

Alma Mater Studiorum - Università di Bologna

DOTTORATO DI RICERCA IN
NANOSCIENZE PER LA MEDICINA E PER L'AMBIENTE

Ciclo 36

Settore Concorsuale: 03/C2 - CHIMICA INDUSTRIALE

Settore Scientifico Disciplinare: CHIM/04 - CHIMICA INDUSTRIALE

SELF-DIAGNOSTIC AND SMART POLYMERS BASED ON FLUORESCENT
PROBES

Presentata da: Valentina Antonia Dini

Coordinatore Dottorato

Matteo Calvaresi

Supervisore

Chiara Gualandi

Co-supervisore

Nelsi Zaccheroni

Esame finale anno 2024

Abstract

This thesis delves into the comprehensive exploration of luminescent molecules, belonging to the category of molecular rotors and aggregachromic dyes, incorporated into polymer matrices to develop self-diagnostic and smart polymers. The research spans different areas of polymer science, encompassing mechanoluminochromism, temperature-dependent behavior, and sensitivity to changes in free volume and chain mobility, providing fresh insights into the dynamic interaction between polymer matrices and luminescent additives when subjected to various environmental factors. In the realm of molecular rotors, our investigations uncover the intrinsic connection between dye emission properties and the mobility and free volume characteristics within polymer matrices. As we incorporate various molecular rotors into amorphous polymer matrices, we challenge conventional assumptions about changes in emission intensity. Our findings reveal that modifications in matrix transparency, the development of microfractures, and waveguide effects wield substantial influence over emission intensity. Utilizing fluorescence lifetime emerges as a robust tool to discern changes in dye properties from variations in the matrix's optical attributes.

Expanding on our research, we identify an innovative approach to better understand chain mobility in complex polymeric materials by measuring the lifetime of a temperature-independent AIE probe. Advanced imaging techniques enable us to quantitatively visualize chain mobility with high spatial and temporal resolution.

Furthermore, we used a phosphorescent probe to explore the change of free volume in various polymers during stress-strain tests and physical aging. The extended lifetimes of this probe lead to the development of materials capable of autonomously monitoring physical aging and mechanical stresses in real-time with exceptional precision and sensitivity, minimizing the impact of instrumental errors.

On the other hand, we explore the inclusion of aggregachromic dyes into polymers with the objective to produce mechanoluminochromic materials. These dyes exhibit extraordinary sensitivity to changes in intermolecular distances and the orientation of chromophores. Part of the research was focused on ascertaining whether the bonding of the dye to the polymer chain provides noticeable

advantages over the simple blending, thus justifying the synthetic efforts of linking the fluorophore to the macromolecules.

In the case of a thermoplastic elastomer functionalized through both covalent bonding and physical dispersion with pyrene derivatives, mechanoresponsiveness arises from the strategic confinement of pyrene chromophores within the soft SEBS block, a feature unattainable in a dispersed dye system. We also explored thermoplastic polyurethanes containing perylene diimide derivatives, highlighting, for this type of polymer matrix, the advantages of both covalent and physically dispersed methods.

Electrospun mechanochromic materials were also developed, emphasizing the importance of fiber orientation in mechanoluminochromic responses.

Overall, this work provides new insights in the use of luminescent dyes within polymer matrices. These materials offer versatility and sensitivity, making them invaluable for a wide range of practical applications, from damage detection and load-bearing devices to wearable technology and mechanochromic textiles. This work paves the way for exciting developments in the future of polymer-based luminescent materials.

Summary

Abstract	1
Acronyms	i
1. Fundamentals	1
1.1. Fluorescent probes for investigation of physico-chemical phenomena in polymers.....	2
1.2. Luminescent probes	6
1.3. T_g and T_v determination by using luminescent probes.....	19
1.4. Physical Aging determination by using fluorescent probes	22
1.5. Determination of mechanical stresses by using luminescent probes	25
1.6. Other processes determination.....	34
1.7. References	39
2. Molecular rotors as rigidification induced emission probes	63
2.1. Emission or scattering? Discriminating the origin of responsiveness in AIEgen-doped smart polymers using the TPE dye	64
2.2. Discrimination of chain mobility and free-volume variations in polymer phase transitions with an absolute AIE probe	89
2.3. A high-sensitivity long-lifetime phosphorescent RIE additive to probe free volume-related phenomena in polymers.....	106
2.4. References	122
3. Aggregachromic dyes.....	125
3.1. Blending or Bonding? Mechanoluminochromism of an Aggregachromic Mechanophore in a Thermoplastic Elastomer	128
3.2. Comparative mechanoluminochromic performances of perylene diimide-doped polyurethanes: blending vs bonding?	154
3.3. In situ monitoring of mechanofluorescent polymeric nanofibers made with excimer-forming telechelic Macromolecule	184
3.4. References	201
4. Overall conclusions.....	205

Acronyms

A: acceptor

A₆Me: hexakis(4-methyl-1-phenylthio)-benzene

AD: bis(adamantyl)1,2-dioxetane

AIE: aggregation induced emission

AMP: 1-Aminomethylpyrene

AMP-Cl: AMP hydrochloride

AP: 1-Aminopyrene

ATR: attenuated total reflection

AZO: azobenzene

BCMDB: 1,4-bis(R-cyano-4-methoxystyryl)-2,5-dimethoxybenzene

BDE: diethyl BODIPY

BODIPY: 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene

BTM: tetramethyl BODIPY

C_{em}: cross-correlation

CB[8]: cucurbit[8]uril

CI: conical intersection

CN-PLLA: poly(L-lactic acid) covalently labeled with the CN₄OH fluorophore

Đ: polydispersity index

D: Dispersed-dye blends

D-x: dispersed dye samples

DABCO: 1,4-diazabicyclo[2.2.2]octane

DBF: dibenzofuran

DCM: dichloromethane

DMA: Dynamic Mechanical Analysis

DMTA: Dynamic mechanical thermal analysis

DMSO-d₆: deuterated dimethyl sulfoxide

Do: donor

DSC: Differential Scanning Calorimetry

E = Young's modulus

EtOH: ethanol

FTIR: Fourier Transformed Infrared

FLIM: fluorescence-lifetime imaging microscopy

FRET: fluorescence resonance energy transfer

HDPE-MAH: high-density maleic anhydride-modified polyethylenes

HMDI: 4,4'-methylenedicyclohexyl diisocyanate

HPS: hexaphenylsilol

HR-ESI-MS: High-resolution electrospray ionization mass spectrometry

HSQC: heteronuclear single quantum correlation

HTMPU: polyurethane modify by including 4,4'-((1Z,3Z)-1,4- diphenylbuta-1,3-diene-1,4-diyl) dibenzyl alcohol in the hard segments

I_E : excimer emission intensity

I_M : monomer emission intensity

I_E/I_M : excimer to monomer emission ratio

k_{nr} : non-radioactive decay rate constant

k_r : radioactive decay rate constant

k_p : phosphorescence constant

LED: light-emitting diode

LLDPE: linear low-density polyethylene

M-C: main-chain

M_n : number average molecular weight

M_w : weight average molecular weight

MALDI: mass spectrometry matrix-assisted laser desorption/ionization

MC: mechanochromic

MDSC: modulated differential scanning calorimetry

MeOH: methanol

ML: mechanoluminescent

MLC: mechanoluminochromic

N_2 : nitrogen molecule

NA: numerical aperture

NBR: nitrile butadiene rubber

NMR: Nuclear Magnetic Resonance

NR: non-reversing heat flow curve

O_2 : oxygen molecule
 OH: hydroxyl group
 OPV: oligo(*p*-phenylene vinylene) derivatives
 PALS: positron annihilation lifetime spectroscopy
 PAS: positron annihilation spectroscopy
 PBA: poly(butylene adipate)
 PBA-PUTHF: semicrystalline polyurethanes elastomer containing poly(tetrahydrofuran) as a soft segment and PBA as hard segments
 PC: poly(Bisphenol A-carbonate)
 PDI: perylene diimide
 PDMS: polydimethylsiloxane
 PE: polyethylene
 PEG: polyethylene glycol
 Per: perylene derivative N,N'-bis(4-amino-1-butyl) perylene-3,4,9,10-tetracarboxylic acid bisimide
 Per-OH: perylene dye functionalized with two alkyl chains bearing hydroxyl groups at each terminus
 PL: photoluminescent PLA: polylactic acid
 PLGA: poly(lactic-co-glycolic acid)
 PLLA: poly(L-lactic acid)
 PLQY: photoluminescence quantum yield
 Poly: PU containing the perylene dye
 PolyPer: PU bearing the Per in the main chain
 PP: polypropylene
 PS: polystyrene
 Ps: positronium atom
 PTFE: Polytetrafluoroethylene
 PU: polyurethane
 PUTHF: highly amorphous polyurethanes elastomer containing poly(tetrahydrofuran) as a soft segment
 PVAc: polyvinyl acetate
 R: reversing heat flow curve
 Rh: rhodamine

RIE: rigidification-induced emission
 RIM: restriction of intramolecular motions
 RIR: restriction of intramolecular rotations
 RIV: restriction of intramolecular vibrations
 S_0 : ground state
 S_1 : excited singlet state
 S_q : root-mean-square roughness
 SAXS: Small-Angle X-ray Scattering
 SBS: poly(styrene-*b*-butadiene-*b*-styrene)
 SEBS: styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene triblock copolymer
 SEBS-MAH: SEBS grafted with maleic anhydride
 SEBS-P: Blend samples of unfunctionalized SEBS and pyrene
 SEM: Scanning Electron Microscopy
 SNOM: scanning near-field optical microscopy
 SP: spiropyran
 STMPU: polyurethane modify by including 4,4'-((1Z,3Z)-1,4-diphenylbuta-1,3-diene-1,4-diyl) dibenzaldehyde in the soft segments
 T: total heat flow curve
 T_1 : excited triplet state
 t_a : aging time
 T_a : annealing temperature
 T_c : crystallization temperature
 T_g : glass transition temperature
 T_m : melting temperature
 T_v : topological freezing transition temperature
 THBA: 10,10',11,11'-tetrahydro-5,5'-bidibenzo[a,d][7]-annulenylidene
 TABD-OH: 4,4'-((1Z,3Z)-1,4-diphenylbuta-1,3-diene-1,4-diyl) dibenzyl alcohol
 TABDAA2: 4,4'-((1Z,3Z)-1,4-diphenylbuta-1,3-diene-1,4-diyl) dibenzaldehyde
 THF: Tetrahydrofuran
 tOPV: cyano-OPV functionalized telechelic poly(ethylene-*co*-butylene)
 TPE: tetraphenylethylene
 TPE-Br: TPE bromo derivative

TPE-EP: tetraphenylethylene functionalized with a pyridinium salt unit

TPE-MRh: TPE-derivative featuring a 3-methyl-rhodanine moiety

TPU: Thermoplastic polyurethane

v : specific volume of a polymer

VLDPE-MAH: very low-density maleic anhydride-modified polyethylenes

WAXS: Wide-Angle X-ray Scattering

XRD: X-ray Diffraction

ΔH_c : crystallization enthalpy

ΔH_m : melting enthalpy

ΔH_{relax} : relaxation enthalpy

ϵ : strain

ϵ_a : molar absorption coefficient

ϵ_b = strain at break

η_{ISC} : efficiency of intersystem crossing between S_1 and T_1

λ_{em} : emission wavelength

λ_{ex} : excitation wavelength

λ_{max} : maximum emission wavelength

σ_b = stress at break

$\sum k$: the sum of all the deactivation process of the excited state T_1

τ_{aged} : lifetime in aged polymers

τ : lifetime

τ_{ph} : phosphorescence lifetime

τ_{glass} : maximum lifetime value obtained in PLGA (glass matrix)

ϕ : photoluminescence quantum yield

Φ_{ph} : phosphorescence quantum yield

1. Fundamentals

Polymers permeate numerous facets of everyday life, spanning from basic container materials to cutting-edge applications in emerging technologies.[1] Polymer science aims to understand the nature and behavior of polymer materials across all their uses from both a scientific and industrial perspective. To assist polymer development, it is fundamental to study their properties, establishing correlations between structure and properties, and unraveling the mechanisms and kinetics of pertinent processes. Such efforts facilitate the determination of material characteristics, evaluation of performance, and even prediction of device lifespan. Moreover, this knowledge underpins the design of innovative tools.

Processes that have the capacity to impact the physical characteristics of polymeric materials encompass a wide array of phenomena. These encompass polymerization, crosslinking, functionalization, and secondary reactions, as well as aging, thermal, photochemical, or chemical degradation. Additionally, these processes involve the transport of small molecules, such as water, solvents, and additives, and are influenced by thermal transitions like relaxations and glass transitions. Morphological alterations, including microphase separation, crystallization, and orientation, play a crucial role, along with self-assembly, gelation, and gel swelling. Each of these processes induces molecular-level transformations within the material, thereby shaping and influencing the material properties and their corresponding applications.

A multitude of advanced methods and techniques have been developed to monitor and track these processes. Spectroscopic methods (UV-Vis, Fourier Transformed Infrared (FT-IR), Raman, Nuclear Magnetic Resonance (NMR)), thermal methods such as differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and gravimetry, microscopy, mechanical tests, viscometry, chemical analysis, and scanning electron microscopy (SEM) are the most spread ones for studying polymers. However, despite the valuable insights they provide into polymer materials, these techniques have certain limitations. These include the need for sampling, the potentially destructive nature of tests, or inadequate sensitivity. These factors make these techniques less suitable for in-situ process monitoring. Furthermore, conventional techniques are ill-equipped to capture dynamic images of

polymer synthesis, structural evolution, and functional performance. In this context, emerging diagnostic techniques such as fluorescence, or more generally, luminescent methods appear as a promising and powerful non-destructive tool. They are efficient, sensitive, and minimally demanding for real-time, in-situ monitoring and visualization of polymer structures and their dynamic processes.[2,3]

This thesis examines the applications of luminescent-based techniques to monitor various polymer properties. To this aim, the photophysical response of different dyes included in polymeric matrices has been investigated during temperature variations and mechanical stresses. Changes of dye's photophysical properties were successfully correlated with variations of their microenvironment occurring as a consequence of physico-chemical processes taking place in the polymer matrices. The comparison between the outcomes of this approach with the information obtained by conventional methods (e.g., DSC, mechanical tests), demonstrates that reliable real-time and in-situ analysis can be performed, eliminating the need for sampling.

1.1. Fluorescent probes for investigation of physico-chemical phenomena in polymers

The wide variety and diversity of polymer properties represent the primary reason for their extensive utilization in materials science over the years.[1] Present-day applications encompass many sectors, including biomedicine, sensing technology, electronics, aerospace, automotive, and the production of various everyday objects. To better harness the properties of polymers, it is advantageous to develop new techniques and tools for investigating phenomena occurring during processing and material use, in particular when these phenomena involve molecular changes and may result in substantial alterations in properties.

Molecular changes encompass conformational changes, topological variations at the atomic level, as well as morphological changes in the state of aggregation (i.e. crystalline and amorphous phases). The phenomena giving rise to these variations can have either physical or chemical origins, and as previously mentioned, it is of paramount importance to study them thoroughly, since they significantly impact the properties of these materials.

Among the physically-driven phenomena in the world of polymers, two are well-known: the glass transition[4] and the crystallization/melting.[5] With regards to the former, it concerns the amorphous phase of a polymer transitioning from a glassy to a rubbery state and vice versa.[6] Once the glass transition temperature (T_g) is exceeded, the polymer undergoes a significant increase in free volume among the chains (Figure 1.1), endowing them with greater mobility.[7,8] This variation is reflected in a strong change in mechanical properties (decrease of elastic modulus) and thermal properties (increase of heat capacity), commonly exploited for T_g determination by using DMA and DSC, respectively.[9,10] Furthermore, the glassy amorphous phase is subjected to another phenomenon known as physical aging,[11] which results in a gradual decrease in free volume over time and a progressive embrittlement of the material.[12]

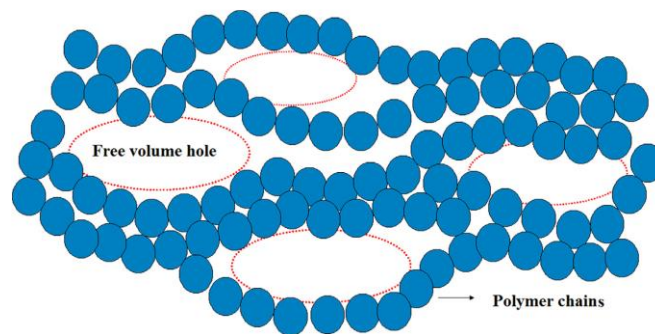


Figure 1.1 Schematic illustration of the free volume within a polymer. Reproduced from ref.[13] with permission from Elsevier Inc., Copyright © 2020.

In the context of semi-crystalline polymers, it's noteworthy that both the quality and quantity of the crystalline phase exert a substantial influence on material characteristics.[14] Crystallization is driven by the thermodynamics of polymer chain arrangement (Figure 1.2) in which the inherent structural units offer enthalpic contributions, such as the establishment of H-bonds or other intermolecular interactions.[15] Understanding the kinetics of the crystallization becomes crucial in order to tailor the polymer properties for a specific application. Indeed, the degree of crystal phase can affect mechanical properties, solvent resistance, and thermal stability.[16]

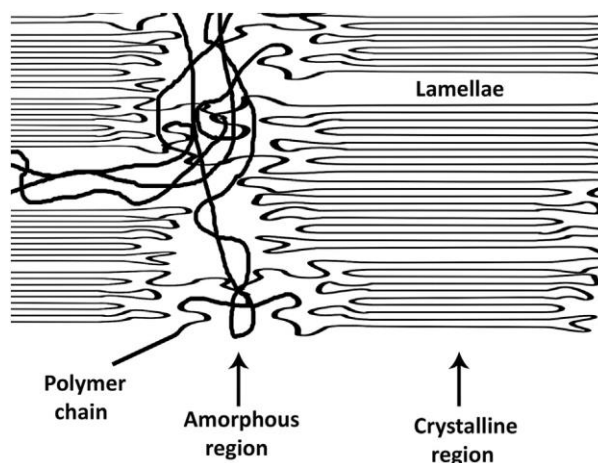


Figure 1.2 Schematic representation of an ideal distribution between the crystalline and amorphous phases in a semi-crystalline polymer. Reproduced from ref. [17] with permission from Elsevier Inc., Copyright © 2017

On the other hand, an example of a chemical process that strongly influences the polymer properties is the crosslinking reaction. It operates on a topological level as it involves the formation of new bonds to create crosslinked networks. While it is not always easily achievable, synthesizing a crosslinked polymer is often worthwhile due to the benefits in terms of dimensional stability, solvent resistance, and often high-temperature resistance.[18] An excellent example of crosslinking process is the vulcanization of rubber. In this process, the interconnection between polymer chains imparts enhanced structural rigidity to the material.[19]

Given the paramount importance of these aspects in the production and utilization of polymeric materials, it is evident that all these phenomena are extensively investigated using a range of specialized techniques. Dilatometry, DMA and DSC are used for the T_g determination and the study of enthalpies of melting and crystallization,[20] as well as physical aging. In addition, X-ray diffraction, IR spectroscopy and NMR are employed to investigate the morphology of the crystalline phase.[21] All these techniques are used in combination with mechanical tests which provide information on the elastic modulus and resistance to different stimuli such as impact, torsion, or stretching.

In this framework, this thesis explores in depth the optical properties taking advantage of spectroscopic methods. Analytical techniques based on luminescence have emerged due to their significant potential to shine light on the structure and properties of polymeric materials and to monitor their microscopic changes. They offer several advantages, such

as high sensitivity, selectivity, and rapid response time, making them ideal for real-time analysis.[22,23] Photophysical techniques include several methods that allow to measure different photophysical features and can be divided in steady-state (e.g., light absorption, excitation and emission spectra, emission anisotropy), and time-resolved (e.g., lifetime, anisotropy decay) ones (Figure 1.3). Unlike traditional methods, luminescence spectroscopy eliminates the need for sampling and enables non-destructive measurements. Furthermore, the intensity and spectral properties of luminescence are highly sensitive to the interaction of excited molecules with other excited molecules, molecules in the ground state, and changes in the molecular environment. While these interactions often limit the direct quantitative diagnostic exploitation of the emission intensity, they offer the opportunity to study other aspects of the system of interest. In the case of polymers, these phenomena can be used, for instance, to investigate chemical interactions in the polymer matrix.[21]

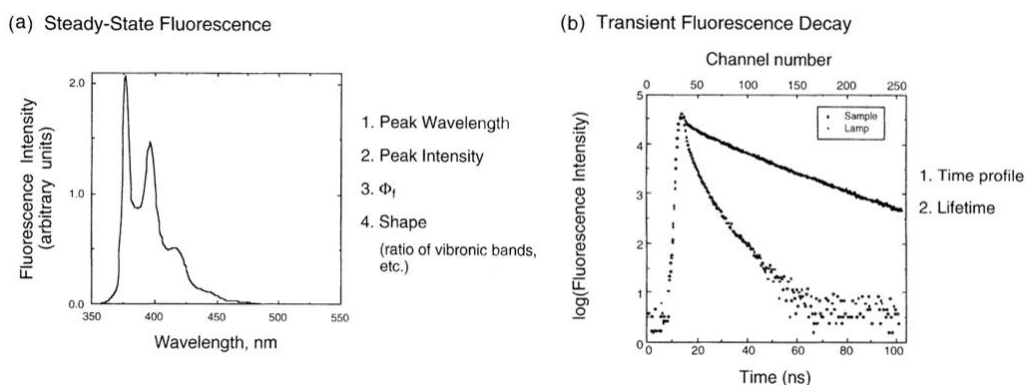


Figure 1.3 Experimental data that can be determined from steady-state fluorescence measurements, specifically from the fluorescence spectrum (a) and time-resolved measurements, from the fluorescence decay curve (b). Adapted from ref. [22] with permission from Elsevier Inc., Copyright © 2000.

The main obstacle in the employment of these techniques in polymers is related to the weak or absent intrinsic luminescence of polymeric materials. To overcome this limitation, luminescent probes can be introduced into the system. The dyes must exhibit adjustable conformations that respond to the microenvironment within the polymer. These molecules must guarantee high-contrast luminescence signals, especially in the solid state, while maintaining stability.[24] When incorporating a luminescent probe into the polymer matrix for the purpose of studying its properties and associated processes, it is

imperative to select the appropriate dye. The chosen dye must indeed exhibit a change in its optical properties in response to the variations of interest experienced by the polymer.

1.2. Luminescent probes

There are various types of luminescent probes presenting different mechanisms for their optical and photophysical properties. Based on their molecular structure, each species, once excited from the ground state (S_0) to the excited state (S_1 or T_1), can undergo either radiative (luminophore) or non-radiative decay, resulting in the presence or absence of luminescence, as shown in the Jablonski diagram in Figure 1.4. These decays are unimolecular ones and influenced by the environment, but also bimolecular processes are possible. In particular, when an excited species is in proximity to another species with the appropriate characteristics to serve as an acceptor, an energy transfer process can occur. During these processes, part of the energy absorbed from the donor molecule is transferred to the acceptor. This leads to the donor relaxation to the ground state and to the acceptor excitation to the excited state. In cases where the acceptor is a luminophore, this energy transfer can result in sensitized light emission (Figure 1.4).

Hence, a suitable probe should possess the capability for radiative emission, and more specifically, this emission should be influenced by the specific phenomenon under investigation within the polymer.

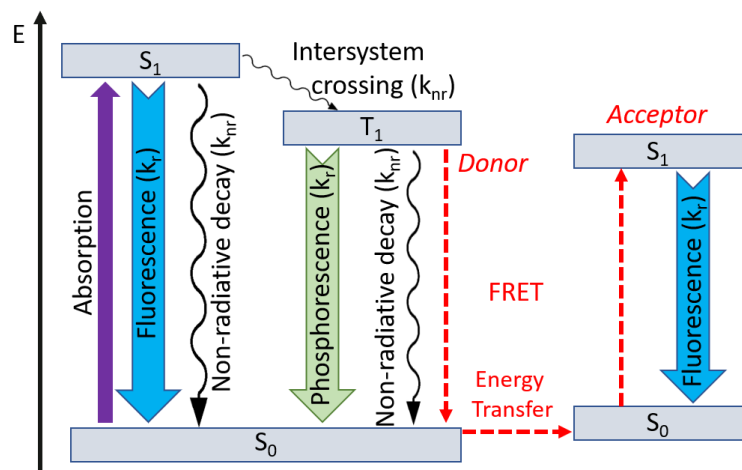


Figure 1.4 Scheme of the Jablonski diagram illustrating the various types of transitions, both radiative and non-radiative, between the energy levels of molecules.

Lastly, it is essential that the alteration in the optical properties of the probe can be easily quantified. The choice of the dye to be employed will depend on the particular phenomenon that one seeks to observe within the polymer matrix.[3,25] Recalling that, as previously mentioned, each phenomenon experienced by polymers that influences their properties has a distinct nature (chemical or physical) and involves molecular changes at multiple levels (conformational, topological, and morphological).

The most commonly used fluorescence probes can be categorized into the following four groups that will be described more in detail in the following sections: (1) molecular rotors, whose luminescence depends on molecular rotations that can be hindered or allowed depending on the surrounding environment; (2) aggregachromic dyes, molecules whose emission depends on their aggregation state; (3) systems involving an excited-state donor and a ground-state acceptor, based on energy transfer; (4) molecules whose luminescence varies or is activated by the breaking of a covalent bond.

1.2.1. Molecular rotors

Molecular rotors are usually organic luminophores, presenting aromatic structures and conjugated systems. However, the primary distinguishing feature of these molecules is their capacity for intramolecular rotations. In a simplified analysis, considering this class of luminophores in high diluted solution, where molecules are

dispersed and non-interacting, their excited state can rapidly decay due to non-radiative pathways favored by their intramolecular motions (rotation and vibration). Indeed, in aromatic structures the radiative decay, yielding luminescence, is maximized by the conjugated configuration with the π -electron delocalization. On the other hand, in solutions at high concentrations, while generally strong π - π stacking interactions in face-to-face packing of luminophore induce their quenching, the hindered helical or twisted structures of molecular rotors prevent their efficient packing. However, the interaction among molecules is sufficient to have the restriction of intramolecular motions (RIM), which results in a radiative decay rate that can effectively compete with non-radiative decay, leading to a higher emission intensity (Figure 1.5).[26,27] This phenomenon, as described so far, was discovered only a few years ago and coined by Tang et al. as "aggregation-induced emission" (AIE) in 2001.[28] It is indeed in stark contrast to the previously known "aggregation-caused quenching" (ACQ) of other dyes.[29–32]

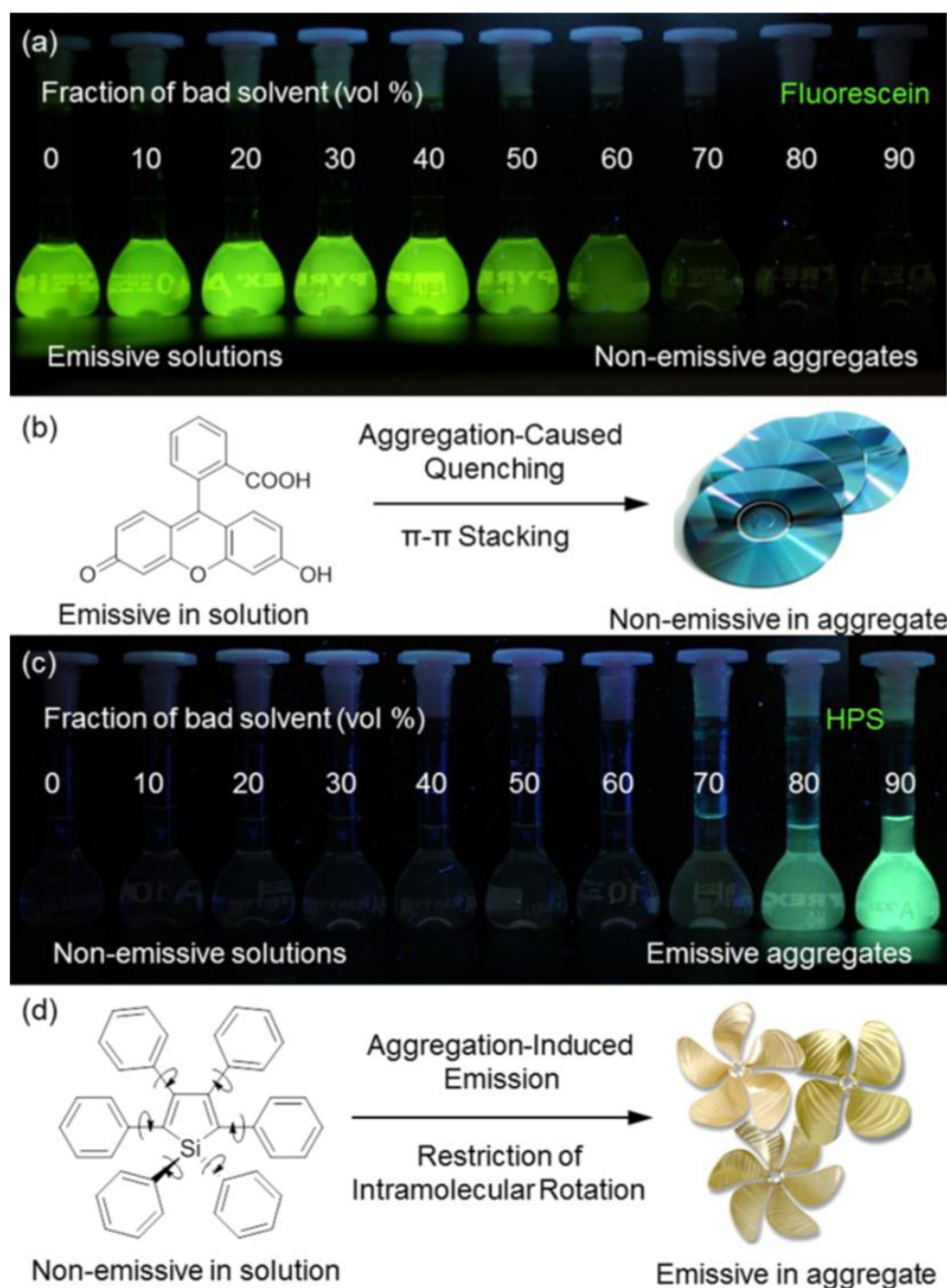


Figure 1.5 Fluorescent digital photographs of (a) fluorescein and (c) hexaphenylsilole (HPS) solutions with different bad solvent fractions. (b) Fluorescein molecules are disk-shaped and become non emissive when forming aggregates where strong π - π interaction quenches the emission. (d) HPS molecules are propeller-shaped and become highly emissive when forming aggregates where the intramolecular rotation is restricted. Reproduced from ref. [27] with permission from American Chemical Society, Copyright © 2018.

Further examples of AIE are shown in Figure 1.6 that schematizes tetraphenylethylene (TPE) and 10,10',11,11'-tetrahydro-5,5'-bidibenzo[a,d][7]-annulenyldiene (THBA) behavior. The twisted chemical structure of both molecules exhibits different allowed

intramolecular motions in solution. Once they are restricted, the dyes show an intense emission.

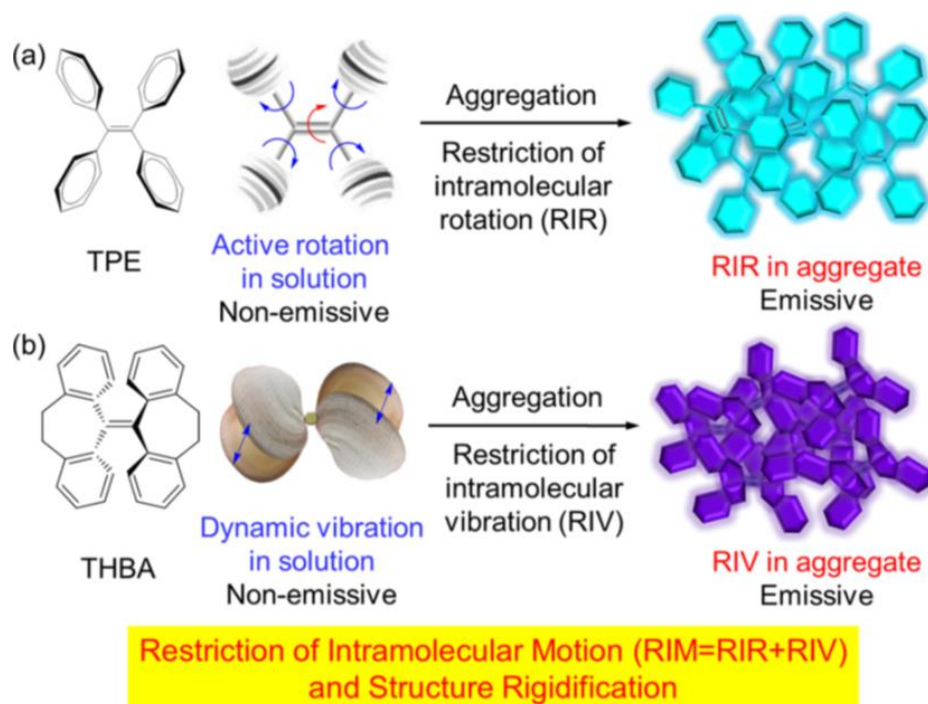


Figure 1.6 (a) Chemical structure of TPE, where the restriction of intramolecular rotations (RIR) causes intense emission. (b) Chemical structure of THBA, which under the restriction of intramolecular vibrations (RIV) enhances its emission. Reproduced from ref. [27] with permission from American Chemical Society, Copyright © 2018.

What has been described so far exclusively regards the AIE phenomenon of molecular rotors in solution. However, the RIM effect satisfies one of the requirements indicated in section 1.2, that make these dyes interesting for investigating polymer properties. Indeed, they are highly sensitive to everything that influences their degree of freedom in the surrounding environment, responding to alterations by modifying their emission properties. Specifically, if they are immersed in a polymeric matrix instead of a solvent, their optical properties are influenced by the phenomena occurring within the polymer (for instance changes of free volume or chain mobility).[33] It is important to emphasize that in this case, we are dealing with dye molecules dispersed among the polymer chains. The emission induction effect of these molecules is no longer due to aggregation but rather due to the hindrance of intramolecular motions caused by the matrix itself. Hence, it is not entirely accurate to label these

molecules as AIE; instead, it would be more appropriate to refer to them as rigidification-induced emission (RIE) dyes. However, since the term RIE is not widely used in the literature, in this thesis molecular rotors will be also indicated as AIE, regardless of the matrix in which they are located and the cause of the emission enhancement.

In the specific case of a polymer serving as a matrix where AIE molecules are dispersed, the phenomena of interest can be physical aging, determination of the T_g , or chain sliding in response to a mechanical stimulus. All these processes result in a variation in the free space between the chains that can be exploited for dye motions, thus changing its emission. For example, the transition of the polymer from the glassy state to the rubbery state, crossing the T_g , would result in the dye emission quenching as the environment passes from rigid to progressively mobile increasing the dye freedom.[34] These dyes have shown a high sensitivity in responding to changes in their surroundings leading to their use in a wide range of applications [33–35] as optoelectronic devices, chemosensors,[36–40] memory chips, [41] data storage, [42–44] as well as in bio-sensing,[45] and security inks.[46,47]

1.2.2. Aggregachromics

Dyes whose emission depends on their aggregation state are referred to as "aggregachromic" compounds.[48] From a chemical and structural perspective, they are characterized by a central planar and highly conjugated aromatic portion capable of promoting π - π stacking interactions among different dye molecules.[49,50] It is possible to modulate the optoelectronic properties or the solubility of these chromophores by adding substituents that increase their dipole moment or dispersibility in various matrices. Additionally, some substituents can make the dye aggregates more flexible and promote their breakage following mechanical deformation. However, it is crucial to choose the functional groups in order to not hinder the self-assembly of molecules by π - π stacking interactions.[50,51] Many examples of dyes belonging to this class can be found, including various aromatic hydrocarbons, such as pyrene,[52–54] naphthalene, anthracene,[55,56] and perylene,[57–59] along with their derivatives,

[60] and recently, studies have also focused on cyanopoly(*p*-phenylene vinylene) and its derivatives.[61–63]

Their optical properties, as mentioned earlier, depend on their state of aggregation. In fact, compared to the emission spectrum of the monomer (isolated dispersed molecule), the spectrum of the aggregate is different in energy and shape.[64]

A specific case occurs when interactions between an excited-state dye molecule and a ground-state molecule leads to the formation of an excimer (excited-state dimer).[65–67] The emission of an excimer is characterized by a broad band at longer wavelengths compared to that of the monomer (Figure 1.8). This is because the formation of the excimer results in a stabilization of the species with the lowering of the excited-state energy decreasing the energy gap with the ground state, causing a redshift of the emission.[50,68] Another variation is represented by the exciplex, where an excited-state molecule encounters a ground-state molecule of a different type, forming a complex in the excited state.[22,65]

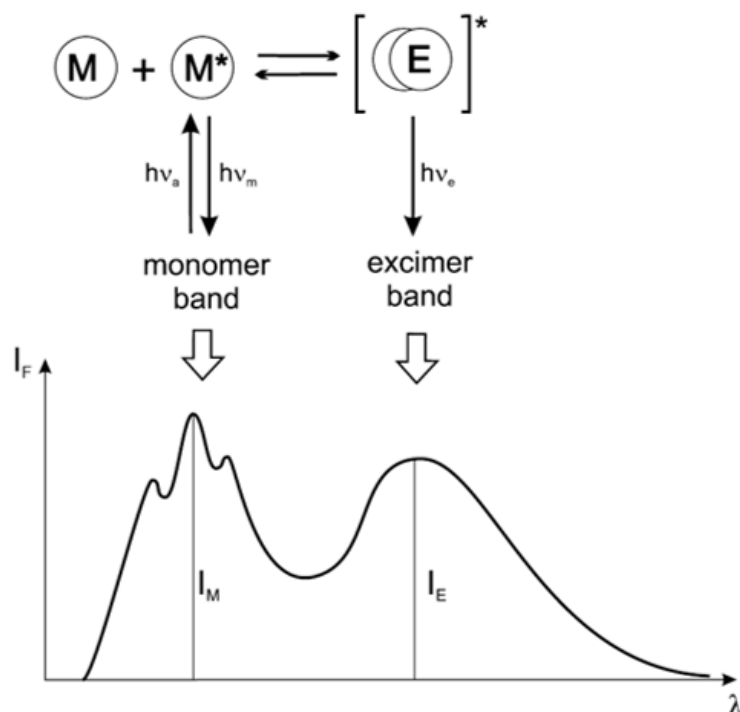


Figure 1.8 Scheme of excimer formation and the respective emission spectrum. Reproduced from ref. [68] with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Copyright © 2012.

The photophysical characteristics of these molecules are well-known and understood in solution. It is important to note that the process of excimer formation in solution is diffusion-controlled, which means that only when a certain concentration threshold is reached a certain number of excited-state monomers will be able to interact with ground-state ones.[68–70] This characteristic can be particularly important when these dyes are included in a polymer matrix. In these systems, the matrix hinders the diffusion due to the matrix rigidity, influencing the molecules interactions and favoring dimers and aggregate formations already at the ground state.

Including this class of dyes in polymer matrices primarily aims to study the mechanical properties of the polymer. In this regard, starting from a state where the excimer signal prevails, due to the neighboring of the dyes in the matrix, through the sliding of polymer chains (mechanical stress) it is possible to disintegrate the dye aggregates changing their luminescence. Materials that respond with a change in emission to a mechanical stimulus are referred to as mechanoluminochromic.[48,50,71,72] In various studies conducted over the years, efforts have consistently aimed to establish a relationship between the variation in the emission spectrum and the specific mechanical property under consideration. For instance, by stretching a polymer matrix containing an aggregachromic dye and monitoring the changes in the spectrum during elongation (Figure 1.9), it is possible to document the variation in the ratio between monomer and excimer intensities (I_M/I_E) as deformation increases. Many examples can be found in literature, but it is important to underline that their behavior can significantly vary and depend on the dye inclusion method. The dye can be dispersed as an additive,[62,70,73–75] attached as a side pendant to the polymer chain,[53,76,77] or incorporated into the main polymer chain.[57,76] A more in-depth discussion of mechanoluminochromism will be provided in section 1.5.

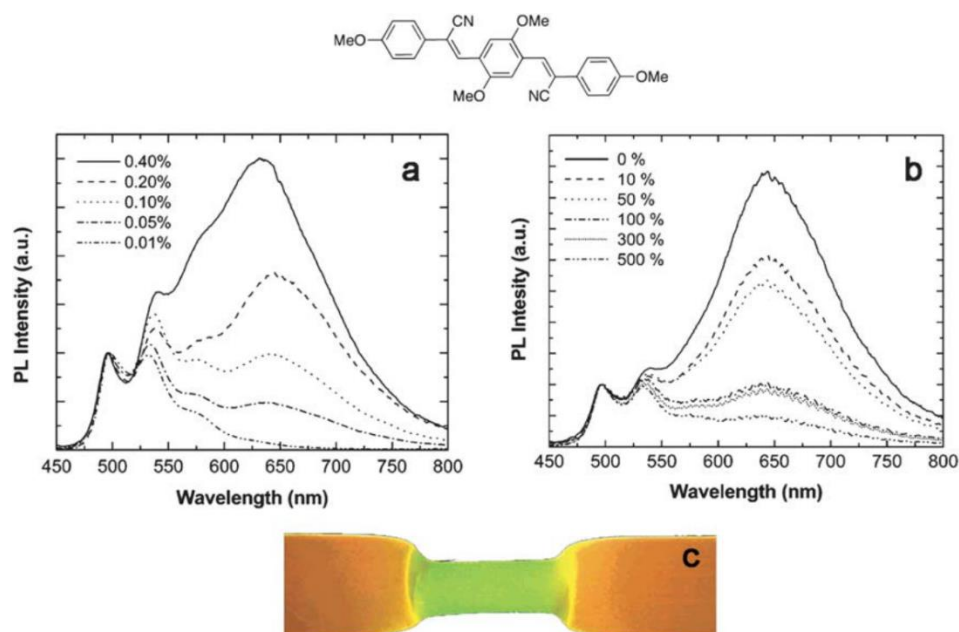
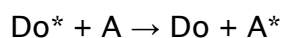


Figure 1.9 The inset of the figure reports the chemical structure of the aggregachromic dye, 1,4-bis(R-cyano-4-methoxystyryl)-2,5-dimethoxybenzene (BCMDB). (a) Emission spectra of BCMDB dispersed in linear low-density polyethylene (LLDPE) films with different concentrations of the dye (wt.%); (b) emission spectra of a 0.20 wt.% BCMDB/LLDPE film at different strain values; (c) image of the same blend after uniaxial deformation (strain = 500%, λ_{ex} = 365 nm) Reproduced from ref. [50] with permission from the Royal Society of Chemistry, Copyright © 2011.

1.2.3. Energy transfer luminophores

Electron transfer is defined as the "photophysical process in which an excited state of a molecular entity (the donor - Do) is deactivated to a lower state, transferring energy to a second molecular entity (the acceptor - A), thereby raising it to a higher energy state".[78] This process can be schematized as follows, where Do represents the donor and A the acceptor.



Generally, it starts with the selective excitation of the donor to take it to its excited state, when the acceptor is at the ground state, then occurs a non-radiative energy transfer between them, thanks to the overlap between the donor emission spectrum and the acceptor absorption one (Figure 1.10).[68,79] In its most common mechanism, the process is known as fluorescence resonance energy transfer (FRET) because, through the energy transfer, the donor emitted light is trivially and readily reabsorbed by the acceptor, that if it is a luminophore itself, can decay via radiative path giving rise to a so-called sensitized emission.[80]

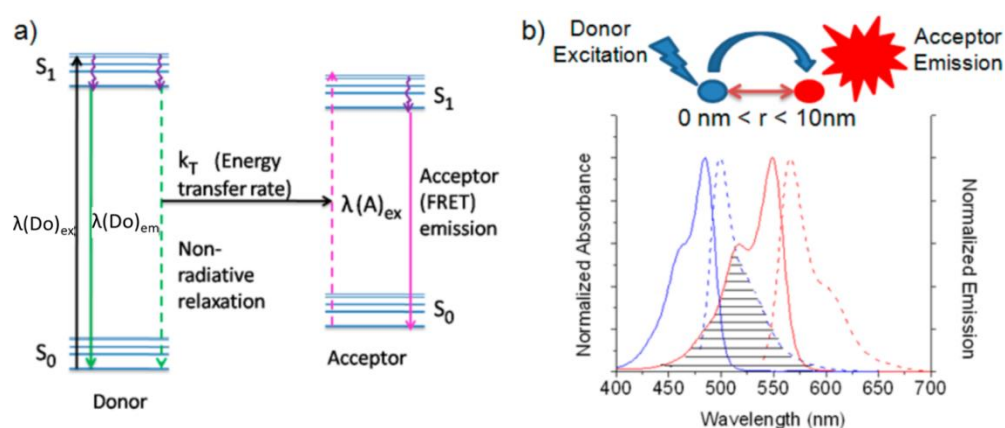


Figure 1.10 (a) Simplified Jablonski diagram for describing FRET phenomenon from donor to acceptor. (b) Scheme of the spectral overlap between the Do emission (dashed, blue) and A absorption (solid, red) where FRET occurs (shaded region). Reproduced from ref. [81] with permission from American Chemical Society, Copyright © 2018.

However, the first theoretical contributions to these types of processes were provided by Dr. L. Dexter and T. Förster, whose names are now associated with two different mechanisms.[79,80,82–84] The first is a spin-conserved process based on electron interactions, while the second does not have spin requirements and is based on coulombic interactions between the dipole moments of molecules.[83] As it might seem intuitive, the dependence of these processes on the distance between the donor and acceptor varies depending on the mechanism involved. In the case of Dexter mechanism, short distances between the two species are crucial for orbital overlap,[68,80] while coulombic interactions occur also at larger distances (Förster mechanism).

The exploitation of energy transfer process for the study of polymers can present several advantages, one of which is the wide variety of acceptor and donor molecules. The acceptor important requirements are high quantum yield and the desired emission wavelength.[25] The choice of the two molecules is virtually limitless, as they can even be two portions of the same molecule. This process is widely used in various fields, especially in biochemistry,[83] where it allows to determine distances between molecules (based on the distance between fluorophores),[68,85] study interactions between proteins[85–87] or DNA components.[88] In the materials field, the

FRET mechanism is exploited to provide mechanochromic properties to the matrix. For example, it is possible to select a molecule (donor) able to release energy in response to mechanical stress even if its emission is weak. Then, it can be combined with the appropriate acceptor which absorbs the donor energy and emits strongly. This strategy makes possible to detect the mechanical stress experienced by the polymer taking advantage of the properties of two different molecules (Figure 1.11).[89,90] In this example light excitation is not even needed since the luminescence is induced by bond cleavage via mechanical stress (see next paragraph). With the same approach, the effects of adding additives to matrices have also been studied.[91]

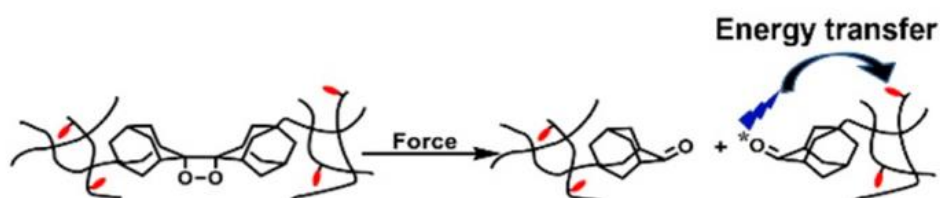


Figure 1.11 A schematic representation of how the application of an external force on the polymer causes the cleavage of a bond and the transfer of energy that gives rise to luminescence. Reproduced from ref. [89] with permission from American Chemical Society, Copyright © 2020.

1.2.4. Covalent bond cleavage-induced luminophores

This class of luminescent compounds includes molecules that possess an easily cleavable bond under the action of an external stimulus. There are various mechanisms that can lead to the scission of the covalent bond, such as ring opening or radical cleavage.[92–96] Depending on the compound, the bond can break due to various stimuli, such as temperature, pH, light, or mechanical stress.[25,97,98] Among the most studied families, we find spiropyrans, diossetanes, oxazines, and rhodamines.

Spiropyrans (SP) are molecules composed of two heterocyclic portions (indoline and benzopyran) linked together by a spirocarbon and arranged perpendicularly to each other.[99–102] This conformation disrupts π -electron conjugation, rendering the molecule colorless. Following a stimulus, which can be electromagnetic radiation, a change in pH,[103]

temperature,[104,105] or mechanical stress,[106–110] the C-O bond breaks. This results in the opening of the spiropyran ring, which rapidly isomerizes into a zwitterionic intermediate with a positively charged indole and a phenolate anion.[111] This intermediate is called merocyanine, and due to its planar and highly delocalized structure, it absorbs in the visible region and becomes colored. These molecules and their derivatives have been widely used as chemo- and biosensors,[112] but also, they have been used to functionalize polymer chains and create mechanochromic materials.[107,113–118] In the latter, the stress experienced by the chains is transmitted to the spiropyran portions, causing their opening and subsequent fluorescence. The relationship between the stress-strain curve and the increase in the photophysical signal due to the color change can be observed, as shown in Figure 1.12.[119]

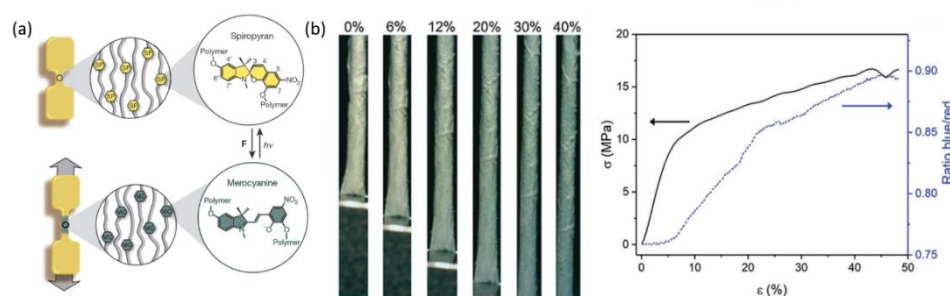


Figure 1.12 (a) Schematic diagram of dog bone samples showing polymeric chains functionalized with spiropyran moieties in the main chain. Zoom in of the isomerization obtained by applying force, between the colorless spiropyran and colored merocyanine. Adapted from [114] with permission from Macmillan Publishers Limited, Copyright © 2009. (b) On the left: a linear glassy polymer carrying a SP moiety in each repeating unit was electrospun into a bundle, stretched and recorded by a CCD camera. During stretching, the blue color continuously increased until sample breaking. This phenomenon can be directly correlated to the increasing amount of mechanically isomerized merocyanine in the backbone of the copolymer chain. On the right: blue to red ratio of the measured intensity color change obtained from the image analysis recorded during the stretching of the electrospun bundle (blue dashed line), together with the specific strain values corresponding to the stress-strain curve (black line). Adapted from ref. [119] with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Copyright © 2018.

Another class of molecules that has been studied is the one presenting the 1,2-dioxetane group.[120–123] This strained 4-membered ring decomposes into two carbonyl portions, one of which is in an electronically excited state.[124] When the excited-state

ketone group returns to the ground state, it emits blue light. The breaking of the bond typically occurs through thermal or mechanical stimuli. Indeed, they are frequently used either in biochemical contexts [125] or for functionalizing polymer chains (incorporated along the main chain or used as crosslinking points) to investigate the effects of mechanical stress on the polymer through a mechanochromic effect (Figure 1.13).[90,120,123,125–127]

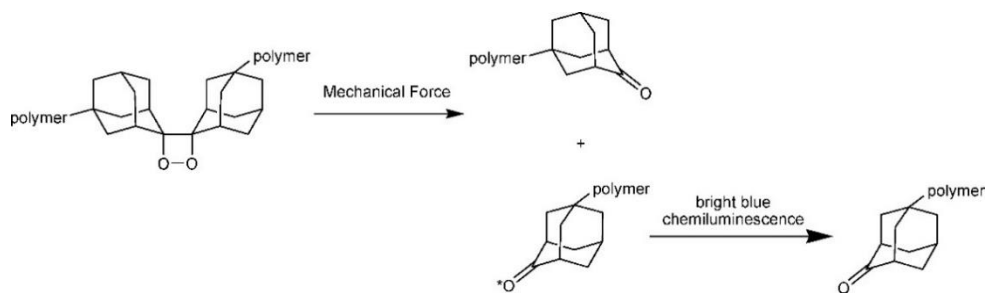


Figure 1.13 Schematic representation of the mechanochromic effect achieved by incorporating bis(adamantyl)dioxetane into a polymer. Reproduced from ref. [120] with permission from American Chemical Society, Copyright © 2014.

In addition to those mentioned, there are other compounds that have been widely used to detect mechanical stress in polymers as the derivatives of rhodamine (Rh).[128] Rhodamine is an excellent fluorophore with a well-known behavior. It exhibits valuable optical properties, good stability, and a high coefficient of absorption and quantum efficiency.[98] As in the case of spiropyrans, these rhodamine spirolactams are colorless in the closed-ring form. However, upon the rupture of the ring, a zwitterion is formed, which, due to the redshift in the absorption spectrum, becomes colored (Figure 1.14).[98] Since the opening and closing of the ring can be controlled by modifying temperature, pH, and mechanical stress, these rhodamine derivatives were initially used as chemosensors and later as fluorophores for super-resolution imaging.[129,130] Recently, these dyes have also been utilized in combination with polymer matrices, where, when bound to the polymer chains, they act as stress sensors exhibiting a mechanochromic behavior.[97,131]

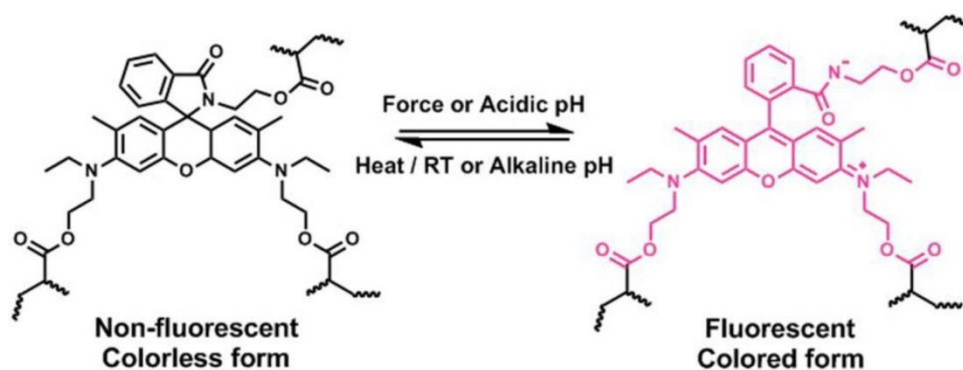


Figure 1.14 Reversible ring-opening/closing isomerization of the Rh-based mechanophore by applying force, temperature or pH variations. Reproduced from ref. [98] with permission from Licensee MDPI, Basel, Switzerland, Copyright © 2018.

There are other classes of dyes belonging to this category of covalent bond cleavage induced luminescence such as diarylbibenzofuranones,[95,96,132] naphthopyrans,[133] and oxazines.[134]

It must be noted that this mechanism of covalent bond breaking has its drawbacks, as will be discussed in detail in section 1.5. Their ability to effectively detect stresses at low levels of polymer deformation is often limited due to their primary operating principle, which involves the breaking of covalent bonds.[119] Furthermore, depending on the type of compound, their application may be limited by the irreversibility of the mechanical activation without the application of an additional external stimulus.

1.3. T_g and T_v determination by using luminescent probes

The glass transition temperature plays a critical role in both the technological and physical aspects of polymeric materials.[135,136] It is during the glass transition that the rotational motions of the chains are activated, leading to a sharp increase in the chain mobility. T_g represents the temperature at which most polymers undergo a reversible transition from the glassy state, characterized by hardness, stiffness and brittleness, to the rubbery state, denoted by softness, elasticity, and flexibility.[8,34,137] T_g directly influences the properties and performance of polymers, making it essential for determining the service

temperature and suitability of polymers for specific applications from engineering to pharmaceuticals.[8,138–141]

Various techniques are employed to determine the glass transitions of polymers, including dilatometry, DMA, and DSC.[142,143] These methods have certain weaknesses, such as poor accuracy, the amount of sample required, and variations in numerical results depending on the technique used. Therefore, the development of nondestructive techniques that allow real-time and in situ analysis for monitoring such transitions can be advantageous.

In this context, fluorescence techniques emerge as a promising approach for studying glassy transitions due to their rapid response, high sensitivity, and ease of detection.[144–153] The determination of T_g through fluorescence can be traced back to the work of Frank in 1975,[154] and later expanded by Torkelson and coworkers.[155–158] Initially, pyrene was used as a fluorescent probe to label polymers.[144,159] Changes in fluorescence emission during the glass transition of the modified polymers allowed the T_g determination. However, with this dye, this technique can be less accurate due to the low dye concentration required to study the emission of the monomer, which can result in less intense fluorescence. Additionally, its low thermal stability is a concern, as there is often a significant reduction in fluorescence intensity as the temperature increases due to the increased nonradiative decay with the thermal energy of the system.[144] To overcome these limitations, the adoption of aggregation-induced emission luminophores has become widespread over the years. As previously mentioned in section 1.2.1, the optical properties of these types of dyes, generally known as molecular rotors, depend on their mobility. Aggregation or any external disturbance that restricts the movement of AIEgens activates the process of restriction of intramolecular motion, which triggers luminescence. [28,160–162] When dispersed in a polymer, the molecular movements of the dye are determined by the mobility of the polymer chains.[163] For this reason, they are particularly suitable for studying processes such as the glass transition, during which the segmental motion of the polymer chain reduces the rigidity of the local microenvironment, leading to a decrease in the emission intensity of the AIEgen molecules (Figure 1.15). This,

combined with the fact that the fluorescence intensity of polymers doped with AIE dyes can be effectively increased by increasing the probe loading without risking quenching,[30,31] forms the basis for using AIE for the rapid and reliable detection of T_g . Several studies on this topic can be found in the literature, including those conducted by Tang and Ma. They successfully determined the T_g of various polymers by measuring changes in emission intensity with increasing temperature, using tetraphenylethylene and its derivatives.[34,164]

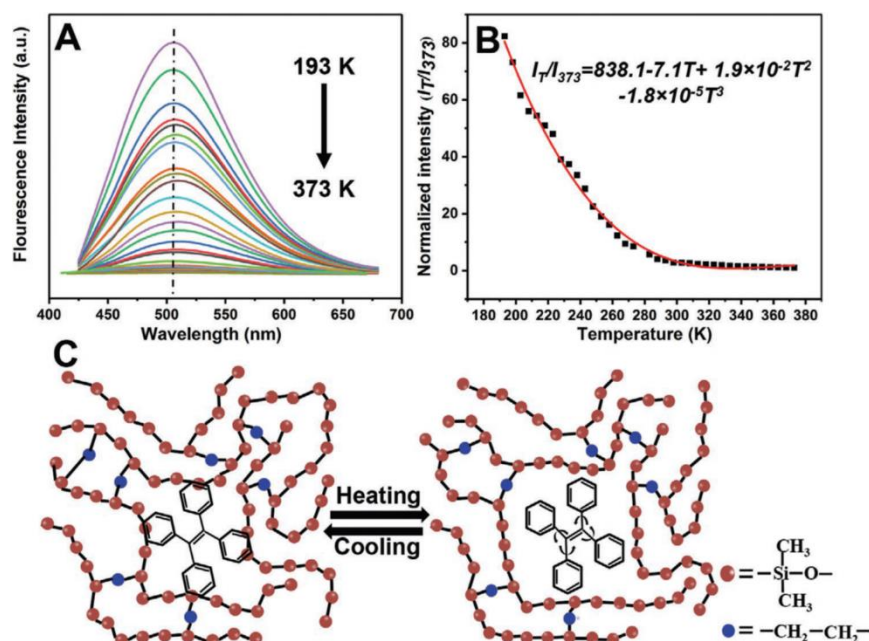


Figure 1.15 A: Fluorescence spectra of a TPE-doped polydimethylsiloxane (PDMS) composite, at different increasing temperatures. B: Plot of normalized fluorescence intensity (I_T/I_{373}) of the same samples as a function of temperature (I_{373} is fluorescence intensity of material at 373 K); C: Schematic representation of TPE intramolecular motions hindered by polymeric chains and then allowed by increasing temperature. Reproduced from ref. [164] with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Copyright © 2020.

The methodologies developed for detecting T_g can also be applied to monitor other transitions in a different class of polymers, such as vitrimers. Vitrimers are crosslinked polymer matrixes, but unlike common thermosets, they are reworkable due to a peculiarity of the crosslinking mechanism based on temperature-adaptable networks.[165–167] Similarly to the T_g of conventional polymers, these matrixes have a temperature parameter called topological freezing transition temperature (T_v). Above T_v , rapid exchange reactions occur at the crosslinking points, allowing vitrimers to be reworked and recycled.[168,169] Below T_v ,

exchange reactions slow down, causing vitrimers to behave like conventional thermosets. T_v not only determines the temperature limits for the use of vitrimers but also significantly affects their performance and reconditioning capabilities, as T_g in other polymers. For this reason, the probes used for T_g determination were also proposed to detect the T_v of vitrimers (Figure 1.16).[170]

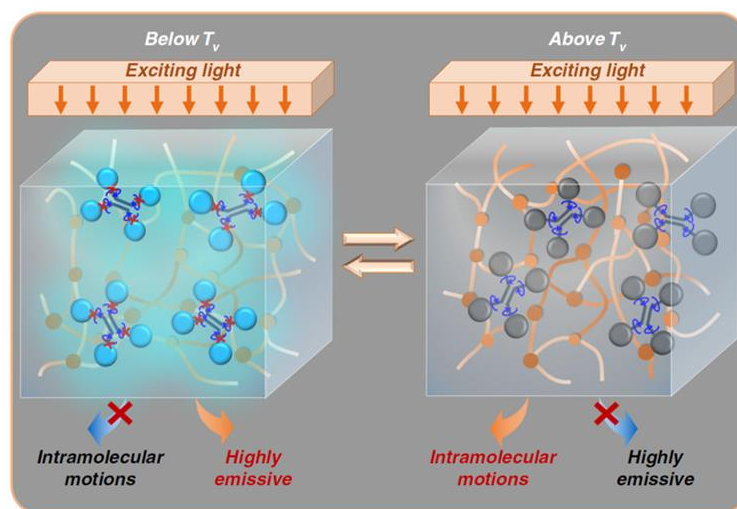


Figure 1.16 Scheme of the principle behind the luminescence variation of an AIE-doped vitrimer below and above its T_v . Reproduced from ref. [170] with permission from Springer Nature, Copyright © 2019,

1.4. Physical Aging determination by using fluorescent probes

It is well known that amorphous polymers are not in thermodynamic equilibrium at temperatures below their glass transition.[171,172] Studies of volumetric relaxation of glassy materials have shown that even below T_g partial rotational movements are allowed and slow chain relaxations attempt to establish equilibrium.[172,173] This non-equilibrium state arises due to the intrinsic kinetic nature of the glass transition. When a polymer is cooled from the rubbery state through the glass transition to the glassy state, there is a rapid decrease in molecular mobility accompanied by a sudden increase in viscosity and modulus, as the glass transition temperature approaches.[174] In essence, the polymer molecules become "frozen" in a nonequilibrium state with higher energy and volume than the corresponding equilibrium state at the same temperature (Figure 1.17). Consequently, there is a thermodynamic

potential or driving force that pushes the molecules towards equilibrium through further packing and/or conformational rearrangement. While molecular mobility significantly decreases in the glassy state compared to the rubbery region, it does not become zero, thereby enabling molecules to gradually approach the equilibrium state characteristic of normal liquid-like packing.[175] This gradual approach to equilibrium affects many material properties and, being time-dependent, is termed "physical aging" to distinguish it from chemical aging (photo-degradation, oxidation, etc.).[176] Physical aging results in a gradual decrease in the fraction of free volume contained in the polymer below T_g and is considered as an enthalpic or volumetric recovery (relaxation).[177,178] Consequently, it impacts all temperature-dependent properties that change dramatically and abruptly at T_g . Indeed, during physical aging, various changes occur in the physical and mechanical properties of the polymer system, such as increased density, tensile and flexural yield stress, and elastic modulus, along with decreased impact strength, fracture energy, elongation at break, and creep rate. Additionally, the material undergoes a transition from ductile to brittle fracture behavior, becoming stiffer and indeed more brittle.[179] To employ polymers effectively as engineering materials, it is crucial to fully understand this phenomenon and develop techniques to diagnose the changes that materials may undergo over time to comprehend their long-term performance.

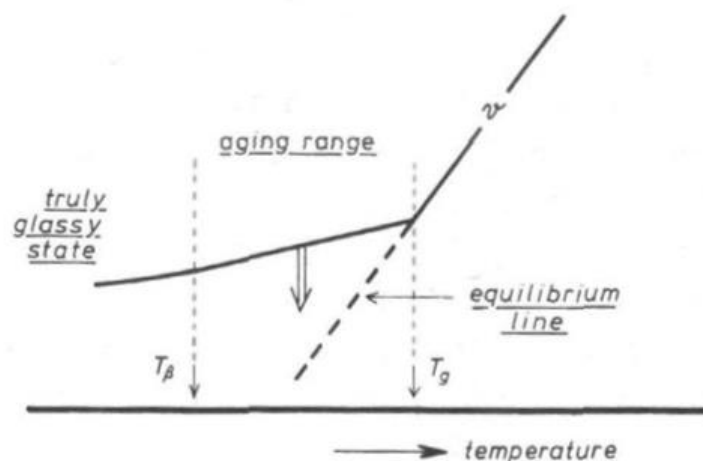


Figure 1.17 Graphical representation of the specific volume (v) of a polymer by varying temperature. It shows the origin of physical aging because by cooling under T_g , the ideal specific volume should be lower than the real one in the glassy state.[174]

As this phenomenon is related to enthalpic relaxation, it can be typically measured using DSC. Specifically, the modulated DSC (MDSC) allows to separate the enthalpic relaxation peak from the glass transition step in the DSC heat flow scan. What makes this operation possible is the fact that, although it is a reversible phenomenon on its own, as it does not cause permanent damage to the polymer matrix (simply raising the polymer above T_g will restore its original properties), when compared to a process like the glass transition, from the perspective of the heat flow exchanged during the DSC measurement, physical aging is an irreversible process. This is why, using MDSC, it is possible to separate the two phenomena: the T_g will be observed in the curve corresponding to reversible heat flow, while the enthalpic peak of physical aging will appear in the non-reversible heat flow curve (Figure 1.18a). Therefore, the extent of aging is quantified by the enthalpy of the corresponding enthalpic relaxation peak in the non-reversing heat flow curve (Figure 1.18b).

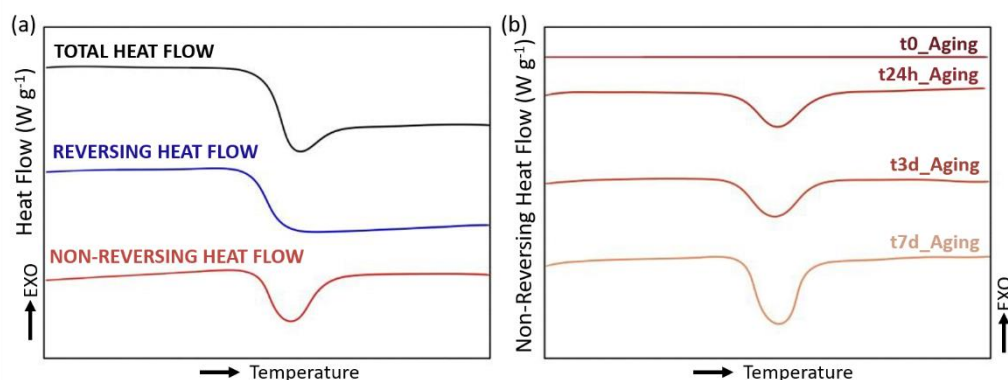


Figure 1.18 (a) Representative MDSC analysis showing the split of the total heat flow curve (black) into the reversing (blue) component and the non-reversing (red) one. (b) An example of an analysis on a sample that has undergone controlled physical aging, with non-reversing heat flow curves at various curing times: zero time ($t0$), 24 hours ($t24h$), 3 days ($t3d$), and 7 days ($t7d$).

Another technique employed to assess free volume, size, and characteristics of nanoscale holes in polymers is positron annihilation spectroscopy (PAS),[180] in particular the technique focused in annihilation lifetime (PALS).[181] PAS techniques involve the irradiation of polymers using positrons, the antiparticles of electrons. Once inside the polymer, a positron quickly loses its kinetic energy and combines with an electron, creating a positronium atom (Ps). Ps is a short-lived entity that annihilates when encountering an electron in the polymer matrix, emitting

two gamma rays. The lifetime of Ps is influenced by the dimensions of the free volume hole in which it is situated. Larger free volume holes result in longer Ps lifetimes. Measuring the Ps lifetime in a polymer sample enables PALS to determine the size and distribution of free volume holes.[182,183]

Fluorescence techniques offer an intriguing avenue for investigation since certain molecules exhibit photophysical properties that depend on the free volume and viscosity of the medium. This dependency is associated with a specific relationship observed in certain fluorophores between their mobility and the intensity of their emission. When these molecules can undergo intramolecular motions, they dissipate their energy through non-radiative pathways, resulting in low luminescence in low-viscosity and high free-volume environments. However, as the free volume of the medium decreases, their mobility becomes restricted, leading to an increase in the emission signal.[179,184–186] As an alternative to molecular rotors, Sung and colleagues have proposed the use of photoisomerizable probes to investigate variations in the free volume of polymer matrices.[185,186] They have found that the cis-trans conversion rate is sensitive to the level of free volume and exhibits a significant decrease during isothermal physical aging in glass after quenching from equilibrium melt. Similarly, Simha and collaborators utilized an excimer formation probe dispersed in a glassy epoxy matrix to observe changes in internal conversion as a function of free volume.[187,188]

1.5. Determination of mechanical stresses by using luminescent probes

The rising use of polymeric materials in industrial contexts has drawn greater scrutiny towards the detection of mechanical deterioration, particularly at the microscale. Although identifying such kinds of damages can be challenging, they significantly jeopardize mechanical robustness and culminate in eventual failure. Presently, prevalent approaches for damage assessment entail the application of ultrasonic waves and X-ray imaging. Nevertheless, these methodologies necessitate substantial and costly apparatus while potentially encountering sensitivity limitations.

[189] Consequently, the main challenge lies in achieving early detection of mechanical injuries in materials, through a simple and highly sensitive approach, to improve their performance. Mechanoresponsive materials, which exhibit an optical response when subjected to a mechanical action such as compression, stretching, or scratching, are particularly attractive and widely investigated.[190] These materials undergo changes in transparency, color, emission intensity, or emission spectrum due to the inclusion of a "mechanophore" within the polymer chains.[191] Mechanophores experience alterations in their absorbance and/or luminescence under mechanical input, caused by conformational changes in the polymer chains. These changes can result in alterations to the mechanophores' aggregation state, cleavage of noncovalent interactions, or even chemical changes like cleavage of covalent bonds.[48,192,193] There are various methods for classifying these materials, and one categorizes them on the basis of the optical property which changes in response to mechanical stimuli. They can be classified as mechanochromic (MC), mechanoluminochromic (MLC), and mechanoluminescent (ML) materials. In the case of MC materials, their absorption spectrum and, consequently, their color under white light changes. For MLC materials, the emission spectrum and often the emission intensity vary. Finally, ML materials do not require any photoexcitation because mechanical stress directly induces photon emission through chemiluminescence.[25,163]

As mentioned earlier, polymers typically do not possess specific optical properties, so they require the incorporation of a mechanophore into the matrix. There are two main strategies to achieve this. In the simpler approach the dye is loaded into the polymer matrix as an additive.[62,72] In this way, the optical properties of the luminophore depend solely on its interactions with the matrix. The mechanochromic properties depend on the polymer's ability to transmit mechanical stress to the mechanophore, which will respond by varying its optical properties. Alternatively, the polymer can be functionalized by covalently linking the mechanophore.[95,114,126] The dye can be included as a pendant group in a side chain or within the main polymer chain. Depending on its placement and the rigidity and conformation of the chains, the

effectiveness of transmitting mechanical stress to the active portion will vary, thus determining the extent of the mechanochromic effect.[194]

Polymer mechanoluminescent response in the bulk can be characterized by a proper use of the photophysical techniques described above, while the material is subjected to mechanical deformation, possibly by applying controlled forces and elongations. A number of different mechanical tests can be carried out by deforming the material in different modes (tension, compression, bending, shear). The most common mechanical characterization is the stress-strain test. Here, the sample with a controlled geometry (typically a dog-bone shape if working under tension) is deformed at a constant rate of strain by applying a controlled force up to failure. The resulting stress-strain curve provides information on the Young's modulus, yield and ultimate stress and strain. The various categories of polymers, i.e thermoplastics, thermoplastic elastomers, thermosettings and crosslinked elastomers, are characterized by different shapes of the stress-strain curve, as described in Figure 1.19.[25]

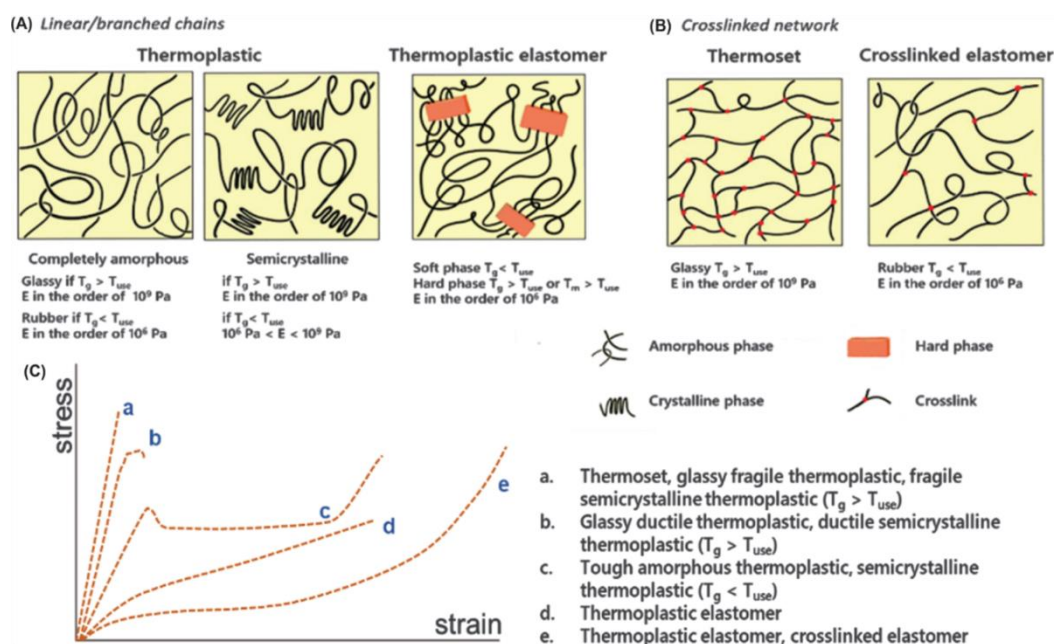


Figure 1.19 Schematic classification of polymers into: (A) systems with linear or branched chains (i.e. thermoplastics and thermoplastic elastomers) and (B) crosslinked polymers (i.e. thermosets and crosslinked elastomers). (C) Theoretical and ideal tensile stress-strain curves of polymeric materials. Reproduced from ref. [25] with permission from The Royal Society of Chemistry, Copyright © 2022.

This analysis makes it possible to quantitatively correlate the optical response with the mechanical stress imparted to polymers that are stretched to different extents.

Hence, below are a few examples of dyes utilized in the fabrication of mechanoresponsive materials, following the classification outlined earlier.

Among the mechanochromic materials, we can easily include compounds whose changes in the absorption spectrum (color) are activated by the rupture of a covalent bond. As seen, spiropyrans are among the most common examples.[99–102,195] In particular, these molecules are commonly incorporated within the polymer's main chain in the case of thermoplastics [114] and at the crosslinking sites of reticulated elastomers [107,196] to achieve a good transmission of the mechanical stress from the chain to the mechanophore (Figure 1.20). Recently, it has been demonstrated that techniques such as electrospinning, which allow the formation of fibers with highly aligned polymer chains inside, further contribute to directing stress onto the mechanophore contained within the polymer, promoting an earlier detection of the mechanochromic signal.[119]

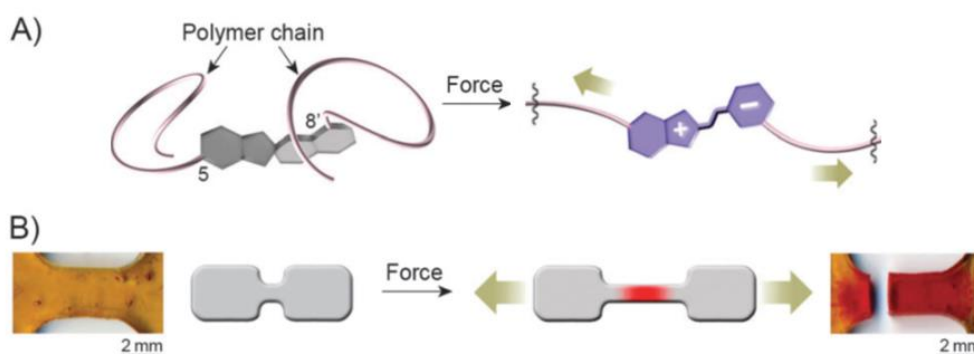


Figure 1.20 Spiropyran as a merocyanine dye inserted into the main chain of the polymer (B) Effect of uniaxial deformation on a dogbone-shaped sampled obtained from the spiro-modify polymer. Reproduced from ref. [99] with the permission from the Royal Society of Chemistry, Copyright © 2014.

In order to provide some examples for the other MLCs category, it is possible to find materials produced using both AIEgens [164,197,198] and aggregachromic [48,50,57,62,70–74,76,77,199] dyes. In the former case, AIE moieties can be covalently bound to the polymer, allowing for precise control over their position and composition within the system. For

instance, the introduction of 4,4'-((1Z,3Z)-1,4-diphenylbuta-1,3-diene-1,4-diyl) dibenzyl derivatives in varying proportions, particularly within the soft or hard segments of PUs,[200,201] resulted in enhanced fluorescence emission under tensile strains (Figure 1.21). Notably, this improvement only happened when the derivatives were included in the soft portions. In this case, stretching caused fluorescence amplification at first, which then started to drop as the tension increased. According to the authors, this behavior results from polyurethane's initial increase in regularity, which promotes aggregation and AIE effects, changing to a dominance of the dilution effect as a result of volume expansion.

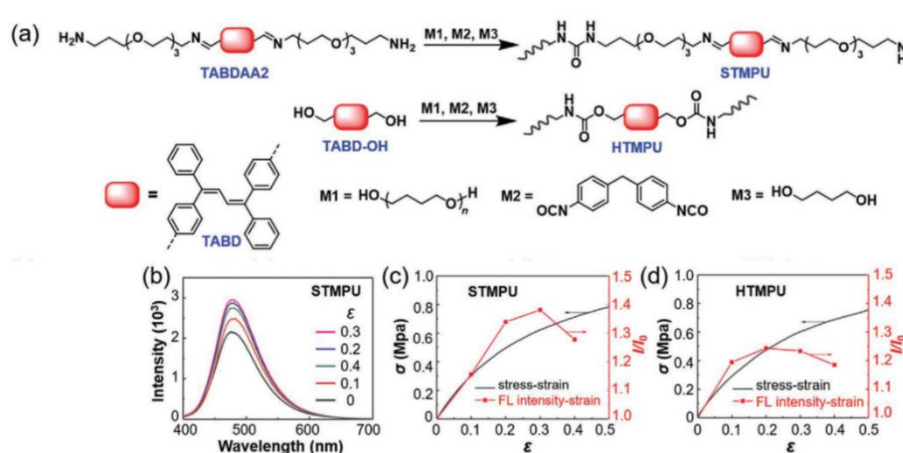


Figure 1.21 a) Two kinds of polyurethanes were modified by including: 4,4'-((1Z,3Z)-1,4-diphenylbuta-1,3-diene-1,4-diyl) dibenzaldehyde (TABDAA2) on the soft segments (STMPU) and with 4,4'-((1Z,3Z)-1,4-diphenylbuta-1,3-diene-1,4-diyl) dibenzyl alcohol (TABD-OH) on the hard segment (HTMPU), respectively. b) Fluorescence spectra of STMPU film at different tensile strains. Stress-strain curve and fluorescence peak intensity-strain curve of STMPU (c) and HTMPU (d) films. Adapted from ref. [202] with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Copyright © 2020.

Aggregachromic dyes are also used to develop MLC materials. When they are included in a polymeric matrix, the formation of aggregates is affected by factors such as their concentration, compatibility, and processing. Then, when subjected to a mechanical stress they can undergo a variation on their emission properties. As discussed above, the optical properties of these materials vary depending on their aggregation state, so the signal measurement is characterized by the change in the emission spectrum from the initial state, often characterized by aggregation, to the more characteristic state of the dispersed monomer. In the case of stretching, the disaggregation of these molecules is induced

by the sliding of the polymer chains. In particular, if crystalline phases are present in the polymer, they significantly contribute to the breaking of the aggregates (Figure 1.22). This results in a progressive increase in the monomer signal as the deformation increases.[57] In the case of compression or a certain impact force, on the other hand, the aggregates will be disassembled by the force itself.[203]

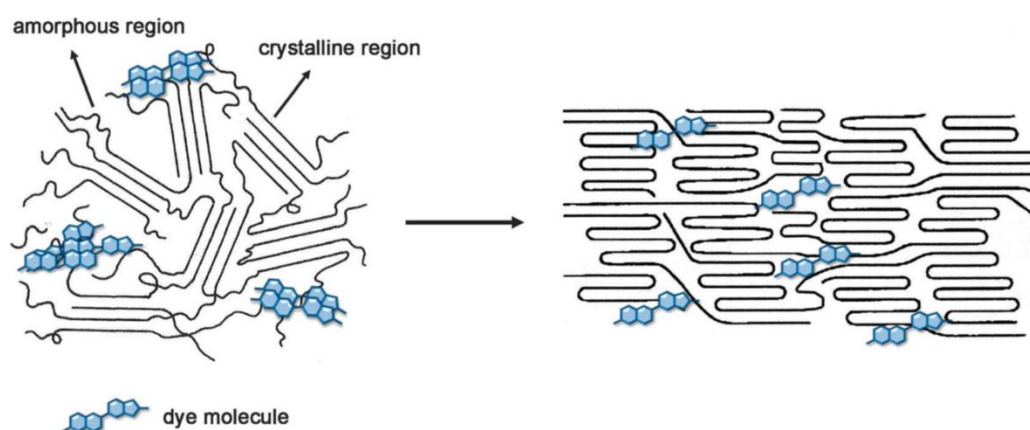


Figure 1.22 Shear induced disaggregation of a MLC dye in response to mechanical uniaxial deformation. Reproduced from ref. [204] with permission from the Royal Society of Chemistry, Copyright © 2013.

One of the most exemplary cases, given their widespread use and extensive study as aggregachromes, involves oligo(phenylene vinylene) derivatives (OPVs). Professor Weder and his research team were pioneers in employing OPVs to create mechanoluminochromic polymer matrices.[62] Through the incorporation of cyano-substituted OPVs in polyethylene, they observed a shift in emission color when the samples underwent mechanical deformation. This shift was attributed to the disruption of dye aggregates, causing the emission spectrum maximum peak to shift from excimer-based emission ($\lambda_{em}^{max} = 650 \text{ nm}$) to monomer-based emission ($\lambda_{em}^{max} = 500\text{-}550 \text{ nm}$). The alteration in the I_M/I_E ratio resulted in a fluorescence color change, with increased deformation, from orange to green (Figure 1.9). Professor Weder's group then focused on investigating various polymer matrices, starting with semi crystalline ones and subsequently exploring amorphous polymers. Their efforts led to the development of a novel class of aggregachromic dyes. By synthesizing telechelic polymers featuring cyanosubstituted dye segments from OPV at their termini,[193] they created dyes capable of getting entangled with the

polymer matrix chains. Consequently, these dyes exhibited remarkable responsiveness to mechanical stress, even in the absence of crystalline domains that typically induce aggregate disruption via strain (Figure 1.23).[205] The introduction of telechelics allowed them to extend the mechanoluminescent effect to a broad spectrum of polymers, yielding diverse outcomes contingent on the matrix's nature.

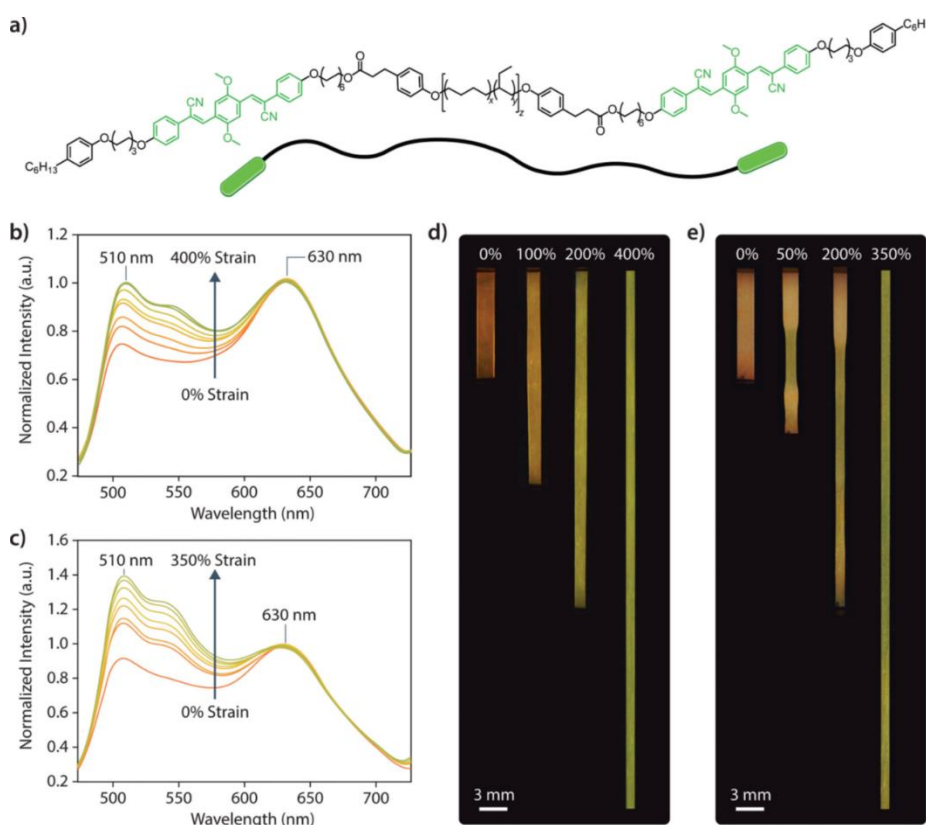


Figure 1.23 a) Chemical structure of the cyano-OPV functionalized telechelic poly(ethylene-co-butylene) (tOPV) that was employed as an additive in thermoplastic polyurethanes to confer mechanoluminescent properties. b, c) Fluorescence spectra of films of (b) a blend between a polyurethane features poly(tetrahydrofuran) as soft segment and 0.2 wt.% of tOPV (PU/tOPV) and (c) a blend between polyurethane contains poly(butylene adipate) (PBA) segments and 0.25 wt.% of tOPV (PBA-PU/tOPV) after being stretched to a strain of up to 400%. Spectra are normalized to the excimer signal at 630 nm. d, e) Images of samples of the (d) PU/tOPV (0.2 wt%) and (e) PBA-PU/tOPV (0.25 wt%) films taken under UV illumination ($\lambda_{\text{ex}} = 365 \text{ nm}$) after deformation to the indicated strains. Reproduced from ref. [205] with permission from Georg Thieme Verlag KG, Copyright © 2020.

Other examples of aggregachromic dyes commonly employed in MLC materials include pyrenes [52,77,199] and perylenes.[57,72,206] Their aggregation behavior is quite similar due to the structural resemblance, and it is well-documented. Typically, these dyes are utilized in material functionalization, either as pendant groups or integrated into the main

polymer chain. This enhances the mechanoluminochromic properties by facilitating more effective force transmission to the active components.

In a specific case, perylene, in the form of 1-Aminopyrene (AP), was grafted onto high-density and very low-density maleic anhydride-modified polyethylenes (HDPE-MAH and VLDPE-MAH).[207] Depending on the polymer matrix, different trends in the I_M/I_E ratio variation were observed as strain increased. Notably, the high-density sample exhibited a significant I_M/I_E ratio reduction, while the low-density variants demonstrated a linear decrease in the I_M/I_E ratio with elongation. This allows the creation of a calibration curve to assess and monitor material deformation.

The third category of mechanophores exploits bond cleavage and in a specific example the energy transfer to an acceptor to increase sensitivity and also obtain color tuning is involved. As mentioned in section 1.2.3, when subjected to mechanical stress, the donor, attached to the polymer, breaks, releasing energy that can be absorbed by the acceptor, thus initiating luminescence.[208] To achieve effective color tuning, the acceptor should possess a high emission quantum yield. For instance, bis(adamantyl)1,2-dioxetane (AD) was incorporated into segmented polyurethanes (PUs) with varying molecular weights and hard segments. [209] This enabled monitoring of diverse microphase separation by enhancing AD emission through FRET to 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole dispersed in the matrix. However, physical blending of the acceptor lacks precise control over key FRET parameters, such as donor-acceptor distance. Therefore, alternative strategies have been proposed for more efficient signaling systems.

In a different approach, mechanoluminescent PUs were synthesized by covalently incorporating both the donor (AD) and the acceptor (9,10-bis-(phenylethynyl) anthracene or 4,7-diphenylbenzo[c][1,2,5]thiadiazole) into the polymer chain. [123] Upon reaching failure strain, bright emission occurred, dependent on the ratio of donor/acceptor units and strain rate, resulting in enhanced mechanical sensitivity and a lowered force threshold to activate mechanoluminescence. The energy transfer mechanism has been utilized to amplify the emission of dioxetanes. As described in section 1.2.4, dioxetanes produce an optical signal in response to mechanical

deformation, which leads to their rupture and photon emission through chemiluminescence. This unique property eliminates the need for an excitation source, reducing background noise and scattered light. To further enhance emission intensity or modify the emission wavelength, the dioxetane can be combined with another molecule acting as an acceptor in the energy transfer process, resulting in more intense luminescence.[123]

Mechanochromism has been accomplished also by exploiting the breaking of non-covalent interactions in supramolecular polymers or polymers doped with supramolecular moieties. In supramolecular networks the building blocks are held together by non-covalent interactions, which are weak and reversible but can also be highly directional and selective. These interactions include multiple hydrogen bonds, π - π stacking, metal coordination, or electrostatic interactions.[210] Due to the multiplicity of interactions on which these polymers are built, their characteristics are extremely versatile. Importantly, because of the fragility of their couplings, supramolecular polymers[211,212] and polymers crosslinked with supramolecular systems can also respond to stimuli in a lower energy range. Specifically, a fluorescence response to mechanical stimuli can arise from the assembly and disassembly of the supramolecular system.[59,213–217] In the case of networks based on host-guest interactions,[218,219] a macrocyclic system (host), including crown ethers, cucurbit[n]urils, calix[n]arenes, and pillar[n]arenes,[220] can accommodate one or more guests (small molecules, typically the fluorophore). Dalcanale et al. have demonstrated the possibility of incorporating these systems both within the main chains of the polymer matrix [221] and at the crosslinking points (Figure 1.24).[222] In both cases, mechanical stress leads to the disassembly of the system. The fluorescence mechanism they employed is unique and advantageous because, initially, when all components are close and the system is assembled, it does not emit (off). However, following the mechanical stimulus that separates them, the fluorophore moves away from the quenching elements and begins to emit (on), hence the name of the off-on mechanism. The latter offers numerous advantages due to its high sensitivity in signal detection and the precision with which

it can be related to the deformation experienced by the material. While the example provided uses perylene as the fluorophore, which is one of the more classic options, supramolecular systems can harness all the photophysical mechanisms discussed so far.[223,224] This keeps the topic and potential applications in a state of constant expansion.

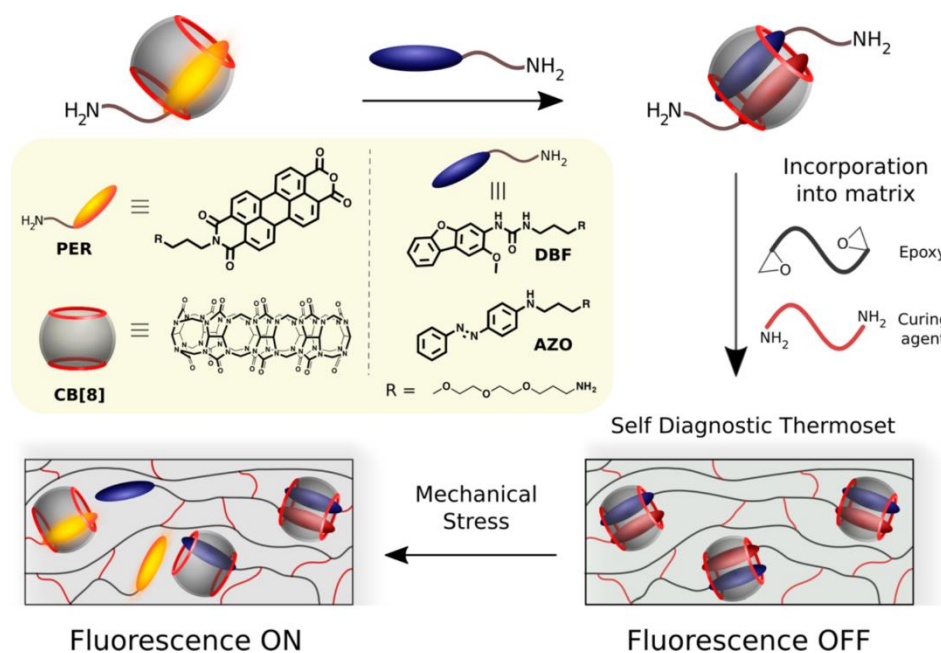


Figure 1.24 Illustration detailing the components of the supramolecular polymer composites developed by Dalcanele et al. and used for self-diagnostic, as well as the mechanism. Reproduced from ref. [222] with permission from American Chemical Society, Copyright © 2019.

1.6. Other processes determination

In addition to T_g and T_v detection, assessment of physical aging and of polymer mechanical failure, other phenomena that affect polymer microstructure and chain mobility can be monitored using fluorescent probes. Indeed, behind processes such as polymerization, crosslinking, polymer degradation, microphase separation, crystallization, and many others, lie variations in chain mobility, free volume, and viscosity changes.

Polymerization is a complex chemical process that transforms monomers into polymeric chains. Depending on the monomers' chemical functionality, this can occur through chain reactions or stepwise reactions. The resulting material can be linear, branched, or crosslinked.[3] As the polymerization progresses, viscosity increases

significantly.[225] Thus, viscosity-sensitive probes are suitable for monitoring these reactions. In this context, various types of luminescent probes have been studied. Lautfy et al., for instance, proposed the use of molecular rotors that emit through a charge transfer mechanism.[226] Their emission is triggered when the viscosity during polymerization prevents the intramolecular rotation of these probes, allowing them to assume the proper conformation for initiating the intramolecular charge transfer process.[24] Subsequently, other studies focused on pyrene probes. It was observed that the ability of this dye to form aggregates was significantly affected by the increasing viscosity during polymerization.[227,228] A linear relationship was established between the progress of polymerization and the ratio of monomer intensity to excimer intensity.[54] Furthermore, researchers were able to determine how the gel point varies with temperature.[229] While these findings related to pyrene may seem promising, as mentioned earlier, molecular rotors are more suitable for viscosity studies, as they do not rely on the probe's diffusion to form excimers and aggregates.

Similarly, during curing process, the matrix viscosity increases significantly. In fact, as the crosslinking reactions progress, fluorescence monitoring of the matrix's stiffening could be carried out, using twisted intramolecular charge transfer fluorescent probes. As molecular rotors, they emit when intramolecular motions are restricted by the surrounding medium.[230]

Leveraging the same principle, molecular rotors can be used also to discern microphase separations occurring in blends of immiscible polymers. An AIE substance dispersed in different matrices will emit inversely proportional to the mobility within the matrix. This approach allows for the creation of true phase separation maps (Figure 1.25).[231] Moreover, in the same way, it is also possible to determine the water uptake by polymers if it acts as a plasticizer, increasing the matrix's mobility.[232]

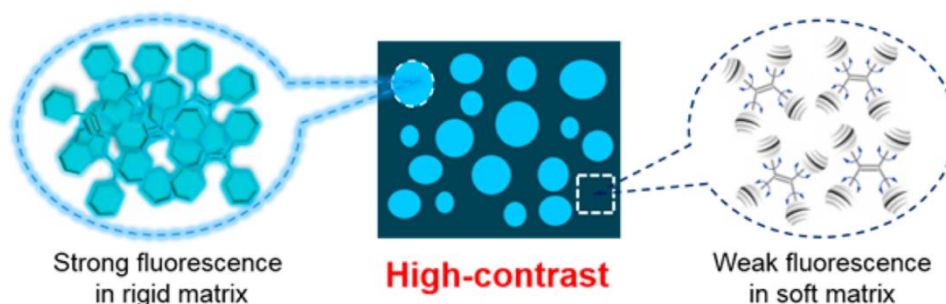


Figure 1.25 Diagram illustrating how phase separation between two matrices of varying rigidity, containing a dispersed AIE luminophore, becomes easily visible thanks to the RIM effect. Adapted from ref. [231] with permission from American Chemical Society, Copyright © 2017.

On the other hand, processes resulting from the action of chemical and physical agents such as oxygen, humidity, UV irradiation, and thermal gradients lead to the decomposition and structural deterioration of polymers, resulting in chain shortening, lower molecular weight, and consequently reduced viscosity.[233] One of the methods available for monitoring chemical aging in common polymers such as polypropylene (PP) and polyethylene (PE), is based on the oxidation of tertiary carbons, leading to the formation of hydroxyl groups(-OH). The formation of these groups can be easily monitored and mapped using specific probes that react with -OH groups and attach to the polymer chain, restricting their internal motions.[234] This technique has enabled the creation of 3D reproductions of areas deteriorated by various aging processes.

Finally, fluorescent probes were used to monitor polymer melting and crystallization. Commonly during polymer processing, crystallization occurs from the melt under non-isothermal conditions [235] and the resulting crystal phase significantly influences key industrial properties such as thermal resistance, toughness, optical transparency, gas permeability, and degradation rate.[236]

Traditional techniques for characterizing polymer crystal phase monitor variations in chain conformation, microstructure, and thermal, mechanical, and optical properties as a function of temperature. For instance, DSC can provide enthalpy values for both crystallization and melting. Other techniques rely on spectroscopic methods, such as ellipsometry, FTIR, and Raman spectroscopy, or on scattering phenomena, including X-ray Diffraction (XRD) and Small/Wide-Angle X-ray Scattering

(SAXS/WAXS). While these techniques are widely used, they often require large-scale equipment and can have limitations in sensitivity.[5,237–242]

In this context, as in other previously discussed areas, the introduction of fluorescence spectroscopic methods is a promising initiative. Since crystallization primarily influences the mobility and conformation of polymer chains, AIE fluorophores have been extensively utilized. When dispersed or covalently bound, AIE fluorophores are excluded from the polymer during the formation of the crystalline phase and are confined to the amorphous regions between crystals,[2,243] reducing their mobility and enhancing their emission.

Several studies have been conducted at varying temperatures to observe changes in the signal intensity of various AIE fluorophores. For instance, Nile et al. investigated the effect of cooling rate in a poly(L-lactic acid) (PLLA) matrix covalently functionalized with the CN4OH fluorophore, which is sensitive to changes in crystallinity (Figure 1.26a). [236,244] Khorloo et al. used a derivative of TPE, whose emission is dependent on polymorphism. This fluorophore emits at different wavelengths (green and yellow) depending on the crystalline form present. By dispersing this fluorophore in PLLA, they were able to identify amorphous regions and distinguish them from the boundaries with the spherulites of the crystalline phase (Figure 1.26b).[245]

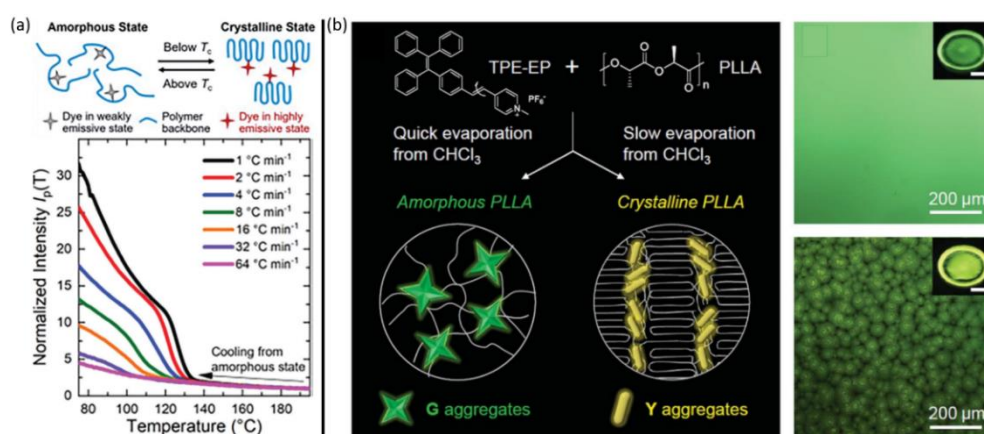


Figure 1.26 (a) Top: Scheme of the PLLA covalently labeled with the CN4OH fluorophore (e.g., CN-PLLA) weakly emissive above crystallization temperature (T_c) and highly emissive below it. Bottom: Normalized emission intensity over temperature of CN-PLLA at various cooling rates. Adapted from ref. [236] with permission from Wiley-VCH GmbH, Copyright © 2023. (b) Left: Different morphology of semicrystalline PLLA embedded with TPE-EP and the schematic representation of TPE-EP different polymorphism. Right: emission images of the amorphous (top) and crystalline (bottom) polymer films. Adapted from ref. [245] with permission from the Royal Society of Chemistry, Copyright © 2020.

1.7. References

- [1] Council, N.R. (1994). *Polymer Science and Engineering: The Shifting Research Frontiers*, The National Academies Press.
- [2] Ge, S. et al. (2022). Aggregation-Induced Emission Boosting the Study of Polymer Science. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.202200080.
- [3] Bosch, P. et al. (2005). Fluorescent probes for sensing processes in polymers. *Chemistry - A European Journal*. DOI: 10.1002/chem.200401349.
- [4] Schneider, H.A. and Di Marzio, E.A. (1992). The glass temperature of polymer blends: comparison of both the free volume and the entropy predictions with data. *Polymer*. DOI: 10.1016/0032-3861(92)91103-9.
- [5] Patki, R. et al. (2007). Crystallization Kinetics of Polymers, in *Physical Properties of Polymers Handbook* (eds.Mark, J.E.), New York, N, pp. 625–640.
- [6] Plazek, D.J. and Ngai, K.L. (2007). The Glass Temperature. *Physical Properties of Polymers Handbook*. DOI: 10.1007/978-0-387-69002-5_12.
- [7] Forrest, J.A. et al. (1996). Effect of free surfaces on the glass transition temperature of thin polymer films. *Physical Review Letters*. DOI: 10.1103/PhysRevLett.77.2002.
- [8] Yang, Z. et al. (2010). Glass transition dynamics and surface layer mobility in unentangled polystyrene films. *Science*. DOI: 10.1126/science.1184394.
- [9] Torres, J.M. et al. (2009). Elastic modulus of amorphous polymer thin films: Relationship to the glass transition temperature. *ACS Nano*. DOI: 10.1021/nn9006847.
- [10] Cheng, S.Z.D. and Wunderlich, B. (1988). Thermal analysis of thermoplastic polymers. *Thermochimica Acta*. DOI: 10.1016/0040-6031(88)85232-8.
- [11] Kong, E.S.-W. (1986). Physical aging in epoxy matrices and composites. DOI: 10.1007/3-540-16423-5_14.
- [12] Schwab, S.D. and Levy, R.L. (1990). Free-Volume-Dependent Fluorescence Probes of Physical Aging in Polymers. DOI: 10.1021/ba-1990-0227.ch023.

- [13] Swapna, V.P. et al. (2020). *Polymer/polyhedral oligomeric silsesquioxane nanocomposite membranes for pervaporation*, INC.
- [14] Nagamatsu, K. (1960). On the viscoelastic properties of crystalline high polymers. *Kolloid-Zeitschrift*. DOI: 10.1007/BF01515798.
- [15] Mileva, D. et al. (2018). Designing polymer crystallinity: An industrial perspective. *Polymer Crystallization*. DOI: 10.1002/pcr2.10009.
- [16] Gahleitner, M. et al. (2016). Crystallinity-based product design: Utilizing the polymorphism of isotactic pp homoand copolymers. *International Polymer Processing*. DOI: 10.3139/217.3242.
- [17] Crawford, C.B. and Quinn, B. (2017). Physiochemical properties and degradation, in *Microplastic Pollutants*, Elsevier, pp. 57–100.
- [18] Nielsen, L.E. (1969). Cross-Linking–Effect on Physical Properties of Polymers. *Journal of Macromolecular Science, Part C*. DOI: 10.1080/15583726908545897.
- [19] Chen, J. et al. (2020). Intramolecularly Cross-Linked Polymers: From Structure to Function with Applications as Artificial Antibodies and Artificial Enzymes. *Accounts of Chemical Research*. DOI: 10.1021/acs.accounts.0c00178.
- [20] Burfield, D.R. (1983). Differential Scanning Calorimetry Characterization of Polypropylene. Dependence of Tg on Polymer Tacticity and Molecular Weight. *Macromolecules*. DOI: 0024-9297/83/2216-0702\$01.50/0.
- [21] Hofstraat, J.W. (2000). Polymer Characterization By Fluorescence Spectroscopy, in *Applied Polymer Science: 21st Century* (eds.Craver, C.D., and Carraher, C.E.), Pergamon, pp. 829–850.
- [22] Itagaki, H. (2000). Fluorescence Spectroscopy, in *Experimental Methods in Polymer Science: Modern Methods in Polymer Research and Technology* (eds.Tanaka, T.), Academic Press, pp. 155–260.
- [23] Díaz-García, M.E. and Badía-Laiño, R. (2019). Fluorescence | Overview, in *Encyclopedia of Analytical Science* (eds.Worsfold, P. et al.), ACADEMIC PRESS, pp. 309–319.
- [24] Wang, Z.J. et al. (1996). Fluorescence probes for monitoring polymerization

- processes. *Journal of Polymer Science, Part B: Polymer Physics*. DOI: 10.1002/(SICI)1099-0488(19960130)34:2<325::AID-POLB13>3.0.CO;2-L.
- [25] Gualandi, C. et al. (2022). Mechanoresponsive luminescence in polymeric materials: strategies and methods, in *Photochemistry*, vol. 50, pp. 458–490.
- [26] Sun, Y. et al. (2022). Twisted aggregation-induced emission luminogens (AIEgens) contribute to mechanochromism materials: a review. *Journal of Materials Chemistry C*. DOI: 10.1039/d2tc02512d.
- [27] He, Z. et al. (2018). Journey of Aggregation-Induced Emission Research. *ACS Omega*. DOI: 10.1021/acsomega.8b00062.
- [28] Luo, J. et al. (2001). Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. *Chemical Communications*. DOI: 10.1039/b105159h.
- [29] Hong, Y. et al. (2009). Aggregation-induced emission: Phenomenon, mechanism and applications. *Chemical Communications*. DOI: 10.1039/b904665h.
- [30] Mei, J. et al. (2015). Aggregation-Induced Emission: Together We Shine, United We Soar! *Chemical Reviews*. DOI: 10.1021/acs.chemrev.5b00263.
- [31] Chen, G. et al. (2015). Conjugation-Induced Rigidity in Twisting Molecules: Filling the Gap between Aggregation-Caused Quenching and Aggregation-Induced Emission. *Advanced Materials*. DOI: 10.1002/adma.201501981.
- [32] Hong, Y. et al. (2011). Aggregation-induced emission. *Chemical Society Reviews*. DOI: 10.1039/c1cs15113d.
- [33] Leung, N.L.C. et al. (2014). Restriction of intramolecular motions: The general mechanism behind aggregation-induced emission. *Chemistry - A European Journal*. DOI: 10.1002/chem.201403811.
- [34] Bao, S. et al. (2015). Sensitive and reliable detection of glass transition of polymers by fluorescent probes based on AIE luminogens. *Polymer Chemistry*. DOI: 10.1039/c5py00308c.
- [35] Pucci, A. (2022). AIE Polymer Films for Optical Sensing and Energy Harvesting. *Handbook of Aggregation-Induced Emission: Emerging applications*. DOI: 10.1002/9781119643098.ch43.
- [36] Han, T. et al. (2012). A novel “turn-on” fluorescent chemosensor for the

- selective detection of Al^{3+} based on aggregation-induced emission. *Chemical Communications*. DOI: 10.1039/c1cc15681k.
- [37] Anuradha et al. (2016). Selective detection of nitrite ion by an AIE-active tetraphenylethene dye through a reduction step in aqueous media. *RSC Advances*. DOI: 10.1039/c6ra06800f.
- [38] Bineci, M. et al. (2016). AIE active pyridinium fused tetraphenylethene: Rapid and selective fluorescent “turn-on” sensor for fluoride ion in aqueous media. *Sensors and Actuators, B: Chemical*. DOI: 10.1016/j.snb.2015.08.087.
- [39] Wu, Y. wei et al. (2017). AIE-active polymers for explosive detection. *Chinese Journal of Polymer Science (English Edition)*. DOI: 10.1007/s10118-017-1882-0.
- [40] Yang, X. et al. (2016). A highly selective and sensitive fluorescent chemosensor for detection of CN^- , SO_3^{2-} and Fe^{3+} based on aggregation-induced emission. *Journal of Materials Chemistry C*. DOI: 10.1039/c5tc02865e.
- [41] Hirata, S. and Watanabe, T. (2006). Reversible Thermoresponsive Recording of Fluorescent Images (TRF). *Advanced Materials*. DOI: 10.1002/adma.200600209.
- [42] Han, T. et al. (2015). A diethylaminophenol functionalized Schiff base: crystallization-induced emission-enhancement, switchable fluorescence and application for security printing and data storage. *Journal of Materials Chemistry C*. DOI: 10.1039/c5tc00891c.
- [43] Li, S. et al. (2015). Color-tunable and highly solid emissive AIE molecules: Synthesis, photophysics, data storage and biological application. *Journal of Materials Chemistry C*. DOI: 10.1039/c4tc02691h.
- [44] Hu, L. et al. (2016). Stimuli-responsive fluorophores with aggregation-induced emission: Implication for dual-channel optical data storage. *Journal of Materials Chemistry C*. DOI: 10.1039/c6tc01179a.
- [45] Yang, Y. et al. (2013). Luminescent chemodosimeters for bioimaging. *Chemical Reviews*. DOI: 10.1021/cr2004103.
- [46] Taniguchi, R. et al. (2014). Stimuli-responsive fluorescence of AIE elastomer based on PDMS and tetraphenylethene. *Macromolecules*. DOI:

10.1021/ma501198d.

- [47] Zhu, X. et al. (2014). An AIE-active boron-difluoride complex: Multi-stimuli-responsive fluorescence and application in data security protection. *Chemical Communications*. DOI: 10.1039/c4cc05913a.
- [48] Traeger, H. et al. (2021). From Molecules to Polymers—Harnessing Inter- and Intramolecular Interactions to Create Mechanochromic Materials. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.202000573.
- [49] Bhosale, S. V. et al. (2021). Naphthalene diimides: Perspectives and promise. *Chemical Society Reviews*. DOI: 10.1039/d0cs00239a.
- [50] Pucci, A. and Ruggeri, G. (2011). Mechanochromic polymer blends. *Journal of Materials Chemistry*. DOI: 10.1039/c0jm03653f.
- [51] Mishra, A. et al. (2000). Cyanines during the 1990s: a review. *Chemical Reviews*. DOI: 10.1021/cr990402t.
- [52] Wang, T. et al. (2020). Pyrene Functionalized Mechanochromic Elastomer with Switchable White Fluorescence. *Macromolecular Chemistry and Physics*. DOI: 10.1002/macp.201900463.
- [53] Rossi, N.A.A. et al. (2009). Synthesis and characterisation of pyrene-labelled polydimethylsiloxane networks: Towards the in situ detection of strain in silicone elastomers. *Journal of Materials Chemistry*. DOI: 10.1039/b908708g.
- [54] Valdes-Aguilera, O. et al. (1990). Pyrene as a Fluorescent Probe for Monitoring Polymerization Rates. *Macromolecules*. DOI: 10.1021/ma00204a055.
- [55] Gao, Y. et al. (2018). Excimer formation and evolution of excited state properties in discrete dimeric stacking of an anthracene derivative: A computational investigation. *Physical Chemistry Chemical Physics*. DOI: 10.1039/c8cp00834e.
- [56] Göstl, R. and Sijbesma, R.P. (2016). π -Extended Anthracenes As Sensitive Probes for Mechanical Stress. *Chemical Science*. DOI: 10.1039/c5sc03297k.
- [57] Traeger, H. et al. (2021). Folded Perylene Diimide Loops as Mechanoresponsive Motifs. *Angewandte Chemie - International Edition*. DOI:

10.1002/anie.202105219.

- [58] Traeger, H. et al. (2022). Strain-correlated mechanochromism in different polyurethanes featuring a supramolecular mechanophore. *Polymer Chemistry*. DOI: 10.1039/d2py00218c.
- [59] Das, A.D. et al. (2020). Damage-reporting carbon fiber epoxy composites. *ACS Applied Polymer Materials*. DOI: 10.1021/acsapm.9b00694.
- [60] Calvino, C. and Weder, C. (2018). Microcapsule-Containing Self-Reporting Polymers. *Small*. DOI: 10.1002/smll.201802489.
- [61] Kunzelman, J. et al. (2008). Oligo(p-phenylene vinylene)s as a “new” class of piezochromic fluorophores. *Advanced Materials*. DOI: 10.1002/adma.200701772.
- [62] Löwe, C. and Weder, C. (2002). Oligo(p-phenylene vinylene) excimers as molecular probes: Deformation-induced color changes in photoluminescent polymer blends. *Advanced Materials*. DOI: 10.1002/1521-4095(20021118)14:22<1625::AID-ADMA1625>3.0.CO;2-Q.
- [63] Lavrenova, A. et al. (2016). Deformation-Induced Color Changes in Melt-Processed Polyamide 12 Blends. *Macromolecular Materials and Engineering*. DOI: 10.1002/mame.201500403.
- [64] Roberts, D.R.T. and Holder, S.J. (2011). Mechanochromic systems for the detection of stress, strain and deformation in polymeric materials. *Journal of Materials Chemistry*. DOI: 10.1039/c0jm04237d.
- [65] Birks, J.B. (1975). Excimers. *Rep. Prog. Phys.*
- [66] Jenekhe, S.A. and Osaheni, J.A. (1994). Excimers and exciplexes of conjugated polymers. *Science*. DOI: 10.1126/science.265.5173.765.
- [67] Jenekhe, S.A. (1995). Excited-state complexes of conjugated polymers. *Advanced Materials*. DOI: 10.1002/adma.19950070314.
- [68] Valeur, B. (2001). *Molecular Fluorescence Principles and Applications*.
- [69] Lakowicz, J.R. (2006). *Principles of fluorescence spectroscopy*.
- [70] Pucci, A. et al. (2005). Luminescent bis(benzoxazolyl)stilbene as a molecular probe for poly(propylene) film deformation. *Macromolecular Rapid*

Communications. DOI: 10.1002/marc.200500227.

- [71] Pucci, A. et al. (2011). Polymer composites with smart optical properties. *Soft Matter*. DOI: 10.1039/c0sm01038c.
- [72] Donati, F. et al. (2008). Modulation of the optical response of polyethylene films containing luminescent perylene chromophores. *Journal of Physical Chemistry B*. DOI: 10.1021/jp711193u.
- [73] Pucci, A. et al. (2007). Bis(benzoxazoly)stilbene excimers as temperature and deformation sensors for biodegradable poly(1,4-butylene succinate) films. *Journal of Materials Chemistry*. DOI: 10.1039/b612033d.
- [74] Kunzelman, J. et al. (2006). Self-assembly and dispersion of chromogenic molecules: a versatile and general approach for self-assessing polymers. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.200600642.
- [75] Kinami, M. et al. (2006). Polyesters with built-in threshold temperature and deformation sensors. *Chemistry of Materials*. DOI: 10.1021/cm052186c.
- [76] Crenshaw, B.R. and Weder, C. (2006). Self-assessing photoluminescent polyurethanes. *Macromolecules*. DOI: 10.1021/ma061685b.
- [77] Cellini, F. et al. (2016). Mechanochromic response of pyrene functionalized nanocomposite hydrogels. *Sensors and Actuators, B: Chemical*. DOI: 10.1016/j.snb.2016.04.149.
- [78] Union, I. et al. (2014). Glossary of Terms Used in Photochemistry. *Chemistry International -- Newsmagazine for IUPAC*. DOI: 10.1515/ci.2003.25.1.16c.
- [79] Strieth-Kalthoff, F. et al. (2018). Energy transfer catalysis mediated by visible light: principles, applications, directions. *Chemical Society Reviews*. DOI: 10.1039/c8cs00054a.
- [80] May, V. and Kühn, O. (2011). Excitation Energy Transfer, in *Charge and Energy Transfer Dynamics in Molecular Systems: Third Edition*, Wiley-VCH Verlag, pp. 467–558.
- [81] Rajdev, P. and Ghosh, S. (2019). Fluorescence Resonance Energy Transfer (FRET): A Powerful Tool for Probing Amphiphilic Polymer Aggregates and Supramolecular Polymers. *Journal of Physical Chemistry B*. DOI: 10.1021/acs.jpcb.8b09441.

- [82] Skourtis, S.S. et al. (2016). Dexter Energy transfer pathways. *Proceedings of the National Academy of Sciences of the United States of America*. DOI: 10.1073/pnas.1517189113.
- [83] Bai, S. et al. (2019). Quantum interferences among Dexter energy transfer pathways. *Faraday Discussions*. DOI: 10.1039/c9fd00007k.
- [84] Cravcenko, A. et al. (2020). Interplay between Förster and Dexter Energy Transfer Rates in Isomeric Donor-Bridge-Acceptor Systems. *Journal of Physical Chemistry A*. DOI: 10.1021/acs.jpca.0c05035.
- [85] Lakowicz, J.R. et al. (1990). Conformational distributions of melittin in water / methanol mixtures from frequency-domain measurements of nonradiative energy transfer. *Biophysical Chemistry*. DOI: 10.1016/0301-4622(90)85014-W.
- [86] Rye, H.S. (2001). Application of fluorescence resonance energy transfer to the GroEL-GroES chaperonin reaction. *Methods*. DOI: 10.1006/meth.2001.1188.
- [87] Chapman, E.R. et al. (1992). Fluorescence Energy Transfer Analysis of Calmodulin ·Peptide Complexes. *Biochemistry*. DOI: 10.1021/bi00166a016.
- [88] Tsuji, A. et al. (2000). Direct observation of specific messenger RNA in a single living cell under a fluorescence microscope. *Biophysical Journal*. DOI: 10.1016/S0006-3495(00)76862-7.
- [89] Yang, F. et al. (2020). Sensitized Mechanoluminescence Design toward Mechanically Induced Intense Red Emission from Transparent Polymer Films. *Macromolecules*. DOI: 10.1021/ACS.MACROMOL.9B02221/SUPPL_FILE/MA9B02221_SI_003.AVI.
- [90] Yuan, Y. et al. (2021). Mechanically Induced Bright Luminescence from 1,2-Dioxetane Containing PDMS Boosted by Fluoroboron Complex as an In-Chain Fluorophore. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.202000575.
- [91] Wu, M. et al. (2021). Semi-IPNs Reinforced with Silica Janus Nanoparticles and Their Stress Sensing with Mechanoluminescent Probe. *Macromolecular Rapid Communications*. DOI: 10.1002/MARC.202000442.
- [92] Kato, S. et al. (2021). Visualization of the Necking Initiation and Propagation

- Processes during Uniaxial Tensile Deformation of Crystalline Polymer Films via the Generation of Fluorescent Radicals. *ACS Macro Letters*. DOI: 10.1021/acsmacrolett.1c00185.
- [93] Stratigaki, M. and Göstl, R. (2020). Methods for Exerting and Sensing Force in Polymer Materials Using Mechanophores. *ChemPlusChem*. DOI: 10.1002/cplu.201900737.
- [94] Willis-Fox, N. et al. (2018). Polymer Mechanochemistry: Manufacturing Is Now a Force to Be Reckoned With. *Chem*. DOI: 10.1016/J.CHEMPR.2018.08.001.
- [95] Imato, K. et al. (2015). Mechanophores with a reversible radical system and freezing-induced mechanochemistry in polymer solutions and gels. *Angewandte Chemie - International Edition*. DOI: 10.1002/anie.201412413.
- [96] Imato, K. et al. (2015). Mechanochromic Dynamic Covalent Elastomers: Quantitative Stress Evaluation and Autonomous Recovery. *ACS Macro Letters*. DOI: 10.1021/acsmacrolett.5b00717.
- [97] Wang, T. et al. (2017). Novel Reversible Mechanochromic Elastomer with High Sensitivity: Bond Scission and Bending-Induced Multicolor Switching. *ACS Applied Materials and Interfaces*. DOI: 10.1021/acsami.7b00176.
- [98] Wang, L. et al. (2018). Rhodamine-functionalized mechanochromic and mechanofluorescent hydrogels with enhanced mechanoresponsive sensitivity. *Polymers*. DOI: 10.3390/polym10090994.
- [99] Klajn, R. (2014). Spiropyran-based dynamic materials. *Chemical Society Reviews*. DOI: 10.1039/c3cs60181a.
- [100] Minkin, V.I. (2004). Photo-, thermo-, solvato-, and electrochromic spiroheterocyclic compounds. *Chemical Reviews*. DOI: 10.1021/cr020088u.
- [101] Kortekaas, L. and Browne, W.R. (2019). The evolution of spiropyran: Fundamentals and progress of an extraordinarily versatile photochrome. *Chemical Society Reviews*. DOI: 10.1039/c9cs00203k.
- [102] Towns, A. (2021). Spiropyran dyes. *Physical Sciences Reviews*. DOI: 10.1515/psr-2020-0197.
- [103] Keyvan Rad, J. et al. (2022). Spiropyran-based advanced photoswitchable

- materials: A fascinating pathway to the future stimuli-responsive devices. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. DOI: 10.1016/j.jphotochemrev.2022.100487.
- [104] Cottone, G. et al. (2004). Theoretical study of spiropyran-merocyanine thermal isomerization. *Chemical Physics Letters*. DOI: 10.1016/j.cplett.2004.03.016.
- [105] Wojtyk, J.T.C. et al. (2007). Elucidating the mechanisms of acidochromic spiropyran-merocyanine interconversion. *Journal of Physical Chemistry A*. DOI: 10.1021/jp068575r.
- [106] Zhang, H. et al. (2014). Spiropyran as a mechanochromic probe in dual cross-linked elastomers. *Macromolecules*. DOI: 10.1021/MA500760P/SUPPL_FILE/MA500760P_SI_001.PDF.
- [107] Kim, T.A. et al. (2018). Mechanical Reactivity of Two Different Spiropyran Mechanophores in Polydimethylsiloxane. *Macromolecules*. DOI: 10.1021/acs.macromol.8b01919.
- [108] Lee, C.K. et al. (2010). Force-induced redistribution of a chemical equilibrium. *Journal of the American Chemical Society*. DOI: 10.1021/ja106332g.
- [109] Weder, C. (2009). Polymers react to stress. *Nature*. DOI: 10.1038/459045a.
- [110] O'Bryan, G. et al. (2010). Stress sensing in polycaprolactone films via an embedded photochromic compound. *ACS Applied Materials and Interfaces*. DOI: 10.1021/am100050v.
- [111] Mandal, M. et al. (2022). Spiropyran-Merocyanine Based Photochromic Fluorescent Probes: Design, Synthesis, and Applications. *ACS Omega*. DOI: 10.1021/acsomega.2c04969.
- [112] Ali, A.A. et al. (2020). Chemo- and biosensing applications of spiropyran and its derivatives - A review. *Analytica Chimica Acta*. DOI: 10.1016/j.aca.2020.01.057.
- [113] Li, M. et al. (2018). Let spiropyran help polymers feel force! *Progress in Polymer Science*. DOI: 10.1016/j.progpolymsci.2017.11.001.
- [114] Davis, D.A. et al. (2009). Force-induced activation of covalent bonds in

- mechanoresponsive polymeric materials. *Nature*. DOI: 10.1038/nature07970.
- [115] Chen, H. et al. (2017). A Novel Design of Multi-Mechanoresponsive and Mechanically Strong Hydrogels. *Advanced Materials*. DOI: 10.1002/adma.201606900.
- [116] Cao, Z. (2020). Highly Stretchable Tough Elastomers Crosslinked by Spiropyran Mechanophores for Strain-Induced Colorimetric Sensing. *Macromolecular Chemistry and Physics*. DOI: 10.1002/macp.202000190.
- [117] Sommer, M. (2021). Substituent Effects Control Spiropyran–Merocyanine Equilibria and Mechanochromic Utility. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.202000597.
- [118] Rohde, R.C. et al. (2019). Mechanochromic composite elastomers for additive manufacturing and low strain mechanophore activation. *Polymer Chemistry*. DOI: 10.1039/c9py01053j.
- [119] Raisch, M. et al. (2018). Highly Sensitive, Anisotropic, and Reversible Stress/Strain-Sensors from Mechanochromic Nanofiber Composites. *Advanced Materials*. DOI: 10.1002/ADMA.201802813.
- [120] Chen, Y. and Sijbesma, R.P. (2014). Dioxetanes as mechanoluminescent probes in thermoplastic elastomers. *Macromolecules*. DOI: 10.1021/ma500598t.
- [121] Clough, J.M. et al. (2017). Mechanoluminescent Imaging of Osmotic Stress-Induced Damage in a Glassy Polymer Network. *Macromolecules*. DOI: 10.1021/acs.macromol.6b02540.
- [122] Yan, C. et al. (2019). Phase-Locked Dynamic and Mechanoresponsive Bonds Design toward Robust and Mechanoluminescent Self-Healing Polyurethanes: A Microscopic View of Self-Healing Behaviors. *Macromolecules*. DOI: 10.1021/ACS.MACROMOL.9B02089/SUPPL_FILE/MA9B02089_SI_001.PDF.
- [123] Yuan, W. et al. (2018). Improving Mechanoluminescent Sensitivity of 1,2-Dioxetane-Containing Thermoplastic Polyurethanes by Controlling Energy Transfer across Polymer Chains. *Macromolecules*. DOI: 10.1021/acs.macromol.8b01668.
- [124] Zaklika, K.A. et al. (1979). Mechanisms of 1,2-Dioxetane Decomposition: the

- Role of Electron Transfer. *Photochemistry and Photobiology*. DOI: 10.1111/j.1751-1097.1979.tb07111.x.
- [125] Beck, S. and Köster, H. (1990). Applications of Dioxetane Chemiluminescent Probes to Molecular Biology. *Analytical Chemistry*. DOI: 10.1021/ac00220a003.
- [126] Chen, Y. et al. (2012). Mechanically induced chemiluminescence from polymers incorporating a 1,2-dioxetane unit in the main chain. *Nature Chemistry*. DOI: 10.1038/nchem.1358.
- [127] Hirano, T. and Matsushashi, C. (2022). A stable chemiluminophore, adamantylideneadamantane 1,2-dioxetane: from fundamental properties to utilities in mechanochemistry and soft crystal science. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. DOI: 10.1016/J.PHOTOCHEMREV.2022.100483.
- [128] Beija, M. et al. (2009). Synthesis and applications of rhodamine derivatives as fluorescent probes. *Chemical Society Reviews*. DOI: 10.1039/b901612k.
- [129] Kim, H.N. et al. (2008). A new trend in rhodamine-based chemosensors: Application of spirolactam ring-opening to sensing ions. *Chemical Society Reviews*. DOI: 10.1039/b802497a.
- [130] Berro, A.J. et al. (2012). Super-resolution optical measurement of nanoscale photoacid distribution in lithographic materials. *ACS Nano*. DOI: 10.1021/nn304285m.
- [131] Woodcock, J.W. et al. (2017). Observation of Interfacial Damage in a Silk-Epoxy Composite, Using a Simple Mechanoresponsive Fluorescent Probe. *Advanced Materials Interfaces*. DOI: 10.1002/admi.201601018.
- [132] Imato, K. et al. (2017). Dynamic covalent diarylbibenzofuranone-modified nanocellulose: Mechanochromic behaviour and application in self-healing polymer composites. *Polymer Chemistry*. DOI: 10.1039/c7py00074j.
- [133] Osler, S.K. et al. (2021). Comparison of the reactivity of isomeric 2H- and 3H-naphthopyran mechanophores. *Journal of Polymer Science*. DOI: 10.1002/pol.20210417.
- [134] Qi, Q. et al. (2021). Force-Induced Near-Infrared Chromism of Mechanophore-Linked Polymers. *Journal of the American Chemical Society*.

- DOI: 10.1021/jacs.1c05923.
- [135] Greco, R. and Nicolais, L. (1976). Glass transition temperature in nylons. *Polymer*. DOI: 10.1016/0032-3861(76)90005-7.
- [136] Baker, G.L. et al. (2008). Glass transitions in polylactides. *Polymer Reviews*. DOI: 10.1080/15583720701834208.
- [137] Qiu, Z. et al. (2017). A Simple and Sensitive Method for an Important Physical Parameter: Reliable Measurement of Glass Transition Temperature by AIEgens. *Macromolecules*. DOI: 10.1021/acs.macromol.7b01070.
- [138] Hale, A. et al. (1991). Glass Transition Temperature as a Function of Conversion in Thermosetting Polymers. *Macromolecules*. DOI: 10.1021/ma00009a072.
- [139] Mohammadi, M. et al. (2017). The glass transition temperature of PMMA: A molecular dynamics study and comparison of various determination methods. *European Polymer Journal*. DOI: 10.1016/j.eurpolymj.2017.03.056.
- [140] Ahmad, M. et al. (2011). Synthesis and characterization of polyurethane-based shape-memory polymers for tailored Tg around body temperature for medical applications. *Macromolecular Chemistry and Physics*. DOI: 10.1002/macp.201000540.
- [141] Omelczuk, M.O. and McGinity, J.W. (1992). The Influence of Polymer Glass Transition Temperature and Molecular Weight on Drug Release from Tablets Containing Poly(DL-lactic Acid). *Pharmaceutical Research: An Official Journal of the American Association of Pharmaceutical Scientists*. DOI: 10.1023/A:1018967424392.
- [142] Li, R. (2000). Time-temperature superposition method for glass transition temperature of plastic materials. *Materials Science and Engineering: A*. DOI: 10.1016/s0921-5093(99)00602-4.
- [143] Jiang, W. et al. (2012). Thermo-mechanical behaviors of epoxy resins reinforced with nano-Al₂O₃ particles. *Journal of Industrial and Engineering Chemistry*. DOI: 10.1016/j.jiec.2011.11.140.
- [144] Ellison, C.J. and Torkelson, J.M. (2002). Sensing the glass transition in thin and ultrathin polymer films via fluorescence probes and labels. *Journal of*

- Polymer Science, Part B: Polymer Physics*. DOI: 10.1002/polb.10343.
- [145] Priestley, R.D. et al. (2005). Structural relaxation of polymer glasses at surfaces, interfaces, and in between. *Science*. DOI: 10.1126/science.1112217.
- [146] Mok, M.M. and Lodge, T.P. (2012). Temperature-based fluorescence measurements of pyrene in block copolymer micelles: Probing micelle core glass transition breadths. *Journal of Polymer Science, Part B: Polymer Physics*. DOI: 10.1002/polb.23029.
- [147] Domingues, R.A. et al. (2010). Fluorescence spectroscopy and thermal relaxation processes of anthracenyl-labeled polysiloxanes. *Journal of Polymer Science, Part B: Polymer Physics*. DOI: 10.1002/polb.21845.
- [148] Xu, J. et al. (2014). Sensitive characterization of the influence of substrate interfaces on supported thin films. *Macromolecules*. DOI: 10.1021/ma500864k.
- [149] Atvars, T.D.Z. et al. (2013). Modulation of the photophysical properties of pyrene by the microstructures of five poly(alkyl methacrylate)s over a broad temperature range. *Photochemistry and Photobiology*. DOI: 10.1111/php.12103.
- [150] Oba, T. and Vacha, M. (2012). Relaxation in thin polymer films mapped across the film thickness by astigmatic single-molecule imaging. *ACS Macro Letters*. DOI: 10.1021/mz3002269.
- [151] Katzenstein, J.M. et al. (2012). Nanoconfined self-diffusion of poly(isobutyl methacrylate) in films with a thickness-independent glass transition. *Macromolecules*. DOI: 10.1021/ma202362j.
- [152] Flier, B.M.I. et al. (2012). Heterogeneous diffusion in thin polymer films as observed by high-temperature single-molecule fluorescence microscopy. *Journal of the American Chemical Society*. DOI: 10.1021/ja208581r.
- [153] Loutfy, R.O. (1986). Fluorescence probes for polymer free-volume. *Pure and Applied Chemistry*. DOI: 10.1351/pac198658091239.
- [154] Frank, C.W. (1975). Observation of Relaxation Processes Near the Glass Transition by Means of Excimer Fluorescence. *Macromolecules*. DOI: 10.1021/ma60045a012.

- [155] Kim, S. and Torkelson, J.M. (2011). Distribution of glass transition temperatures in free-standing, nanoconfined polystyrene films: A test of de Gennes' sliding motion mechanism. *Macromolecules*. DOI: 10.1021/ma200617j.
- [156] Evans, C.M. et al. (2011). Glass transition temperature of a component near infinite dilution in binary polymer blends: Determination via fluorescence spectroscopy. *Macromolecules*. DOI: 10.1021/ma201259w.
- [157] Rittigstein, P. et al. (2007). Model polymer nanocomposites provide an understanding of confinement effects in real nanocomposites. *Nature Materials*. DOI: 10.1038/nmat1870.
- [158] Ellison, C.J. and Torkelson, J.M. (2003). The distribution of glass-transition temperatures in nanoscopically confined glass formers. *Nature Materials*. DOI: 10.1038/nmat980.
- [159] Ellison, C.J. et al. (2002). Confinement and processing effects on glass transition temperature and physical aging in ultrathin polymer films: Novel fluorescence measurements. *European Physical Journal E*. DOI: 10.1140/epje/i2001-10057-y.
- [160] Chen, J. et al. (2003). Synthesis, light emission, nanoaggregation, and restricted intramolecular rotation of 1,1-substituted 2,3,4,5-tetraphenylsiloles. *Chemistry of Materials*. DOI: 10.1021/cm021715z.
- [161] Ding, D. et al. (2013). Ultrabright organic dots with aggregation-induced emission characteristics for real-time two-photon intravital vasculature imaging. *Advanced Materials*. DOI: 10.1002/adma.201301938.
- [162] Wang, Z. et al. (2013). Long-term fluorescent cellular tracing by the aggregates of AIE bioconjugates. *Journal of the American Chemical Society*. DOI: 10.1021/ja312581r.
- [163] Zhang, J. et al. (2021). Stimuli-Responsive AIEgens. *Advanced Materials*. DOI: 10.1002/adma.202008071.
- [164] Meng, B. et al. (2020). Composites with AIEgens for Temperature Sensing and Strain Measurement. *Macromolecular Chemistry and Physics*. DOI: 10.1002/macp.201900552.
- [165] Brutman, J.P. et al. (2014). Polylactide vitrimers. *ACS Macro Letters*. DOI:

10.1021/mz500269w.

- [166] Yang, Y. et al. (2021). Functional epoxy vitrimers and composites. *Progress in Materials Science*. DOI: 10.1016/j.pmatsci.2020.100710.
- [167] Denissen, W. et al. (2015). Vinylogous urethane vitrimers. *Advanced Functional Materials*. DOI: 10.1002/adfm.201404553.
- [168] Luo, J. et al. (2022). Elastic vitrimers: Beyond thermoplastic and thermoset elastomers. *Matter*. DOI: 10.1016/j.matt.2022.04.007.
- [169] Krishnan, B.P. et al. (2022). Design, Synthesis and Characterization of Vitrimers with Low Topology Freezing Transition Temperature. *Polymers*. DOI: <https://doi.org/10.3390/polym14122456> Academic.
- [170] Yang, Y. et al. (2019). Detecting topology freezing transition temperature of vitrimers by AIE luminogens. *Nature Communications*. DOI: 10.1038/s41467-019-11144-6.
- [171] Möller, J. et al. (2006). Freezing-in and production of entropy in vitrification. *Journal of Chemical Physics*. DOI: 10.1063/1.2346673.
- [172] Kovacs, A.J. (1968). Applicability of Free Volume Concept to Relaxation Phenomena in the Glass Transition Range. *Rubber Chemistry and Technology*. DOI: 10.5254/1.3547193.
- [173] Struik, L.C.E. (1966). Volume relaxation in polymers. *Rheologica Acta*. DOI: 10.1007/BF02009739.
- [174] Struik, L.C.E. (1977). *Physical aging in amorphous polymers and other materials*.
- [175] Tant, M.R. and Wilkes, G.L. (1981). An overview of the nonequilibrium behavior of polymer glasses. *Polymer Engineering & Science*. DOI: 10.1002/pen.760211403.
- [176] Elias, H.G. (1977). Chemical Aging, in *Macromolecules*, Springer, pp. 375–388.
- [177] Hutchinson, J.M. (1995). Physical aging of polymers. *Progress in Polymer Science*. DOI: 10.1016/0079-6700(94)00001-I.
- [178] Ian M., H. (1995). Physical Aging in Polymer Glasses. *Science*.

- [179] Schwab, S.D. and Levy, R.L. (1990). Free-Volume-Dependent Fluorescence Probes of Physical Aging in Polymers, pp. 397–408.
- [180] Widakdo, J. et al. (2023). Positron annihilation spectroscopy for the free volume depth profile analysis of multilayer and 2D materials composite membranes: A review. *Separation and Purification Technology*. DOI: 10.1016/j.seppur.2023.124366.
- [181] Hill, A.J. (1995). Positron Annihilation Lifetime Spectroscopy To Probe Free-Volume Effects in High-Temperature Polymers and Composites. DOI: 10.1021/bk-1995-0603.ch005.
- [182] Liu, J. et al. (1995). Free-Volume Hole Properties of Polymer Blends Probed by Positron Annihilation Spectroscopy: Miscibility. *Macromolecules*. DOI: 10.1021/ma00121a012.
- [183] Consolati, G. et al. (2023). Probing the Free Volume in Polymers by Means of Positron Annihilation Lifetime Spectroscopy. *Polymers*. DOI: 10.3390/polym15143128.
- [184] Oster, G. and Nishijima, Y. (1956). Fluorescence and Internal Rotation: Their Dependence on Viscosity of the Medium. *Journal of the American Chemical Society*. DOI: 10.1021/ja01589a021.
- [185] Meyer, E.F. et al. (1990). Free volume changes in polyvinyl acetate measured by fluorescence spectroscopy. *Polymer*. DOI: 10.1016/0032-3861(90)90113-D.
- [186] Loutfy, R.O. (1982). FLUORESCENCE PROBES FOR POLYMERIZATION REACTIONS - BULK POLYMERIZATION OF STYRENE, n-BUTYL METHACRYLATE, ETHYL METHACRYLATE, AND ETHYL ACRYLATE. *Journal of polymer science. Part A-2, Polymer physics*. DOI: 10.1002/pol.1982.180200505.
- [187] Shmorhun, M. et al. (1990). Free volume changes in epoxy adhesives during physical ageing: fluorescence spectroscopy and mechanical stress relaxation. *Polymer*. DOI: 10.1016/0032-3861(90)90039-2.
- [188] Al-Hassan, K.A. and Rettig, W. (1986). Free volume sensing fluorescent probes. *Chemical Physics Letters*. DOI: 10.1016/S0009-2614(86)80082-3.
- [189] Naresh Kumar, S. et al. (2020). Damage Detection in Composite Materials

- Using Lamb Wave method. *IOP Conference Series: Materials Science and Engineering*. DOI: 10.1088/1757-899X/998/1/012066.
- [190] Weder, C. (2011). Mechanoresponsive materials. *Journal of Materials Chemistry*. DOI: 10.1039/c1jm90068d.
- [191] Kucharski, T.J. and Boulatov, R. (2011). The physical chemistry of mechanoresponsive polymers. *Journal of Materials Chemistry*. DOI: 10.1039/c0jm04079g.
- [192] Jiang, S. et al. (2013). Mechanoresponsive PS-PnBA-PS triblock copolymers via covalently embedding mechanophore. *ACS Macro Letters*. DOI: 10.1021/mz400198n.
- [193] Calvino, C. et al. (2019). Mechanoresponsive, Luminescent Polymer Blends Based on an Excimer-Forming Telechelic Macromolecule. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.201800705.
- [194] Robb, M.J. et al. (2016). A robust damage-reporting strategy for polymeric materials enabled by aggregation-induced emission. *ACS Central Science*. DOI: 10.1021/acscentsci.6b00198.
- [195] Vidavsky, Y. et al. (2019). Enabling Room-Temperature Mechanochromic Activation in a Glassy Polymer: Synthesis and Characterization of Spiropyran Polycarbonate. *Journal of the American Chemical Society*. DOI: 10.1021/jacs.9b04229.
- [196] Zhang, H. et al. (2014). Spiropyran as a mechanochromic probe in dual cross-linked elastomers. *Macromolecules*. DOI: 10.1021/ma500760p.
- [197] Zhang, H. et al. (2021). A multi-stimuli responsive tetraphenylethene derivative: Self-reversible mechanochromism, mechanoluminescence, switchable photochromism. *Dyes and Pigments*. DOI: 10.1016/j.dyepig.2020.109128.
- [198] Qiu, Z. et al. (2018). Dynamic Visualization of Stress/Strain Distribution and Fatigue Crack Propagation by an Organic Mechanoresponsive AIE Luminogen. *Advanced Materials*. DOI: 10.1002/adma.201803924.
- [199] Rossi, N.A.A. et al. (2009). Synthesis and characterisation of pyrene-labelled polydimethylsiloxane networks: towards the in situ detection of strain in silicone elastomers †. DOI: 10.1039/b908708g.

- [200] Wang, K. et al. (2019). Mechano-fluorochromic behavior of AEE polyurethane films and their high sensitivity to halogen acid gas. *RSC Advances*. DOI: 10.1039/c8ra10486g.
- [201] Wang, K. et al. (2018). Multi-stimuli-responsive fluorescence of AEE polyurethane films. *European Polymer Journal*. DOI: 10.1016/j.eurpolymj.2018.02.014.
- [202] Han, T. et al. (2021). Mechanochromic Fluorescent Polymers Enabled by AIE Processes. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.202000311.
- [203] Kunzelman, J. et al. (2009). Pressure-sensitive chromogenic polyesters. *Macromolecular Materials and Engineering*. DOI: 10.1002/mame.200800299.
- [204] Ciardelli, F. et al. (2013). Dye-containing polymers: Methods for preparation of mechanochromic materials. *Chemical Society Reviews*. DOI: 10.1039/c2cs35414d.
- [205] Kiebal, D.J. et al. (2020). Mechanoresponsive Elastomers Made with Excimer-Forming Telechelics. *Organic Materials*. DOI: 10.1055/s-0040-1721052.
- [206] Pucci, A. et al. (2009). Linear low density polyethylene (LLDPE) films containing perylene dyes as stress-strain luminescent indicators. *E-Polymers*. DOI: 10.1515/epoly.2009.9.1.716.
- [207] Zych, A. et al. (2019). Strain-reporting pyrene-grafted polyethylene. *European Polymer Journal*. DOI: 10.1016/j.eurpolymj.2018.12.016.
- [208] Yang, F. et al. (2020). Sensitized Mechanoluminescence Design toward Mechanically Induced Intense Red Emission from Transparent Polymer Films. *Macromolecules*. DOI: 10.1021/acs.macromol.9b02221.
- [209] Liu, S. et al. (2020). An optomechanical study of mechanoluminescent elastomeric polyurethanes with different hard segments. *Polymer Chemistry*. DOI: 10.1039/c9py01850f.
- [210] Yang, L. et al. (2015). Supramolecular Polymers: Historical Development, Preparation, Characterization, and Functions. *Chemical Reviews*. DOI: 10.1021/cr500633b.

- [211] Brunsveld, L. et al. (2001). Supramolecular polymers. *Chemical Reviews*. DOI: 10.1021/cr990125q.
- [212] De Greef, T.F.A. et al. (2009). Supramolecular polymerization. *Chemical Reviews*. DOI: 10.1021/cr900181u.
- [213] Zhang, Y.M. et al. (2018). Multi-stimuli-responsive supramolecular gel constructed by pillar[5]arene-based pseudorotaxanes for efficient detection and separation of multi-analytes in aqueous solution. *Soft Matter*. DOI: 10.1039/c8sm01838c.
- [214] Sagara, Y. et al. (2019). Rotaxane-Based Mechanophores Enable Polymers with Mechanically Switchable White Photoluminescence. *ACS Central Science*. DOI: 10.1021/ACSCENTSCI.9B00173/SUPPL_FILE/OC9B00173_SI_006.MP4.
- [215] Chen, P. et al. (2015). White-Light-Emitting Lanthanide Metallogels with Tunable Luminescence and Reversible Stimuli-Responsive Properties. *Journal of the American Chemical Society*. DOI: 10.1021/jacs.5b07394.
- [216] Liang, A. et al. (2015). White light-emitting diodes based on an all-phosphorescent supramolecular polymer. *Polymer Chemistry*. DOI: 10.1039/c5py00832h.
- [217] Xu, P. et al. (2023). Design of a pH-sensitive supramolecular fluorescent probe for selective cancer cell imaging. *Dyes and Pigments*. DOI: 10.1016/j.dyepig.2023.111366.
- [218] Kyba, E.P. et al. (1977). Host-Guest Complexation. 1.
- [219] Qu, D.H. et al. (2015). Photoresponsive Host-Guest Functional Systems. *Chemical Reviews*. DOI: 10.1021/cr5006342.
- [220] Xue, M. et al. (2015). Development of Pseudorotaxanes and Rotaxanes: From Synthesis to Stimuli-Responsive Motions to Applications. *Chemical Reviews*. DOI: 10.1021/cr5005869.
- [221] Fröh, A.E. et al. (2017). Strain Field Self-Diagnostic Poly(dimethylsiloxane) Elastomers. *Chemistry of Materials*. DOI: 10.1021/ACS.CHEMMATER.7B02438/SUPPL_FILE/CM7B02438_SI_001.PDF.
- [222] Das, A.D. et al. (2019). Damage-Reporting Carbon Fiber Epoxy Composites.

- ACS Applied Polymer Materials*. DOI: 10.1021/acsapm.9b00694.
- [223] Lou, X. and Yang, Y. (2020). Aggregation-induced emission systems involving supramolecular assembly. *Aggregate*. DOI: 10.1002/agt2.1.
- [224] Liu, K. et al. (2012). From bola-amphiphiles to supra-amphiphiles: The transformation from two-dimensional nanosheets into one-dimensional nanofibers with tunable-packing fashion of n-type chromophores. *Chemistry - A European Journal*. DOI: 10.1002/chem.201200898.
- [225] Moritz, H.U. (1989). Increase in viscosity and its influence on polymerization processes. *Chemical Engineering & Technology*. DOI: 10.1002/ceat.270120112.
- [226] Loutfy, R.O. (1981). High-Conversion Polymerization Fluorescence Probes. 1. Polymerization of Methyl Methacrylate. *Macromolecules*. DOI: 10.1021/ma50003a009.
- [227] Schreiber, H.P. et al. (1963). Viscosity/Molecular weight relation in bulk polymers-I. *Polymer*. DOI: 10.1016/0032-3861(63)90042-9.
- [228] Aktaş, D.K. (2006). A fluorescence study on the critical exponents for the linear polymerization of butyl-methacrylate. *Phase Transitions*. DOI: 10.1080/01411590600916218.
- [229] Okay, O. et al. (1999). Free-radical crosslinking copolymerization of styrene and divinylbenzene: Real time monitoring of the gel effect using fluorescence probe. *Polymer*. DOI: 10.1016/S0032-3861(98)00831-3.
- [230] Peinado, C. et al. (2001). Fluorescent probes for monitoring the UV curing of acrylic adhesives, 1: FTIR and fluorescence in real time. *Macromolecular Chemistry and Physics*. DOI: 10.1002/1521-3935(20010601)202:9<1924::AID-MACP1924>3.0.CO;2-C.
- [231] Han, T. et al. (2017). High-Contrast Visualization and Differentiation of Microphase Separation in Polymer Blends by Fluorescent AIE Probes. *Macromolecules*. DOI: 10.1021/acs.macromol.7b00973.
- [232] Hakala, K. et al. (2001). Monitoring water uptake of polyurethanes by in situ fluorescence technique. *Journal of Applied Polymer Science*. DOI: 10.1002/app.1998.

- [233] Haider, T.P. et al. (2019). Plastics of the Future? The Impact of Biodegradable Polymers on the Environment and on Society. *Angewandte Chemie - International Edition*. DOI: 10.1002/anie.201805766.
- [234] Zhang, Z. et al. (2020). Three-Dimensional Visualization for Early-Stage Evolution of Polymer Aging. *ACS Central Science*. DOI: 10.1021/acscentsci.0c00133.
- [235] Alizadehaghdam, M. et al. (2020). Following isothermal and non-isothermal crystallization of poly(3-hexylthiophene) thin films by UV-vis spectroscopy. *Polymer*. DOI: 10.1016/j.polymer.2020.122959.
- [236] Nile, R. et al. (2023). Crystallization Behavior of Semicrystalline Polymers Characterized by an In Situ Fluorescence Technique and its Sensing Mechanism. *Macromolecular Chemistry and Physics*. DOI: 10.1002/macp.202300230.
- [237] Kong, Y. and Hay, J.N. (2002). The measurement of the crystallinity of polymers by DSC. *Polymer*. DOI: 10.1016/S0032-3861(02)00235-5.
- [238] Zuo, B. et al. (2016). Stepwise crystallization and the layered distribution in crystallization kinetics of ultra-thin poly(ethylene terephthalate) film. *Journal of Chemical Physics*. DOI: 10.1063/1.4953852.
- [239] Wu, T. et al. (2005). Study on the nonisothermal crystallization process of mLLDPE/EVA blends using FTIR micro-spectroscopy. *Journal of Applied Polymer Science*. DOI: 10.1002/app.20953.
- [240] Liu, X. and Yu, W. (2021). Weak Shear-Induced Slowdown in Crystallization of Less-Entangled Poly(ϵ -caprolactone). *Macromolecules*. DOI: 10.1021/acs.macromol.1c00204.
- [241] Zhang, Q. et al. (2020). In-situ tracking polymer crystallization during film blowing by synchrotron radiation X-ray scattering: The critical role of network. *Polymer*. DOI: 10.1016/j.polymer.2020.122492.
- [242] Nakanishi, Y. et al. (2022). Morphological study of isotactic polypropylene thin films on different substrates using grazing incidence wide-angle X-ray diffraction. *Polymer*. DOI: 10.1016/j.polymer.2022.124665.
- [243] Jager, W.F. et al. (2005). Novel color-shifting mobility sensitive fluorescent probes for polymer characterization. *Macromolecular Symposia*. DOI:

10.1002/masy.200551136.

- [244] Nile, R. et al. (2021). Sensing the melting transition of semicrystalline polymers via a novel fluorescence technique. *Polymer*. DOI: 10.1016/j.polymer.2021.124070.
- [245] Khorloo, M. et al. (2020). Polymorph selectivity of an AIE luminogen under nano-confinement to visualize polymer microstructures. *Chemical Science*. DOI: 10.1039/c9sc04239c.

2. Molecular rotors as rigidification induced emission probes

Molecular rotors have been demonstrated to be especially well-suited for investigating specific aspects and phenomena associated with chain mobility and free volume in polymer matrices since their emission capabilities are intrinsically linked to their mobility. When these molecules are integrated into a polymeric matrix, their sensitivity to the rigidity of the surrounding polymer becomes evident.[1]

In the present thesis, different molecular rotors have been incorporated as additives in various amorphous polymer matrices. The optical properties of the dyes were characterized across polymer glass transition temperature, after physical aging and under tensile deformation. Both the emission intensity and the probe's lifetime were measured while varying sample temperature or during uniaxial deformations. The emission intensity can be affected by a variety of instrumental conditions, sample geometry and morphology. Differently, the lifetime is an absolute measure, independent from any instrumental errors or imperfections in the matrix, thus allowing for more reliable and reproducible results. Therefore, the use of both steady-state and time-resolved techniques allows for a complete characterization of the dye properties in the polymer matrices, thus helping to correctly interpreting the occurring phenomena.

In the following sections, various techniques to measure luminescent signals will be described, which are simple in terms of instrumentation, requiring only a light source and a detector, easily adaptable to different conditions, non-destructive and allowing for in situ and real-time monitoring.

Section 2.1 of this work presents results concerning TPE-doped polymers exposed to thermal and mechanical stress, as well as physical aging. In these conditions, variations in emission intensity are typically associated with changes in photoluminescent quantum yield (PLQY). However, this study challenges that assumption. During exposure to external stimuli, other matrix changes were observed, such as variations in polymer matrix transparency, possibly arising from local alterations in the refractive index and the development of microfractures. Consequently, this research utilized fluorescence lifetime as an absolute fluorescence parameter and combined it

with different characterization techniques to demonstrate that scattering can impact apparent emission intensity. Therefore, we demonstrated that lifetime measurements can be employed to determine whether the observed phenomenon results from modifications in the photophysical properties of AIE dyes (RIM effect) or from alterations in the matrix's optical properties.

In section 2.2, various fluorescent molecular rotors were tested to identify the most suitable one for T_g detection. These dyes were incorporated into different polymer matrices and by analyzing the decay of lifetime during heating ramps, a dye was selected based on its temperature-independent photophysical behavior, which instead was closely related to matrix T_g . Moreover, utilizing confocal microscopy and fluorescence-lifetime imaging microscopy (FLIM), this fluorescent probe successfully identified the different components in immiscible polymer blends. Therefore, the fluorescence lifetime of this temperature-invariant AIE probe emerges as a straightforward and versatile parameter for quantitatively visualizing the absolute chain mobility of complex polymeric materials in real time and with sub-micrometer resolution.

Finally, section 2.3 reveals the outcomes of investigating the lifetime of a phosphorescent molecular rotor within various polymer matrices. Its lifetime was measured during stress-strain tests and subsequent annealing heat treatments, which allow the controlled physical aging of the samples. These tests, which induce alterations in chain mobility, provided insights into the transformations occurring at the free volume level, based on the variations in lifetime. As a result, materials with the potential to self-monitor physical aging and mechanical stresses in real-time were developed.

2.1. Emission or scattering? Discriminating the origin of responsiveness in AIEgen-doped smart polymers using the TPE dye

2.1.1. Introduction

Tetraphenylethylene, the simplest and most common AIE, has been frequently used in combination with various polymeric matrices to endow materials with different new functionalities. In this context, TPE has been easily blended with the polymer[2–4] incorporated within microcapsules dispersed throughout a polymer matrix,[5,6]

covalently linked to macromolecular chains,[7] or confined in a specific layer within a multilayer architecture.[8,9] For instance, Robb et al. harnessed the RIM effect to visually discern micro damages across a broad spectrum of polymers: within crack regions, TPE is released from solvent-containing microcapsules and subsequent solvent evaporation prompts TPE aggregation, leading to intense fluorescence.[5] Meng et al. established a connection between polymer tensile deformation and TPE emission intensity.[10]

Functioning as an additive, TPE has also been proposed as a probe for polymer T_g [2] and T_v associated with topology changes in vitrimers.[11] In this context, the decline in TPE fluorescence intensity upon heating has been ascribed to the mobility alteration that takes place during the polymer transition. The fundamental premise behind this is that the rigidity of glassy polymer chains prevents TPE's intramolecular motions, thus intensifying emission is observed at temperatures below the polymer T_g . Upon surpassing T_g , elevated temperatures confer mobility to polymer chains, enabling intramolecular movements in TPE, resulting in a subsequent decline in emission. Correspondingly, within vitrimers, the polymer gains dynamism and mobility as the T_v is exceeded.

Nevertheless, it remains one problem that has not yet been mentioned but is crucial to consider. It is imperative to acknowledge that the observed luminescence of solid matrices containing fluorophores, characterized solely by intensity fluctuations, can be substantially affected by the optical traits of the material. These are particularly relevant for scattering phenomena, which frequently manifest due to refractive index disparities within the sample, stemming from factors such as local density fluctuations, microcracks, or microbubbles. Scattering can markedly influence emission intensity, giving rise to apparent enhancements in the emission signal. Consequently, the mere assessment of fluorescence emission intensity, without a comprehensive analysis of the emission quantum yield, might prove inadequate under specific conditions, potentially yielding misleading outcomes.

Emission intensity represents a relative measurement of quantum yield, remaining valid only when the optical system under

consideration, encompassing geometry, absorption and scattering, remains unaltered. Thus, it is crucial to evaluate parameters unaffected by matrix scattering in order to expound upon observed phenomena using more reliable data. In contrast to emission intensity, fluorescence lifetime constitutes an intrinsic property of a fluorophore, featuring an absolute value not susceptible to scattering influences or measurement methodologies.[12] In fact, the lifetime demonstrates a direct relationship with the quantum yield (Equations 2.1 and 2.2) when quenching mechanisms exclusively involves changes in non-radiative decay kinetics (k_{nr}), such as the RIM mechanism in AIEgens.

$$\tau = 1/(k_r + \sum_i k_{nr,i}) \dots \dots (\text{Eq. 2.1})$$

$$\Phi = k_r/(k_r + \sum_i k_{nr,i}) \dots \dots (\text{Eq. 2.2})$$

Consequently, in complex experimental scenarios, especially those involving low-scattering optical configurations, the quantification of fluorescence lifetime emerges as a straightforward method to assess the quantum yield. This study is directed towards a comprehensive evaluation of the photophysical characteristics exhibited by TPE dispersed within various polymeric microenvironments. These matrixes are subject to fluctuations in temperature, physical aging, and mechanical deformation. The investigative approach encompasses independent emission spectroscopy measurements, transmittance analysis, imaging techniques, and time-resolved spectroscopy measurements.

The ultimate objective concerns the exploration of scattering effects on TPE's emission behavior, thus enhancing the comprehension of the mechanism governing the application of this AIE fluorophore for polymer property detection. In pursuit of this goal, TPE was introduced into three distinct commercially available polymers: poly(lactic-co-glycolic acid) (PLGA), polyvinyl acetate (PVAc), and poly(Bisphenol A-carbonate) (PC). These polymers, representing completely amorphous materials with varying T_g values, were selected to sound out TPE's emission attributes under varying temperatures.

Of particular interest is the investigation of PVAc, recognized for its robustness and exceptional deformability. This polymer was additionally subjected to mechanical stretching, further augmenting the scope of the analysis.

2.1.2. Results and discussion

Investigation of the thermolumineschromic response

The polymers under investigation, i.e. PVAc, PLGA and PC, were processed as depicted in Figure 2.1. Figure 2.2 shows the second DSC scans of the TPE-doped polymer matrices from which the T_g values were derived (i.e. 39°C, 47°C and 148 °C for PVAc, PLGA and PC, respectively). We verified that no remarkable changes in the T_g of the polymers are observed after the addition of the TPE (Figure 2.2 and Table 2.1), meaning that the 0,1 wt.% of TPE does not affect polymer thermal properties, at least in the amount used in the present work.

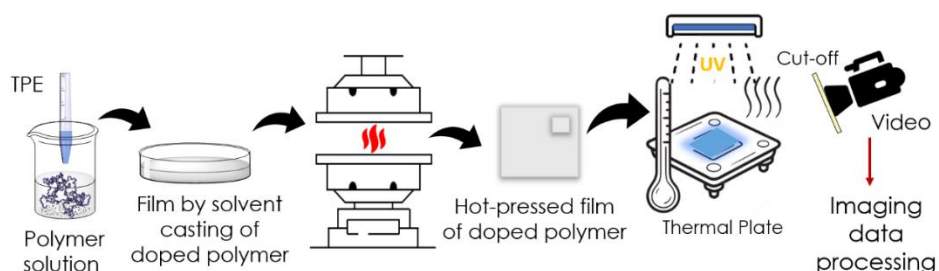


Figure 2.1 Scheme of the experimental setup for the measurement of sample fluorescence variation under thermal treatment: polymer films doped with TPE were obtained by solvent casting followed by hot-pressing; a specimen was positioned over a heating stage to carry out heating/cooling treatments under a controlled rate; the specimen was irradiated with UV light and the sample emission was monitored with a camera; images were processed by analyzing greyscale intensity, using ImageJ software. Reproduced from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

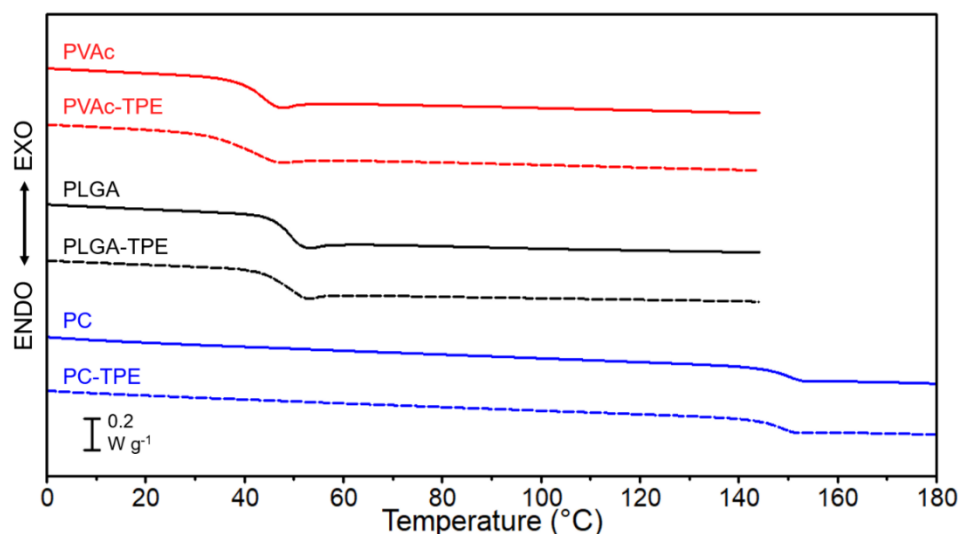


Figure 2.2 DSC second heating scans of pristine (solid line) and doped polymers (dashed line): PVAc (red), PLGA (black), and PC (blue). Adapted from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

Table 2.1 Thermal data of undoped and doped polymers (T_g is determined at the midpoint at the half height; ΔC_p = specific heat capacity variation).

Sample	T_g [°C]	ΔC_p [J g ⁻¹ °C ⁻¹]
PVAc	42	0.51
PVAc-TPE	39	0.53
PLGA	48	0.57
PLGA-TPE	47	0.51
PC	149	0.27
PC-TPE	148	0.26

To determine fluorescence variation over temperature, UV light-irradiated samples were heated at a rate of 5 °C min⁻¹. Figure 2.3b, c and d show the fluorescence intensity behavior of the analyzed matrices as a function of temperature. The emission intensity was quantitatively expressed by the grayscale values obtained from the digital images, as previously reported by Z. Qui et al.[14] and B. Meng et al.[10] Images of the tested polymers at different temperatures are

also reported for each polymer. In the case of PVAc and PLGA, the almost complete quenching of the sample emission is obtained reaching 100 °C, whereas, for PC, which has a higher T_g , only at around 250 °C. By observing sample images and graphs in Figure 2.3, it is evident that emission intensity decreases with temperature and that the greatest fluorescence variation occurs across polymer T_g where a step-like change of the emission is observed. This temperature-dependent change in fluorescence can be reasonably ascribed to the RIM effect. Since the emission quantum yield of TPE is directly related to its mobility, below polymer T_g , where chains are vitrified in a random coil conformation, a higher quantum yield of TPE is expected, as a consequence of the RIM effect, in comparison with above T_g , where chain mobility and free volume strongly increase together with the dye intramolecular motions.[15,16]

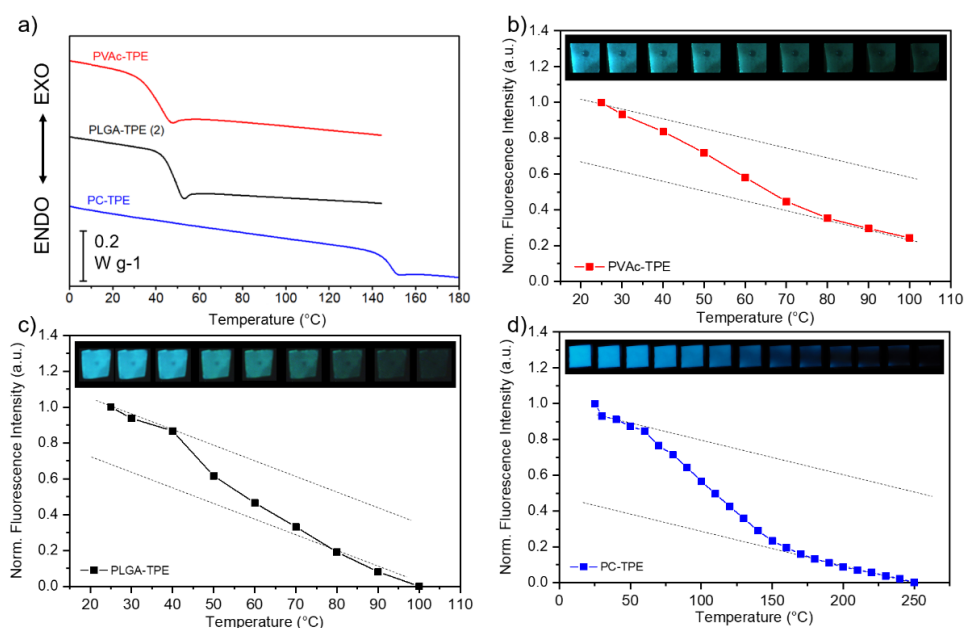


Figure 2.3 a) DSC second heating scans of PVAc-TPE (red), PLGA-TPE (black) and PC-TPE (blue). Fluorescence as a function of temperature, obtained from greyscale intensity analysis of TPE-doped sample images: PVAc-TPE (b), PLGA-TPE (c) and PC-TPE (d). Dotted lines are added to better highlight the step-like change of sample emission across T_g . Images of samples acquired at different temperatures are also reported in sequence. Adapted from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

In order to get a deeper understanding of the fluorescence changes across polymer T_g , physical aging, a common phenomenon of the amorphous state, has been considered. Physical aging is a

thermodynamic phenomenon whereby the material approaches a state of equilibrium through structural relaxations that slowly reduce the excessive free volume and cause volume contraction. This phenomenon occurs at temperatures below T_g and is thermoreversible since, by heating the polymer above T_g , the free volume lost during aging is recovered.[17] The occurrence of physical aging is expected to reduce the free volume available for the AIE rotational motions, thus enhancing its radiative deactivation. In other words, TPE is expected to be sensitive to polymer densification due to physical aging.

To verify this hypothesis, TPE-doped PLGA, which shows the clearest fluorescence variation in correspondence to its T_g among the tested polymers, was selected and subjected to cycles of heating, cooling and isotherm, as described in Figure 2.4a, while measuring fluorescence emission by grayscale analysis. In detail, a “highly aged” sample of PLGA-TPE, obtained by storing the polymer at room temperature for several weeks, was heated above its T_g (1st heating ramp, Figure 2.4a, green segment) and quickly cooled (fast cooling ramp, Figure 2.4a, blue segment) to erase its thermal history and gain an “unaged” sample. The latter was subsequently re-heated (2nd heating ramp, Figure 2.4, black segment). The same sample was then “aged overnight” at 35°C on the heating stage before being heated above its T_g (3rd heating ramp, Figure 2.4, red segment). During these thermal treatments, the fluorescence of the sample was continuously recorded by the camera. In parallel, the sample was also characterized by DSC to identify the T_g and the extent of physical aging.

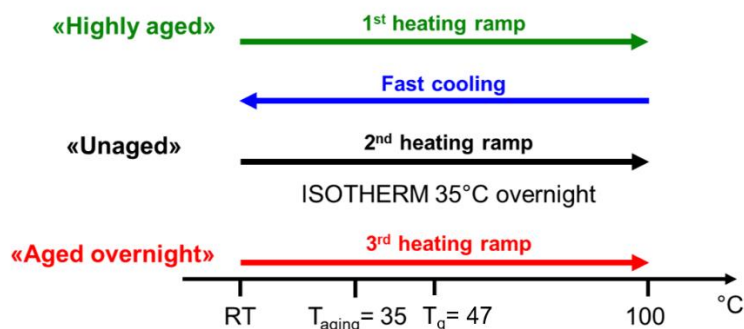


Figure 2.4 Thermal program applied to PLGA-TPE sample: the starting “highly aged” specimen was heated above T_g and quickly cooled to gain the “unaged” sample, the latter, after being heated above T_g , was maintained at 35 °C overnight to induce physical aging (“aged overnight” sample) and heated again to monitor its fluorescence. Adapted from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

Figure 2.5 shows the change in sample fluorescence during the above-described heating scans, together with the corresponding DSC scans. In the latter, the step-change in the heat flow ascribable to the glass transition overlaps with the enthalpic relaxation peak caused by physical aging. As expected, the highly aged sample shows the more intense peak, followed by the sample aged overnight and by the unaged one. In all the scans, the fluorescence gradually decreases with increasing temperature. It is worth noting that by heating the highly aged sample (green curve), the slope of the curve drastically changes, forming a step-like pattern, in a narrow temperature range around T_g . The step almost disappears by heating the unaged sample; yet, after aging overnight, the step is clearly visible again, even if less marked compared to the sample aged for several weeks. A further interesting observation is that the path of fluorescence vs temperature above T_g is the same for the differently aged samples, which is consistent with the achievement of the equilibrium state, while the fluorescence below T_g is different and correlates well with the degree of aging of the sample at the time of the scan. Indeed, the more aged the sample (green curve), the greater its initial fluorescence intensity, while, when the thermal history was erased (black curve), the sample's initial fluorescence was lower. DSC curves reported in Figure 2.5 allow to appreciate that not only the step-like fluorescence decrease occurs at T_g , but also that its entity matches

closely with that of the enthalpy relaxation peaks. These results apparently suggest that TPE, via the RIM mechanism, is sensitive to small variations in free volume since at the T_g the fluorescence intensity curve presents a step-like change, whose magnitude can be attributed to the amount of free volume recovered during the transition.

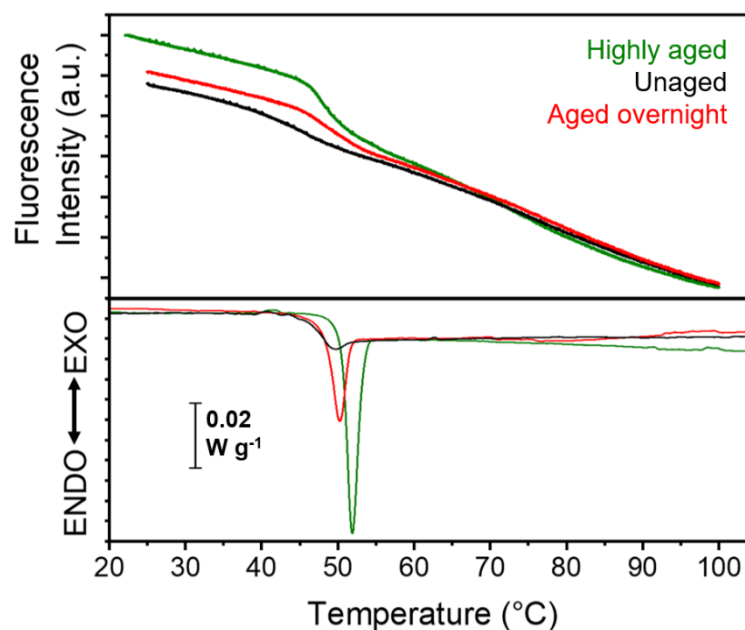


Figure 2.5 Normalized variation of greyscale in terms of fluorescence intensity as a function of temperature for the differently aged PLGA samples; the corresponding DSC heating scans are also reported. Adapted from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

Nonetheless, it is worth reminding that the measured emission intensities are proportional to quantum yields of the dyes only if the optical system is perfectly constant during the temperature ramp. This may not be strictly true for optically complex samples, such as solid and partially transparent polymer films. Indeed, when subjected to thermal treatments, solids show defects, such as fluctuation in thickness and density, or they present areas in which the refractive index of the material itself changes. It is particularly important to consider such defects, as they are spots that trigger scattering and often affect emission intensity measurements. To bypass the limitations posed by the scattering phenomenon, we measured the lifetime, an absolute and quantitative parameter that is directly

proportional to the quantum yield and depends only on the radiative and non-radiative decay constants. In other words, lifetime is sensitive to the RIM effect [18,19] without being affected by the scattering.

TPE lifetime was measured in the three different polymer matrices, by varying the temperature. Figure 2.6a reports the average lifetime of TPE dispersed in the polymers as a function of temperature. The lifetime decreases during heating with a very similar trend in PVAc, PLGA and PC, independently from the polymer T_g . It is worth noting that this drop has a very different trend compared to the one observed for fluorescence intensity (Figure 2.3). The independent decrease of the lifetime from the T_g of the matrix suggests that the temperature variation directly influences the non-radiative relaxation path of TPE (i.e. on its internal conversion). Meanwhile, the effect of the increased chain mobility, induced by overcoming the glass transition, is not predominant.

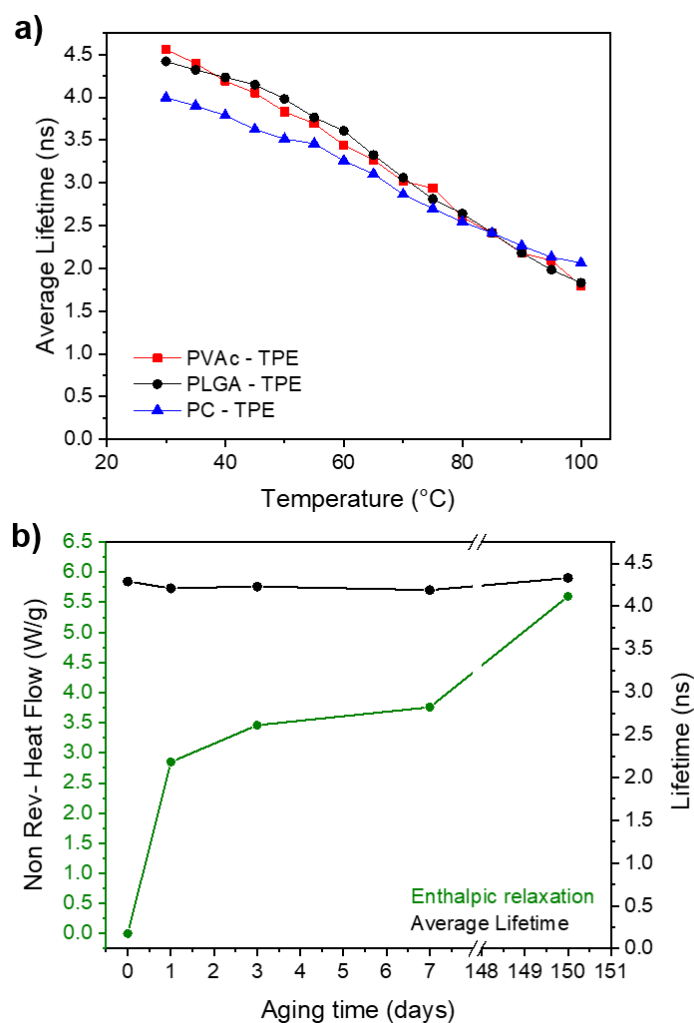


Figure 2.6 a) TPE average lifetime as a function of temperature when embedded in PVAc (red), PLGA (black) and PC (blue). Lifetime detection as a function of temperature in PLGA was carried out on a film containing 0.1 wt.% TPE. b) Lifetime measured at room temperature as a function of aging time in PLGA. Reproduced from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

In the case of PLGA, TPE lifetime was measured after different aging times of the polymer matrix. MDSC measurements were also carried out to quantify the enthalpy of relaxation of physically aged samples from the non-reverse heat flow curves (reported in Figure 2.7).

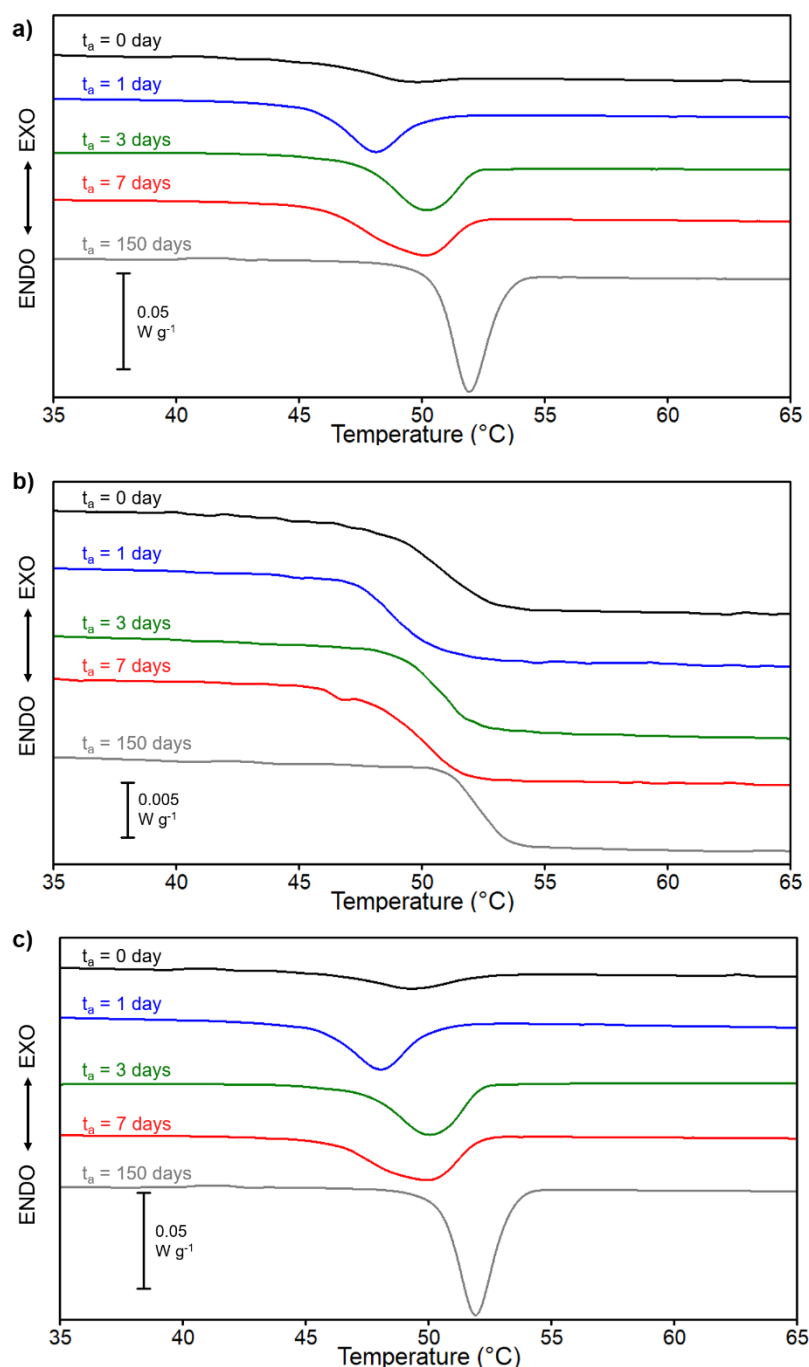


Figure 2.7 MDSC curves of PLGA- TPE after different aging times (t_a): unaged (black), 1 day (blue), 3 days (green) and 7 days (red). (a) non-reversing heat flow, (b) reversing heat flow, and (c) total heat flow. Reproduced from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

Also, in the case of physical aging, lifetimes are not consistent with the emission measurements (Figure 2.3b). From Figure 2.6b it is evident that, albeit the polymer free volume decreases with aging time (as proven by the increase of the enthalpy of relaxation), TPE lifetime is not affected by polymer physical aging, thus proving that TPE is not responsive to the small changes in free volume occurring during the

physical aging process, as instead previously hypothesized. As a matter of fact, the considerations made about the sensitivity of TPE on free volume and polymer T_g based on the emission intensity were not confirmed by the lifetime measurements. This indicates that the observed emission variations are not the consequence of RIMs and the source of these changes must be traced back to something else.

To assess whether the scattering can be the cause of the emission intensity variation, we measured the transmittance (%) of films of equal thickness in the wavelength range 300-800 nm. Figure 2.8a shows the average transmittance values (from multiple measurements in different areas of the sample, with error bars) obtained from differently aged PLGA-TPE samples. It is evident that, as aging time increases, the sample becomes less and less transparent. By repeating the same analysis on undoped PLGA films we observed the same behavior, proving that the decrease in the transmittance is not ascribable to the absorbance of the dye (see Figure 2.8b). These data corroborate previous observations demonstrating that during the process of physical aging, the approaching polymer chains induce local and inhomogeneous changes in the material density.[20,21] These physical defects lead to the phenomenon of scattering which, by opposing to the waveguide effect of the polymer matrix, can justify the observed enhancement in fluorescence intensity in differently aged samples (Figure 2.5). The same phenomenon can explain the decrease in fluorescence under temperature variations (Figure 2.3). Therefore, the measurement of the lifetime, combined with transmittance, highlight that the fluorescence variations detected at the T_g and in differently aged samples are ascribable to the combined effect of TPE photophysical properties temperature dependence and of the changes in the optical properties of the matrix where the TPE is dispersed, rather than to the restriction of TPE intramolecular motions. Hence, even if changes in fluorescence intensity are related to the polymer's T_g , they cannot be correlated to the AIE properties of the TPE, but rather to collective scattering effects).

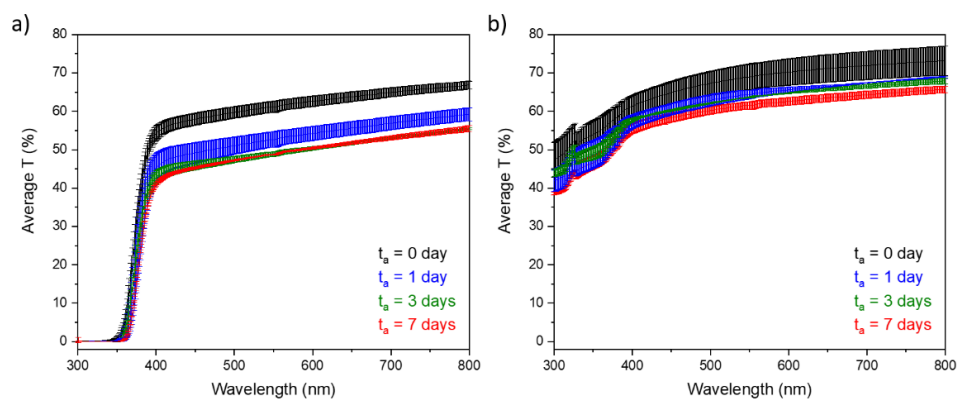


Figure 2.8 Average transmittance (%) of PLGA-TPE (a) and PLGA without TPE (b) after different aging times (t_a): unaged sample (black), $t_a = 1$ day (blue), $t_a = 3$ days (green), and $t_a = 7$ days (red). Adapted from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

Investigation of the mechanoluminochromic response

TPE has been also explored in combination with polymer matrices to develop mechanoluminochromic materials.[16] To this aim, TPE has been dispersed in poly(styrene-*b*-butadiene-*b*-styrene) (SBS)[3] and in PDMS[10] or bonded to the main chain of a polyurethane.[7]

In this work, PVAc-TPE was tested under tensile deformation to elucidate the mechanism behind the change of emission intensity under stretching. PVAc was selected being a tough, highly deformable polymer, that allows to investigate the change of sample fluorescence over a wide range of strains. The mechanical data are reported in Figure 2.9 and Table 2.2.

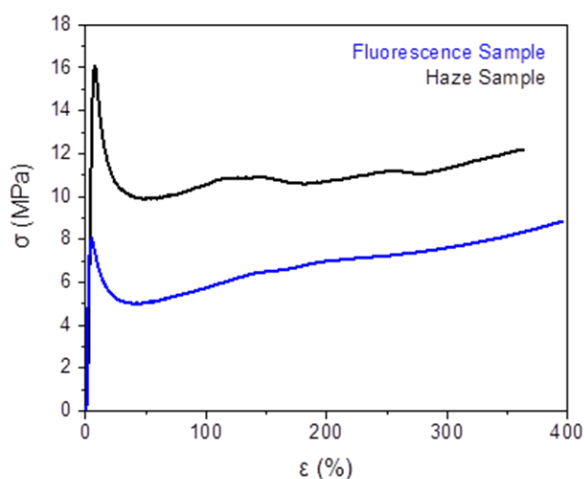


Figure 2.9 Stress-strain curves of PVAc-TPE specimens tested under UV light (blue) and white transversal light (black). Reproduced from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

Table 2.2 Mechanical data of PVAc doped with TPE (E = Young's modulus obtained from the slope of the elastic range; ϵ_b = strain at break; σ_b = stress at break).

Sample	E [MPa]	ϵ_b [%]	σ_b [MPa]
PVAc-TPE	620 ± 180	275 ± 75	12 ± 2

As shown in Figure 2.10, in a first experiment, the sample was irradiated with a UV lamp (365 nm) and the tensile test was recorded with a camera. A second experiment was then carried out similarly, by replacing the UV source with a white lamp. The comparison between the two experiments should help in assessing whether the change of fluorescence is ascribable to a change in TPE emission or rather depends on changes in the physical property of the matrix. It is pointed out that the analysis was not limited to the central part of the sample, but the whole sample was digitized for the determination of the intensities. This approach reduces the effect of dye dilution on the outcomes of the analysis.

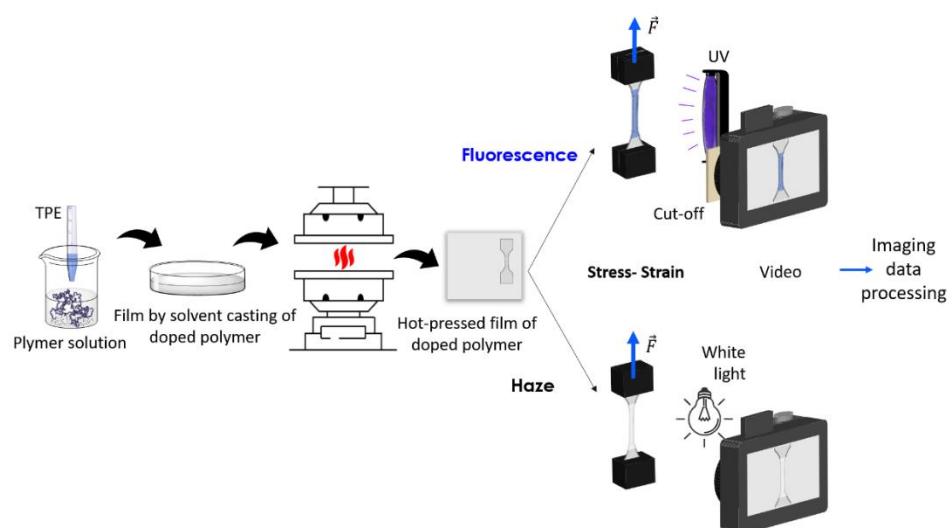


Figure 2.10 Scheme of the experimental setup for the measurement of sample fluorescence and brightness variation during the stress-strain test: polymer films doped with TPE were obtained by solvent casting followed by hot-pressing; a dog-bone specimen was irradiated with either a UV light or a white light and the test was recorded with a camera; images were processed by analyzing greyscale intensity, using ImageJ software. Reproduced from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

Figure 2.11a shows that the emission intensity of the specimen under UV light is constant up to about 100% strain and then displays a positive correlation with the strain. This result differs from previous data reported in the literature, where a negative correlation between the emission intensity and the strain was found and ascribed either to the reduced concentration of the dye in the excited area of the sample or to the disruption of TPE aggregates.[3,7,10] Differently from the previous studies, our analysis was not limited to the central part of the sample, but the whole sample was analyzed for the determination of the intensities. This approach reduces the effect of dye dilution on the outcomes of the analysis and can justify why emission fluorescence does not decline in our experiments. However, the observed emission increase above 100% strain is somehow unexpected, since sample stretching would suggest the occurrence of TPE disaggregation, with a consequent emission decrease owing to reduced RIM effect.

The second experiment, performed with the white lamp, allowed to determine the change in transparency of the sample, since a

gradual opaqueness was distinctly visible to the naked eye during the stretching (Figure 2.11b). Image analysis yielded the greyscale values of the sample versus strain, corresponding to a measurement of average scattering. It is evident that the trend of fluorescence emission (blue line in Figure 2.11a) and of haze (black line in Figure 2.11a) are very similar. This suggests that the origin of the emission increment above 100% strain lies on the emergence of scattering phenomena during the analysis, rather than an increase in the quantum yield of TPE. Scattering, indeed, can increase the observed emission intensity not only as stray light (i.e., light at the excitation wavelength that is mistaken for emission, a contribution that can be minimized with good quality emission filters) but also due to the interruption of waveguide effect.[22] Homogeneous polymers films have a larger refractive index than air, resulting in partial waveguide of the emission light originated inside the sample, which is then transported to its edges. This can drastically reduce the amount of photons that are originated and detected in the central part of the film. The occurrence of scattering interrupts the waveguide effect, increasing the detection of the emitted photons nearby their origin, rather than at the edges of the film.

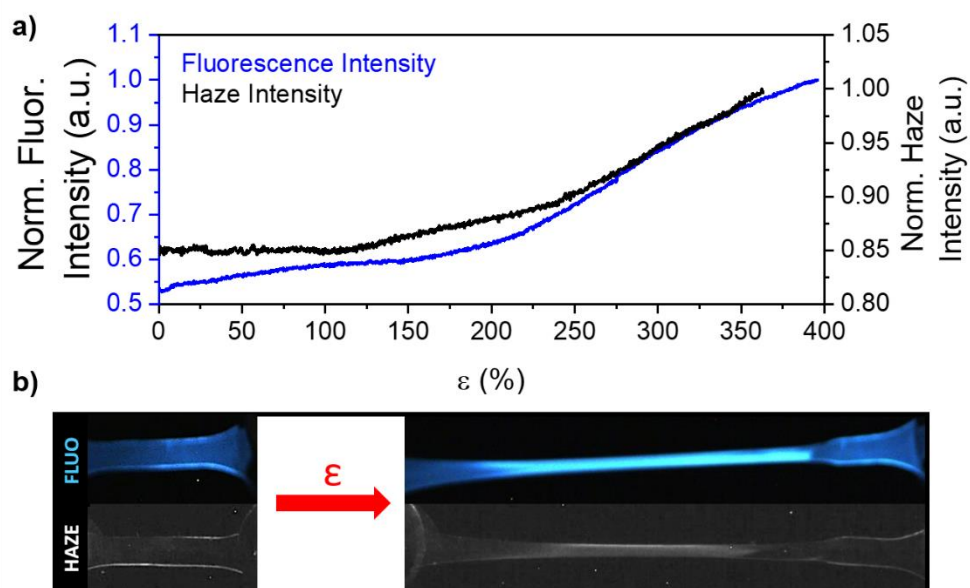


Figure 2.11 a) Plotting of the data obtained by the analysis of the videos recorded during stress-strain test in-situ fluorescence emission (blue line) and haze (black line). b) Pictures of PVAc-TPE sample at the pristine (right) and the stretched state (left) under UV (top) and transversal white light (bottom). Adapted from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

A further evidence that supports this hypothesis is provided by the TPE lifetime – a parameter that is proportional to the quantum yield – measured at different strain values, which remains constant (lifetime values are reported in Figure 2.12 and differ less than 3%). It is thus confirmed that mechanical deformation, despite changing the arrangement of polymer chains, does not significantly affect TPE mobility and its radiative decay.

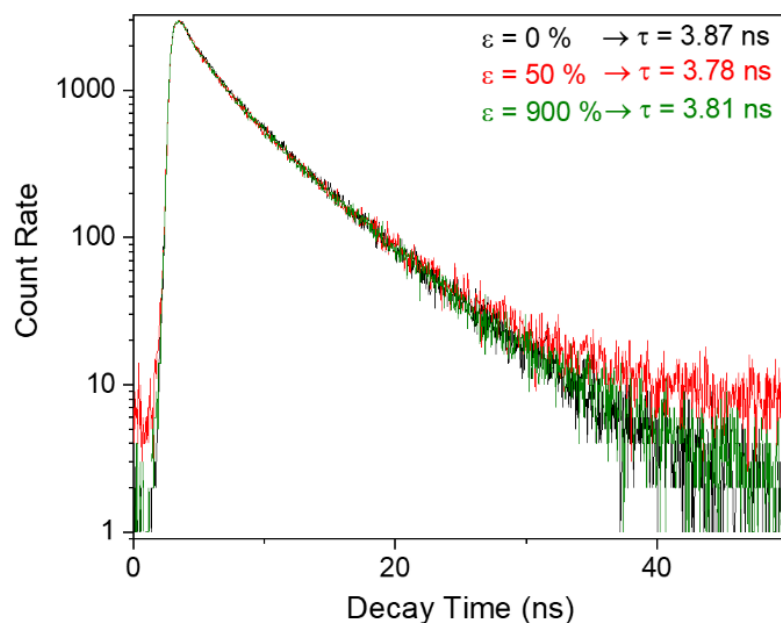


Figure 2.12 Fluorescence decays of PVAc-TPE stretched at different strain values (ϵ). Adapted from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

The images obtained with the wide-range fluorescence optical microscope (Figure 2.13) better clarify what happens on the polymer sample during stretching above 100% strain. Upon deformation, microcracks are formed,[23] clearly observable during the acquisition of images at various extensions. Cracks and microcracks are usually formed during polymer use and reveal in advance permanent failure of the matrix. Notably, cracks are visible both in bright field microscopy, as dark lines, and in fluorescence imaging, where these cracks appear more emissive than the rest of the sample. Here, the waveguide effect of the polymer matrix is interrupted by these defects, which results in an only apparently increased fluorescence, which is instead due to the amount of light that is not anymore waveguided to the edges of the sample.[24,25]

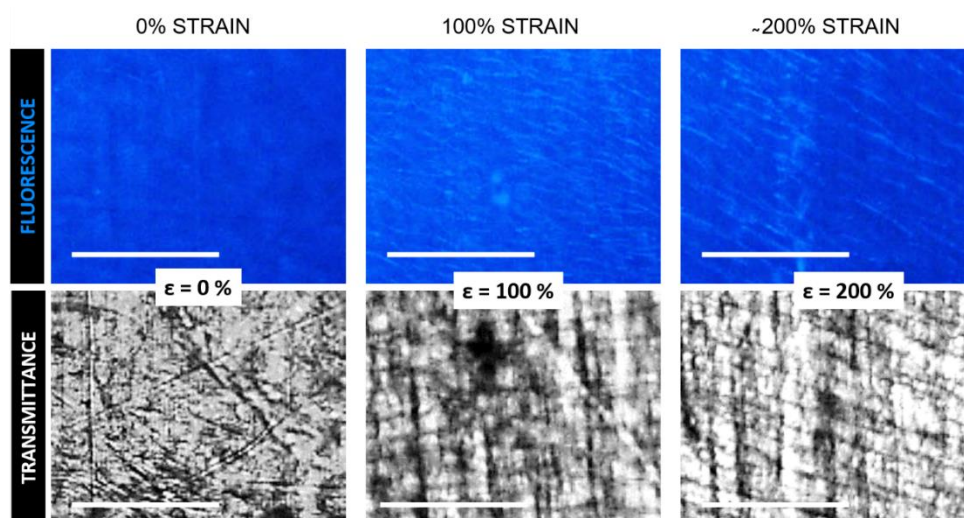


Figure 2.13 Wide range microscope images of PVAc-TPE at 0%, 100% and 200% ϵ under fluorescence (top) and transmission (bottom) microscopy. Scale bar = 100 μm . Reproduced from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

In fluorescence images acquired with confocal microscopy, the microcracks formed on the sample are no longer visible (Figure 2.14a). This technique, indeed, allows to minimize waveguiding and scattering contributions, since both excitation and emission light are confined in the sub-micrometric confocal volume. Therefore, in confocal microscopy, microcracks cannot act as the spot of emergence of emission light waveguided from other original spots. Finally, the FLIM technique confirmed that the lifetime of the sample does not change across the sample, not even in the proximity of the microcracks (Figure 2.14b), further confirming that the increase in intensity observed in wide-field microscopy and in fluorescence imaging (Figures 2.11 and 2.13) arises by the interplay of waveguiding and scattering, and it is not ascribable to changes in the photophysics of the AIE probes.

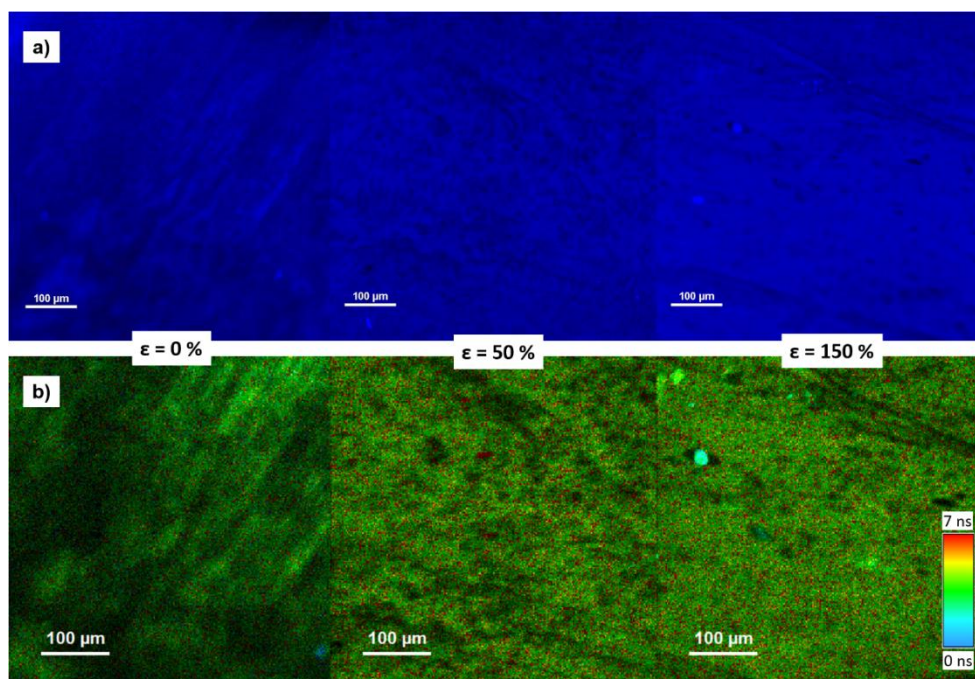


Figure 2.14 Confocal microscopy (a) and FLIM images of PVAc-TPE (b) at 0%, 50% and 150% strain (ϵ). Reproduced from ref. [13] with permission from SCUT, AIEI, and John Wiley & Sons Australia, Ltd., Copyright © 2023.

2.1.3. Conclusions

TPE, the simplest and most widely known AIE, was used as an additive in various polymer matrices to investigate the effects of temperature and mechanical deformation over sample optical properties with the aid of various characterization techniques that provided novel and complementary data. We confirmed previously reported phenomena, such as emission changes in correspondence of T_g , and we observed novel, unreported behavior, such as emission increases in response to strain. Concerning the variations in correspondence of T_g , we observed an evident drop whose amplitude positively correlates to the physical aging of the sample. Accurate analysis of lifetime decays showed that these changes could only be detected via measurements of emission intensity but did not correlate with the expected variation of the fluorescence lifetime. Transmittance and microscopy measurements showed the correlation between the emergence of light scattering and the variation of emission intensity, both under thermal and mechanical stimuli, suggesting that changes in the optical transparency and the

interruption of the waveguide effect could be the main cause for the observed changes in emission intensity. This has also been confirmed by confocal microscopy and FLIM investigations, that showed again the invariability of the lifetime during polymer deformation, as well as of the fluorescence intensity, when measured under the condition that the contribution of scattered light is made negligible (in confocal microscopy). As a conclusion, TPE can be a useful probe to study thermo- and mechanoluminochromism of polymeric matrices. Yet, measurements of an absolute fluorescence parameter such as the fluorescence lifetime is essential to discriminate between variations of the photophysical properties of the AIE dyes, related to the RIM effect, and variations that are instead related to the optical homogeneity of the polymer matrix. It is envisaged that the proposed methodology applied to other AIE dyes will facilitate a more precise identification of fluorophores that exhibit genuine sensitivity to the polymer environment.

2.1.4. Experimental section

Materials. PVAc (Sigma Aldrich, $M_w = 5 \times 10^5 \text{ g mol}^{-1}$), and PLGA 75:25 mol% (Evonik, inherent viscosity $0.71 - 1.0 \text{ dL g}^{-1}$), PC (Sigma Aldrich, $M_w = 4.5 \times 10^4 \text{ g mol}^{-1}$) were used to prepare polymeric films. Dichloromethane (DCM, $\geq 99.8\%$), Methanol (MeOH, $\geq 99.9\%$), Ethanol (EtOH, 97.2%), TPE were provided by Sigma Aldrich and used without further purification.

Film preparation. Films were obtained by solvent casting from polymeric solutions. PLGA and PC were dissolved in DCM at a concentration of $4\% \text{ w v}^{-1}$ while PVAc was dissolved in a mixture of MeOH: EtOH=80:20 (v/v) at $4\% \text{ w v}^{-1}$. TPE was then added to the polymeric solutions to gain 0.1 wt.% TPE in the final films of PVAc and PC and 2 wt.% TPE in PLGA film. TPE concentration was set to achieve a detectable emission from the samples. After stirring until complete polymer dissolution, each mixture (70 mL) was poured into a glass petri dish ($d = 110 \text{ mm}$) and left under the fume hood for solvent evaporation. The resulting films were hot-pressed at a temperature of $T_g + 100 \text{ }^\circ\text{C}$ and rapidly cooled to room temperature.

Accelerated physical aging experiments. To investigate the effect of physical aging, all samples were thermally treated to erase their thermal history. They were heated to a temperature of $T_g + 100\text{ }^{\circ}\text{C}$ for 10 min and then quenched using liquid nitrogen. Once prepared, samples were immediately analyzed at t_0 . Then they were kept at a temperature corresponding to $T_g - 15\text{ }^{\circ}\text{C}$, to achieve controlled aging, and analyzed after 1, 3 and 7 days.

Characterization methods. DSC was carried out using a Q2000 DSC apparatus (TA instruments) equipped with a refrigerated cooling system (RCS90). About 6 mg of sample were placed in Tzero aluminum pans and subjected to a heating scan at $20\text{ }^{\circ}\text{C min}^{-1}$ from $-90\text{ }^{\circ}\text{C}$ to $+150\text{ }^{\circ}\text{C}$, quenched to $-90\text{ }^{\circ}\text{C}$, and then heated up to $150\text{ }^{\circ}\text{C}$ at $20\text{ }^{\circ}\text{C min}^{-1}$, under nitrogen atmosphere. From this acquired data, the T_g was taken at half-height of the glass transition heat capacity step in the second heating scan. MDSC was also performed from $-20\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$. The heating rate was $1\text{ }^{\circ}\text{C min}^{-1}$, the modulation amplitude was $0.159\text{ }^{\circ}\text{C}$ and the oscillation period was 40 s. The enthalpic recovery of the aged samples was calculated as the area of the endothermal relaxation peak in the non-reversing heat flow signal.[26] Transmittance spectra were measured using an UV/Vis Perkin Elmer Spectrophotometer Lambda-45 in a wavelength range from 800 nm to 300 nm. Fluorescence analysis under temperature was carried out by positioning the TPE-doped polymer sample ($1.5 \times 1.5\text{ cm}^2$) on a heating stage (Linkam TH 600 hot stage). The sample is then irradiated with a UV light at 365 nm, while undergoing different heating and cooling scans (from RT to $150/200\text{ }^{\circ}\text{C}$) under a controlled rate of temperature variation ($5\text{ }^{\circ}\text{C min}^{-1}$), using He flow to cool the sample (Figures 2.1 and 2.4). During these ramps, an RGB camera, with a 415 nm cut-off placed in front of the lens to filter UV light reflections, was used to capture an image sequence of the emitting sample. With the aim of obtaining a graph correlating the fluorescence intensity with sample temperature, data were processed using ImageJ software. The grayscale intensity values of the image sequence were obtained by analyzing the entire sample area and were then plotted with respect to the temperature values. An Edinburgh FLS920

fluorometer equipped with a high-speed HS773-04 photomultiplier and connected to a PCS900 PC card was used for the fluorescence lifetime measurements based on time-correlated single photon counting technique (TCSPC). Sample lifetimes as a function of temperature were taken inserting the heating stage with the sample into the sample chamber of the instrument. Lifetimes were acquired every 5 °C during a temperature ramp of 5 °C min⁻¹ from 25 °C to 100 °C. A 340 nm pulsed diode laser Picoquant was used to excite the sample and the emission signal was collected at 480 nm (380 nm cut-off filter). The obtained decays were then analyzed and a good fitting obtained with a monoexponential equation results in an average lifetime. To determine sample lifetimes during mechanical deformation, we used a homemade tensile tester working under strain control. Stress-strain tests were carried out using an Instron Testing Machine 4465 and the Series IX software package. Dog-bone-shaped samples (gage length = 20 mm, width = 5 mm, thickness = 0.1-0.3 mm) cut from each film were tested in traction mode with a load cell of 100 N. The crosshead speed was set at 10 mm min⁻¹. During mechanical tests, samples were irradiated either with a UV lamp (led at 365 nm, Thorlabs) positioned in front of the sample or with a white light positioned at 90° to the front of the sample (Figure 2.10). The stress-strain tests were recorded with a camera (DCC1645C - USB 2.0 CMOS, Thorlabs) placed in front of the sample. To detect fluorescence intensity and avoid stray light from UV excitation, a 400 nm cut-off filter was used in front of the camera. Image J software was used to determine the sample fluorescence during the stress-strain test under UV irradiation and the change of sample haze in greyscale during the stress-strain test under white light irradiation. More in detail, the integration over a ROI was performed and taken as fluorescence or haze intensity values, respectively, to be correlated with the strain of the sample. Mechanical data are provided as average value $\pm$ standard deviation. Fluorescence microscopy was carried out using an Olympus IX 71 inverted microscope equipped with a LED (365 nm, Thorlabs) for fluorescence excitation with a bandpass excitation filter (MF390-18, Thorlabs US), then projected to the sample through reflection on a dichroic mirror (MD416, Thorlabs US) and the emission was imaged

through an emission filter (wavelength interval 510 ± 42 nm) with a Basler Scout scA640-70gc CCD RGB camera for image acquisition. Images with 10X magnification were taken using the objective Olympus UPLFLN10X2. At the same time, using the same microscope with bright field illumination, transmission images were also obtained. Samples were analyzed also by using a Nikon A1R confocal microscope system with 20x magnification, numerical aperture, NA, 0,75 of Nikon Plan-Apo objective lens. The samples were excited by a continuous wave laser at 405 nm. The emission of the films was collected in the range 500 - 620 nm. In FLIM a TCSPC system of Picoquant GmbH Berlin was used with a 405 nm pulsed excitation laser at 10 MHz repetition frequency, the same dichroic mirror, a 482/35 nm bandpass emission filter, a Hybrid PMA detector and a Picoquant TimeHarp correlation board.

2.2. Discrimination of chain mobility and free-volume variations in polymer phase transitions with an absolute AIE probe

2.2.1. Introduction

Up to now, application of reported AIE probes for local mobility in polymer-based materials are severely limited by the dependence of their emission also on other parameters, firstly and foremost, on temperature, a representative example being TPE, as reported in the previous section (Figure 2.6a). With such premises, the use of luminescent probes should only be feasible at a given and constant temperature, with important limitations to the quantitative estimation of molecular mobility as a function of temperature, which often remains relative to the used measurement system.

In this work, we have screened a library of rotors and AIE luminogens (Figure 2.15) to select a probe that shows minimal intrinsic dependence on temperature in a broad range, up to 120 °C, and whose emission is strongly dependent on local mobility of polymer chains. To overcome the common issue of relativity of luminescence intensity information, we monitor an absolute luminescence parameter, i.e., the fluorescence lifetime. Indeed, this parameter is expected to provide, in a single measurement and without the need of calibration curves, a quantitative estimate of the local chain mobility. The 3-methyl-rhodanine TPE derivative (TPE-MRh), which was synthesized and characterized by Prof. Pucci's research group at the University of Pisa, was selected from various dyes tested. TPE-MRh is an AIE molecular rotor with a strong dependence on the local mobility of polymer chains. It exhibits minimal temperature sensitivity over an extensive temperature range, approximately up to 200°C. Utilizing this dye and monitoring its lifetime during temperature scans, it became possible to establish a correlation between photophysical data and the mobility of several polymer matrices. In fact, by selecting polymers with different T_g to cover a wide range of temperature, it was possible to investigate the behavior of the dye in different mobility conditions. Further investigation, carried out with confocal microscopy and fluorescence lifetime microscopy, permits to identify the components of immiscible

polymer blends and to gain information about the UV-curing of a crosslinked polymer.

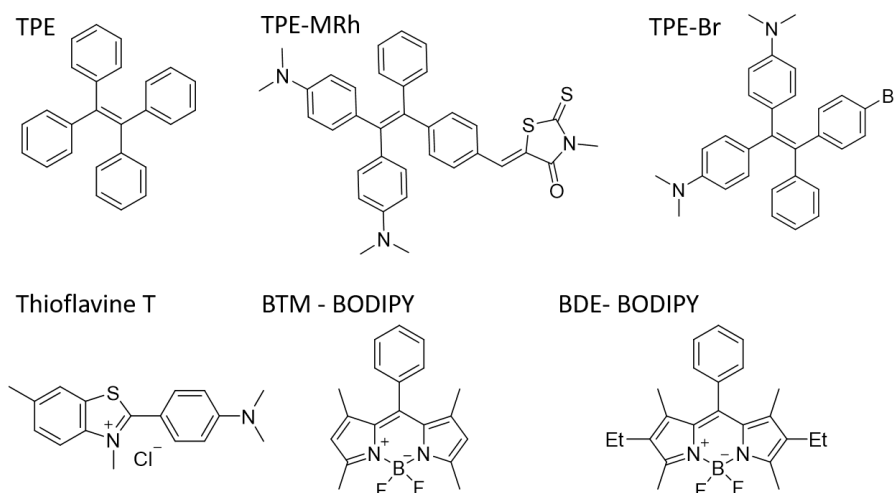


Figure 2.15 Chemical structure of the tested dyes: TPE, TPE bromo derivative (TPE-Br) and TPE-MRh synthesized by Prof. Pucci's group at the University of Pisa. [27] Additionally, thioflavin T (ThT) and two derivatives of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (commonly known as BODIPY): tetramethyl (BTM) and diethyl (BDE) provided, by Prof. Prodi's group from the University of Bologna.

2.2.2. Results and discussion

For a preliminary screening of the dyes (Figure 2.15), casted films were prepared from two different polymer matrices: PLGA and nitrile butadiene rubber (NBR). The former is an amorphous glassy polymer and the latter is a rubbery material. Each polymer was blended with 0.1 wt.% of six distinct fluorophores, including TPE, along with two derivatives (TPE-Br and TPE-MRh), thioflavin and two derivatives of BODIPY (BTM and BDE). Figure 2.16 shows the different emission color of the six different PLGA samples under UV light.

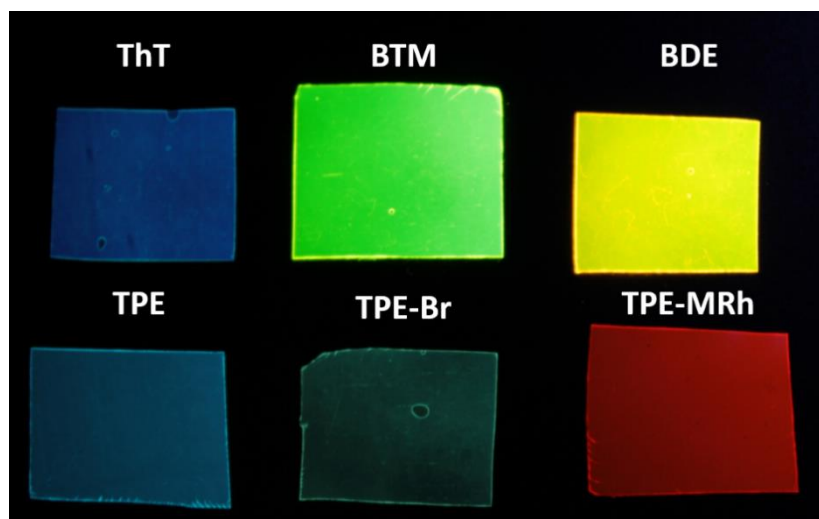


Figure 2.16 PLGA samples doped with the different dyes (0.1 wt.%) observed under UV light.

The tested fluorophores are well-known molecular rotors or AIE compounds, and they exhibit photophysical properties that depend on their mobility. To evaluate their performance, the films prepared with these fluorophores were subjected to temperature variation, inducing changes in polymer mobility. The decay behavior of the different samples was continuously monitored as the temperature increased, allowing us to determine both emission intensity values and lifetime measurements. The samples were subjected to a first heating ramp, aimed at erasing any thermal history effects in the material, followed by a cooling at $5\text{ }^{\circ}\text{C min}^{-1}$, a second heating scan, that was the main focus of data collection, and a final cooling to room temperature. Figure 2.17a reports the normalized emission intensities during the second heating ramp and Figure 2.17b shows the lifetimes, calculated as the average of the values obtained during the second heating and the final cooling. Lifetimes were normalized to the maximum lifetime value obtained in PLGA, referred to as τ_{glass} , as it corresponds to the matrix in the glassy state at room temperature.

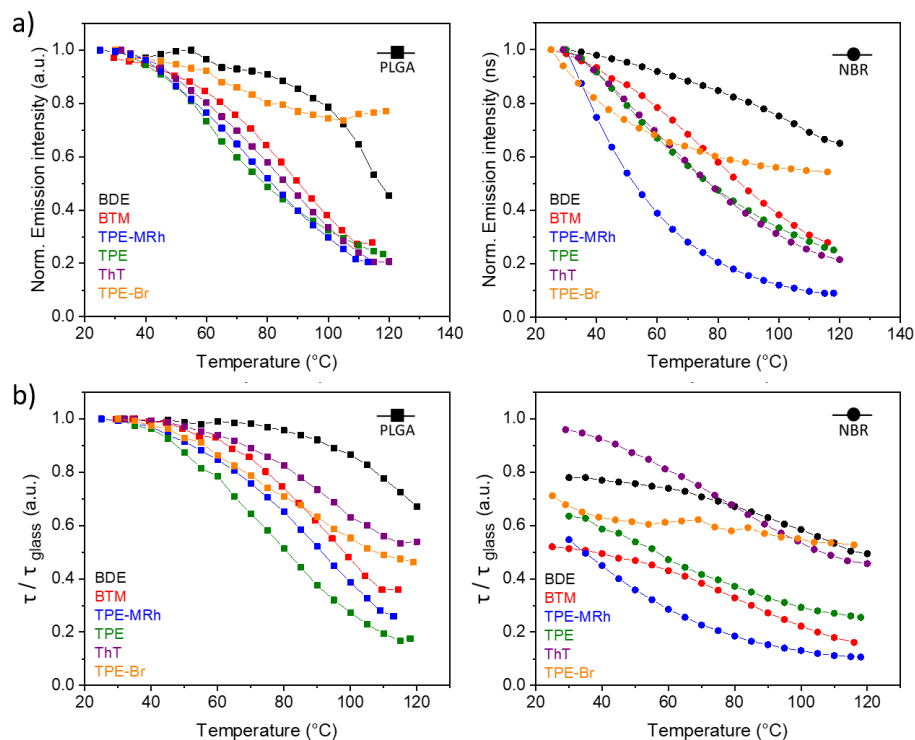


Figure 2.17 a) Normalized emission intensity of the sample decays during the second heating ramp, after erasing thermal history. PLGA samples are displayed on the left, while NBR samples are shown on the right. b) Lifetimes of PLGA (left) and NBR (right) samples, normalized to τ_{glass} .

As observed in Figure 2.17, the NBR samples consistently exhibited lower lifetimes compared to the corresponding PLGA samples loaded with the same dye. This observation can be readily explained by considering that, at room temperature, NBR is well beyond its T_g , while the PLGA matrix reaches its T_g at approximately 50 °C. Therefore, at room temperature, the two polymers display a noticeable difference in chain mobility. It is also worth noting that the addition of the different dyes does not interfere with the T_g of the polymers.

Table 2.3 Thermal data of undoped and doped polymers: T_g , determined at half-height of the glass transition heat capacity step, and ΔC_p).

Sample	T_g (°C)	ΔC_p (J g⁻¹ °C⁻¹)
PLGA	48	0.58
PLGA-TPE	49	0.53
PLGA-TPE-Br	48	0.55
PLGA-TPE-MRh	49	0.60
PLGA-BDE	50	0.57
PLGA-BTM	50	0.58
PLGA-ThT	50	0.51
NBR	-16	0.29
NBR-TPE	-17	0.26
NBR-TPE-Br	-15	0.24
NBR-TPE-MRh	-15	0.28
NBR-BDE	-15	0.23
NBR-BTM	-16	0.27
NBR-ThT	-16	0.30

The aim of this analysis is to pinpoint the dye that, among the tested ones, is more responsive to the variation in matrix mobility with temperature. In other words, we expect that the optical characteristics of the probe change around the glass transition temperature of the polymer in which it is embedded. Ideally, beyond this point, both the intensity and lifetime of the dye should decrease. According to this criterion, the BDE can be excluded from the candidates: in PLGA it exhibits a significant intensity variation (black squares of Figure 2.17a left) at temperatures much higher than T_g , as well as its lifetime (black squares Figure 2.17b left). On the other hand, the lifetime of BTM, TPE, and ThT in PLGA (red, green and purple squares respectively, in Figure 2.17b left) reveals a behavior consistent with expectations, showing an initial plateau and a decrease around polymer T_g . In NBR (red, green and purple circles of Figure 2.17b right), however, the decrease in lifetime occurs with some delay. A small plateau is observed at the beginning of the scan, whereas it would be expected to occur immediately, given that this is

a matrix already well above T_g , indicating high mobility. A similar behavior is observed in emission intensity (Figure 2.17a).

The dyes that best meet the above-cited criteria are TPE-Br and TPE-MRh. In PLGA (Figure 2.17b left, orange and blue curves respectively), they exhibit an initial plateau followed by a decrease at PLGA T_g , while in NBR (Figure 2.17b right, orange and blue curves respectively), the lifetimes decrease right from the beginning with a steep gradient, leading to a final plateau. Also in this case, the emission intensity has a similar pattern (Figure 2.17a).

Among these two dyes, TPE-MRh displays the most significant variation in both intensity and lifetime and is thus selected to continue the study. The choice can be further justified by presenting the results in a slightly different manner. When measuring an absolute parameter like lifetime, it is possible to correlate measurements taken on different samples and under different experimental conditions. This allows us to compare the photophysical behavior of dyes as a function of temperature relative to the mobility that polymers exhibit beyond T_g , irrespective of the matrix. The same is not possible with a relative measure as the intensity. Figure 2.18 displays the same data as Figure 2.17, but the x-axis features temperature values shifted to $T - T_g$, considering the T_g of each specific polymer. This adjustment aligns the value at 0 °C with the condition where the matrix, irrespective of its composition, is precisely at its glass transition point. The expectation is that a fluorophore closely correlating its photophysical properties with polymer mobility should exhibit an unchanged behavior up to 0 °C, after which it would begin to decrease steeply. Therefore, it is clear that the intensity graph (Figure 2.18a) is less informative as all curves originate from the same initial value. Conversely, the lifetimes graph concerning $T - T_g$ (Figure 2.18b) reveals that only TPE-Br and TPE-MRh exhibit behavior independent of the polymer matrix, aligning primarily with T_g . Notably, the experimental points determined from PLGA matrix (orange and blue squares of Figure 2.18b) adheres to the anticipated trend, and the ones related to NBR matrix (orange and blue circles of Figure 2.18b) closely match in the overlapped interval of $T - T_g$. This matching is more evident for

TPE-MRh (blue), reinforcing its status as the most suitable probe, demonstrating the strongest correlation with polymer properties. For the other dyes, apparently, there are additional dependencies influencing the photophysical trend with temperature, resulting in discrepancies between the curves.

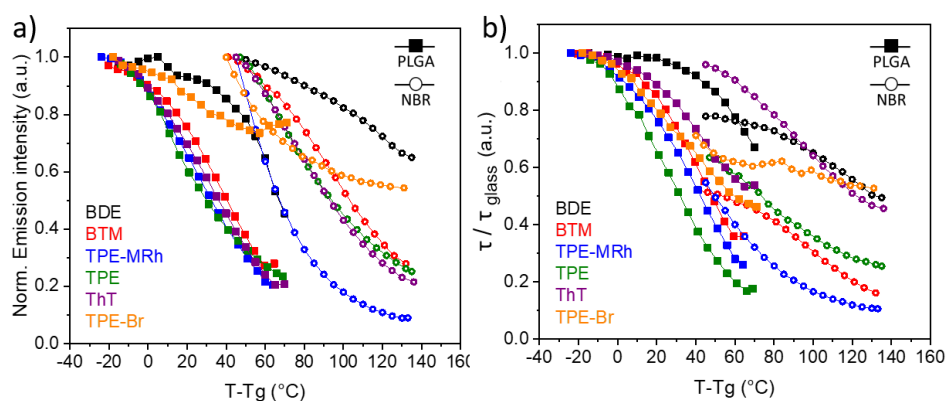


Figure 2.18 Normalized emission intensity (a) and normalized lifetime (b) of PLGA and NBR dye-doped samples during the second ramp as a function of $T - T_g$.

After selecting TPE-MRh as the ideal fluorophore, we proceeded to study its emission properties in a variety of polymer matrices with different chemical structures and glass transition temperatures, covering a wide temperature range. The new matrices chosen for this study, in addition to the already analyzed NBR and PLGA, are polyethylene glycol (PEG) and polystyrene (PS). Table 2.3 displays the T_g values for these polymers with and without the dye, included as additive at 0.1 wt% of concentration.

Table 2.3 Thermal data of PEG and PS undoped and doped with TPE-MRh: T_g , determined at half-height of the glass transition heat capacity step, and ΔC_p)

Sample	T_g (°C)	ΔC_p (J g ⁻¹ °C ⁻¹)
PEG 400	-75	0,17
PEG-TPE-MRh	-73	0.26
PS	97	0.36
PS-TPE-MRh	91	0.39

The films were subjected to the same temperature ramps applied to the earlier samples. Fluorescence lifetime decays are measured as the temperature increases (Figure 2.19). It is worth noting, that the lower the T_g of the polymer, the lower the lifetime measured at room temperature (RT). In particular, it approaches zero for fluid PEG polymer, with $T_g \ll RT$ and it is very small for rubbery polymer NBR (T_g ca. -15 °C). In polymer matrices with higher T_g , when we increase T from RT to 150°C (or 200°C in PS), the measured lifetime exhibits (i) rather constant values as long as $T \ll T_g$, then (ii) a progressive decrease of lifetime in the range $(T_g - 10^\circ\text{C}) < T < (T_g + 110^\circ\text{C})$, and finally again a rather constant value, yet now approaching zero, for $T \gg T_g$.

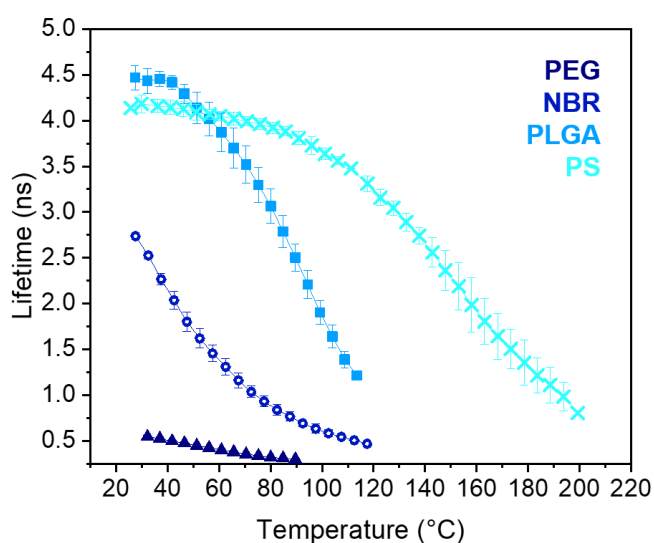


Figure 2.19 Lifetime trends at increasing temperature in different matrices containing 0.1 wt.% of dispersed TPE-MRh.

Remarkably, if the lifetime trends are overlapped by shifting the T axis to $T - T_g$ (i.e., when all curves are relative to T_g which is set the zero point in the abscissa axis) a sigmoidal curve is obtained that is common to all polymer matrices, independently from the polymer composition and from the absolute temperature value (Figure 2.20). This sigmoid represents a sort of “master” curve where all fluorescence lifetime data correlate with a common property of all polymers and only dependent on T_g , which we ascribe to the absolute mobility of polymer chains.

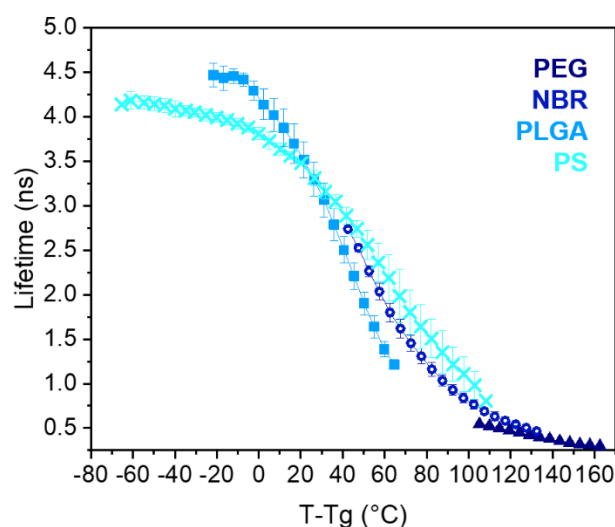


Figure 2.20 “Master” curve of the average fluorescence lifetime vs. $T - T_g$. Average fluorescence lifetimes are obtained by fitting the fluorescence decay.

At the best of our knowledge, this is the first example of a common curve obtained from fluorescence data acquired on different polymer matrices, without the need of correction for the different chemical environments or for intrinsic temperature dependence of the emission properties of the probe.

The sigmoidal trend of the fluorescence lifetime in the range of polymer T_g provides an absolute calibration curve that allows direct assessment of local chain mobility via measurement of fluorescence lifetime. The dynamic range of this sensing system, i.e., the equivalent temperature range in which local mobility can be quantitatively assessed, is ~ 120 °C, mostly above T_g .

To further check the invariance of the fluorescence lifetime with respect to the polymer matrix, we measured the lifetime in each polymer film in the glassy state at -196 °C (77 K) (where chain mobility

is null and equal for all polymers). We take this lifetime as the «characteristic lifetime» of each polymer matrix, τ_0 . The obtained values are presented in Table 2.4. A slight discrepancy between the values is evident, which can be attributed to experimental error. In this case, the value of the dye, when immobilized, is considered the same, regardless of the matrix, indicating that the properties of this fluorophore remain consistent and independent of further interactions with the matrix.

Table 2.4 Lifetime values of TPE-MRh dye in different polymer matrices at -196 °C (77 K).

Sample	τ_0 (ns)
PEG-TPE-MRh	4.9
NBR-TPE-MRh	5.1
PLGA-TPE-MRh	5.0
PS-TPE-MRh	4.6

To further investigate the sensitivity of this fluorophore to variations in the free space between polymer chains, controlled physical aging studies were conducted. Indeed, it is well-known that in glassy polymers chain mobility decreases as consequence of physical aging, namely of small-scale chain relaxations that alter the local packing of the chains and cause volume contraction. Films of PS-TPE-MRh were thermally annealed at a temperature 15°C below T_g for specific durations. To quantify the aging process, the samples were analyzed using MDSC, which provides the signal corresponding to enthalpy relaxation. The values of ΔH_{relax} related to different aging times are presented in Table 2.5. At the same time, the lifetime of the dye was measured to establish a possible correlation with the aging of the sample.

Table 2.5 ΔH_{relax} values determined from the non-reversing signal of MDSC of PS-TPE-MRh aged sample

Sample	Aging time (h)	ΔH_{relax} (J g ⁻¹)
PS-TPE-MRh	0	0.003
	24	1.816
	72	2.168
	168	2.554

Figure 2.21 illustrates that enthalpy relaxation increases rapidly at short aging times and then continues to increase slowly. Given its molecular rotor nature, one might expect the dye's lifetime to exhibit a similar pattern as enthalpy relaxation. Surprisingly, the lifetime of the dye remains constant during this period, despite the noticeable changes in free volume that the polymer undergoes during the treatment. Thus, the results indicate that this fluorophore is not as sensitive to these small changes in mobility as it is to the significant changes that occur near the glass transition temperature.

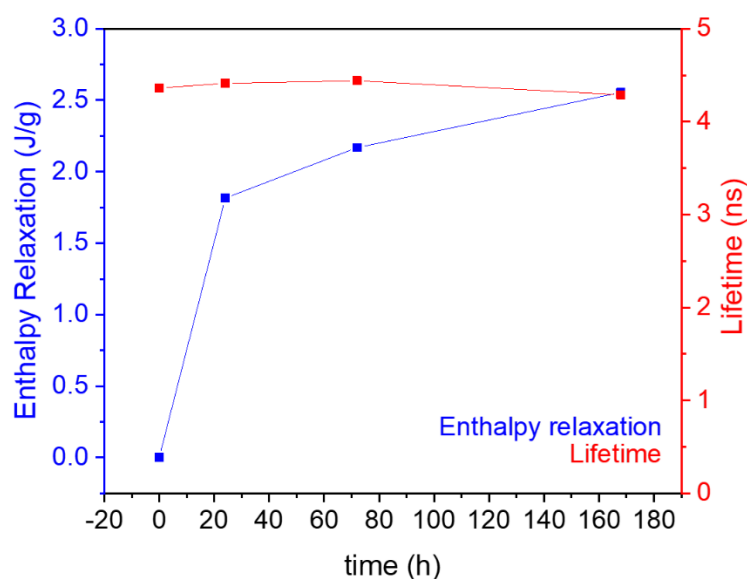


Figure 2.21 ΔH_{relax} (blue) and lifetime (red) of TPE-MRh as a function of ageing time for PS.

After gauging the level of sensitivity of our fluorophore to matrix mobility, the detection of fluorescence lifetimes can be applied in various applications. For instance, drawing inspiration from the calibration performed with the “master” curve in Figure 2.20, we can leverage fluorescence lifetime imaging techniques like FLIM. FLIM

enables rapid, quantitative and submicron mapping of local mobility. In this work, FLIM was applied in (i) microstructured polymer blends at different temperatures (see Figure 2.22) and (ii) during the photopolymerization of a commercial resin (see Figure 2.23) in real time and with submicron resolution.

In the first example, we tested the possibility to monitor the microscopic phase structure of a polymer blend and its dynamic response to temperature variations. We blend two immiscible polymers that were previously doped and tested with TPE-MRh, i.e., PS and PLGA, which respectively feature T_g just above room temperature (PLGA, $T_g = 48^\circ\text{C}$) and at the limit of temperature range that could be accessed in our microscopy setup (PS, $T_g = 86^\circ\text{C}$). PS and PLGA were dissolved in a good solvent for both polymers (THF), mixed in 1:1 weight ratio, doped with 0.1% wt.% of the AIE probe and casted on a cover glass for microscopy. Confocal and FLIM images of the polymer blend at room temperature show that the dye is distributed in both phases (Figure 2.22a), with a higher intensity in the dispersed phase, which may suggest a favorable partition of the dye in this polymer matrix. Analysis of FLIM image reveals that the lifetime is similar in both phases (Figure 2.22a), which can be expected since both polymers are well below T_g at room temperature. The similar lifetime suggests a similar PLQY and similar brightness of the TPE-MRh dye in the two phases, thus corroborating the hypothesis of a slight preferential partition of the dye in the dispersed phase. In these conditions, the dispersed and dispersing phases cannot be confidently assigned to either PS or PLGA. Yet, when we locally increased the temperature with a heating plate to nominal 60°C , we observed a clear difference in the variation of the local lifetimes of the two phases (Figure 2.22b): the dispersed phase shows only a minor variation of τ from ~ 3.1 ns to ~ 3.0 ns, suggesting that this phase is only approaching the T_g range. Conversely, the dispersing phase shows a major decrease of the lifetime from ~ 3.5 to ~ 2.6 ns, which matches well with the variation that can be expected to occur $\sim 20^\circ\text{C}$ above T_g , according to the “master” curve discussed beforehand. It may be noted that local lifetimes measured with FLIM (Figure 2.22c) are slightly higher than reported in Figure 2.20, an effect probably

ascribable to the microscopic heterogeneity of the blend, in particular on the interfaces between the two polymer phases. Based on these observed variations the dispersing phase can be confidently assigned to the polymer with T_g close to RT, i.e., to PLGA, and the dispersed phase can be assigned to the polymer whose T_g is not fully reached in this experiment, i.e., to PS.

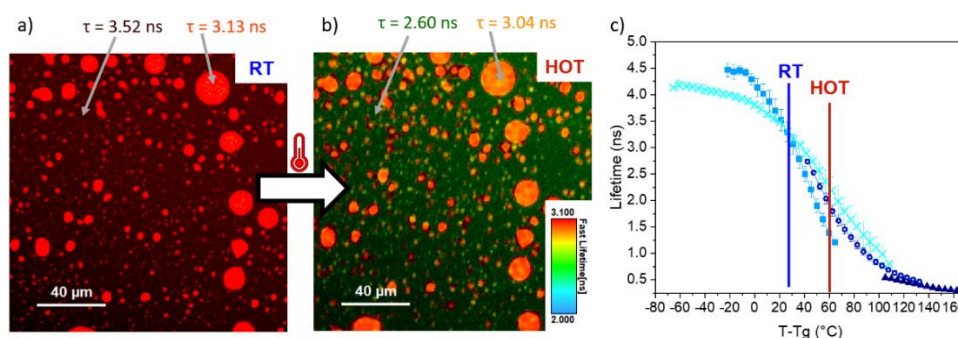


Figure 2.22 FLIM images of the PS:PLGA = 50:50 blend doped with TPE-MRh at room temperature (a) and heated to over 50 °C (b), along with the dye lifetime in both the dispersed and dispersing phases. (c) “Master” curve, indicating both the RT and heated state for reference.

As a second application, we explored the possibility of monitoring changes in the mobility of polymer chains over time by triggering a photopolymerization reaction, rather than varying temperature. We used a commercial photopolymer (“optical glue”) and doped it with 0.1 wt% of the TPE-MRh dye, keeping it in the dark. Subsequently, we deposited a small drop of the mixture on a cover glass and captured images of the sample using confocal microscopy and FLIM (Figure 2.23) over time. The excitation wavelengths were 488 nm and 405 nm, respectively. At the beginning, the optical glue was in a fluid state, and both the intensity and fluorescence lifetime were low (around 1 ns). Under the imaging conditions (wavelength and laser intensity), the sample properties remained stable, with no significant changes observed during the first 100 consecutive acquisitions. We then proceeded to irradiate the sample using the FLIM laser (405 nm) while gradually increasing the intensity by a factor of 1000. After 30 seconds of irradiation, a small square within the confocal field of view became visible. The image acquisition was repeated with FLIM. This irradiation process was performed in 30-second intervals, totaling 90 seconds, which allowed the sample to become rigid. The progressive

increase in intensity and the change in lifetime observed with longer irradiation times indicated a correlation with the advancing polymerization of the matrix, which gradually became more rigid. Considering that after 90 s of irradiation, the matrix reached a state resembling a rubbery polymer above its T_g , by measuring the probe lifetime more accurately and in combination with the “master” curve, it would be possible to estimate the local mobility of the polymer.

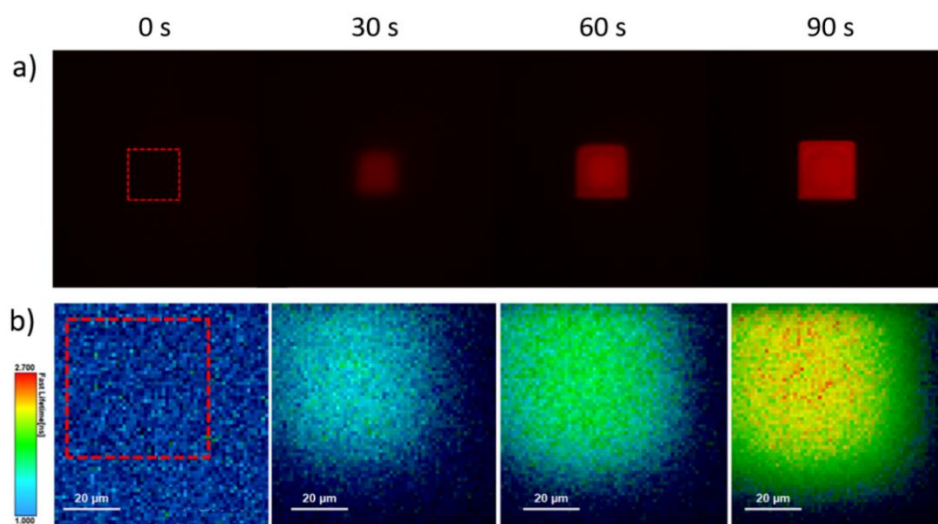


Figure 2.23 a) Confocal images ($\lambda_{ex} = 488$ nm) of the TPE-MRh doped optical glue at increasing times of irradiation (405 nm laser 1000 times more intense than in the image conditions), which show an increase of the emission intensity (4x zoom). b) FLIM images ($\lambda_{ex} = 405$ nm) in the same conditions showing the variation in lifetime with the proceeding of the polymerization.

2.2.3. Conclusions

After conducting a screening of various fluorescent molecular rotors as additives in two distinct polymers, the one exhibiting the most consistent response solely to changes in matrix mobility with increasing temperature was selected. Subsequent controlled aging studies revealed that this fluorophore is sensitive primarily to significant alterations in free volume, such as those occurring at the glass transition, as opposed to minor changes in physical aging. The chosen probe was subsequently tested in different polymer matrices, leading to the creation of a sort of “master” curve capable of correlating the photophysical properties of the fluorophore exclusively with matrix mobility, regardless of its composition. This

correlation was achieved as a function of temperature relative to T_g . Finally, two application examples were presented, demonstrating the utility of fluorescence lifetime imaging microscopy in distinguishing components of immiscible polymer blends with varying T_g and identifying the level of polymer mobility during the crosslinking process. In summary, this represents the first molecular rotor fluorescent probe for temperature-independent local mobility across a wide temperature range, facilitating quantitative monitoring of local mobility with high temporal and spatial resolution based on fluorescence lifetime.

2.2.4. Experimental section

Materials. PLGA 75:25 mol% (Evonik, inherent viscosity = 0.71 - 1.0 dL g⁻¹), NBR (Acrylonitrile-butadiene copolymer, 27% of Acrylonitrile, Nipol 1072CGX Zeon Chemicals L.P.), PEG (Sigma Aldrich, $M_n = 400$ g mol⁻¹), and PS ($M_w = 30.5 \times 10^4$ g mol⁻¹, Carlo Erba) were used to prepare polymeric films. Dichloromethane (DCM, $\geq 99.8\%$) and THF ($\geq 99.8\%$ Sigma Aldrich) were used without further purification. TPE-MRh and TPE-Br were provided by Prof. Pucci's group from University of Pisa, TPE were provided by Sigma Aldrich and used without further purification. ThT, BDE and BTM were provided by Pro. Prodi's group from the University of Bologna. The optical glue NOA81, was provided by Thorlabs.

Samples preparation. Films were obtained by solvent casting from polymeric solutions. PLGA, NBR and PVAc were dissolved in DCM at a concentration of 4% w v⁻¹ while PS was dissolved in THF. The dyes were then added to the polymeric solutions to gain 0.1 wt.% in the final films. Dyes concentration was set to achieve a detectable emission from the samples. After stirring until complete polymer dissolution, each mixture (50 mL) was poured into a glass petri dish (d = 110 mm) and left under the fume hood for solvent evaporation. The resulting films were hot-pressed at a temperature of $T_g + 100$ °C and rapidly cooled to room temperature. The PEG sample was prepared by simply mixing the right amount of TPE-MRh to gain 0.1 wt.% in the final sample. For the photopolymerization experiment the optical glue was

simply mixed with the right amount of dye, corresponding to a concentration of 0.1 w.t%

Accelerated physical aging experiments. To investigate the effect of physical aging, PS-TPE-MRh was thermally treated to erase its thermal history. More precisely, it was heated to a temperature of $T_g + 100\text{ }^{\circ}\text{C}$ for 10 min and then quenched using liquid nitrogen. Once prepared, the sample was immediately analyzed at t_0 . Then it was kept at a temperature corresponding to $T_g - 15\text{ }^{\circ}\text{C}$, to achieve controlled aging, and analyzed after 24h, 72h and 168h (7 days).

Characterization methods. DSC was carried out using a Q2000 DSC apparatus (TA instruments) equipped with a refrigerated cooling system (RCS90). About 6 mg of sample were placed in Tzero aluminum pans and subjected to a heating scan at $20\text{ }^{\circ}\text{C min}^{-1}$ from $-90\text{ }^{\circ}\text{C}$ to $+150\text{ }^{\circ}\text{C}$ (to $200\text{ }^{\circ}\text{C}$ in PC and PS), quenched to $-90\text{ }^{\circ}\text{C}$, and then heated up to $150\text{ }^{\circ}\text{C}$ (to $200\text{ }^{\circ}\text{C}$ in PC and PS) at $20\text{ }^{\circ}\text{C min}^{-1}$, under nitrogen atmosphere. From this acquired data, the T_g was taken at half-height of the glass transition heat capacity step in the second heating scan. MDSC was also performed from $-20\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$. The heating rate was $1\text{ }^{\circ}\text{C min}^{-1}$, the modulation amplitude was $0.477\text{ }^{\circ}\text{C}$ and the oscillation period was 60 s. The enthalpic recovery of the aged samples was calculated as the area of the endothermal relaxation peak in the non-reversing heat flow signal.[26] Fluorescence analyses at different temperatures were carried out by positioning a dye-doped polymer sample ($1.5 \times 1.5\text{ cm}^2$) on a heating stage (Linkam TH 600 hot stage). The sample is then irradiated with a solid state pulsed laser at 405 nm (Picoquant), during different heating scans at $5\text{ }^{\circ}\text{C min}^{-1}$ from RT to $120/200\text{ }^{\circ}\text{C}$. Between heating ramps, the sample is cooled almost at the same rate without a cooling control system. During these ramps, an Edinburgh FLS920 fluorimeter equipped with a high-speed HS773-04 photomultiplier and connected to a PCS900 computer card was used for the fluorescence lifetime measurements based on time-correlated single photon counting technique (TCSPC). Sample lifetimes at $-196\text{ }^{\circ}\text{C}$ (77 K) were measured by dipping polymer film into liquid nitrogen inside a quartz dewar into the sample chamber of the instrument.

A 405 nm pulsed diode laser Picoquant was used to excite the sample and the emission signal was collected at 630 nm (450 nm cut-off filter). The obtained decays were then analyzed and a good fitting obtained with a monoexponential equation results in an average lifetime. Samples were analyzed also by using a Nikon A1R confocal microscope system with 20x magnification, numerical aperture, NA, 0,75 of Nikon Plan-Apo objective lens. The samples were excited by a pulsed Picoquant laser at 401 nm. The emission of the films was collected in the range 575 - 620 nm. In FLIM a TCSPC system of Picoquant GmbH Berlin was used with a 401 nm pulsed excitation laser at 10 MHz repetition frequency, the same dichroic mirror, a 550 nm cut-off filter, a Hybrid PMA detector and a Picoquant TimeHarp correlation board.

2.3. A high-sensitivity long-lifetime phosphorescent RIE additive to probe free volume-related phenomena in polymers

2.3.1. Introduction

In contrast to the preceding section, where the focus was on studying fluorescent AIE molecular rotors, this work takes a significant step forward by harnessing the potential of phosphorescence. Phosphorescence offers distinct advantages over fluorescence due to its spin-forbidden nature. It is inherently slower than the spin-allowed fluorescence process. The extended phosphorescence lifetime facilitates time-gated detection, where the emission signal is recorded after an appropriate delay following excitation. This measurement method enhances precision and allows for the elimination of unwanted signals, such as matrix autofluorescence or excitation light scattering. To explore the benefits of using phosphorescent RIE dyes as polymer additives, the AIEgen hexakis(4-methyl-1-phenylthio)-benzene (A6Me) was selected. It is known as one of the most phosphorescent organic molecules in the solid state.[28,29] It is non-emitting in solution at room temperature but in a rigid environment (i.e. in a frozen solution or a solid phase) it exhibits enhanced photophysical properties, with a very intense green phosphorescence and a long lifetime (Table 2.6) as a consequence of RIM.[30]

Table 2.6 Photophysical data of A6Me under different experimental conditions[29]: molar absorption coefficient (ϵ_a), maximum emission wavelength ($\lambda_{\max}$), phosphorescence lifetime (τ_{ph}) and phosphorescence quantum yield (Φ_{ph}).

Absorption in CH ₂ Cl ₂ , 298 K		Emission in solid phase, 298 K		
λ^a [nm]	ϵ_a^b [M ⁻¹ cm ⁻¹]	$\lambda_{\max}$ [nm]	τ_{ph}^c [μ s]	Φ_{ph}^d
326	19200	510	3.0	1.0

A6Me is currently available on the market from several chemical suppliers, which incredibly increases its scientific impact on industry and academia. The selected matrixes are polymers of industrial relevance, i.e. polystyrene (PS), polyvinyl acetate, and polylactic acid

(PLA). They have been used in a completely amorphous state and their T_g cover a wide range of temperatures (from 40 to 120 °C).

This work is divided in two main studies. Starting with a generic photophysical characterization of the dye included in the different matrices, the first focus of the work was to assess if lifetime measurements can provide information on local changes of polymer free volume. To this aim, the dye emission properties were characterized by measuring lifetime rather than the emission intensity since the latter brings many problems associated with its very nature. Indeed, the absolute value of emission intensity is massively affected by the optical properties of the polymer matrix (i.e. optical density, refractive index, sample thickness, presence of voids/microcracks that can induce waveguide effects or scattering, etc.) and the instrumentation parameters. Therefore, a reliable comparison between the emission of two different samples cannot be separated from the calculation of the emission quantum yield. Differently, lifetime, being an absolute measure, is not affected by the measuring conditions. In this study, lifetime observation represents the keystone for the application within the field of polymeric materials. In glassy polymers, chain mobility decreases due to the free volume reduction to reach a thermodynamically stable state. This phenomenon, known as physical ageing, is due to small scale chain relaxations that alter the local packing of the chains and cause volume contraction. The practical consequence of physical ageing is the increase of material brittleness, impairing long-term applications.[31] Experimentally, ageing can be investigated by dilatometry, calorimetry and spectroscopic techniques such as PALS, FTIR, and UV-Vis spectroscopy based on photochromic probes and labels.[31]4 By using A6Me as a probe, we can take advantage of the long lifetime of the excited state and monitor lifetime variations in polymers subjected to accelerated physical ageing, without destroy the samples. The second focus of the work was to again exploit lifetime measurements to investigate the nature of the chain mobility changes that occur by applying a tensile deformation to the matrix.

2.3.2. Results and discussion

A6Me was physically blended at a concentration of 2 wt.%, with PS, PVAc, and PLA, by preparing films through solvent casting (see experimental section 2.3.4). The selected polymers are completely amorphous with T_g in the range of 40–120 °C, whose values (Table 2.7) are not affected by the addition of A6Me.

Table 2.7 T_g and emission properties of polymeric films loaded with 2 wt.% of A6Me.

Sample	T_g ^a [°C]	λ_{max} ^b [nm]	τ_{ph} ^c [μs]
PS-A6Me	97	530	8.5 ± 0.8
PVAc-A6Me	43	520	18.7 ± 0.4
PLA-A6Me	59	550	22.6 ± 0.4

^aDetermined by DSC; ^bEmission wavelength; ^cPhosphorescence lifetime.

Figure 2.23 reports the DSC curves of the pure polymeric films, and of the corresponding films loaded with A6Me to assess the possible effect of A6Me on polymer thermal transitions. For a reliable comparison, all samples have been subjected to a first heating followed by a fast cooling to erase polymer thermal history. The atactic polystyrene (Figure 2.24a) and the polyvinyl acetate (Figure 2.24b) only show a heat capacity step at the expected glass transition temperature, 97 °C and 43 °C, respectively. Differently, the stereoregular PLA has the capability to partially crystallize. This is evident in the DSC scan, since, after the glass transition region, the polymer shows a cold crystallization exotherm peak followed by a melting endotherm peak of exactly the same entity ($\Delta H_c = \Delta H_m = 45 \text{ J g}^{-1}$), meaning that the quenched PLA film is completely amorphous since the fast cooling prevents the polymer from crystallizing. The addition of 2 wt.% of A6Me does not affect polymer T_g but the enthalpy of cold crystallization and the subsequent melting of the same entity are lower ($\Delta H_c = \Delta H_m = 33 \text{ J g}^{-1}$), suggesting that A6Me reduces the polymer rate of crystallization. It is worth mentioning that also in the first heating scan PLA samples obtained after hot-pressing did not present any crystalline phase and were thus completely amorphous.

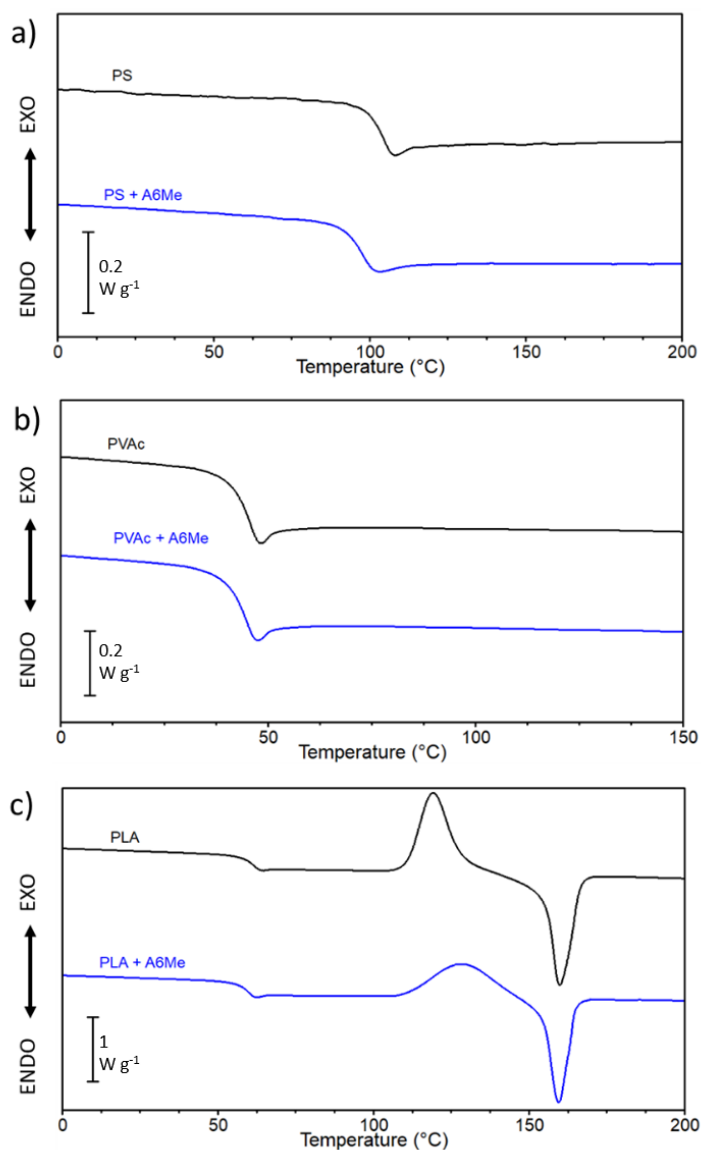


Figure 2.24 DSC 2nd heating curves of doped (blue) and undoped (black) films: PS (a); PVAc (b); PLA (c). Reproduced from ref. [32] with permission from the Royal Society of Chemistry, Copyright © 2023

The films obtained by blending the dye with various polymer matrices were subsequently characterized by measuring both the emission spectrum and the lifetime (Figure 2.25).

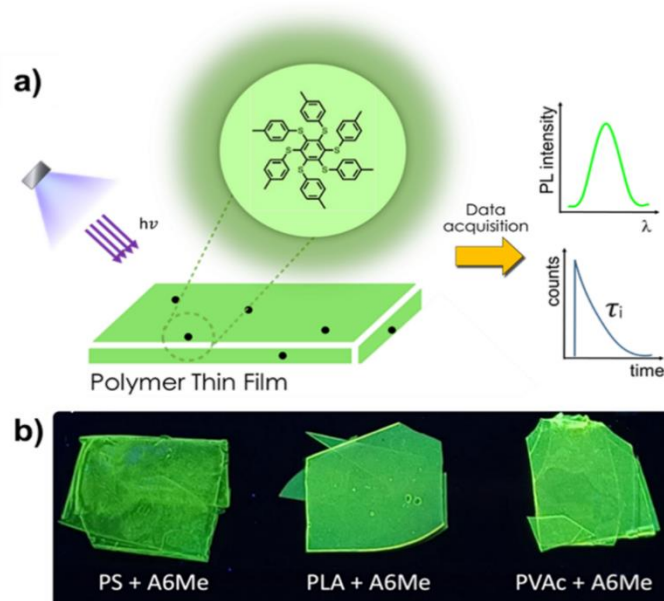


Figure 2.25 a) Sketch of the methodology applied to characterize starting films doped with A6Me; b) image of the polymeric samples under UV light. Adapted from ref. [32] with permission from the Royal Society of Chemistry, Copyright © 2023

The photophysical characterization is shown in Figure 2.26, where the behavior of the pristine dye is compared with the emissions obtained in the different unaged polymeric films. In the case of A6Me, it was previously demonstrated that the nature of the excited state has a significant charge transfer contribution,[28] which in turn is notoriously strongly influenced by the polarity of the environment. The emission maximum of A6Me varies in the different polymers, probably due to different intermolecular interactions between the matrix and the dye. This interaction can be determined by the nature of polymer side groups, which can favor the “solubilization” of A6Me, depending on the overlap of the electronic clouds of the dye and the polymer. The effect of the matrix becomes more evident when recording lifetimes (Table 2.7). In the case of the complete immiscibility of dye and polymer, the lifetime is expected to be equal to that of the pristine dye in the solid state (i.e. 3 μ s, Table 2.6). However, when dispersed in the glassy polymers, A6Me always displays longer lifetimes, indicating a good dispersion of the molecule in the matrices and a possible effect of the matrix itself on the RIM mechanism.

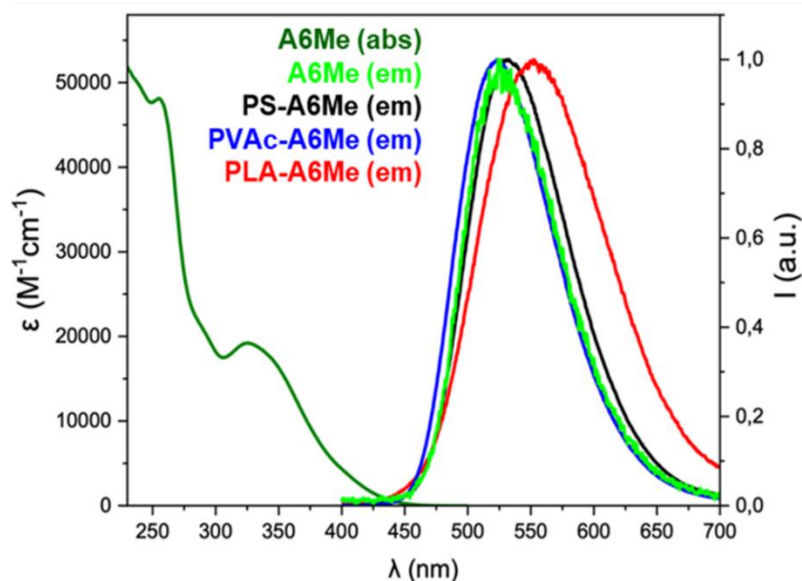


Figure 2.26 Optical behavior of A6Me: absorption spectra in DCM solution (left) and emission spectra (right) of the chromophore in the solid phase and dispersed in polymeric films of PS, PLA, and PVAc with $\lambda_{exc}=320$ nm. Adapted from ref. [32] with permission from the Royal Society of Chemistry, Copyright © 2023

The next step was to investigate local changes in polymeric free volume by measuring lifetime values. The polymeric films were thermally annealed at a temperature below T_g for a specific time. In order to quantify this aging process, the samples were analyzed using MDSC. This technique of analysis allows to separate the change of heat capacity occurring at T_g from the endothermic peak caused by the enthalpic relaxation process of physically aged samples. Figure 2.27 reports a representative MDSC analysis performed on an aged PVAc sample. The curves of the total heat flow (T), reversing heat flow (R) and non-reversing heat flow (NR) are displayed. As expected, the total heat flow shows both the step-change in heat flow at T_g and the enthalpy relaxation, the reversing signal displays only the T_g while the enthalpy relaxation appears only in the non-reversing curve. ΔH_{relax} can thus be determined from the non-reversing heat flow and results are reported in Table 2.8 for all aged samples.

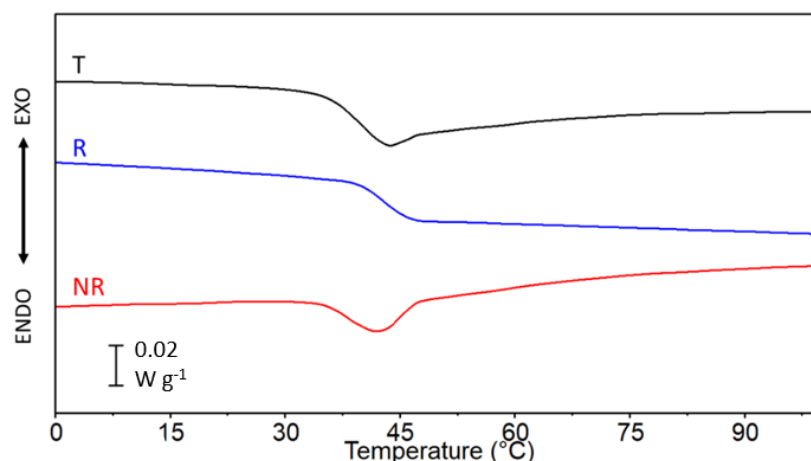


Figure 2.27 Representative MDSC analysis showing the total heat flow (black), the reversing heat flow (blue) and the non-reversing heat flow (red). Reproduced from ref. [32] with permission from the Royal Society of Chemistry, Copyright © 2023

Table 2.8 ΔH_{relax} values determined from the non-reversing signal of MDSC for all aged samples.

Sample	Aging time	ΔH_{relax}
	[hours]	[J g ⁻¹]
PS + A6Me	0	-0.28
	24	2.27
	72	2.77
	168	3.14
PLA + A6Me	0	-0.32
	24	2.41
	72	4.98
	168	7.00
PVAc + A6Me	0	0.25
	24	0.60
	72	0.94
	168	1.97

For each polymer, Figure 2.28 reports the lifetime of the dye and the enthalpy relaxation as a function of ageing time. As expected, the enthalpy relaxation strongly increases at short ageing times for the quenched samples, being far from the thermodynamic equilibrium, and continues to increase up to 7 days, albeit at a slower rate. Concomitantly, the dye's lifetime increases, following the same trend

of enthalpy relaxation. Moreover, the radiative constant of the deactivation of the phosphorescent excited state increases upon ageing, while the non-radiative one decreases (Table 2.9). This result demonstrates that the change in dye lifetime reflects the micro- and nanostructural changes of the glass occurring during thermal annealing and can be related to the reduction of free volume, notoriously accompanied by material densification. In other words, the free volume available for A6Me rotational motions decreases with ageing time, thus limiting the non-radiative decay pathways of the excited state and enhancing the radiative deactivation.

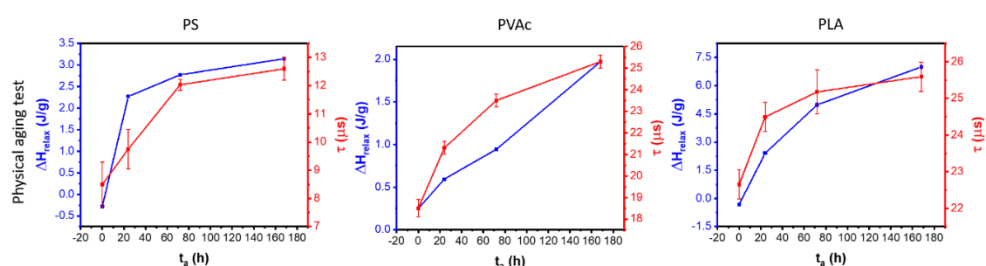


Figure 2.28 ΔH_{relax} (blue) and lifetime (red) of A6Me as a function of ageing time for PS, PVAc, and PLA. Adapted from ref. [32] with permission from the Royal Society of Chemistry, Copyright © 2023

Table 2.9 Emission properties of A6Me in PLA before and after ageing and of pure A6Me.

Sample	Φ	$\tau [\mu\text{s}]$	$k_r [\text{s}^{-1}]$	$k_{nr} [\text{s}^{-1}]$
PLA	0.07	22	3.2×10^3	4.2×10^4
PLA aged (168h)	0.1	25.5	3.9×10^3	3.5×10^4
A6Me	1.0	3	3.3×10^5	0

Lifetime measurements were also carried out during tensile stress-strain tests. As expected by preliminary mechanical test (Figure 2.29), PS and PLA behave as rigid glassy polymers, showing a linear elastic region at low strain characterized by a high Young's module, followed, in the case of PLA, by a fragile fracture and, in the case of PS, by a short plastic deformation before breaking. Differently, PVAc behaves as a thermoplastic tough material, characterized by a lower Young's modulus in the elastic region and a strong yield followed by

plastic deformation at constant stress before breaking (see mechanical data in Table 2.10).

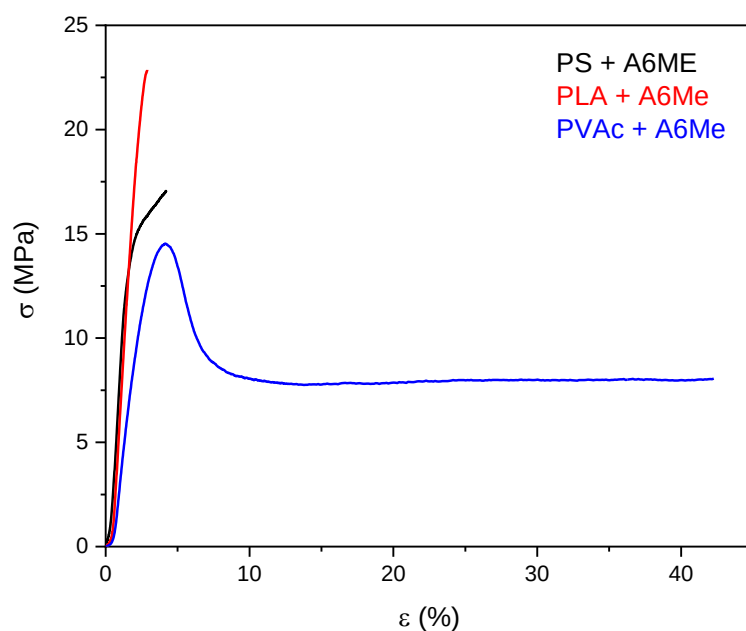


Figure 2.29 Representative stress-strain curves of A6Me doped films: PS (black), PLA (red) and PVAc (blue). Reproduced from ref. [32] with permission from the Royal Society of Chemistry, Copyright © 2023

Table 2.10 Mechanical data of doped polymers (E is obtained from the slope of the elastic range). Values are reported with standard deviations. Comparison between groups was performed using the one-way ANOVA and differences were considered significant for $p < 0.05$.

Sample	E [MPa]	ϵ_b [%]	σ_b [MPa]
PS + A6Me	1030 ± 100	3.4 ± 0.8	16 ± 2
PLA + A6Me	1280 ± 130	3.4 ± 0.8	29 ± 6
PVAc + A6Me	660 ± 60	63 ± 17	10 ± 2
PS	1490 ± 90	2.5 ± 0.1	32 ± 4
PLA	1190 ± 90	5.5 ± 1.7	35 ± 12
PVAc	730 ± 160	77 ± 4	12 ± 4

Young's modulus, E: PS vs PS + A6Me $p < 0.05$; PLA vs PLA + A6Me $p > 0.05$; PVAc vs PVAc + A6Me $p > 0.05$.

strain at break, ϵ_b : PS vs PS + A6Me $p > 0.05$; PLA vs PLA + A6Me $p > 0.05$; PVAc vs PVAc + A6Me $p > 0.05$.

stress at break, σ_b : PS vs PS + A6Me $p > 0.05$; PLA vs PLA + A6Me $p > 0.05$; PVAc vs PVAc + A6Me $p > 0.05$.

Figure 2.30 reports for each polymer both the stress-strain curve and A6Me lifetime resulting from the fitting of experimental data recorded by positioning the optical fibre in front of the central area of the sample under tension (see experimental section 2.3.4 for the fitting procedure). A striking result is the evident reduction of A6Me lifetime during the elastic deformation in all host materials. In the case of PS and PLA, the lifetime linearly decreases in the elastic regime, reaching, in the case of PS, a constant value in the plastic regime. A similar behavior, albeit with some differences, is observed in the lifetime of the dye dispersed in PVAc. Here, again, the fast decrease of A6Me lifetime occurs during matrix elastic deformation, but the decrement persists after yield, up to 20% of deformation, till reaching a constant value. The deformation mechanism of bulk isotropic linear glassy polymers in uniaxial tension has been the subject of intense experiments and numerical simulations aimed at correlating the mechanical behavior with the deformation mechanism at the molecular level.[33] Molecular dynamics simulations of a glassy amorphous polyethylene polymer under uniaxial tensile strength showed that the free volume increases in the elastic region while it reaches a constant value in the plastic deformation.[34] This deduction nicely agrees with PALS analysis conducted on polycarbonate that experiences an increase in free volume when subjected to tensile deformation.[35] Supported by these previous results, it is conceivable that the observed decrease in A6Me lifetime is due to the activation of dye motions in polymer sites where the free volume increases in the elastic regime. Mechanoluminescent polymeric systems, capable of monitoring deformation and stress to gain information on deformation mechanisms, are the subject of intensive research.[36–41] The strain threshold for mechanoactivation can vary over a wide range, depending on the polymer under investigation and on the mechanoresponsive species, but mechanoluminescence is generally achievable only after the yield point. This is the first observation of a luminescent probe sensitive to elastic deformation and represents a significant step forward and, at the same time, a starting point for future methodologies in this area.

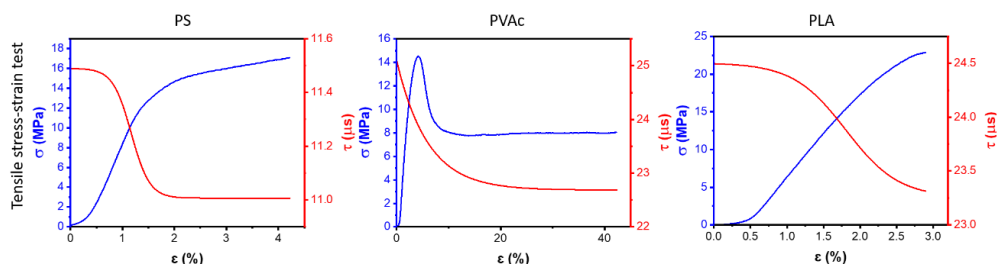


Figure 2.30 Lifetime of A6Me (red curve – sigmoidal fitting) measured in situ during stress-strain analysis of PS, PVAc, and PLA. Adapted from ref. [32] with permission from the Royal Society of Chemistry, Copyright © 2023

2.3.3. Conclusions

In conclusion, it was developed an auto-diagnostic materials where A6Me dye works as a probe of free volume changes in the surrounding polymeric matrices of three different polymers of industrial relevance. This all-organic dye was chosen to exploit its exalted and highly potent luminescence properties under the effect of an AIE-based process. This work is focused on correlating the dye's lifetime with the changes in the surrounding micro- and nano-organized environment. The dye lifetime is thus affected by minor changes of free volume, occurring as a consequence of physical ageing, but also by molecular movements activated by mechanical stresses (Figure 2.31).

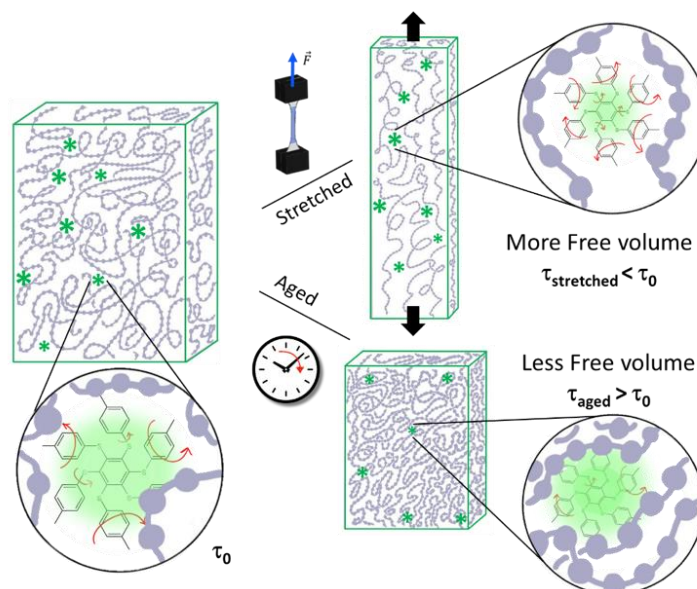


Figure 2.31 Sketch depicting A6Me lifetime (τ_0) variation as a consequence of physical ageing and tensile deformation. Dye's lifetime in aged polymers (τ_{aged}) increases as a consequence of free volume reduction, while dye's lifetime in mechanically stretched samples ($\tau_{\text{stretched}}$) decreases during elastic deformation because of free volume increase. Reproduced from ref. [32] with permission from the Royal Society of Chemistry, Copyright © 2023

Our methodological approach is based on: (i) an affordable, metal-free, relatively non-toxic organic dye with exalted phosphorescent properties; (ii) a simple preparation method consisting in mixing a small amount of A6Me dye with the polymer without compromising its properties, and (iii) on lifetime detection that can be performed in situ and circumvents issues related to sample geometry and scattering effects, that may limit the reliability of emission intensity measurements. These results pave the way for further in-depth studies where phosphorescent AIEgens can be exploited to get helpful information on structural motions and nanostructural evolutions of polymers.

2.3.4. Experimental section

Materials. Polystyrene ($M_w = 30.5 \times 10^4 \text{ g mol}^{-1}$, Carlo Erba), Polyvinyl acetate ($M_w = 50 \times 10^4 \text{ g mol}^{-1}$, Sigma Aldrich), and Poly(L-lactide) ($M_w = 8.4 \times 10^4 \text{ g mol}^{-1}$, PDI = 1.7, Lacea H.100-E) were used. Tetrahydrofuran (THF, $\geq 99.8\%$ Sigma Aldrich) and dichloromethane ($\geq 99.8\%$ Sigma Aldrich) were used without further purification. A6Me is the AIE probe used to dope the polymeric films and was synthesized as previously reported [29] Table 2.6 summarizes the photophysical behavior of A6Me dye.

Film preparation. Homogeneous polymeric solutions were prepared by dissolving each polymer in the proper solvent (DCM in case of PLA and PVAc, THF in case of PS) at a concentration of 4% w v⁻¹. A6Me was added to gain a final concentration of 2 wt.% in the dry film. After stirring until complete polymer dissolution, each mixture (50 mL) was gently poured into a glass petri dish (d = 7.5 mm) and left under the fume hood for solvent evaporation. To eliminate the solvent, the obtained films were separated from the petri, hot-pressed at a temperature of $T_g + 100 \text{ }^\circ\text{C}$ and rapidly cooled to room temperature.

Unaged samples were obtained by keeping the films at a temperature $T = T_g + 50 \text{ }^\circ\text{C}$ for 10 minutes to erase all prior thermal history, then rapidly quenched in liquid nitrogen and kept at $-20 \text{ }^\circ\text{C}$ before analysis.

Accelerated physical ageing experiments. Physical ageing was induced by keeping the unaged films at about 10 °C below their respective T_g : the annealing temperature (T_a) was 35 °C for PVAc, 45°C for PLA and 90°C for PS. The samples were maintained at this temperature for a certain ageing time.

Characterization methods. DSC was carried out using a Q2000 DSC apparatus (TA instruments) equipped with a Refrigerated Cooling System (RCS90). Samples were subjected to a first heating scan in the temperature range -90-200 °C at a rate of 20 °C min⁻¹, followed by a fast cooling to -90 °C and a second heating scan at 20 °C min⁻¹ to 200 °C. T_g was taken at half-height of the glass transition heat capacity step, while the T_c and the melting temperature (T_m) were taken at the peak maximum of crystallization exotherm and melting endotherm, respectively. MDSC was also performed from -90 °C to 200 °C. The heating rate was 3 °C min⁻¹, the modulation amplitude was 0.477 °C and the oscillation period was 60 s. The enthalpic recovery of the aged samples was calculated as the area of the endothermal relaxation peak in the non-reversing heat flow signal, by following a previously reported method [26]. For a more accurate measure of the enthalpic recovery, after heating, the samples were cooled at 3 °C min⁻¹ and the exothermal peak area in the non-reversing signal, resulting from the so-called "frequency effect", was subtracted to gain the enthalpy of relaxation. Photophysical measurements in solution were carried out in dichloromethane at 298 K. Luminescence measurements were performed on solid state samples. UV-vis absorption spectra were recorded with a PerkinElmer I40 spectrophotometer using quartz cells with a path length of 1.0 cm. Emission spectra were obtained with a Perkin Elmer LS55 spectrofluorometer. Lifetimes shorter than 10 µs were measured by an Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution) with a 405 nm laser. Emission intensity decay measurements in the range 10 µs to 1 s for external analysis (ageing and stress-strain tests) were performed on a homemade time-resolved phosphorimeter coupled with two optical fibers. The excitation source was a UV-LED centred at 365 nm

while the detector was a conventional APD. Emission quantum yield was calculated from corrected emission spectra registered by an Edinburgh FLS920 spectrofluorimeter equipped with a barium sulfate coated integrating sphere (4 in.), a 450W Xe lamp (λ excitation tunable by a monochromator supplied with the instrument) as light source, and a R928 photomultiplier tube, following the procedure described by De Mello et al. [42]. Radiative and non-radiative constants are calculated based on the following equations, with the assumption of unitary intersystem crossing efficiency and the absence of photoreactions.

$$\tau_{ph} = \frac{1}{k_r + k_{nr} + k_p} \quad \text{.....(Eq. 2.3)}$$

$$\Phi_{ph} = \frac{\eta_{ISC} k_r}{k_r + k_{nr} + k_p} = \eta_{ISC} k_r \tau_{ph} \quad \text{.....(Eq. 2.4)}$$

Where τ_{ph} is the phosphorescence lifetime, η_{ISC} the efficiency of intersystem crossing between S_1 and T_1 , k_r is the radiative rate constant, k_{nr} is the non-radiative rate constant and k_p is the photoreaction rate constant. The estimated experimental errors are: 2 nm on the absorption and emission band maximum, 5% on the molar absorption coefficient and shorter luminescence lifetime. In the case of longer lifetimes, the error is evaluated each time due to the external set-up (see below). Stress-strain curves of A6Me doped films were recorded using an Instron Testing Machine 4465 and the Series IX software package. Dog-bone shaped specimens (gage length = 20 mm, width = 5 mm, thickness = 0.1-0.2 mm) cut from each film were tested in traction mode with a load cell of 100 N. The crosshead speed was set at 0.5 mm min⁻¹ for PLA and PS and at 3 mm min⁻¹ for PVAc. Load-displacement curves were acquired and converted to stress-strain curves. At least 4 specimens were tested for each polymer and mechanical data were provided as the average value $\pm$ standard deviation.

Oxygen effect during lifetime measurements. To investigate the effect of oxygen during the changes of polymer matrix we record lifetimes in air-equilibrated and under N₂ atmosphere at different aging times. Based on the equation:

$$\tau = \frac{1}{\sum k + k_q [O_2]} \dots\dots(\text{Eq. 2.5})$$

Where $\sum k$ is the sum of all the deactivation process of the excited state T_1 of A6Me, $k_q [O_2]$ is the quenching by oxygen.

The term $\sum k$ is constant for a precise aging time while we could estimate $k_q [O_2]$ by differences of the reverse of the lifetime in air-equilibrated and under N_2 atmosphere. The value we calculated are $k_q [O_2] = 6500 \text{ s}^{-1}$ for low aging time (1 hours) and $k_q [O_2] = 6200 \text{ s}^{-1}$ for long aging time (6 months), differences lower than 5%. Variation of value of k_{nr} and k_r could be estimated with the same process and after aging these variations are 13000 s^{-1} , a value two times higher than the overall effect of oxygen and 40 times higher compared to the differences of $k_q [O_2]$ at low aging and long aging times. Based on these data we could say that the effect of O_2 is negligible compared to the effect of matrix changes.

Lifetime fitting in in situ mechanical tests. Lifetime values obtained during the stress-strain analysis are shown in Figure 2.23 (black curve) and are reported together with the stress-strain profile of the analyzed polymer (blue curve). The fitting curve of lifetime data is reported in red and the fitting function and corresponding parameters are reported in Table 2.8, including the standard error.

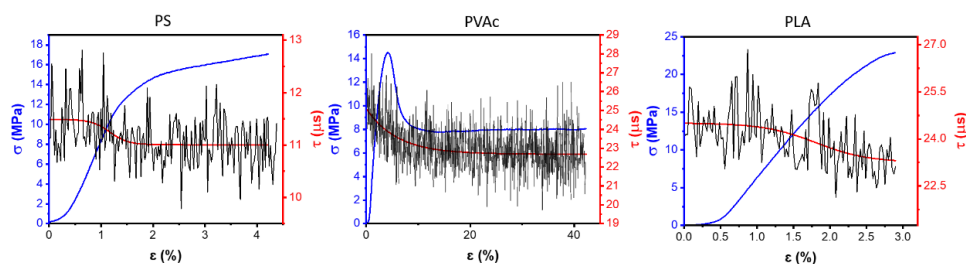


Figure 2.23 Lifetime decay of A6Me, raw data (black), fitting curve (red), and stress-strain curve (blue): a) PS; b) PVAc; c) PLA. Adapted from ref. [32] with permission from the Royal Society of Chemistry, Copyright © 2023

Table 2.8 Schematic representation of the fitting function used to describe the behavior of A6Me lifetime in the composite system during the stress-strain analysis.

Sample	Fitting function	y_0 [μs]	Standard Error of estimate
PVAc	Sigmoidal 5 parameters ^a	22.68	1.06
PS	Sigmoidal 4 parameters ^b	11.01	0.51
PLLA	//	23.26	0.82

^a $f = y_0 + a / (1 + \exp(-(x - x_0)/b))^c$; ^b $f = y_0 + a / (1 + \exp(-(x - x_0)/b))$

[Parameters]

$a = \max(y) - \min(y)$

$b = \text{xwtr}(x, y - \min(y), .5) / 4$

$c = 1$

$x_0 = \text{x50}(x, y - \min(y), .5)$

$y_0 = \min(y)$

* xwtr. This function returns x75-x25 for sigmoidal shaped function.

** This function returns the x value for the y value 50% of the distance from the minimum to the maximum of smoothed data for sigmoidal shaped. Same for x75 and x25 that returns for the y value 25% and 75% respectively of the distance from the minimum to the maximum of smoothed data for sigmoidal shaped.

2.4. References

- [1] Luo, J. et al. (2001). Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. *Chemical Communications*. DOI: 10.1039/b105159h.
- [2] Bao, S. et al. (2015). Sensitive and reliable detection of glass transition of polymers by fluorescent probes based on AIE luminogens. *Polymer Chemistry*. DOI: 10.1039/c5py00308c.
- [3] Pucci, A. (2019). Mechanochromic fluorescent polymers with aggregation-induced emission features. *Sensors (Switzerland)*. DOI: 10.3390/s19224969.
- [4] Iasilli, G. et al. (2014). Aggregation-induced emission of tetraphenylethylene in styrene-based polymers. *Macromolecular Chemistry and Physics*. DOI: 10.1002/macp.201300698.
- [5] Robb, M.J. et al. (2016). A robust damage-reporting strategy for polymeric materials enabled by aggregation-induced emission. *ACS Central Science*. DOI: 10.1021/acscentsci.6b00198.
- [6] Chen, S. et al. (2020). A Facile Strategy to Prepare Smart Coatings with Autonomous Self-Healing and Self-Reporting Functions. *ACS Applied Materials and Interfaces*. DOI: 10.1021/ACSAMI.9B18919/ASSET/IMAGES/LARGE/AM9B18919_0006.JPEG .
- [7] Wu, Y. et al. (2014). Memory chromic polyurethane with tetraphenylethylene. *Journal of Polymer Science, Part B: Polymer Physics*. DOI: 10.1002/polb.23399.
- [8] Qiu, Z. et al. (2018). Dynamic Visualization of Stress/Strain Distribution and Fatigue Crack Propagation by an Organic Mechanoresponsive AIE Luminogen. *Advanced Materials*. DOI: 10.1002/adma.201803924.
- [9] Bu, T. et al. (2018). Stretchable Triboelectric-Photonic Smart Skin for Tactile and Gesture Sensing. *Advanced Materials*. DOI: 10.1002/adma.201800066.
- [10] Meng, B. et al. (2020). Composites with AIEgens for Temperature Sensing and Strain Measurement. *Macromolecular Chemistry and Physics*. DOI: 10.1002/macp.201900552.
- [11] Yang, Y. et al. (2019). Detecting topology freezing transition temperature of vitrimers by AIE luminogens. *Nature Communications*. DOI: 10.1038/s41467-019-11144-6.
- [12] Berezin, M.Y. and Achilefu, S. (2010). Fluorescence lifetime measurements and biological imaging. *Chemical Reviews*. DOI: 10.1021/cr900343z.
- [13] Dini, V.A. et al. (2023). Emission or scattering? Discriminating the origin of responsiveness in AIEgen-doped smart polymers using the TPE dye. *Aggregate*. DOI: 10.1002/agt2.373.
- [14] Qiu, Z. et al. (2017). A Simple and Sensitive Method for an Important Physical Parameter: Reliable Measurement of Glass Transition Temperature by AIEgens. *Macromolecules*. DOI: 10.1021/acs.macromol.7b01070.
- [15] Mei, J. et al. (2014). Aggregation-induced emission: The whole is more

- brilliant than the parts. *Advanced Materials*. DOI: 10.1002/adma.201401356.
- [16] Han, T. et al. (2021). Mechanochromic Fluorescent Polymers Enabled by AIE Processes. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.202000311.
- [17] Schwab, S.D. and Levy, R.L. (1990). Free-Volume-Dependent Fluorescence Probes of Physical Aging in Polymers, in *Polymer Characterization*, pp. 397–408.
- [18] Khalid, A.H. and Kontis, K. (2011). Progress towards absolute intensity measurements of emissions from high temperature thermographic phosphors. *Journal of Luminescence*. DOI: 10.1016/J.JLUMIN.2011.02.018.
- [19] Bur, A.J. et al. (2002). Temperature dependence of fluorescent probes for applications to polymer materials processing. *Applied Spectroscopy*. DOI: 10.1366/0003702021954638.
- [20] Takahara, K. et al. (1999). Physical aging in poly(methyl methacrylate) glass: Densification via density fluctuation. *Polymer*. DOI: 10.1016/S0032-3861(98)00580-1.
- [21] Tant, M.R. and Wilkes, G.L. (1981). An overview of the nonequilibrium behavior of polymer glasses. *Polymer Engineering & Science*. DOI: 10.1002/pen.760211403.
- [22] Gualandi, C. et al. (2022). Mechanoresponsive luminescence in polymeric materials: strategies and methods, in *Photochemistry*, vol. 50, pp. 458–490.
- [23] Awaja, F. et al. (2016). Cracks, microcracks and fracture in polymer structures: Formation, detection, autonomic repair. *Progress in Materials Science*. DOI: 10.1016/j.pmatsci.2016.07.007.
- [24] Debijs, M.G. and Verbunt, P.P.C. (2012). Thirty years of luminescent solar concentrator research: Solar energy for the built environment. *Advanced Energy Materials*. DOI: 10.1002/aenm.201100554.
- [25] Pucci, A. (2018). Luminescent Solar Concentrators Based on Aggregation Induced Emission. *Israel Journal of Chemistry*. DOI: 10.1002/ijch.201800028.
- [26] Thomas, L.C. (2005). Modulated DSC® Paper #5: Measurement of Glass Transitions and Enthalpic Recovery. *TA Series*.
- [27] Micheletti, C. et al. (2022). Red-emitting tetraphenylethylene derivative with aggregation-induced enhanced emission for luminescent solar concentrators: A combined experimental and density functional theory study. *Aggregate*. DOI: 10.1002/agt2.188.
- [28] Bergamini, G. et al. (2013). A persulfurated benzene molecule exhibits outstanding phosphorescence in rigid environments: From computational study to organic nanocrystals and OLED applications. *Journal of Materials Chemistry C*. DOI: 10.1039/c3tc00878a.
- [29] Fermi, A. et al. (2014). Molecular asterisks with a persulfurated benzene core are among the strongest organic phosphorescent emitters in the solid state. *Dyes and Pigments*. DOI: 10.1016/j.dyepig.2014.04.036.

- [30] Baroncini, M. et al. (2017). Rigidification or interaction-induced phosphorescence of organic molecules. *Chemical Communications*. DOI: 10.1039/c6cc09288h.
- [31] Cangialosi, D. et al. (2013). Physical aging in polymers and polymer nanocomposites: Recent results and open questions. *Soft Matter*. DOI: 10.1039/c3sm51077h.
- [32] Dini, V.A. et al. (2023). A high-sensitivity long-lifetime phosphorescent RIE additive to probe free volume-related phenomena in polymers. *Chemical Communications*. DOI: 10.1039/d2cc05908h.
- [33] Oleinik, E.F. et al. (2018). Plasticity Mechanism for Glassy Polymers: Computer Simulation Picture. *Polymer Science - Series A*. DOI: 10.1134/S0965545X18010042.
- [34] Hossain, D. et al. (2010). Molecular dynamics simulations of deformation mechanisms of amorphous polyethylene. *Polymer*. DOI: 10.1016/j.polymer.2010.10.009.
- [35] Xie, L. et al. (1995). Evolution of nanometer voids in polycarbonate under mechanical stress and thermal expansion using positron spectroscopy. *Journal of Polymer Science Part B: Polymer Physics*. DOI: 10.1002/polb.1995.090330109.
- [36] Traeger, H. et al. (2021). From Molecules to Polymers—Harnessing Inter- and Intramolecular Interactions to Create Mechanochromic Materials. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.202000573.
- [37] Willis-Fox, N. et al. (2018). Polymer Mechanochemistry: Manufacturing Is Now a Force to Be Reckoned With. *Chem*. DOI: 10.1016/j.CHEMPR.2018.08.001.
- [38] Guo, Q. and Zhang, X. (2021). A review of mechanochromic polymers and composites: From material design strategy to advanced electronics application. *Composites Part B: Engineering*. DOI: 10.1016/j.compositesb.2021.109434.
- [39] Chen, G. et al. (2020). Mechanochromism of Structural-Colored Materials. *Advanced Optical Materials*. DOI: 10.1002/ADOM.202000984.
- [40] Ciardelli, F. et al. (2013). Dye-containing polymers: Methods for preparation of mechanochromic materials. *Chemical Society Reviews*. DOI: 10.1039/c2cs35414d.
- [41] Li, J. et al. (2015). Polymer Mechanochemistry: From Destructive to Productive. *Accounts of Chemical Research*. DOI: 10.1021/acs.accounts.5b00184.
- [42] de Mello, J.C. et al. (1997). An Improved Experimental Determination of External Photoluminescence Quantum Efficiency. *Advanced Materials*. DOI: 10.4324/9781003392064-5.

3. Aggregachromic dyes

Aggregachromic dyes, as previously explained, offer valuable potential as probes when incorporated into polymer matrices to create mechanoluminochromic materials. These dyes exhibit absorption and emission properties that are highly responsive to variations in intermolecular distances and the relative orientation of chromophore molecules within the material. This remarkable sensitivity makes them effective as ratiometric signal units. Their distinct dual emission bands provide significant practical applications, as the ratio between the emission intensity $\lambda_{em}^{max}(monomer)$ and the emission intensity at $\lambda_{em}^{max}(excimer)$ can be used to monitor the disaggregation process. In the absence of mechanical stress, the material predominantly emits excimer fluorescence. The application of strain gradually disrupts the excimer aggregates, leading to an increase in monomer emission. Consequently, by monitoring the intensity changes of these two signals during mechanical stress, a mathematical correlation can be established between ratiometric intensity and applied strain, effectively turning the material into an intrinsic strain sensor. This capability enables the real-time, in-situ assessment of mechanical stresses within the embedded polymer. Given these exceptional properties, aggregachromic dyes can be employed to develop both covalently functionalized mechanoluminochromic polymers and mechanoluminochromic blends with the dye as a dispersed additive. The latter approach is particularly attractive due to its versatility, allowing for the rapid and straightforward creation of various mechanoluminochromic polymers.[1–6] Nonetheless, there are challenges associated with using these dyes, especially when dealing with large aggregates and materials with high segmental mobility. In such cases, the lack of strong interactions between the polymeric matrix and the dye molecules can result in poor disaggregation, leading to a limited mechanoluminochromic response.[7] In light of these challenges, there is a current research focus on developing covalently functionalized systems that incorporate aggregachromic mechanophores.

This thesis, therefore, investigates how different methods of including these dyes into polymer matrices affect their mechanoluminochromic properties.

In section 3.1, a pyrene derivative was selected as a probe due to its well-studied photophysical properties. The dye was either dispersed within a block

copolymer at various concentrations or included via functionalization in the copolymer's soft block. The distinct distribution of the probe within the polymer led to varying aggregation and disaggregation abilities, which greatly influenced the mechanoluminochromic outcomes. In the case of the chemically bonded probe, a substantial decrease in the excimer-to-monomer emission ratio was observed starting at 50% strain, confirming significant mechanoluminochromism. This effect was corroborated through emission lifetime measurements and near-field investigations. Furthermore, the mechanoluminochromic response exhibited good reversibility after repeated stress-relaxation cycles. Conversely, the samples where the probe was physically dispersed showed weak excimer emission intensity and a negligible mechanoluminochromic response, up to a doping level about five times higher than the functionalized polymer. Only at such high dye concentrations a noticeable decrease in the I_E/I_M ratio became evident, although excimer emission remained predominant even at maximum strain. In summary, the covalent approach proved to be an elegant method for confining the chromogenic unit in the soft phase of the block copolymers, resulting in an elastomeric film with a detectable and reversible mechanoluminochromic response using a modest amount (i.e., ~1 wt %) of pyrene molecules, which is 10 times less than in the dispersed system.

In section 3.2, we examine the mechanoluminochromism of a commercial thermoplastic polyurethane containing a perylene diimide probe, either covalently bonded to a specially synthesized polyurethane or simply blended. The goal was to assess how dye concentration and the two incorporation methods influence mechanoluminescence performance. The results indicated that binding the chromophore to the polymer chains reduces their tendency to aggregate, resulting in a less noticeable color change compared to systems with dispersed dye undergoing uniaxial tensile deformation. Nevertheless, this study reaffirms the findings of the previous research, demonstrating that covalently incorporating the dye provides greater sensitivity and a better alignment between the stress relaxation process and the mechanochromic response through stress relaxation experiments.

Lastly, in section 3.3, we harnessed a new-generation macromolecular additive featuring excimer-forming oligo(*p*-phenylene vinylene) dyes at the termini,[8] introducing highly sensitive mechanoluminochromism to various

polymers when incorporated in small quantities. Specifically, we utilized this additive to create MLC nanofibrous materials through the electrospinning of polyurethane solutions containing trace amounts of tOPV mechanoluminochromic additive. The resulting fibrous mats consisted of continuous fibers with diameters ranging from 300 to 700 nm, arranged either randomly or aligned, depending on the type of collector used during electrospinning. When subjected to tensile deformation, the mats exhibit a strain-dependent shift in fluorescence color from orange to green, monitored through spectroscopy and fluorescence microscopy. Interestingly, an in-situ analysis of single fibers reveals that those aligned with the direction of applied strain change their emission more significantly compared to fibers aligned perpendicularly or obliquely. We anticipate that these findings and insights into the transfer of mechanical force within nanofibrous polymer mats will promote the widespread use of self-reporting nanofibers in applications like load-bearing devices, wearable technology, and mechanochromic textiles.

3.1. Blending or Bonding? Mechanoluminochromism of an Aggregachromic Mechanophore in a Thermoplastic Elastomer

3.1.1. Introduction

The goal of this initial study is to assess the efficiency of the two potential methods for polymer functionalization in producing a mechanoluminochromic matrix. To achieve this, we first outline the production and analysis of a thermoplastic elastomer covalently functionalized with pyrene moieties (Figure 3.1a). Subsequently, we compare its chromogenic performance with that of a physically blended mixture containing similar fluorophores. As a thermoplastic elastomer potentially capable of reversible mechanoluminochromism, styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene triblock copolymer (SEBS) was selected. This material offers several advantages, such as a low Young's modulus, excellent processability and good chemical and UV resistance, making it suitable for both indoor and outdoor applications. We employed a commercially available SEBS grafted with maleic anhydride (SEBS-MAH) to allow a simple functionalization procedure (Figure 3.1b). We chose 1-Aminomethylpyrene (AMP) as a pyrenic derivative since it can readily react with the anhydride grafted to the polymer chains, and its aggregachromic properties, characterized by efficient excimer formation, are well known. In the selected matrix, the functionalization with the pyrene moieties interested only the soft domains of ethylene-butylene. The mechanoluminochromic response is evaluated in terms of sensitivity and reversibility, and it is compared with that of blended samples obtained with a similar polymeric matrix without grafted maleic anhydrides (SEBS), in which pyrene could be potentially dissolved in both blocks.

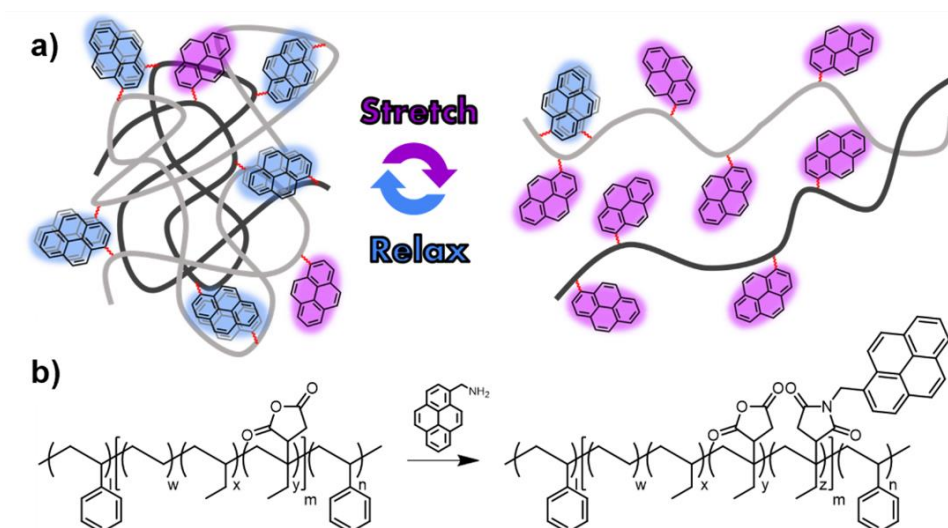


Figure 3.1 (a) Schematic representation of the AMP-functionalized SEBS: when no stress is applied, the emission of the material is dominated by the excimer. The deformation causes the gradual breaking of the excimer aggregates leading to the increase of the monomer emission; (b) covalent functionalization of SEBS-MAH with AMP. Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

3.1.2. Results and discussion

Preparation and Characterization of SEBS-Based Mechanoluminochromic Systems

The synthesis of the polymers under investigation and their characterization (FTIR, NMR and stress-strain tests) was performed by the Group of Prof. Andrea Pucci of the University of Pisa. AMP was selected as a fluorophore because of the suitable and rich photophysical properties of the pyrene core, together with its optimal thermal and chemical stability. In particular, the two fluorescence emissions of pyrene, as a monomer and as an excimer, are characterized by a large spectral separation and high luminescence quantum yields, with long lifetimes of the excited states that are also affected by oxygen concentration.[10,11]

Pyrene-functionalized SEBS (SEBS-AMP) was synthesized starting from a SEBS-MAH, exploiting its straightforward reaction with the amino groups of AMP forming a robust succinimide (Figure 3.1b). [12,13] The proceeding of the reaction was then easily monitored via FT-IR spectroscopy thanks to the disappearance of the absorption bands around 1788 cm^{-1} (strong) and 1866 cm^{-1} (weak), which are characteristic of saturated cyclic anhydrides (originating from the anti-

symmetric and symmetric C=O stretching vibration, respectively),[14–16] and the formation of a signal around 1711 cm^{-1} , ascribable to the imide formation (Figure 3.2). The absence of NH stretching at 1530 and 1650 cm^{-1} excludes the formation of amide derivatives.[16]

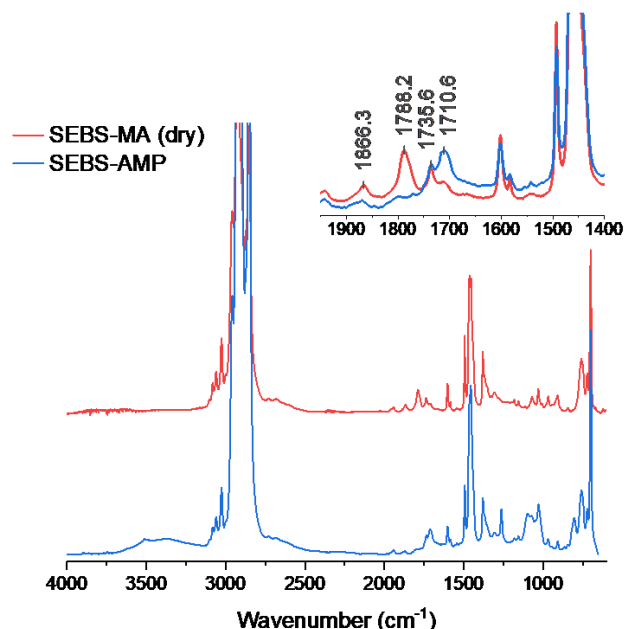


Figure 3.2 IR spectra of starting polymer matrix (SEBS-MAH, red) and after functionalization (SEBS AMP, blue). Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

The obtained SEBS-AMP was purified by Kumagawa extraction to ensure the complete removal of unreacted pyrene, and the weight percentage of grafted pyrene was calculated to be 1.1 wt.% by UV-vis analysis (Figure 3.3).

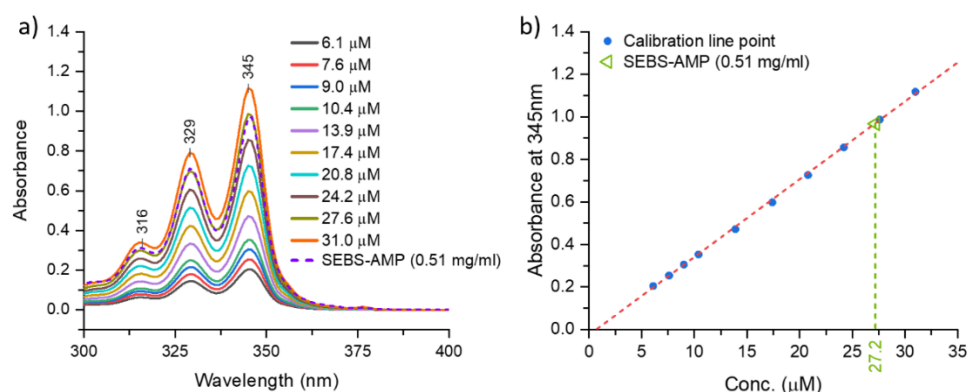


Figure 3.3 a) UV-Vis spectra of AMP at different concentrations in toluene (line), and SEBS-AMP dissolved in toluene (dash). b) Calibration line and data for SEBS-AMP. Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

Blend samples of unfunctionalized SEBS and pyrene were also prepared by physical dispersion (SEBS-P) in order to compare the optical and mechanical properties of the covalently functionalized matrix to those of dispersed samples. In this latter case, pyrene was introduced, ranging from 1 to 10 wt.%. Films were prepared by hot compression molding. The UV-vis spectra of the SEBS-P and SEBS-AMP films (Figure 3.4 as an example) showed a slight bathochromic shift of 2 nm as well as a broadening of the absorption bands with respect to toluene solutions (Figure 3.3), thus suggesting the occurrence of pyrene preassociation or ground state excimer formation in the polymer environment.[10] This behavior was confirmed from the ratio P_A of the absorption intensity of the most intense band to that of the adjacent minimum at shorter wavelength, which decreased from 2.5 in the toluene solution to 1.9 in the case of the SEBS-AMP film.

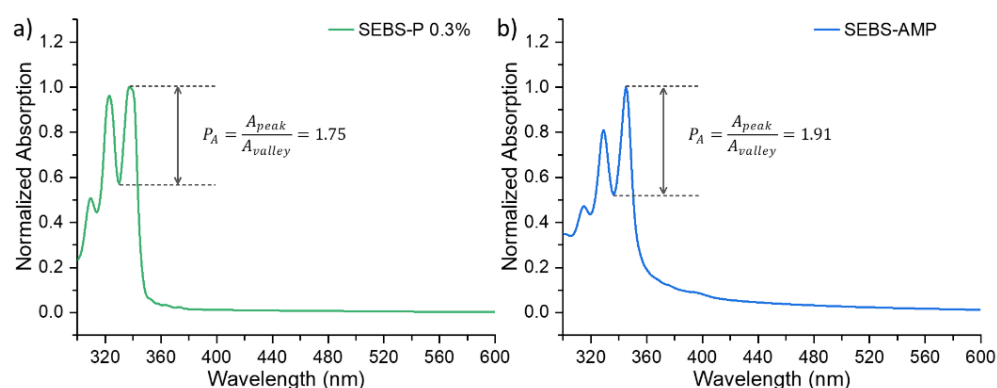


Figure 3.4 UV-Vis spectra of polymeric films: SEBS-P 0.3% (a) and SEBS-AMP (b). P_A represents the peak-to valley ratio for the (0,0) transition, and A_{peak} and A_{valley} are the absorption intensity of the most intense band and the adjacent minimum at shorter wavelength respectively. [10] Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

Tensile stress-strain tests, before and after the introduction of the fluorophore, are reported in the following Figure 3.5.

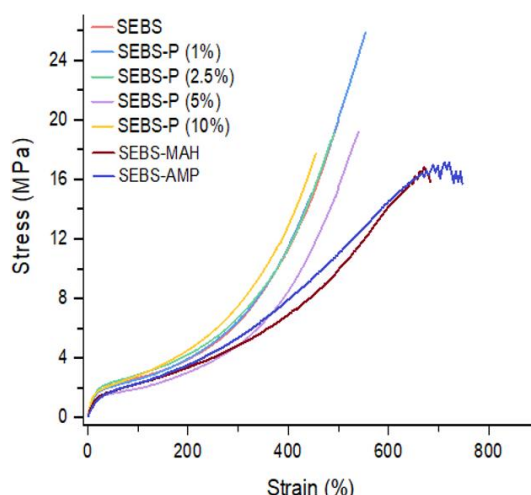


Figure 3.5 a) Stress-strain curves of pristine polymer, polymer blended with different amounts of pyrene and covalently functionalized polymers. Adapted from ref. [9] with permission from American Chemical Society, Copyright © 2023.

Young's modulus and deformation at break are shown in Figure 3.6. These characterizations assessed that mechanical properties of covalently functionalized, blend samples and pristine polymers were almost identical, thus demonstrating that functionalization and dispersion processes do not substantially affect the mechanical behavior.

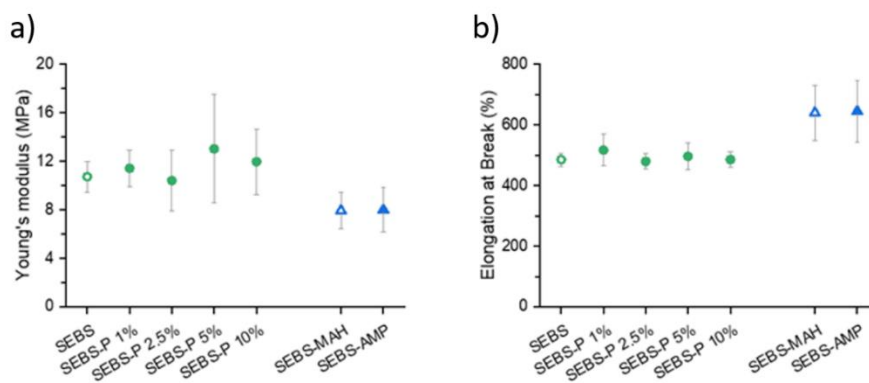


Figure 3.6 Young's moduli (a) and elongation at break (b) for the pristine polymeric matrices (empty symbols) and for functionalized/dispersed samples (filled symbols); three replicates were performed for each sample and the result is reported as mean $\pm$ SD. Adapted from ref. [9] with permission from American Chemical Society, Copyright © 2023.

SEBS-P and SEBS-AMP Fluorescence Characterization

The amount of excimer in covalently functionalized (SEBS-AMP) and blend samples (SEBS-P) was assessed by fluorescence emission

spectroscopy (Figure 3.7a). In particular, we calculated the excimer to monomer emission ratio at their maxima, 465 and 394 nm, respectively (I_E/I_M). In the case of SEBS-P systems, the sample containing the lowest amount of pyrene (1 wt.%) showed poor excimer formation ($I_E/I_M < 0.1$, Figure 3.7b).

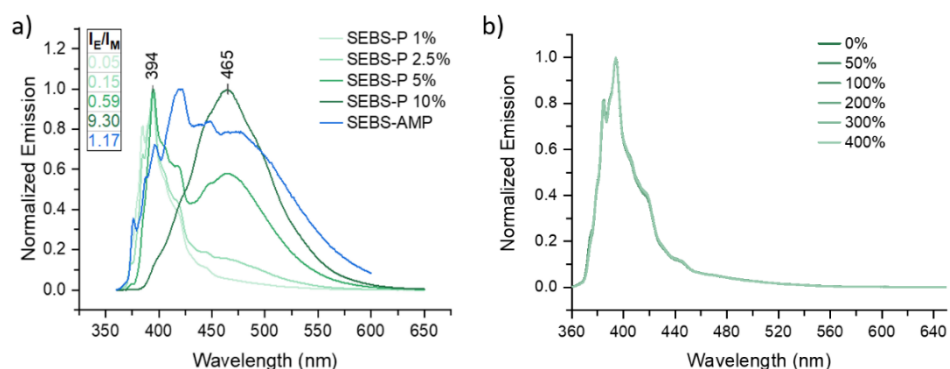


Figure 3.7 Normalized emission spectra $\lambda_{exc} = 345$ nm of SEBS-P with different amounts of dispersed pyrene and SEBS-AMP. b) Normalized emission (λ_{exc} : 345 nm) for SEBS-P 1% at different stress. Adapted from ref. [9] with permission from American Chemical Society, Copyright © 2023.

The presence of excimer started to be evident from 2.5% of dispersed pyrene (although with low intensity, $I_E/I_M = 0.15$, Figure 3.8) and grew on reaching 5% ($I_E/I_M = 0.59$) and 10% ($I_E/I_M = 9.30$). In the latter sample, a pronounced broad peak around 465 nm is evident, while the emission from monomeric species was negligible. Remarkably, the covalently functionalized sample showed an evident excimer band ($I_E/I_M = 1.17$) despite comprising only 1 wt.% of pyrene functionalities. In this sense, we can estimate the I_E/I_M for SEBS-AMP to be about 23 times larger than the SEBS-P 1% sample doped with the same amount of pyrene (and even about 2 times larger than SEBS-P 5%), thus indicating the higher tendency of pyrene moieties to form fluorescent aggregates in the covalently functionalized SEBS-AMP system compared to the dispersed system.

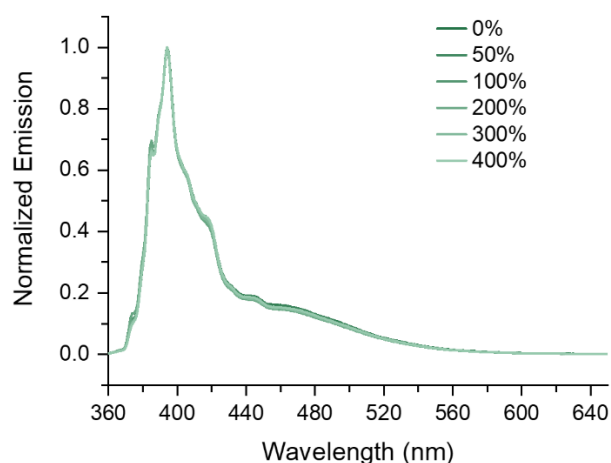


Figure 3.8 Normalized emission (λ_{exc} : 345 nm) for SEBS-P 2.5% at different stress. Adapted from ref. [9] with permission from American Chemical Society, Copyright © 2023.

This observation can be partially explained considering that, in the covalently linked sample, the functionalization interests only the ethylene-butylene soft block of the polymeric matrix, while in the blend samples, the fluorophores are dispersed throughout the polymeric matrix (including the styrene hard block). Therefore, in the SEBS-AMP system, the pyrene units are, on average, closer to each other and the formation of excimers and aggregates is enhanced. This hypothesis is also confirmed by the larger $I_{\text{E}}/I_{\text{M}}$ ratio shown by the SEBS-AMP system compared to that reported by Dalcanale et al. for pyrene-grafted polyethylene containing similar pyrene concentration.[17] The confinement of the chromogenic probe into one single domain allows the formation of the excimer band at lower dye contents.

Consistently, the monomer emission had a shorter lifetime (Figure 3.9) in SEBS-AMP than in SEBS-P 1%, in agreement with the most extensive excimer band observed in the emission spectra of SEBS-AMP:[18] the monomeric emission lifetime of SEBS-AMP is shorter because a larger fraction of the excited states of pyrenes leads to either formation of excimers or to the excited state of aggregates, which are responsible for the red-shifted emission at 465 nm.

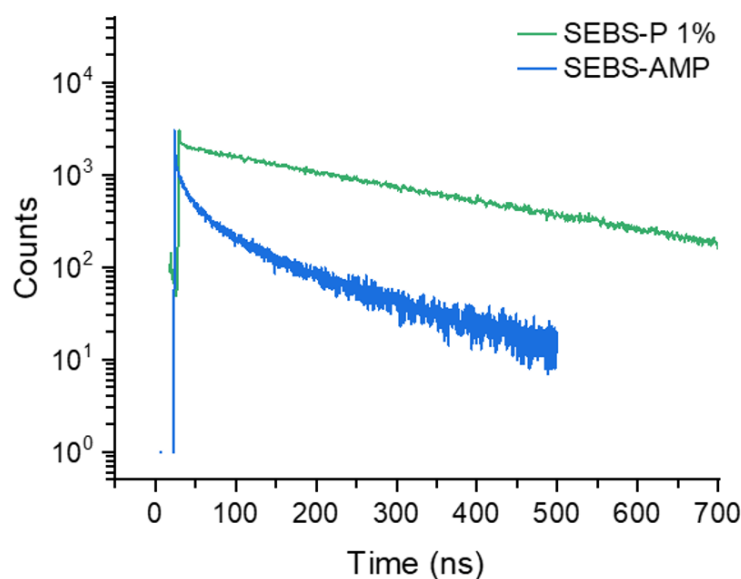


Figure 3.9 Lifetimes of monomeric emission $\lambda_{em} = 394$ nm in SEBS-P 1% and SEBS-AMP. Adapted from ref. [9] with permission from American Chemical Society, Copyright © 2023.

We then characterized the fluorescent behavior of these systems under uniaxial deformation. SEBS-P with 1 and 2.5 wt % of dispersed pyrene showed only limited changes in the emission spectra (Figures 3.7b and 3.8). These results are consistent with the poor excimer band formation observed in the unstrained samples: if excimers and aggregates are only barely present in the sample, we cannot expect relevant mechanoluminochromism based on spectral variations.

In SEBS-P 5% (Figure 3.10a, spectra normalized on the monomeric emission), the excimer band is clearly present in the unstrained sample, and we observed a significant mechanoluminochromism during deformation, even though only starting from 200% of strain. Drops of excimer content of around 11 and 33% were observed at 200 and 400% of strain, respectively. In the sample comprising 10 wt.% of dispersed pyrene (Figure 3.10b, spectra normalized on the monomeric emission), the emission spectrum is characterized by the presence of almost only the excimer band, and a signal ascribable to the monomeric band started to appear during the deformation already from 50% strain onward. However, the excimer band remained dominant in the whole deformation range explored. In this case, a drop of excimer content of around 34 and 79% can be estimated at 50 and 400% of strain, respectively. In the case of the covalently

functionalized SEBS-AMP sample (Figure 3.10c), the excimer band decreases upon deformation and the drop of excimer is already evident at 50% of strain. The excimer to monomer emission ratio changed by 30 and 78% applying 50 and 400% of strain, respectively.

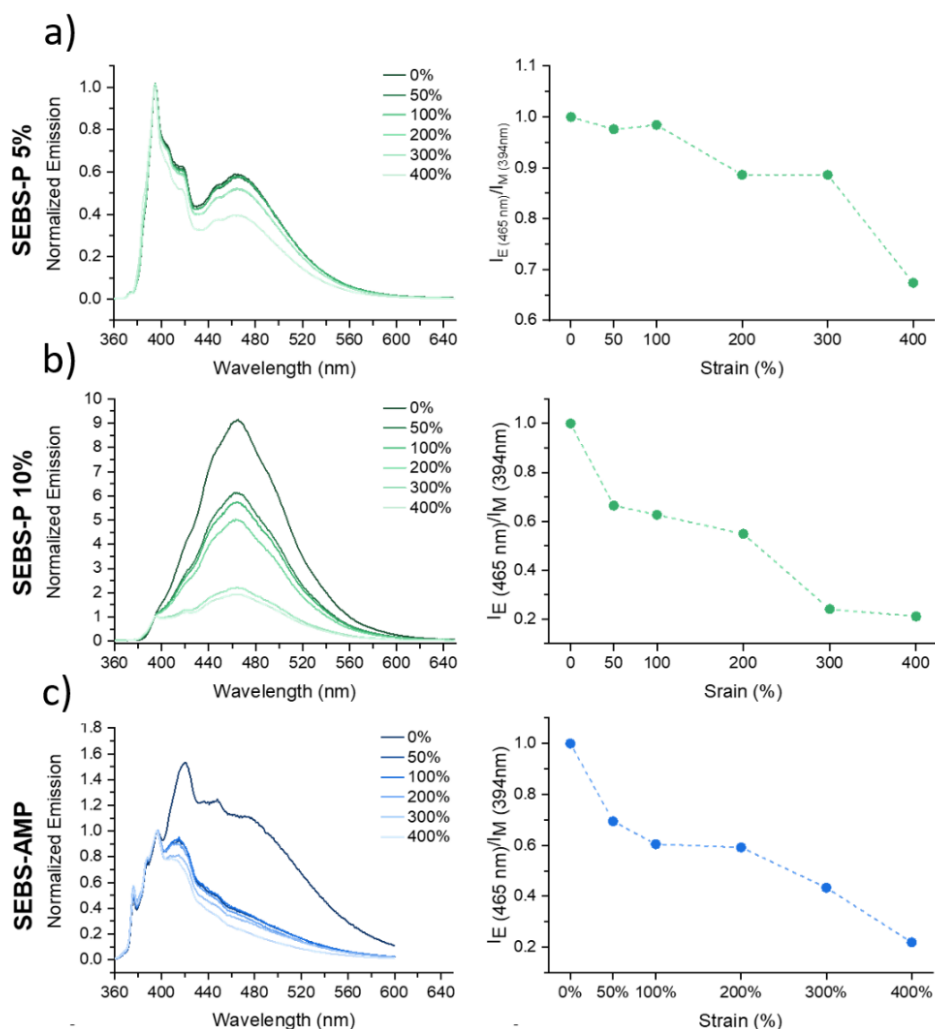


Figure 3.10 Emission ($\lambda_{\text{exc}} = 345\text{ nm}$, normalized at 396 nm) and normalized I_E/I_M for SEBS-P 5% (a), SEBS-P 10% (b), and SEBS-AMP (c) at different strains. Adapted from ref. [9] with permission from American Chemical Society, Copyright © 2023.

The covalently functionalized system shows an improved mechanoluminescent response with respect to the corresponding blend doped with 1 wt.% of pyrene. Ultimately, the mechanoluminescent properties of SEBS-AMP were similar in amplitude and in the slope of the response to those of SEBS-P 10%, which contains about 10 times the amount of pyrene molecules. This can be explained on the basis that in the former, the pyrenic units are confined within the ethylene-butylene soft block of the polymeric

matrix, thus resulting in a higher local concentration leading to increased excimer formation. Yet, the enhanced response and sensitivity to applied stress are not a mere effect of concentration. The amorphous soft block grants the elastic properties to the matrix; therefore, fluorophores are strategically localized in the phase that bears the earliest mechanical stress, resulting in a more efficient breakage of the excimers and aggregates during deformation, an enhanced mechanoluminochromic response, and an improved sensitivity toward the applied force. In other words, the covalent functionalization of the ethylene-butylene soft block allowed the formation of (possibly smaller) pyrene excimers, which appeared, however, more responsive than the mixed 5 wt.%. The mechanoluminochromic response in the blend films required larger amounts of pyrene since it can be preferentially incorporated in the polystyrene blocks that are less active during the uniaxial solicitation. A deeper analysis will be given by the SNOM characterization, carried out at the University of Pisa by Prof. Fuso's group, described in the following division. Since SEBS-P 10% and SEBS-AMP showed the best I_E/I_M variation between pristine and 400% stress (–79 and –78%, respectively), these samples were further characterized to investigate the reversibility of the mechanoluminochromic response. To this aim, the films were tested under successive cycles of strain (up to 400%, Figure 3.11a,b). The I_E/I_M values remained within 10% of their initial values across 5 cycles for both systems. These experiments show that the hard phase of the styrene blocks acts effectively as anchor points for the macromolecular chains in both SEBS-P 10% (Figure 3.11a) and SEBS-AMP (Figure 3.11b) samples, leading to reversible deformation and reversible mechanoluminochromic response.

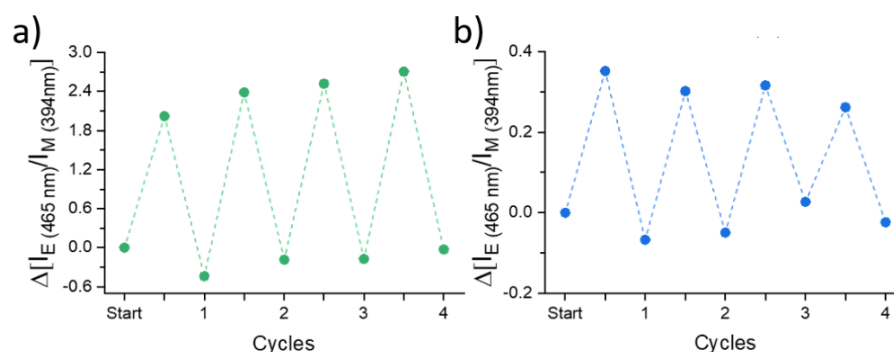


Figure 3.11 variation of the excimer to monomer intensity ratio, $\Delta(I_E/I_M) = (I_E/I_M)_{\text{Start}} - (I_E/I_M)_{400\%}$, under uniaxial loading and unloading cycles for SEBS-P 10% (a) and SEBS-AMP (b). Adapted from ref. [9] with permission from American Chemical Society, Copyright © 2023.

For a more detailed comparison of SEBS-P 10% and SEBS-AMP, Figure 3.12 shows the results of time-resolved emission measurements after film deformation at different predefined strains. More in detail, Figure 3.12a,b report, for each sample, the emission decay of the monomer (measured at 398 nm) at different strains. It is evident that these emission decays can be divided into a long component (which is actually made of two contributions, one at about 25 ns and one at ca. 130–170 ns, matching the expected monomeric pyrene decays in the presence and in the absence of oxygen as a quencher, respectively) which represents the unquenched monomeric pyrene moieties; the other contribution is instead characterized by a short decay (0.6–3 ns) that accounts for those pyrene moieties involved in the formation of excimers and aggregates with a distribution of quenching rates, owing to different pyrene-pyrene distances. These two fractions are quantified by a three-exponential fitting and by plotting the two pre-exponential coefficients. After a preliminary fitting, 3 fixed lifetimes (2, 25, and 130 ns for the SEBS-AMP and 1, 25, and 170 ns for the SEBS-P 10%) were selected to optimize the quantification of pre-exponential factor contributions. Since the pyrene moieties feature the same radiative constants, these coefficients can be regarded as roughly proportional to the molar fraction of pyrene moieties which are involved in excimer formation ($B1$) with respect to the monomers that are not involved in the excimer formation ($B2 + B3$). Notably, with the increase of strain, the fraction

of excimer-forming pyrene moieties decreases and, concomitantly, the fraction of unquenched pyrene monomers increases. In SEBS-AMP, i.e., in the presence of covalently bound pyrene, this transition appears to be sharper and to involve a larger fraction of pyrene moieties, with respect to what observed in SEBS doped with 10 wt.% of physically dispersed pyrene.

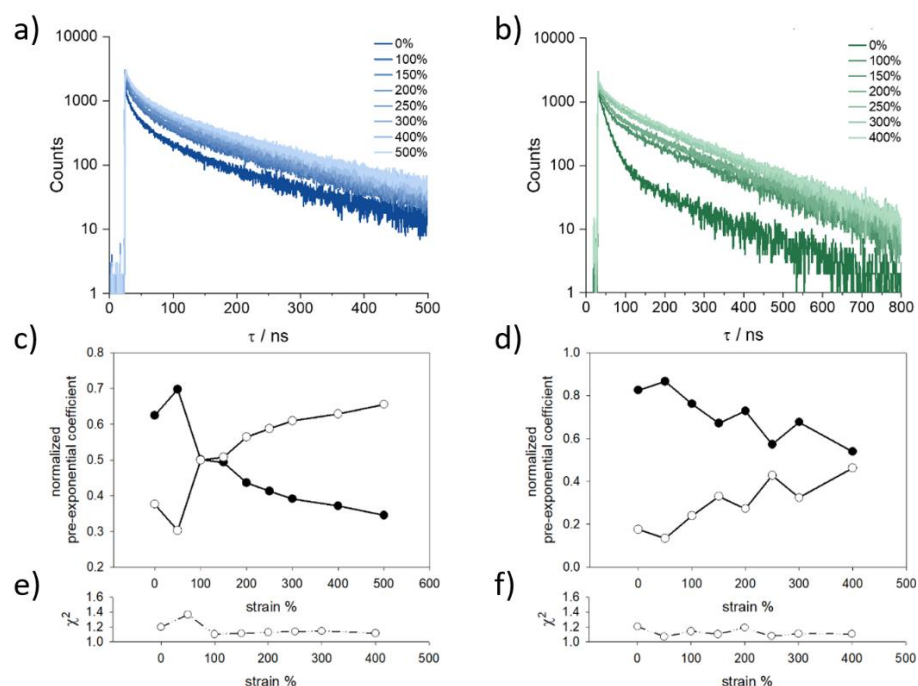


Figure 3.12 Emission decays of SEBS-AMP (a) and SEBS-pyrene 10% (b); (c,d) pre-exponential factors obtained with a fixed lifetime, three-exponential decay fittings of data shown in (a,b), respectively. B1 (solid circles) represents the fraction of quenched pyrenes (excimer forming pyrene moieties), while B2 + B3 (hollow circles) represents the fraction of unquenched pyrenes (non-excimer forming moieties); χ^2 (e,f) of the fittings is also reported as an indication of the good quality of the fitting. Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

Characterization by scanning near-field optical microscopy (SNOM)

To get further confirmation of what has been shown so far, Professor Fuso's group at the University of Pisa performed SNOM analyses on the same samples.

A relevant aspect concerns the spatial distribution of the emission at the sample surface. To get useful insight in this direction, SNOM on SEBS-AMP, SEBS-P 5%, and SEBS-P –10% was performed to evaluate the morphological features before and after 100% of strain and near-field operation assessed as in Figure 3.13. The fluorescence emission,

stimulated in the near-field at 365 nm and collected in the far-field, was split and sent onto two separate detectors equipped with interference filters centered at 405 and 458 nm (bandwidth 10 nm), respectively. In this way, maps representative of the spatial distribution of monomer and excimer emission, respectively, were simultaneously acquired.

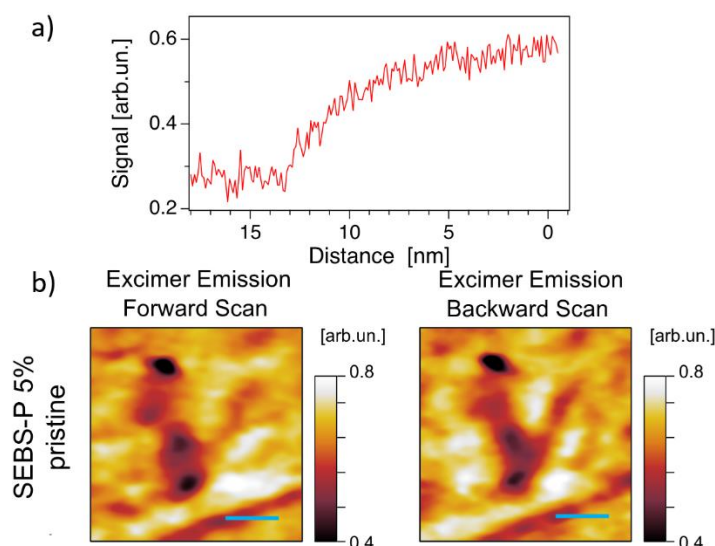


Figure 3.13 Emission signal as a function of the probe-to-sample distance acquired during an approach a); emission maps collected during the forward and backward directions of the SNOM raster scan b). Markers size is 400 nm; relative variations of the signal in forward and backward scans are typically within $\pm 10\%$. Data shown in the examples refer to the excimer emission from SEBS-P 5% in pristine conditions. Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

The emission maps acquired on pristine and strained SEBS-P 10% film turned out almost homogeneous, possibly because of the strong excimer emission that saturated the signal collected by the analysis. Therefore, this sample was not further investigated. Figure 3.14 shows examples of the so-realized maps acquired during $4\ \mu\text{m} \times 4\ \mu\text{m}$ scans on both pristine and strained SEBS-P 5% and SEBS-AMP samples. In addition to the emission maps, we also included the topographies reconstructed during the same scans. Inhomogeneous topographical features were detected, possibly affected by surface irregularities in the mold. Roughness analysis conducted on SEBS-P 5% and SEBS-AMP topographies resulted in a root-mean-square roughness (S_q) of 20 ± 4 and 27 ± 6 nm, respectively. The uniaxial deformation, oriented

approximately along the diagonal of the images, produced an increase in roughness due to the formation of elongated structures in the stretching direction, clearly visible in the maps (Figure 3.14). For the strained SEBS-P 5% sample, S_q was found to be 41 ± 9 nm; for the SEBS-AMP sample, S_q was 36 ± 12 nm. Although generally correlated with topography, emission maps exhibit qualitatively different morphologies. For the excimer band, emission domains, i.e., regions where the emission intensity is almost homogeneous, extend over relatively large areas (typical of a few μm). By contrast, the emission of the monomer is more spatially dispersed and granular, featuring submicrometric domains appearing, in particular, in the SEBS-AMP sample. In near-field scans, only the outmost layers are subjected to excitation since the near-field extinguishes on a length scale of a few tens of nanometers. Therefore, the finding can be ascribed to the uneven spatial distribution of the pyrene units at the sample surface, possibly leading to the granular morphology of monomer emission maps. Conversely, agglomeration involved in the excimer formation occurs on a larger length scale, giving rise to more extended and homogeneous domains.

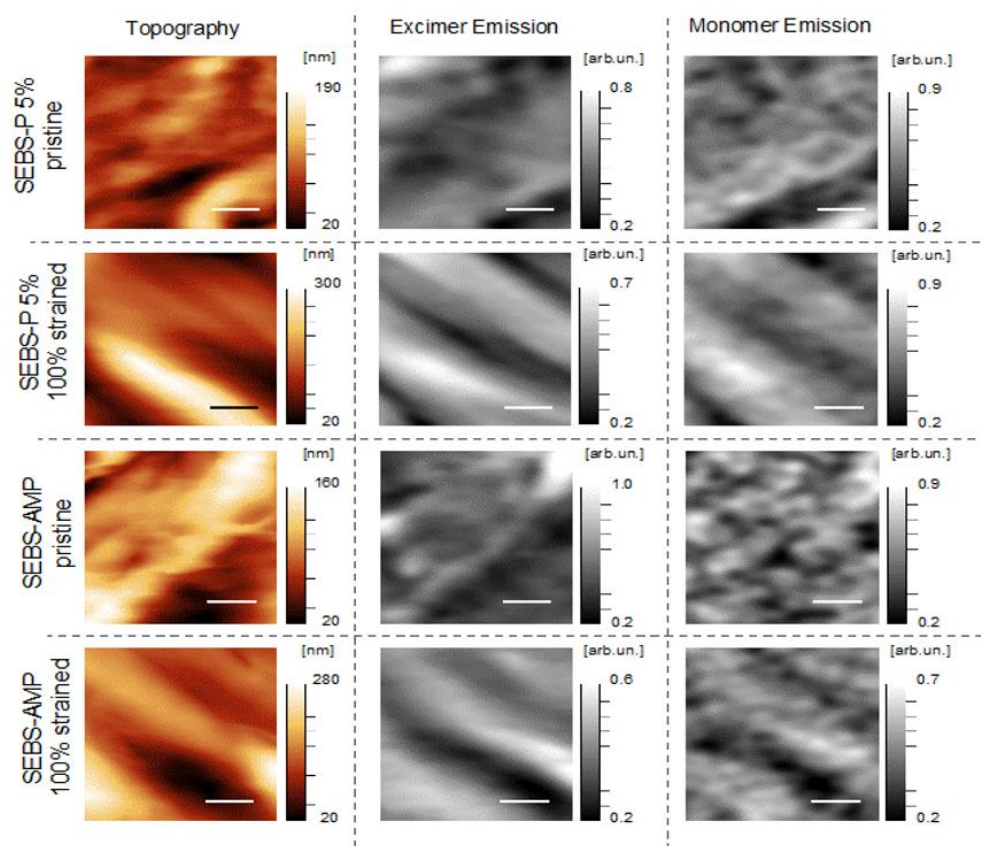


Figure 3.14 Topography and emission maps for SEBS-P 5% and SEBS-AMP samples, both in pristine and strained conditions. Marker size is 1 μm ; $\lambda_{\text{exc}} = 365 \text{ nm}$. Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

According to this analysis, strain induces changes in the morphology of photoluminescent (PL) domains. In particular, in the PL maps of the excimer, domains of typically 1–2 μm width and elongated shape along the stretching direction are clearly visible. For their size and shape, they are comparable to topographic structures. Similar elongated domains in the stretching direction are also observed in the case of the monomer, despite being more finely divided, as mentioned earlier. A standard cell-counting algorithm, based on the Otsu method (Figure 3.15), has been applied to the whole set of emission maps produced in the experiment, corresponding to a total scanned area of about 200 μm^2 per sample.

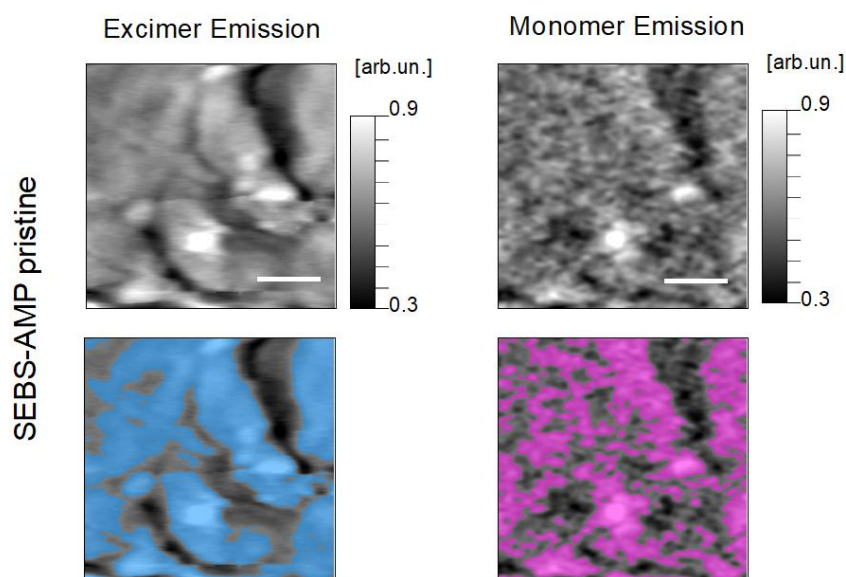


Figure 3.15 Examples of the Otsu algorithm applied to the SEBS-AMP film in pristine conditions (excimer emission): in the bottom line, the obtained emission domains are superposed to maps. Marker size is 2 μm . Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

This analysis enabled determining an average area of the emission domains in different samples and strain conditions (Figure 3.16a). They confirm the granular distribution of the monomer emission domains that, in fact, show in most samples an average smaller area than the excimer ones. There is, however, a notable exception for the strained SEBS-P 5% sample, where maps suggested an increase of the monomer domain area by a factor ca. 5 upon application of the mechanical strain. We note that, conversely, the average emission intensity calculated on the same maps, summarized in Figure 3.16b, did not increase with respect to the pristine conditions. This means that, rather than modifying the monomer/excimer intensity ratio, strain led to an improved homogeneity of the monomer distribution at the sample surface driven by mechanical stress. This is in line with the constant monomer/excimer intensity ratio recorded by emission spectroscopy for the SEBS-P 5% sample at 100% strain, as reported in Figure 3.10a.

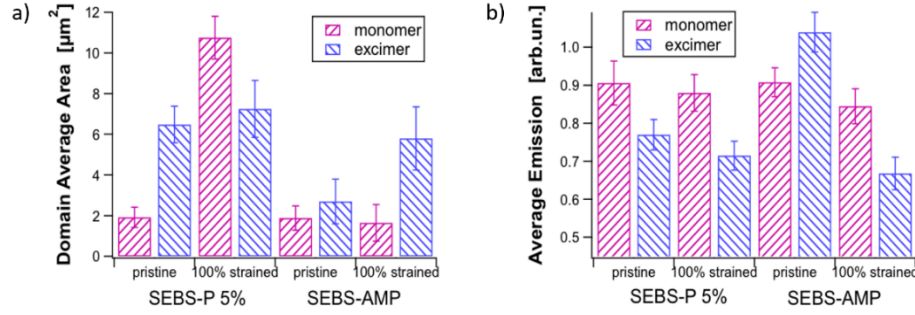


Figure 3.16 Average area of the emission domains in SEBS-P 5% and SEBS-AMP samples before and after stretching (a) and corresponding average emission intensity (b). Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

The marked mechanoluminescence of SEBS-AMP is also confirmed in near-field investigations. As shown in Figure 3.16b, mechanical strain promotes a decrease in the average intensity of the excimer emission, in substantial agreement with the macroscopic fluorescence measurements. This is accompanied by an increase in the grain area by a factor of about 3, suggesting that, upon strain, the surviving excimer species reorganize their spatial distribution within wider domains at the sample surface. The behavior is, therefore, similar to that of the monomer species in the dispersed material. However, we can hypothesize a slightly different mechanism, where, on the one hand, the mechanical stress acts to distribute over larger areas the pyrene units are covalently linked to the polymer matrix, while, on the other hand, it promotes efficient segregation of excimers and aggregates.

In addition, we evaluated the morphological correlation between the spatial distribution of excimer and monomer domains (Figure 3.17). As detailed in the following equations

$$e'_{i,j} = 2 \frac{e_{i,j} - e_{avg}}{e_{max} - e_{min}} \quad (\text{Eq. 3.1})$$

$$m'_{i,j} = 2 \frac{m_{i,j} - m_{avg}}{m_{max} - m_{min}} \quad (\text{Eq. 3.2})$$

Cross-correlation (C_{em}) is a term used to describe the distribution of different variables in a set and can have values between 1 and -1, with 1 and -1 describing an interdependence of the variables and 0 representing a random relation between the two. In the case

presented herein, C_{em} between excimer and monomer emission intensities was always found to be positive. This result indicates that the local trends of the intensities are similar and may be interpreted assuming a similar spatial distribution of the dye (in the monomeric and aggregated forms) on the surface of the samples. In both SEBS-P 5% and SEBS-AMP, the application of a strain resulted in features roughly aligned with the uniaxial deformation, confirming that mechanical stress effectively drives the dye's spatial distribution. There are, however, qualitative differences in the investigated samples. First of all, in SEBS-P 5%, cross-correlation is higher, on average, with respect to SEBS-AMP, as demonstrated by the color scale range in Figure 3.17. This means that spatial distributions of monomer and excimer emission domains are similar to each other, being substantially ruled by the local surface density of the dispersed dye molecules. In this case, mechanical stress induces a spatial rearrangement of such density. On the contrary, when the dye is covalently linked to the polymer matrix, regions exist at the sample surface where the emission of the excimer, detected in the scan, is poorly correlated with that of the monomer and vice-versa. Although with the limitations inherently related to the finite spatial resolution of the technique (the minimum transverse size of the features observed in cross-correlation maps is on the order of 100 nm, or slightly smaller), this result may be interpreted as the evidence of a different spatial distribution of the dye molecules accompanied with a possibly increased local density of pyrene molecules, hence an enhanced probability of aggregation. In such conditions, the applied mechanical stress promotes molecular segregation, leading to a slight increase in the cross-correlation due to the co-location of monomer and excimer domains, meaning that the strain had the effect of converting part of the excimers into monomers, thus confirming the emission results. Moreover, as mentioned earlier, the spatial distribution of the surviving aggregates becomes more homogeneous.

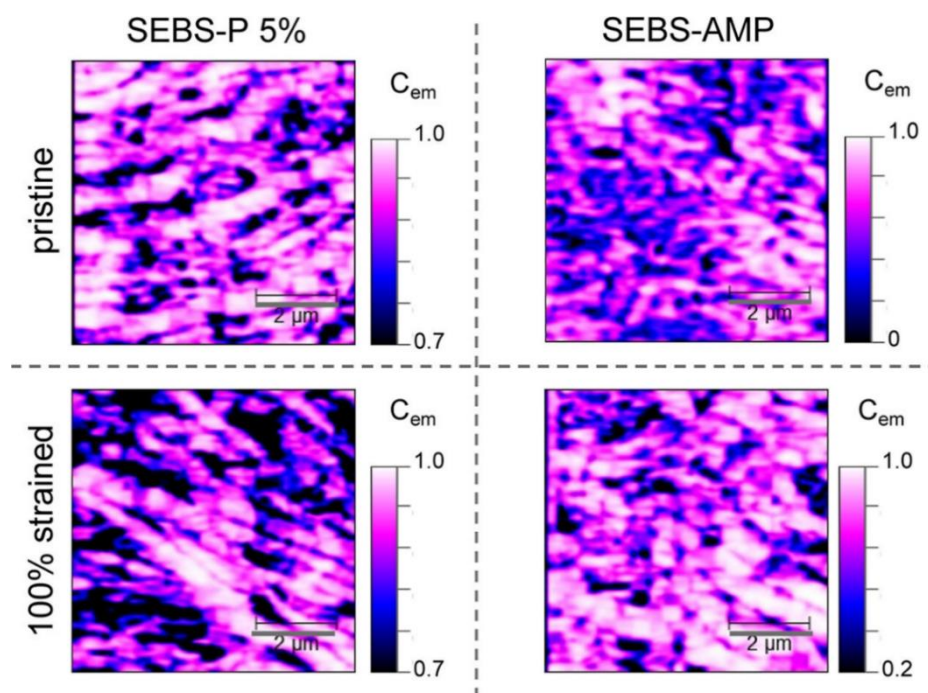


Figure 3.17 Excimer/monomer correlation maps for SEBS-P 5% and SEBS-AMP samples. Scale bar = 2 μm . Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

3.1.3. Conclusions

In this work, two different procedures were proposed for the preparation of SEBS elastomers endowed with mechanoluminochromic properties. The covalent approach provided ~1 wt.% of pyrene molecules grafted on the flexible ethylene-butylene blocks of SEBS (SEBS-AMP), which was compared with the physical dispersion of blend films containing variable pyrene contents, i.e., from 1 to 10 wt.% (SEBS-P 1–10%). Both procedures did not substantially affect the mechanical behavior of the derived films. Spectroscopic and SNOM investigations evidenced a modest chromogenic response under uniaxial stress for the blend films up to 5 wt.% of pyrene content, possibly due to the insufficient formation of pyrene excimers. Conversely, SEBS-AMP displayed an evident pyrene excimer band at about 480 nm, possibly caused by the strategic confinement of the pyrene chromophores in the soft block of SEBS. The larger mobility of the aliphatic phase, which thus also bears most of the mechanical stress, causes an early and noticeable drop of the I_E/I_M ratio and a marked mechanoluminochromism already at 50% of

strain due to the (reversible) rupture of the pyrene excimers. A similar chromogenic response occurred in blend films containing dispersed 10 wt.% of pyrene. Such a high concentration was required in the physically dispersed blend for the formation of a responsive excimer band, probably due to a favorable solubility of pyrene and also in the styrene blocks of SEBS. For this reason, notwithstanding the clear decrease in the I_E/I_M ratio, the excimer emission remained predominant up to the greatest deformation. These results highlight the significant potential for low-cost materials based on widely used commodity elastomers capable of showing reversible mechanoluminochromic response. There is no doubt that the physical mixing offers a simpler route in gathering mechanoluminochromism, but the optimization of the I_E/I_M ratio seems less straightforward. Conversely, the covalent approach presents high potentialities and some advantages, especially when the probe is confined in a segregated domain. Modest amounts of the chromogenic probe are actually required for the emersion of the excimer band, thus allowing better control of the aggregation/de-aggregation process and a complete chromogenic effect.

3.1.4. Experimental section

Materials. THF, toluene, MeOH, deuterated dimethyl sulfoxide (DMSO- d_6), AMP hydrochloride (AMP-Cl, 95%), pyrene (98%), and ammonium hydroxide aqueous solution (25%) were obtained from Sigma-Aldrich (Germany) and used as received. SEBS functionalized on the aliphatic segment with MAH (SEBS-MAH, 1 wt.% of grafted anhydrides) was kindly provided by Auser Polimeri S.R.L. (Italy). The product exhibits a degree of functionalization of grafted anhydride equal to 1 wt.%, a percentage of styrene of 28 mol %, an amount of residual unsaturation below 3%, and a density equal to 0.919 g cm⁻³. SEBS used in this work (SEBS YH-501) was supplied by Sinopec (China) in the form of a white powder. The product has a linear structure and consists of 30 mol % of styrene units. Both SEBS and SEBS-MAH were purified by dissolution in toluene and reprecipitation in MeOH (toluene/MeOH = 1:20 v/v). The polymer was recovered by filtration and dried under vacuum. After purification, SEBS-MAH was dried for 4

h at 170 °C under vacuum to convert all carboxylic acid groups, formed upon hydrolysis, back to anhydrides. Thermal treatment was monitored by FT-IR in attenuated total reflection (ATR) mode (Figure 3.18).

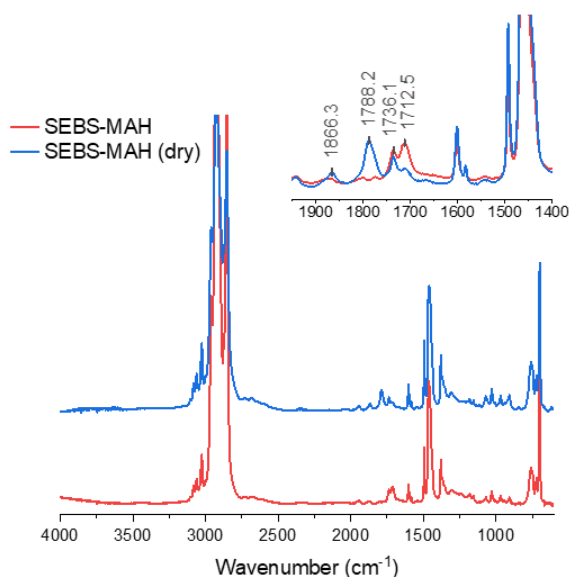


Figure 3.18 IR spectra of SEBS-MAH before (red) and after (blue) dried under vacuum to convert all carboxylic acid groups, formed upon hydrolysis, back to anhydrides. Reproduced from ref. [9][9] with permission from American Chemical Society, Copyright © 2023.

Converting AMP-Cl in AMP. AMP-Cl (0.43 g, 1.5 mmol) was dissolved in MeOH (35 mL), and NH_4OH (40 mL) was added. A color change from yellow to colorless was observed (Figure 3.19).



Figure 3.19 AMP-Cl before (left) and after (right) the addition of NH_4Cl . Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

The day after, AMP was recovered by filtration (white solid), washed with cold methanol, and dried under vacuum. 0.28 g was recovered (1.2 mmol, yield 80%). AMP was utilized without further

purification. AMP was characterized by ^1H NMR in $\text{DMSO}-d_6$ (Figure 3.20a) and by FT-IR in ATR mode (Figure 3.20b).

^1H NMR (500 MHz, $\text{DMSO}-d_6$, 25 °C) δ : 8.42 (d, $J = 9.2$ Hz, 1H), 8.32–8.24 (m, 3H), 8.21 (d, $J = 9.2$ Hz, 1H), 8.19–8.10 (m, 3H), 8.06 (t, $J = 7.6$ Hz, 1H), 4.47 (s, 2H), 2.08 (s, 2H).

FT-IR (ATR) cm^{-1} : 3365, 3306, 3038, 2917, 2890, 2851, 1603, 1587, 1488, 1451, 1432, 1415, 1314, 1282, 1185, 1069, 886, 842, 818, 811, 791, 762, 723, 712, 680.

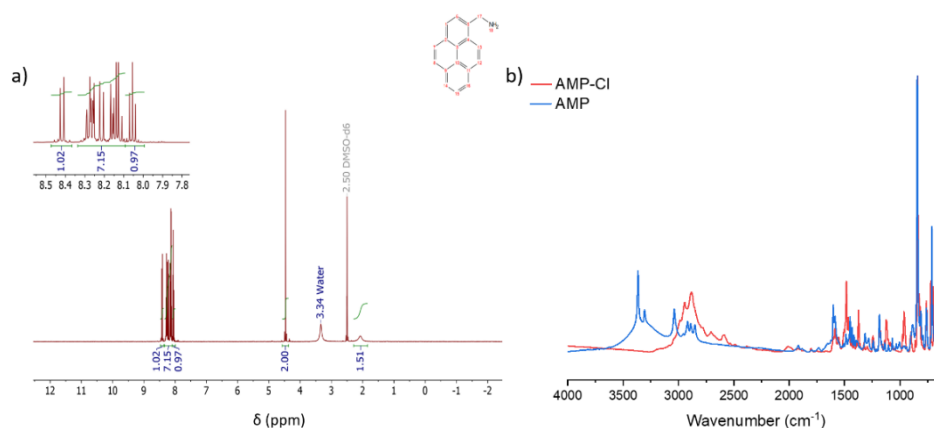


Figure 3.20 a) ^1H -NMR (500 MHz, $\text{DMSO}-d_6$, 25 °C) of AMP. b) IR spectra of AMP-Cl (red) and AMP (blue). Adapted from ref. [9] with permission from American Chemical Society, Copyright © 2023.

Preparation of SEBS-AMP and UV-Vis Analysis to Determine the Grafting Extent. 4.84 g of SEBS-MAH (0.45 mmol of grafted anhydrides) was dissolved in dry THF (30 mL). Then, 64 mg of AMP (0.28 mmol, 0.6 eq) was added, and the reaction was carried out at reflux for 48 h under stirring. The polymer was precipitated in MeOH (THF/MeOH = 1:20 v/v) and recovered by filtration (4.24 g). To remove the unreacted AMP, the crude product was purified by Kumagawa extraction in MeOH for 48 h and then dried under vacuum. The extent of the reaction was monitored by FT-IR in ATR mode (Figure 3.2) by observing the disappearance of the peaks at 1866 and 1788 cm^{-1} ($\nu_{\text{C=O}}$ of anhydride) and the appearance of the peak at 1711 cm^{-1} ($\nu_{\text{C=O}}$ of imide). To determine the degree of functionalization, UV-vis spectroscopy was employed. First of all, a calibration curve was obtained by plotting the absorbance at 345 nm of stock solutions of AMP in toluene. The range of concentration spanned between $6.1 \times$

10^{-6} and 3.1×10^{-5} M, corresponding to absorbances in the range of 0.2–1.1 (Figure 3.3). A solution of SEBS-AMP (0.51 mg mL^{-1}) in toluene was prepared, and the degree of functionalization with respect to the grafted anhydride (85.6%) and the weight percentage of grafted pyrene unit were calculated (1.1 wt.%).

Preparation of Blends of Pyrene in SEBS. 1.00 g of SEBS was dissolved in 50 mL of toluene, then the proper amount of pyrene (1–10 wt.%) was added, and the solution was left under stirring overnight. The solvent was removed under vacuum, and the polymer was recovered.

Film Preparation. About 1.0 g of pelletized pyrene in SEBS (SEBS-P) or SEBS-AMP was pressed twice for 5 min at 150°C and 150–200 bar. Before compression, the polymer was allowed to soften between the hot plates for 2 min.

Characterization methods. ^1H NMR spectra were carried out at room temperature and recorded on a JEOL spectrometer operating at 500 MHz and using 5 mm tubes and by setting 32 scans. The residual solvent peak was employed as an internal standard. FT-IR spectra were acquired by a Nicolet iS50 spectrometer (Thermo Fisher). The samples were analyzed in the ATR mode in the spectral range between 4000 and 600 cm^{-1} by setting 32 or 64 scans and a resolution of 4 cm^{-1} . The ATR accessory (ATR ITX) contained a diamond crystal (by employing this crystal, the penetration of infrared radiation is about $2 \mu\text{m}$ at wavelength numbers 1000 cm^{-1}) at a nominal incident angle of 45° . UV-vis absorption spectroscopy was performed using a Cary 5000 UV-vis-NIR spectrophotometer (Agilent). Fluorescence spectra were acquired on a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer equipped with a 450 W xenon arc lamp, double-grating excitation, and single-grating emission monochromator. The selected excitation wavelengths were close to the absorption peak at longer wavelengths. For polymeric films, the samples were rotated 30° with respect to the excitation beam, and the detector was set in the front-face mode. An Edinburgh FLS920 fluorometer equipped with a photomultiplier Hamamatsu R928P and connected to a PCS900 PC card was used for the fluorescence lifetime measurements based on the time-correlated single photon counting technique. Scanning near-field optical

microscopy (SNOM) in the emission mode was carried out with a custom-made apparatus, making use of a tapered and apertured optical fiber (LovaLite, 50 nm apical aperture) coupled with a 365 nm light-emitting diode (LED) (ThorLabs M365) as the near-field probe. Fluorescence emission, collected in the far field at 45° off-normal by a long working distance microscope objective (Mitutoyo 10× Plan Apo), was spectrally analyzed by interference filters (CVI Laser Optics) and detected by miniaturized photomultipliers (Hamamatsu R9880U-01). A sketch of the experimental configuration is shown in Figure 3.21. Amplitude modulation of the LED radiation and lock-in demodulation of the signal (Stanford Research SR830DSP) were used to improve the signal-to-noise ratio. DSC analyses were performed with a TA Instruments Discovery DSC 250 calorimeter. About 9 mg of polymer film obtained by compression molding was put in a 3 mm aluminum Tzero Pan plugged with a Tzero hermetic lid. The samples were analyzed according to the following cycle: heating from RT to 150 °C at 10 °C min⁻¹; cooling from 150 to -90 °C at 10 °C min⁻¹; and a second heating scan to 150 °C at 10 °C min⁻¹. An isotherm of 5 min was set between each heating-cooling scan. Stress-strain analyses were performed on Tinius Olsen H10KT equipped with a 500 N load cell, using an extension rate of 10 mm min⁻¹. Dog-bone specimens with a gauge length of 20 mm and a width of 5 mm were used. Three replicates were analyzed for each sample, and the results are given in terms of mean and standard deviation. The thickness was measured for each sample using a microcaliper.

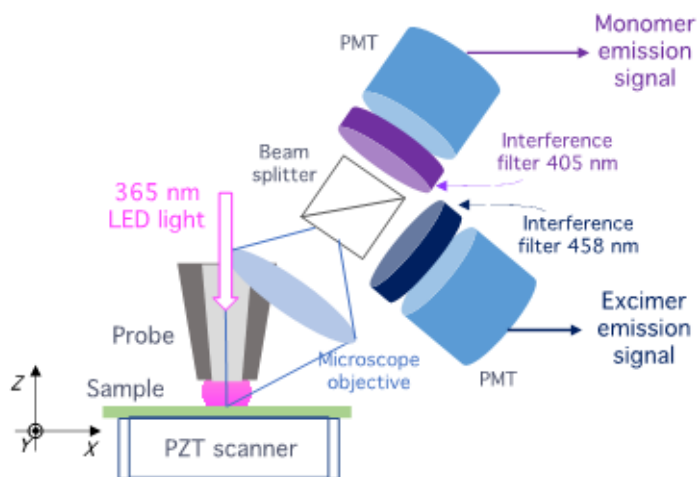


Figure 3.21 Simplified sketch of the SNOM setup: two distinct miniaturized photomultipliers (PMT) collect emission of the monomer and excimer bands. The sample is held by a piezoelectric (PZT) scanner of the hollow-tube kind, enabling sub-nm controlled displacements along the three (X, Y, Z) directions. Reproduced from ref. [9] with permission from American Chemical Society, Copyright © 2023.

SNOM. The Scanning Near-field Optical Microscope setup is custom-built according to the configuration described in [19] as sketched in Figure 3.21. The adopted probe is a tapered single-mode optical fiber featuring an apical aperture of 50 nm (nominal); the shear-force method is employed to monitor the probe-to-sample distance and keep it within the near-field range.

Operation in the near-field is assessed by the consistent increase of the collected signal during the probe-to-sample approach (Figure 3.13a), demonstrating its effective coupling with the material. Sub-wavelength lateral resolution is achieved in the actual conditions of the experiment: both maps acquired during the forward and backward directions of the SNOM raster scan show features with minimum size below 200 nm (Figure 3.13b).

Emission domains are identified in the SNOM maps by using a cell-counting algorithm based on the Otsu method.[20,21] The algorithm sets a threshold in an intensity map, enabling separation in two distinct classes; threshold is determined via maximization of the intensity variance pertaining to each class. Figure 3.14 shows examples of the algorithm output. In the experiment, the approach has been applied to the whole set of available emission maps, leading

to the domain average area and the relevant standard deviation plotted in Figure 3.16a of main text.

Cross-correlation analysis is used to determine the spatial interdependence between excimer and monomer emission. To this aim, individual maps simultaneously acquired during the same sample scan are first normalized to their dynamic range, according to equations Eq. 3.1 and Eq. 3.2, where $e_{i,j}$ and $m_{i,j}$ are the excimer and monomer emission signals detected at the i,j point of the map, e_{max} , m_{max} the maximum, e_{min} , m_{min} the minimum, and e_{avg} , m_{avg} the average signals detected in the corresponding maps. The so-determined normalized signals $e'_{i,j}$ and $m'_{i,j}$, ranging from -1 to +1, are then used to build a cross-correlation map, whose elements $c_{i,j}$ are calculated as

$$c_{i,j} = \sum_{k=0}^{N-1} \sum_{\ell=0}^{N-1} e'_{i+k,j+\ell} m'_{k,\ell} \dots (\text{Eq. 3.3})$$

where summations extend over the whole map, N being the number of points in every line and column of the square map (N is typically equal to 256). The cross-correlation map C_{em} showing $c_{i,j}$ values can finally be drawn. A simple Python code has been used for calculations. The mean value of C_{em} was found lower for pristine and drawn SEBS-AMP compared to SEBS-P (Table 3.1). This agrees with the more efficient dispersion of PL domains in SEBS-AMP.

These results support the hypothesis that the stretching affects the distribution of the domains, in particular, increasing the cross-correlation between the distribution of pyrene in the monomeric and excimer forms. This effect is particularly evident in the case of SEBS-AMP, which presented a more dispersed distribution in the pristine state.

Table 3.1 The mean value of C_{em} for SEBS-P 10% and SEBS-AMP at 0% and 100% of strain.

	C_{em}	
	pristine	drawn
SEBS-P 5%	0.83±0.11	0.88±0.10
SEBS-AMP	0.60±0.16	0.75±0.14

3.2. Comparative mechanoluminochromic performances of perylene diimide-doped polyurethanes: blending vs bonding?

3.2.1. Introduction

In previous research, an in-depth comparison between mixed systems and their corresponding covalently functionalized counterparts consistently demonstrated that the covalently bonded systems offer a superior mechanoluminochromic response, a result that is in alignment with findings reported in existing literature.[2,22] This difference in performance is attributed to the distinct disaggregation mechanisms occurring in the two types of systems. Specifically, it is hypothesized that the conformational change-driven disaggregation in the bound systems is more efficient than the shear-induced disaggregation in the blended systems.[8] These findings were obtained through a precisely designed smart molecular system that is challenging to replicate on a larger scale. Therefore, in this study, blended and covalently bonded systems were compared using a different dye, perylene derivatives (Per), incorporated into a commercial thermoplastic polyurethane (TPU). The covalently bound system was realized by mixing the TPU with a second PU (named PolyPer), bearing the Per in the main chain. The blended system was attained by blending the TPU with the free chromophore and adding, at the same time, a second PU (named Poly) not containing the dye. Therefore, these two systems only differed in the dye incorporation approach, keeping constant the chemical structure and the composition of the polymer matrix (TPU-Poly). Differently from previous reports[22,23] the PolyPer bearing the dye in the main chain was synthesized without controlling the chromophore distribution along the chain, aiming for a straightforward and potentially scalable synthetic procedure. Two concentrations of both bonded and blended chromophores were tested. The photophysical properties of the films were measured at rest and under tensile deformation in stress-strain tests and stress-relaxation experiments.

3.2.2. Results and discussion

Characterization of synthesized polyurethanes

The perylene matrixes used in this work were synthesized at the University of Parma by Prof. Dalcanale's group. They also performed the characterizations both through spectroscopic techniques such as ^1H NMR, heteronuclear single quantum correlation (HSQC) and the mass spectrometry matrix-assisted laser desorption/ionization (MALDI).

Two different perylene-based chromophores were synthesized by applied a synthetic procedure adapted from the literature:[24] Per, bearing two unreactive butyl chains to be used as an additive in the preparation of dispersed-dye samples (D-x), and Per-OH, functionalized with two alkyl chains bearing hydroxyl groups at each terminus, as shown in Figure 3.22.

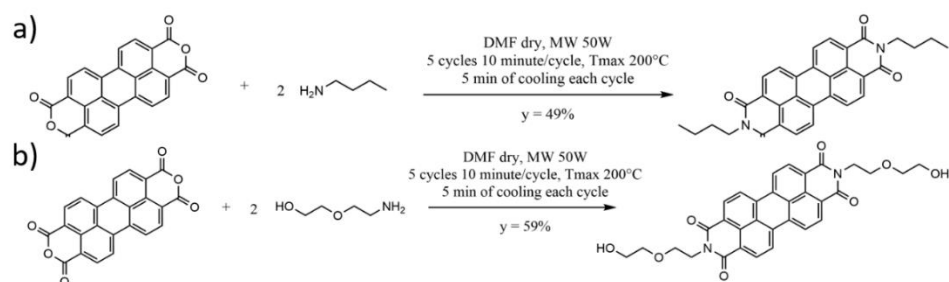


Figure 3.22 Schemes of Per (a) and Per-OH (b) synthesis.

Both Per and Per-OH were fully characterized, and the corresponding ^1H NMR and HSQC spectra, conducted as the synthesis at the University of Parma by Dalcanale's group, are reported in Figure 3.23.

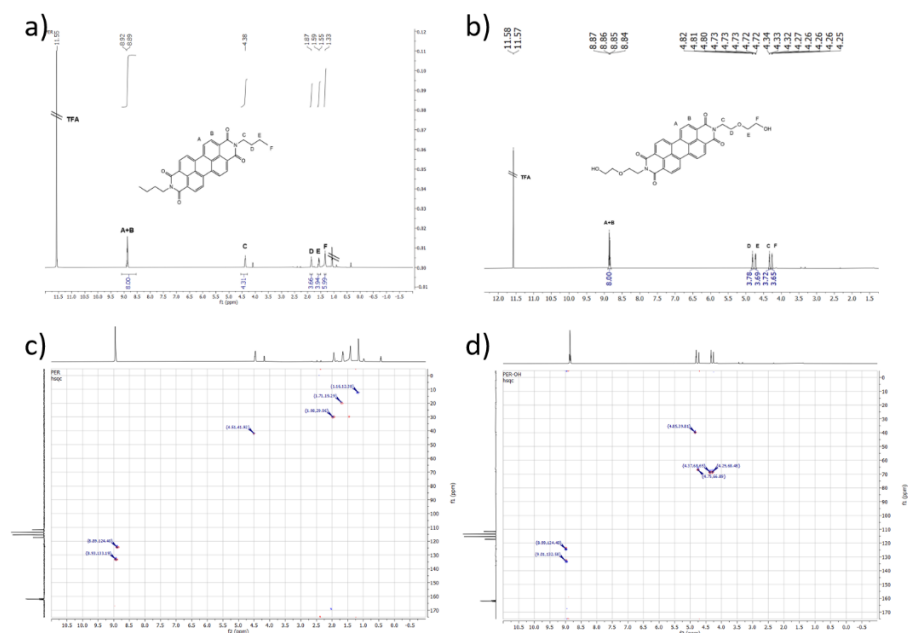


Figure 3.23 ^1H NMR of Per (a) and Per-OH (b) (deuterated TFA, 600 MHz, 298 K). HSQC of Per (c) and Per-OH (d) (deuterated TFA, 151 MHz, 298 K).

Per-OH was used for the preparation of PolyPer1 and PolyPer5, together with PEG 1500, 4,4'-methylenedicyclohexyl diisocyanate (HMDI), and 1,4 butanediol, in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as catalyst as shown in the scheme of Figure 3.24.

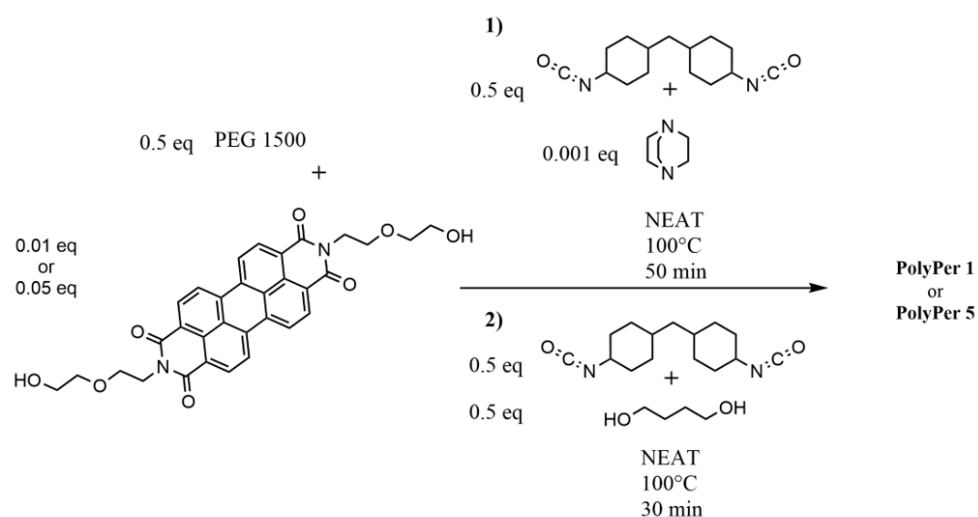


Figure 3.24 Synthesis scheme of PolyPer1 and PolyPer5.

The quantity of chromophore Per-OH present in PolyPer1 was too low to allow its detection and quantification through ^1H NMR

functionalization with Per-OH does not influence the synthetic process.

Table 3.2 GPC data of TPU, Poly, PolyPer1 and PolyPer5: M_n , weight average molecular weight (M_w) and polydispersity index ($\mathcal{D}$).

Sample	M_n [g mol ⁻¹]	M_w [g mol ⁻¹]	$\mathcal{D}$
TPU	93410	310570	3.3
Poly	1960	3630	1.9
PolyPer1	1960	3360	1.7
PolyPer5	2300	4640	2.0

DSC analyses were performed to evaluate how the different degrees of functionalization affect the thermal properties (Figure 3.27). After erasing polymer thermal histories by melting and cooling at 10 °C min⁻¹, heating scans are analyzed. All synthesized PU are semicrystalline with a glass transition temperature (T_g) below RT. Above T_g , the DSC heating scan of Poly shows a narrow melting peak (T_m = 42 °C), which can be ascribed to PEG segments (pure PEG1500 shows a T_m at *ca.* 45 °C [25]). The DSC traces of PolyPer1 and PolyPer5 similarly display a narrow melting peak that, also in these cases, can be attributed to the melting of PEG1500 segments.

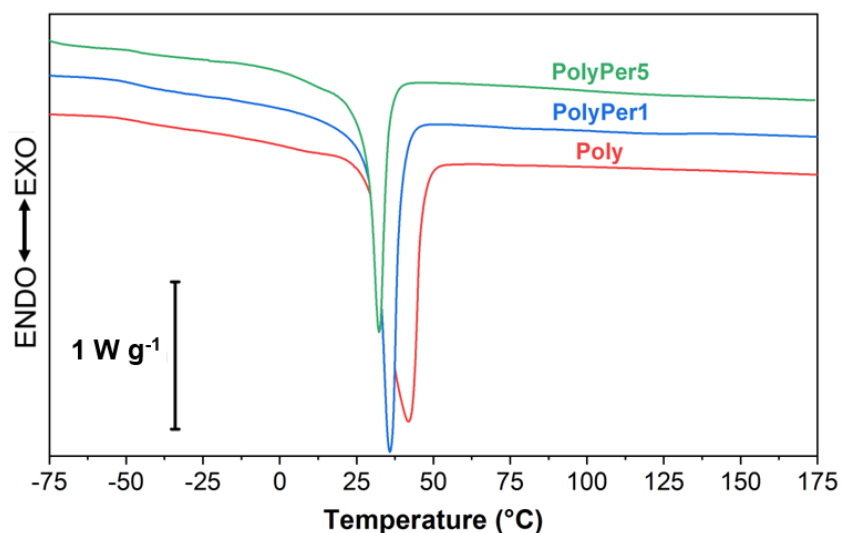


Figure 3.27 DSC scans after controlled cooling at 10 °C min⁻¹ of Poly (red), PolyPer1 (blue), and PolyPer5 (green)

Calorimetric data of PolyPer1, PolyPer5, and Poly reported in Table 3.3 show that, upon increasing the amount of Per-OH in the main polymeric chain, both T_m and ΔH_m decrease. This result indicates that the presence of the chromophore in the main polymeric chain reduces the capability to crystallize, possibly due to the proximity of the chromophore to the PEG segments.

Table 3.3 Calorimetric data of bulk PU and films.

a)

Sample	T_g [°C]	ΔC_p [J·g ⁻¹ ·°C ⁻¹]	T_m [°C]	ΔH_m (PEG segments) [J·g ⁻¹]
Poly ^a	-45	0.16	42	63.1
PolyPer1 ^a	-46	0.18	36	52.6
PolyPer5 ^a	-46	0.11	32	40.1
D-0.15 ^b	-45	0.37	44	12.2
D-0.78 ^b	-46	0.23	41	15.6
MC-0.15 ^b	-44	0.36	40	11.8
MC-0.78 ^b	-43	0.39	42	8.3

Calorimetric data are referred to the heating scan after controlled cooling at 10 °C min⁻¹.

b) Calorimetric data are referred to the first heating scan.

UV-Vis absorption and fluorescence spectra of Per, Per-OH, PolyPer, and PolyPer5 solutions in THF were recorded (Figure 3.28a,b). The absorption spectra show an absorption maximum at 522 nm for all the materials under analysis, along with two higher vibronic transitions located at ~486 and ~456 nm, characteristic of perylene diimide (PDI) chromophores in solutions.[26,27] Additionally, the fluorescence spectra represent a mirror image of the absorption spectra and maintain the vibronic pattern accompanied by well-resolved fine structures, with the highest emission band at 526 nm for all the materials under analysis. The similarities in the shapes and positions of dyes and polymers' absorption and emission spectra indicate that the different imide substituents do not significantly affect their photophysical properties. Furthermore, for both polymers, ground-state aggregation does not occur in solution.

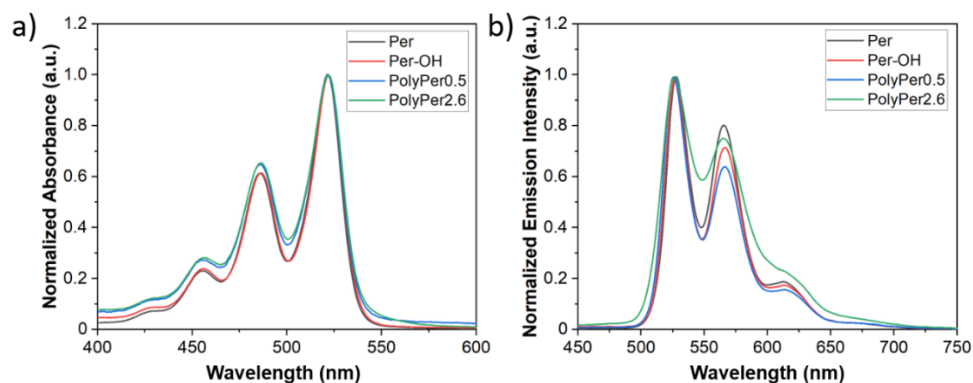


Figure 3.28 UV-Vis (a) and (b) emission spectra ($\lambda_{\text{ex}} = 485 \text{ nm}$) of THF solutions of Per ($c = 15 \text{ }\mu\text{M}$, black), Per-OH ($c = 15 \text{ }\mu\text{M}$, red), PolyPer1 ($c_{\text{Per-OH in the polymer}} = 20 \text{ }\mu\text{M}$, blue), and PolyPer5 ($c_{\text{Per-OH in the polymer}} = 20 \text{ }\mu\text{M}$, green).

Characterization of Per-based films

The synthesized polyurethanes were employed as additives of a high-MW commercial TPU presenting $M_n = 93410 \text{ g mol}^{-1}$ and $\bar{D} = 3.3$ (Table 3.2), a T_g below RT and a broad melting between $100 \text{ }^\circ\text{C}$ and $180 \text{ }^\circ\text{C}$ [28] (Figure 3.29 and Table 3.4). PolyPer1 and PolyPer5 were added at 30 wt.% concentration to TPU to prepare main-chain (MC) compounds. Dispersed-dye blends (D) were also produced by dispersing the free Per dye into a TPU:Poly 70:30 w/w blend.

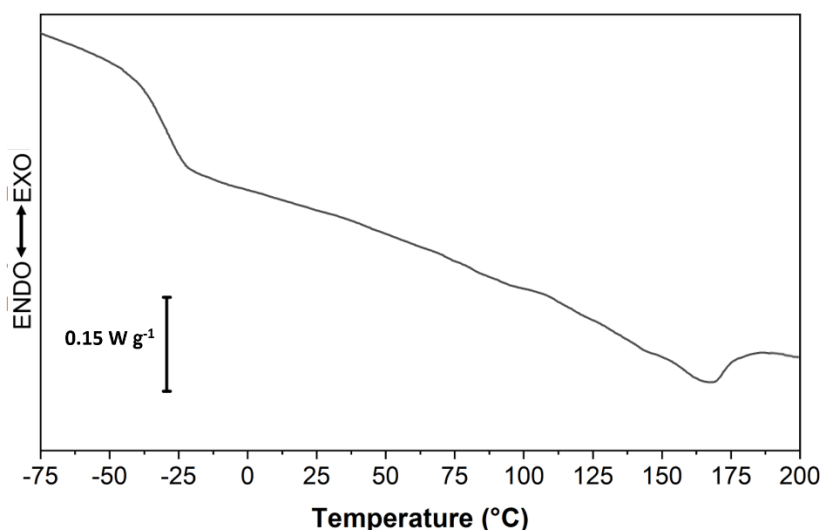


Figure 3.29 DSC heating scan after controlled cooling at $10 \text{ }^\circ\text{C min}^{-1}$ of TPU.

Table 3.4 Calorimetric data are referred to the heating scan after controlled cooling at 10 °C min⁻¹.

Sample	T _g [°C]	ΔC _p [J·g ⁻¹ ·°C ⁻¹]	T _m [°C]	ΔH _m [J·g ⁻¹]
TPU	-30	0.41	164	13.4

The thermal behavior of both dispersed-dye blends and main-chain systems is shown in Figure 3.30a,b and the corresponding calorimetric data are reported in Table 3.3. First heating scans of samples stored at RT for two weeks are analyzed in this case, this scan being representative of the starting condition for mechanoluminescent characterization. All films are semicrystalline and display a single T_g at *ca.* -45 °C suggesting that Poly-based materials and TPU form a miscible blend.

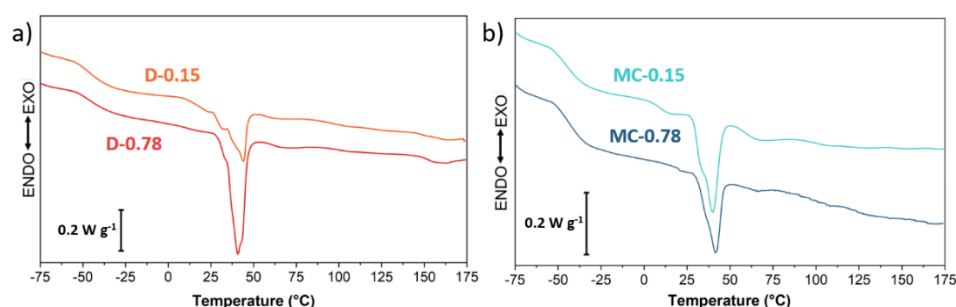


Figure 3.30 DSC first heating scans of D-0.15 (orange) and D-0.78 (red); b) DSC first heating scans of MC-0.15 (cyan) and MC-0.78 (blue).

This result was further confirmed by Dynamic mechanical thermal analysis (DMTA) reported in Figure 3.31. Therefore, DSC and DMTA results suggest that, both in the dispersed-dye blends and in the main-chain systems, the chromophore, typically located in the amorphous phase, is closely in contact with both the blend components, without any preferential segregation. All samples show a broad melting endotherm in the range 20 – 55 °C, which can be attributed to the melting of PEG segments of the synthesized PU since plain Per does not show any transition in this temperature range (data not shown), and a weak and hardly measurable endothermal signal above 150 °C, ascribable to the melting of the commercial TPU (Table 3.4). Upon increasing the amount of dispersed Per in D blends, the

ΔH_m of the PEG segments increases, indicating a possible nucleating action of Per excimers. This behavior is not observed in MC systems, where, instead, upon increasing the amount of the chromophore in the main polymeric chain, a decrease in T_m is observed, as previously seen for the corresponding bulk materials.

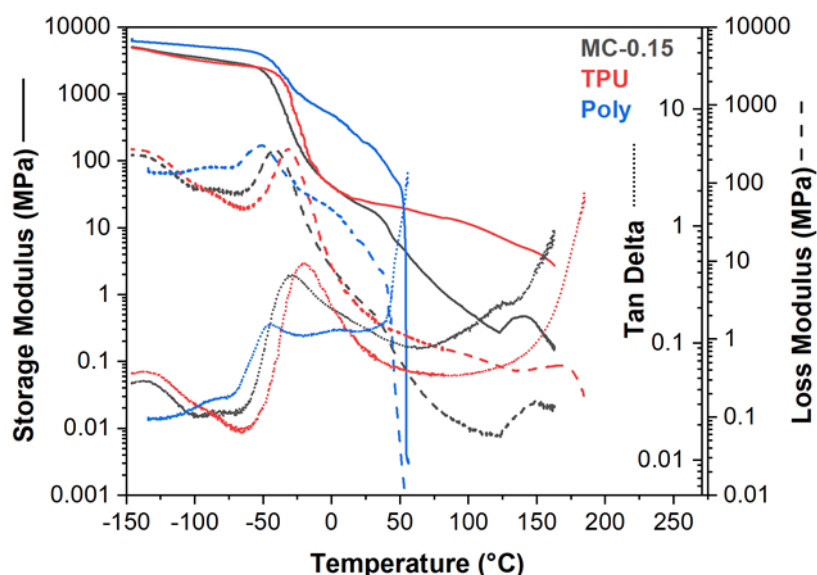


Figure 3.31 DMTA analysis of MC-0.15 (black), TPU (red), and Poly (blue). Storage modulus (solid line), loss modulus (dashed line) and $\tan\delta$ (dotted line) are reported.

Notably, all the materials under analysis display similar mechanical properties, typical of common TPU, with a low Young's modulus and a high deformation at break, thus indicating that the presence of the chromophore either in the main polymeric chain or as a dispersed additive does not affect the mechanical properties of the material (Figure 3.32 and Table 3.5).[26,27]

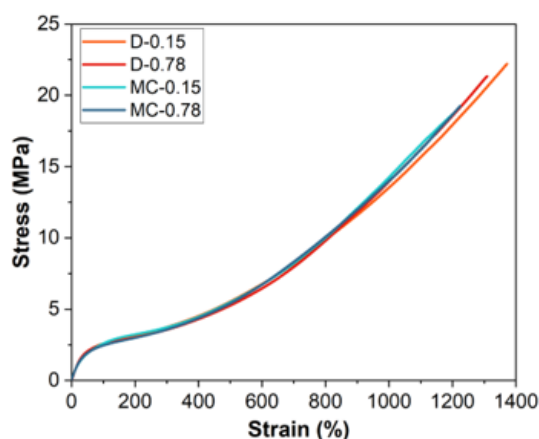


Figure 3.32 Representative stress-strain curves of D-0.15 (orange), D-0.78 (red), MC-0.15 (cyan) and MC-0.78 (blue).

Table 3.5 Mechanical data of D and MC samples.

Sample	Stress at break [MPa]	Strain at break [%]	Young's Modulus [MPa]
D-0.15	20 ± 3	$1.32 \cdot 10^3 \pm 0.05 \cdot 10^3$	5.3 ± 0.4
D-0.78	17 ± 4	$1.2 \cdot 10^3 \pm 0.1 \cdot 10^3$	6.0 ± 0.3
MC-0.15	19 ± 4	$1.2 \cdot 10^3 \pm 0.1 \cdot 10^3$	5.4 ± 0.4
MC-0.78	18 ± 6	$1.2 \cdot 10^3 \pm 0.1 \cdot 10^3$	6 ± 1

When excited with UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$), D samples exhibit a bright red fluorescence, while MC samples display a green-yellow fluorescence (Figure 3.33a). When compared with the monomeric emission of Per, these results indicate that a certain dye ground-state aggregation occurs in all the investigated blends. Indeed, the fluorescence spectra of both MC and D samples under static conditions (Figure 3.33b), normalized at the excimers maximum emission ($\lambda = 660 \text{ nm}$), show the emissions of both monomeric Per ($\lambda = 568 \text{ nm}$) and of the Per excimers. However, the contributions of these two emissions differ among the samples: in MC samples, the monomer emission dominates, presenting only a shoulder, while D samples show similar contributions, with the aggregation emission gaining weight as the Per doping increases.

By comparing the ratio between the intensities at monomer emission maximum ($\lambda_{em}^{max}(monomer) = 568\text{ nm}$, I_M) and at the excimer emission maximum ($\lambda_{em}^{max}(excimer) = 660\text{ nm}$, I_E) of D and MC samples, we can evaluate how the Per inclusion mode in the film affects the aggregation process: the lower this ratio (I_M/I_E), the higher will be the amount of Per excimers. The values of the emission intensity ratio calculated for all the MC and D samples are reported in Figure 3.33c. As expected, increasing the dye concentration (i.e., lower I_M/I_E) favors the aggregation. Moreover, it can be observed that Per aggregation occurs more easily in the dispersed system rather than in the covalently linked one at the same dye concentration. This can be explained by the reduced mobility of the dye linked to the polymer chains compared to the dispersed ones.

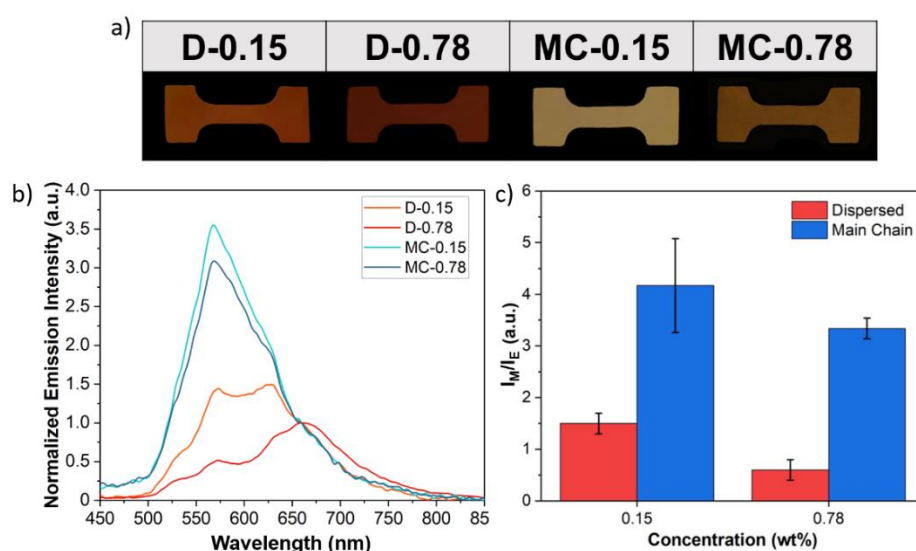


Figure 3.33 a) Images under UV light ($\lambda_{ex}=365\text{ nm}$) of films of D and MC samples. b) Solid-state emission spectra of D-0.15 (orange), D-0.78 (red), MC-0.15 (cyan), and MC-0.78 (blue). c) I_M/I_E versus concentration of the chromophore for D (red) and MC (blue) samples. The results reported are averaged between three replicates for each sample.

Mechanoluminochromic properties of Per-based samples

After determining how the different concentrations of the chromophore and the different incorporation approaches (i.e., blended or bonded) affect the aggregation of Per chromophores in the investigated samples, their mechanoluminochromism was evaluated by collecting their emission spectra in situ during stress-strain and

stress-relaxation experiments. under UV light excitation ($\lambda_{\text{ex}} = 365 \text{ nm}$). Figure 3.34 pictures the employed setup.

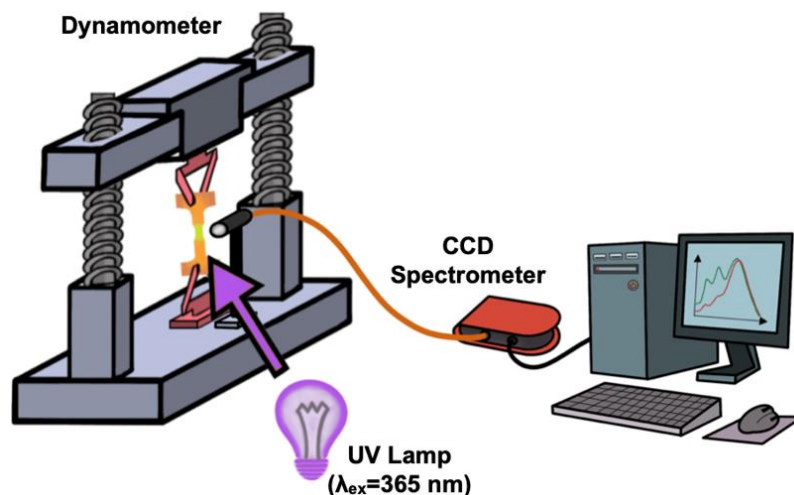


Figure 3.34 Schematic representation of the setup employed for the mechanoluminescent characterizations.

Figures 3.35 and 3.36 report, for both D and MC samples, respectively, the normalized spectra obtained at different strains during stress-strain experiments.

A noticeable variation in the emission spectrum is observed upon stretching for D blends (Figures 3.35a, and 3.35b). In D-0.78, the spectrum is initially dominated by the emission of the excimers; as the deformation increases, the emission attributed to Per monomer progressively increases (see schematic representation of the Per disaggregation under stretching in Figure 3.34c). This behavior is also observed in the blend doped with a lower concentration of the dye, i.e., D-0.15, albeit the starting $I_{\text{M}}/I_{\text{E}}$ is lower compared to D-0.78. These changes are visually apparent as the color shifts from orange to yellow in D-0.15 and from red to orange in D-0.78 (Figures 3.35a,b). In contrast, MC samples show only a slight change in the emitted intensity (Figures 3.36a and 3.36b). This result can be attributed to the limited aggregation observed for MC systems (Figure 3.33c) which, in turn, leads to a minimal shift in the observed fluorescence color even at high strain (Figure 3.36c).

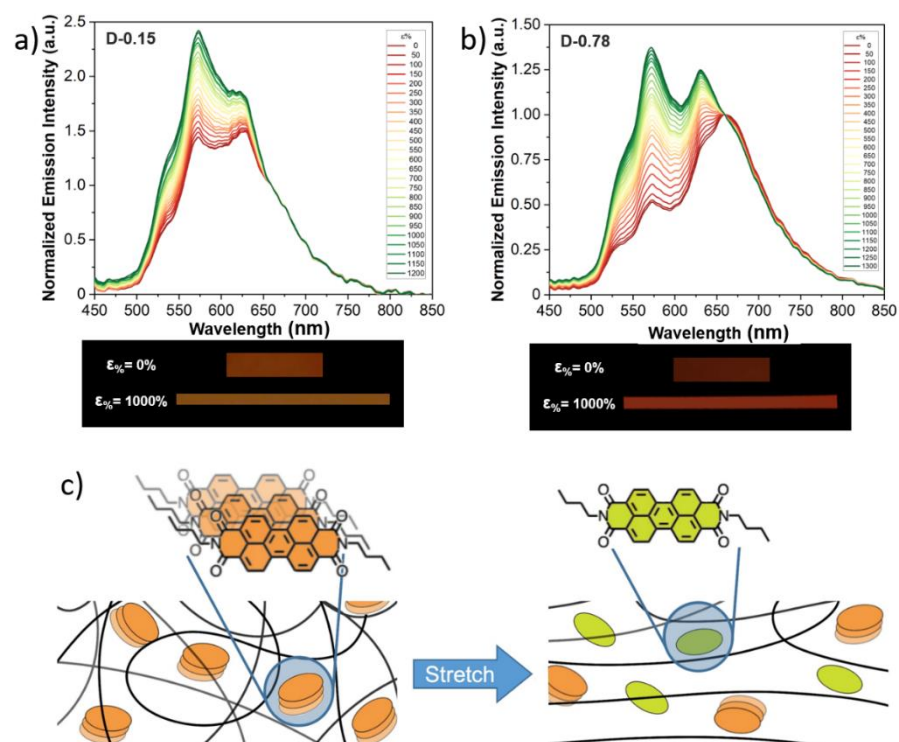


Figure 3.35 Solid-state emission spectra at increasing strains of a) D-0.15 and b) D-0.78 with the respective fluorescence images under UV light ($\lambda_{\text{ex}} = 365$ nm) of films at 0% and 1000% strains ($\epsilon_{\%}$); (c) schematic representation of the mechanoluminescence in D blends.

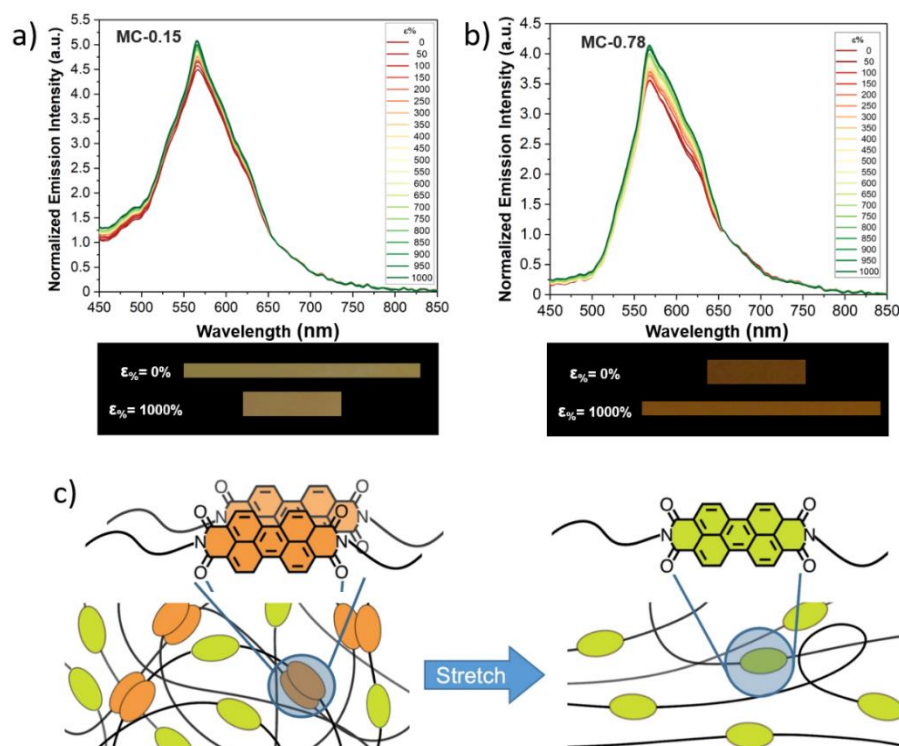


Figure 3.36 Solid-state emission spectra at different strains of a) MC-0.15 and b) MC-0.78 with the respective fluorescence images under UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$) of films at 0% and 1000% strains; (c) schematic representation of the mechanoluminescence in MC blends.

Then, the ratio between the intensity at the emission maximum of the monomer (I_M , with $(\lambda_{em}^{max}(\text{monomer}) = 568 \text{ nm})$ and of the excimer (I_E , with $(\lambda_{em}^{max}(\text{excimer}) = 660 \text{ nm})$) was plotted versus the applied strain (Figure 3.37). For all the samples, I_M/I_E increases with deformation, and a linear response is observed in the plastic deformation range. This indicates that rearrangements of the chains associated with disentanglement processes must occur to achieve disaggregation of the dyes in both MC and D samples. Notably, in MC samples, the trend of I_M/I_E appears highly scattered as a consequence of the small spectral variations recorded for these samples.

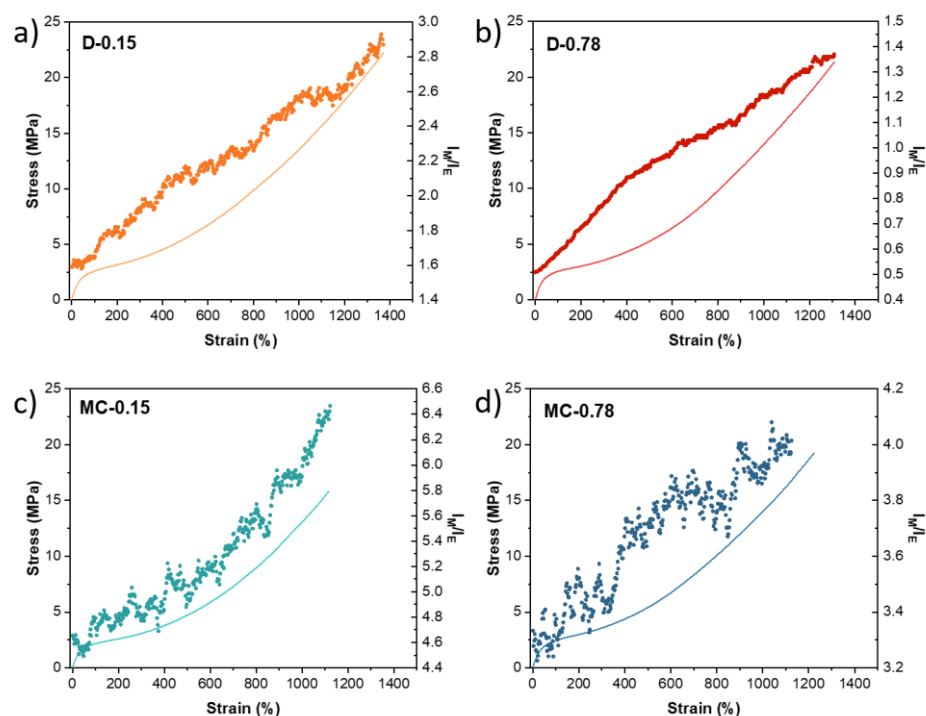


Figure 3.37 Stress-strain curves (solid lines) and I_M/I_E (dots) of a) D-0.15, b) D-0.78, c) MC-0.15, and d) MC-0.78. The results reported are averaged among three samples.

To better compare the mechanoluminescent performances of D and MC samples, the ratiometric emission intensity was plotted versus the strain in the linear mechanoluminescent range (i.e., strain comprised between 250% and 950%) and fitted with a linear function (Figure 3.38). By comparing the slopes of the linear fits reported in Table 3.6, for D blends, D-0.15 displays slightly higher mechanoluminescent sensitivity than D-0.78. This result might be attributed to the larger size of the aggregates in the sample at higher concentration. Similar results are obtained for MC systems, where the sample displaying the lowest concentration of dye (MC-0.15) shows the highest sensitivity.

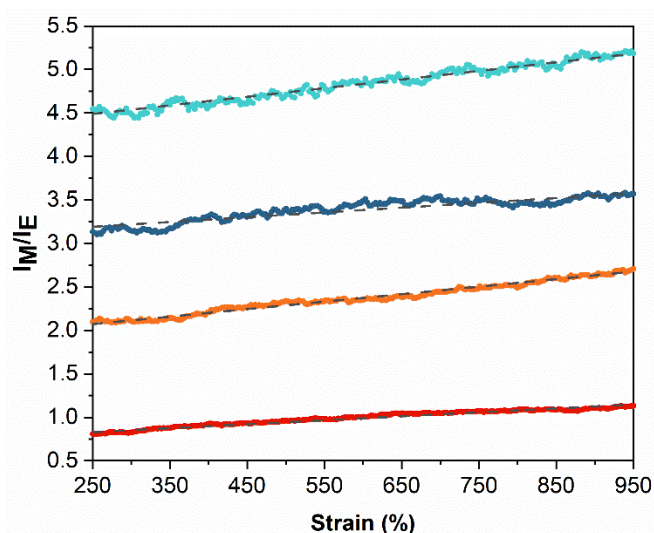


Figure 3.38 I_M/I_E (dots) plotted versus strain in the range 250% - 950%, fitted with a linear function (dashed line): D-0.15 (orange), D-0.78 (red), MC-0.15 (cyan,) and MC 0.78 (blue). The results reported are averaged among three samples.

Table 3.6 Results of the linear fit for D and MC samples.

Sample	Slope	R^2
D-0.15	$8.62 \cdot 10^{-4} \pm 0.07 \cdot 10^{-4}$	0.98
D-0.78	$4.55 \cdot 10^{-4} \pm 0.05 \cdot 10^{-4}$	0.97
MC-0.15	$9.9 \cdot 10^{-4} \pm 0.1 \cdot 10^{-4}$	0.96
MC-0.78	$5.5 \cdot 10^{-4} \pm 0.1 \cdot 10^{-4}$	0.86

When comparing D and MC systems, MC samples have slightly higher slopes for both concentrations, albeit, as previously discussed, the idle states present most of the dye in the monomeric form. This result does not contradict those reported in the literature for aggregachromic dyes, where mechanoluminochromic polymers with the dye bound to the main polymeric chain generally display much higher mechanoluminochromic sensitivities than their dispersed-dye counterparts.[22] It is worth noting that, in the low range of dye concentration explored in this work, the amount of dye excimers achieved in MC samples is insufficient to induce useful spectral variations under stretching (see Figure 3.36). Therefore, if a perceptible color variation is aimed, the direct comparison, performed

by maintaining a constant dye concentration, demonstrates that, for polyurethanes, the blending approach is more effective in obtaining mechanoluminochromic polymers than the bonding approach, at least in the low regime of dye concentration pursued with a focus on cost-effectiveness. Our finding is somehow supported by a study conducted by Weder and co-workers, wherein they reported mechanoluminochromism when oligo(*p*-phenylene vinylene) derivatives were covalently incorporated into TPU at high concentration, specifically in the range 4-9 wt.%. In contrast, for the blend, they used a lower dye concentration in the range of 0.1-0.4 wt.%, but a direct comparison between blending and bonding at the same concentration was not reported by the authors.[2]

In the previously reported work (section 3.1), we addressed the comparison between blending and bonding, employing an elastomeric SEBS triblock copolymer. In that study, we achieved a discernible and reversible mechanochromic response with a modest dye concentration when the dye was covalently linked to the polymer chain. In contrast, achieving a detectable mechanochromism through physical dispersion necessitated a dye concentration ten times higher. These findings contrast with those reported in the present work and could be achieved by exploiting the intrinsic phase separation of the SEBS copolymer which allowed to selectively confine the dye units to the soft phase by covalently bonding the dye to the central block.

Samples D-0.15 and MC-0.15 were also subjected to deformation to 200% strain followed by rapid unloading to 100% strain, over 4 cycles, while the fluorescence intensity ratio, I_M/I_A , was continuously monitored. Discarding the first cycle, which is affected by the Mullins effect (Figure 3.39), in the subsequent cycles both samples experience dye disaggregation and re-aggregation. Indeed, I_M/I_A display a cyclic trend that synchronizes with the loading and unloading phases. However, in the D-0.15 sample the I_M/I_A curve exhibits a drift towards lower values. This implies that after each cycle the degree of dye aggregation progressively increases, probably as a consequence of the fast and frequent chain re-arrangements, facilitating the assembly of the highly mobile dye molecules. In MC-

0.15, instead, the minimum and maximum values of I_M/I_A remain almost constant across the different cycles. This indicates that the extent of disaggregation and aggregation effectively mirrors the applied strain throughout the repeated deformation and relaxation steps.

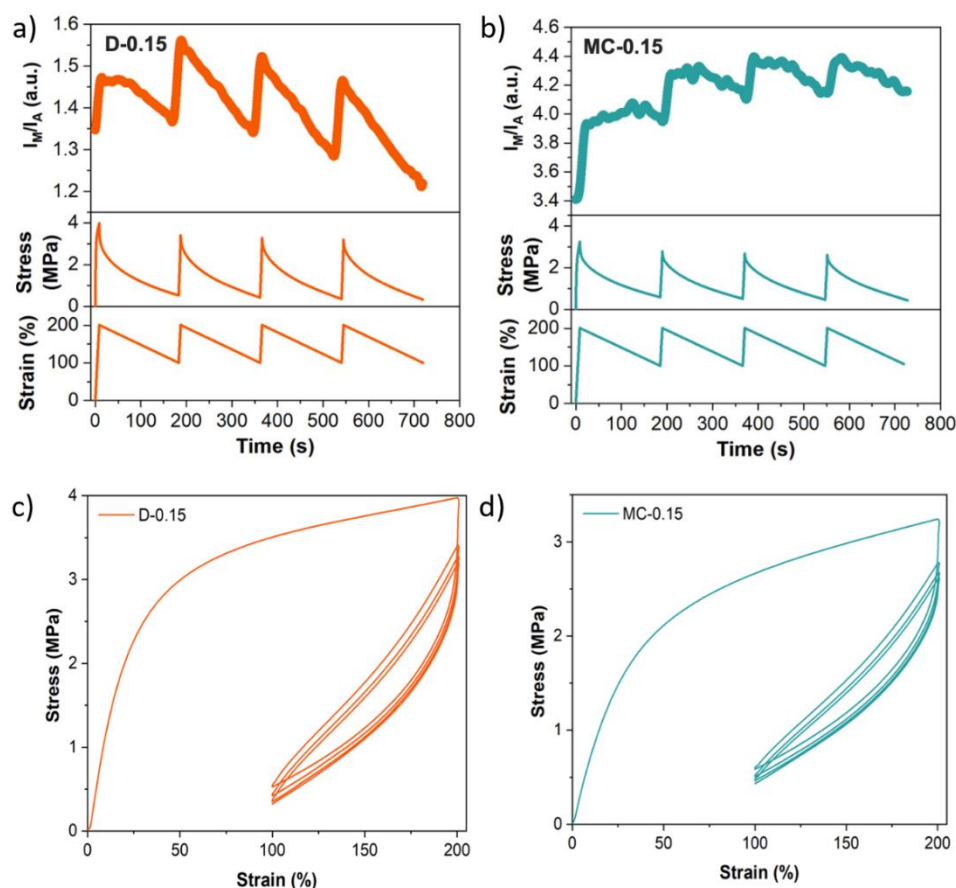


Figure 3.39 Cyclic loading-unloading experiments performed on a) D-0.15 and b) MC-0.15 over 4 cycles between 100 and 200% strain: stress, strain and I_M/I_A as a function of time.; stress-strain behavior of c) D-0.15 and d) MC-0.15 when deformed through multiple cycles correspond to the loading-unloading cycles of a) and b) respectively.

Lastly, the stress-relaxation behavior of D blends was assessed (Figure 3.40). For all the samples under analysis, the stress-relaxation curves are that of common TPUs, with an initial rapid decrease in the stress, followed by a slower relaxation process.[29] For all samples, the stress applied was not fully relaxed at the end of the experiment (30 minutes). In both D-0.15 and D-0.78, upon stress application, I_M/I_E increases (disaggregation phase, Figure 3.40(i)), similarly to what was observed in stress-strain experiments. After this initial disaggregation phase, which is concomitant with the strain phase of the experiment,

a progressive increase of I_M/I_E is observed, indicating that disaggregation of the material is still occurring during the first phase of stress relaxation. This phase lasts ca. 130 s for both D-0.15 and D-0.78 and is followed by a plateau region, which lasts ca. 280 s for both blends (Figure 3.40(ii)). Surprisingly, I_M/I_E decreases after this second phase, meaning that the dye monomers re-aggregate (aggregation phase, Figure 3.40(iii)). In D-0.15, the final I_M/I_E is higher than the value measured at idle state, meaning that the initial dye aggregation degree is not reached after 30 min of stress relaxation; in contrast, for D-0.78, the final I_M/I_E measured is lower than the initial value (Table 3.7).

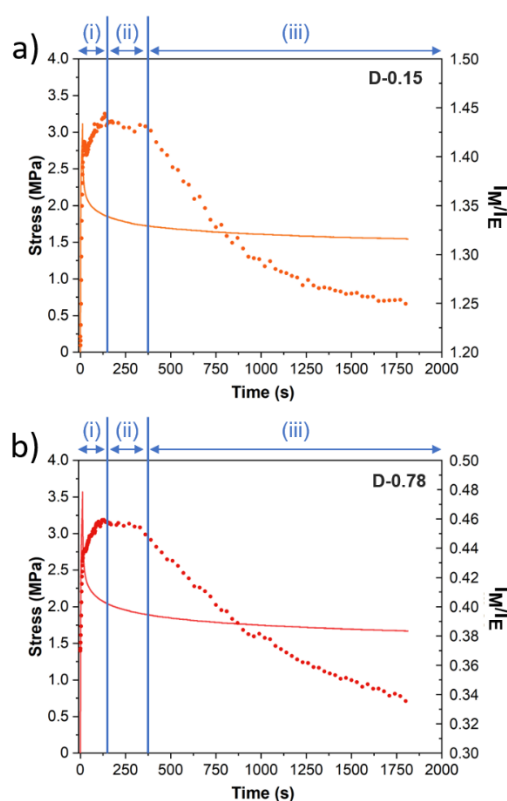


Figure 3.40 Stress-relaxation curves (solid lines) and I_M/I_E (dots) of a) D-0.15, and b) D-0.78. The trend of I_M/I_E over time can be divided into three regions: an initial disaggregation phase (i), followed by a plateau region (ii), and a reaggregation phase (iii).

Table 3.7 Calorimetric and mechanoluminochromic data before and after stress-relaxation experiments.

Sample	Initial ΔH_m [J g ⁻¹]	ΔH_m after relaxation [J g ⁻¹]	Initial I_M/I_A	I_M/I_A max	I_M/I_A after relaxation
D-0.15	12.2	16.0	1.216	1.44a	1.250
D-0.78	15.6	15.9	0.370	0.46b	0.336
MC-0.15	11.8	12.4	3.538	4.41c	3.294

a) at 135 s

b) at 130 s

c) at 130 s

The mechanoluminochromism during stress-relaxation tests in the dispersed-dye system can be justified by considering the microstructural rearrangements during stress relaxation, depicted in Figure 3.41a for the D-0.15 sample. When TPU is stretched, the dye disaggregates (Figure 3.41a(i)) while the polymeric network is deformed, thus changing its conformation from the highly entropically favored random coil conformation to a more aligned one, leading to a decrease in entropy that is rapidly recovered when the strain is fixed. Since this driving force does not affect the dispersed dyes, they will retain their inertial motion longer, with no driving force for reaggregation (plateau region, Figure 3.41a(ii)). Reaggregation of the dyes will then occur, possibly triggered by the decrease of free volume induced by strain-induced crystallization, thus leading to the observed decrease of I_M/I_A (Figure 3.41a(iii)). This hypothesis is well supported by analysis of the ΔH_m before and after the stress-relaxation experiment (Table 3.8), which clearly shows that the material undergoes a strain-induced crystallization, with the final ΔH_m comparable for all the blends under analysis. This effect is more evident upon increasing the dye concentration, with the D-0.78 sample reaching a lower I_M/I_A at the end of the experiment than the starting one.

Stress-relaxation analysis was also performed on MC-0.15 (Figure 3.41b) to compare the response of MC and D systems at the same

concentration. Also, for MC-0.15, the stress-relaxation response is that of common TPUs, with an initial rapid decrease in the stress, followed by a slower relaxation process without a complete relaxation of the applied stress at the end of the experiment. We observe the presence of an initial disaggregation phase (Figure 3.41b(i)), immediately followed by an aggregation phase (Figure 3.41b(iii)), with a final aggregation degree higher than that at the idle state. As seen for D-0.15, MC-0.15 shows a delay between the mechanical stress-relaxation phase and the end of the mechanoluminescent disaggregation (*ca.* 170 s for MC-0.15, *ca.* 120 s for D-0.15); however, for this blend, no plateau region is observed and the I_M/I_A ratio in MC-0.15 better follows the mechanical stress relaxation than the dispersed-dye blend at the same concentration. It is pointed out that MC-0.15 also undergoes strain-induced crystallization, but in this case, the increment of ΔH_m is lower than what was observed for D-0.15 (Table 3.7). Therefore, this moderate increase of crystal domains, justified by the lower crystallization capacity of the MC sample due to the presence of the chromophore in the chain, hardly explains the high final aggregation degree achieved by Per units at the end of the experiment.

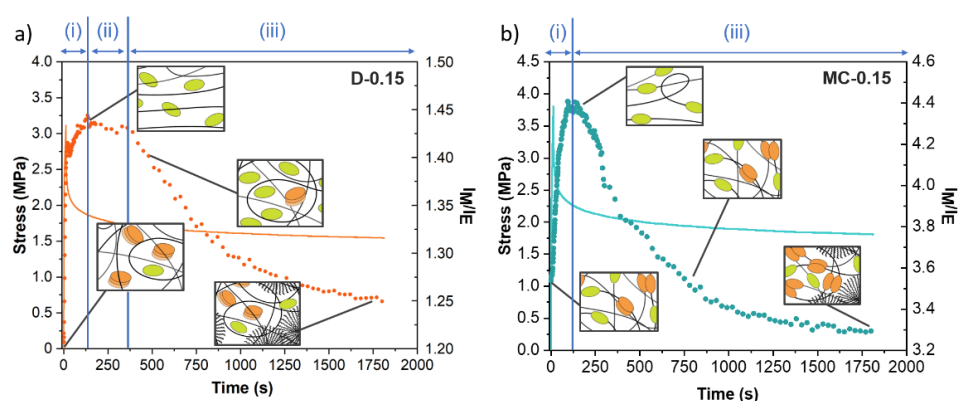


Figure 3.41 Stress-relaxation curves (solid lines) and I_M/I_E (dots) of a) D-0.15, and b) MC-0.15. For D-0.15 sample, the trend of I_M/I_E during time can be divided into three regions: an initial disaggregation phase (i), followed by a plateau region (ii) and a reaggregation phase (iii); for MC-0.15 sample, the trend of I_M/I_E during time show only two regions: an initial disaggregation phase (i), followed by a reaggregation phase (iii), with no plateau region. The sketches provide a schematic representation of how the dye aggregation state changes during the stress-relaxation experiment.

To justify this behavior, Bergström's constitutive model for hysteresis and stress-relaxation in elastomers[29] can be considered. According to this model,[29] stress-relaxation in elastomers is mainly affected by the reptation and Brownian displacement of macromolecules that are "elastically inactive", namely chains that can be highly stretched during fast applied macroscopic deformation but with loose connectivity to the main load-bearing chains. In our MC sample, being the two components miscible in the amorphous phase, the chains of PolyPer are entangled with the chains of commercial TPU and subjected together to deformation. However, PolyPer chains, being shorter in length are unlikely involved in more than one physical crosslink point. For these reasons, they can be considered the elastically inactive chains while TPU is the load-bearing component. Based on this assumption, the mechanochromism of MC sample during the stress-relaxation test can be explained as follows: the initial fast stress-relaxation process, which impacts mainly the unfunctionalized TPU, is followed by a delayed rearrangement of the polymeric chains containing the chromophore, which promotes the dye reaggregation. Thanks to this reaggregation mechanism, which differs from that of the dye-dispersed blend mainly driven by strain-induced crystallization, MC-0.15 better follows the mechanical stress relaxation than the dispersed-dye blend at the same concentration.

Overall, stress-relaxation experiments show that, even if the number of excimers formed with the bonding approach is significantly lower compared to the blending one, the MC sample allows for a full recovery of the initial excimers during stress relaxation, in contrast to the D sample in which excimers are not recovered during relaxation of the stress and their rupture is irreversible in this phase. In a second phase, the phenomenon of strain-induced crystallization results, in both MC and D approaches, in the formation of further excimers as a consequence of dye concentration in the remaining amorphous phase.

3.2.3. Conclusions

The mechanoluminochromic performances of thermoplastic polyurethanes containing a perylene diimide derivative, either covalently linked to main polymeric chains or simply used as an additive, were evaluated to determine the effects of the two incorporation approaches. To this purpose, polyurethanes covalently functionalized with a perylene diimide derivative in different mol% were synthesized and blended with a commercial TPU (MC samples). Parallely, blends of commercial TPU and unfunctionalized synthetic PU were prepared and doped with different concentrations of dispersed perylene dye (D samples). Thermal characterization of the materials proved that dye aggregates favor polymer crystallization in dispersed blends. Conversely, increasing the chromophore concentration in the main chain decreases ΔH_m , possibly because the chromophore is linked to the crystallizing segments of the synthesized PU. However, no significant differences were observed in the mechanical behavior of these materials. As expected, spectroscopic characterization at rest highlights that the relative emission intensities of the dyes in monomeric and aggregate forms strongly depend on the dye concentration for both D and MC systems. However, at the same dye concentration, the aggregate emission in MC samples is significantly lower compared to D counterparts, probably due to a reduced mobility and conformational freedom of the dyes linked to the polymer chains compared to the dispersed ones. For this reason, under uniaxial tensile strain, D samples display a higher emission color variation, well appreciable by the naked eye. These results prove that covalently functionalizing the dye to the main polymeric chain does not significantly improve the mechanoluminochromic response under uniaxial strain for this type of material compared to simpler and more cost-effective blending approach, at least in the low concentration regime of the dye investigated in the present work. In stress-relaxation experiments and in cyclic loading-unloading experiments, conversely, a comparison between dispersed and main chain systems at the same dye concentration highlighted that the latter showed an improved

correspondence between the mechanical data and the mechanoluminochromic response. Considering the literature on this topic, it can be concluded that the polymeric matrix plays a key role in determining the aggregation state of the dye and both the covalent approach and the physical blend can be advantageous depending on the type of polymer. However, as for the mechanoresponse, the results of cyclic deformation and stress-relaxation experiments corroborates previous findings stating that the covalent bonding of the dye elicits a better force-dependent fluorescence response than the physical dispersion. Overall, these results highlight the potential of mechanoluminochromic elastomers based on physical dispersions of aggregachromic dyes, providing a more straightforward and cheaper synthetic route than covalent incorporation while still retaining high sensitivity and visibly discerning color changes. Due to its improved responsiveness to stress-relaxation phenomena, the covalent incorporation of dyes remains an attractive alternative for damage detection.

3.2.4. Experimental section

Materials. All used solvents were of reagent quality and commercially purchased. All solvents were dried and distilled using standard procedures. All purchased starting materials were used without further purification.

Characterization methods. NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz) and on a JEOL ECZ600R (600 MHz) spectrometer at 298 K. All chemical shifts (δ) were reported in ppm relative to the proton resonances resulting from incomplete deuteration of the NMR solvents. High-resolution MALDI-TOF was performed on an AB SCIEX MALDI TOF-TOF 4800 Plus (matrix: *a*-cyano-4-hydroxycinnamic acid). High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) was performed on a Mass Spectrometer LTQ ORBITRAP XL Thermo. GPC was carried out using a KNAUER system equipped with a refractive index detector and a TSKgel SuperHM-M column (length = 150 mm, internal diameter = 6 mm). THF was used as an eluant with a 0.6 mL min⁻¹ flow and sample

concentrations of about 5 mg mL⁻¹. The analyzed samples were solubilized in THF, stirred overnight, and filtered on a 0.450 µm polytetrafluoroethylene (PTFE) filter. A molecular weight calibration curve was obtained with polystyrene standards in the molecular weight range 580 - 990500 g mol⁻¹. UV-Vis absorption spectroscopy was performed using a Cary 5000 UV-Vis-NIR spectrophotometer (Agilent). The emission spectra were recorded with an Edinburgh FLS920 fluorometer equipped with a high-speed HS773-04 photomultiplier Hamamatsu R928P. Emission spectra in the solid state were acquired by exploiting a Thorlabs compact spectrometer (CCS200M, optical fiber with a 200 µm apical aperture) coupled to a 365 nm LED (ThorLabs SOLIS-365c) as the near-field probe. DSC was carried out using a Q2000 DSC apparatus (TA instruments) equipped with a Refrigerated Cooling System (RCS90). The analyses were performed on 4-6 mg samples placed inside aluminum pans under nitrogen flow. The samples under analysis were subjected to three heating scans at a rate of 20 °C min⁻¹ alternated with two cooling scans, the first of which was a fast cooling (quenching) and the second of which was a controlled cooling scan at 10 °C min⁻¹. DMTA was carried out on films (gauge length = 10 mm, width 5 mm, thickness = 0.2-0.5 mm) by means of a TA Instrument dynamic mechanical analyzer (DMA Q800) under tensile configuration. The specimens were tested with a heating ramp from - 140 °C to 200 °C at 3 °C·min⁻¹, adopting a frequency of 1 Hz under displacement control. Stress-strain tests were conducted using an Instron Testing Machine 4465 and the Series IX software package. Dog-bone-shaped samples were prepared following ASTM D170837 (gauge length = 14 mm, width = 5 mm, thickness = 0.2-0.5 mm) and were tested in traction mode with a load cell of 100 N. The crosshead speed was set at 200 mm·min⁻¹. Cyclic deformation tests were carried out with the same setup on dog-bone samples. Samples were stretched using a crosshead speed of 200 mm·min⁻¹ up to 200% of deformation, the deformation was then relaxed to 100% using a crosshead speed of 5 mm·min⁻¹. This cycle was repeated four times. Stress-relaxation tests were carried out with the same setup on dog-bone samples. Samples were stretched using

a crosshead speed of $200 \text{ mm} \cdot \text{min}^{-1}$ up to 300% of deformation, which was kept constant for 30 minutes. During stress-strain, stress-relaxation and cyclic tests, emission spectra were acquired by exploiting a Thorlabs compact spectrometer (CCS200M, optical fiber with a $200 \text{ }\mu\text{m}$ apical aperture) coupled to a 365 nm LED (ThorLabs SOLIS-365c) as the near-field probe. Spectra were recorded at a 10 Hz frequency in stress-strain analysis while, in stress-relaxation analysis, a 1 Hz frequency was employed for the first 60 s of the experiment, and a 0.03 Hz frequency was employed for the remaining time of the experiment. In cyclic tests spectra were recorded with a 2 Hz frequency.

Synthesis of N,N'-bis(4-amino-1-butyl) perylene-3,4,9,10-tetracarboxylic acid bisimide (Per). In a pressure-tight microwave tube under nitrogen (CEM Discover purchased from CEM Corp, 3 mm thick, 10 mL volume), 100 mg of perylene-3,4,9,10-tetracarboxylic bisanhydride were suspended in 5 mL of dry N, N-dimethylformamide (DMF), and 2 eq. of butyl amine were added. The red suspension was sonicated for five minutes before heating under microwave irradiation at 50 W for 10 min. The heating was repeated for five cycles, with cooling intervals of 5 minutes. The maximum temperature was set at $200 \text{ }^{\circ}\text{C}$. After cooling, the solution color turned dark red. The reaction was quenched by adding 50 mL of NaOH 1M and then stirred for 30 min (Figure 3.22a). The obtained precipitate was filtered and washed abundantly with water until neutral pH and finally dried using a vacuum pump. The final product was obtained as a brown-red solid. Yield 49%.

^1H NMR (CF_3COOD , 600 MHz, 298K), δ (ppm) = 8.89 – 8.85 (m, 8H, HA and HB), 4.38 (bt, 4H, HC), 1.86 – 1.84 (m, 4H, HD), 1.61 – 1.55 (m, 4H, HE), 1.33 (bt, 6H, HF).

^{13}C NMR (CF_3COOD , 151 MHz, 298K), δ (ppm) = 133.2, 124.4, 41.9, 29.9, 19.3, 12.4.

HR-ESI-MS: Calculated for $\text{C}_{32}\text{H}_{27}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 503.19653; found: 503.19569

Synthesis of N,N'-bis(2-[2-hydroxyethoxy]ethyl) perylene-3,4,9,10-tetracarboxylic acid bisimide (Per-OH). In a pressure-tight microwave tube under a nitrogen atmosphere, 100 mg of perylene-3,4,9,10-tetracarboxylic bisanhydride were suspended in 5 mL of dry DMF, and 2 eq. of 2-(2-aminoethoxyethanol) were added. The red suspension was sonicated for five minutes before heating under microwave irradiation at 50 W for 10 min. The heating was repeated for five cycles, with cooling intervals of 5 minutes. The maximum temperature was set at 200 °C. After cooling, the solution color turned dark red. The reaction was quenched by adding 50 mL of NaOH 1M and stirring for 30 min (Figure 3.22b). The obtained precipitate was filtered and abundantly washed with water until neutral pH and finally dried using a vacuum pump. The final product was obtained as a brown-red solid. Yield 59%.

¹H NMR (CF₃COOD, 600 MHz, 298K) δ (ppm): 8.86 (dd, J = 7.0 Hz, 8H, HA and HB, AB system), 4.81 (t, J = 5.4 Hz, 4H, HD), 4.76 – 4.70 (m, 4H, HE), 4.33 (t, J = 5.4 Hz, 4H, HC), 4.29 – 4.24 (m, 4H, HF).

¹³C NMR (CF₃COOD, 151 MHz, 298K), δ (ppm) = 132.6, 124.4, 68.6, 68.5, 66.9, 39.8.

MALDI-TOF: calculated for C₃₂H₂₇N₂O₈[M+H]⁺: 567.1767, found: 567.1732

General procedure for the synthesis of PolyPer and Poly. All the equivalents are intended with respect to 1 equivalent of HDMI. In a 3-neck round bottom flask, under nitrogen flux, polyethylene glycol (MW = 1500 g mol⁻¹, 0.5 eq.) was melted at 100 °C under mechanical stirring. Per-OH (0.01 eq. for PolyPer1, 0.05 eq. for PolyPer5, respectively) was added, and the mixture was stirred to disperse the chromophore homogeneously. Then, 0.5 eq. of 4,4-methylenebis(cyclohexyl isocyanate) (HDMI) and 0.001 eq. of 1,4-diazabicyclo[2.2.2]octane (solution 18 mM in acetonitrile) was added and the stirring was maintained for 50 minutes, obtaining a dark viscous mixture. Finally, the remaining 0.5 eq. of HDMI and 0.5 eq. of 1,4-butanediol were added, and the mixture was stirred for about 30

minutes until it became too viscous to be efficiently stirred. The obtained polymer was poured onto an aluminum foil and dried under vacuum at 45°C for one night. The final product was obtained as a dark red solid (Figure 3.23). Poly was obtained by applying the same synthetic procedure without adding Per-OH (Figure 3.26). The as-prepared materials were named according to their composition, where Poly stands for polyurethane, Per for N,N'-bis(2-[2-hydroxyethoxy]ethyl) perylene-3,4,9,10-tetracarboxylic acid bisimide, and the number 1 and 5 corresponds to 0.01 and 0.05 of dye eq., respectively. Poly, PolyPer1, and PolyPer5 were purified by dissolution in THF (4% g mL⁻¹ solution) and filtration under vacuum. The filtered solution was then cast in a glass petri dish for 24 hours.

PolyPer5.

¹H NMR (DMSO-d₆, 400 MHz, 298K), δ (ppm) = 8.85 (d, J = 8.2 Hz, 0.2 H, HB PER-OH), 8.51 (d, J = 7.9 Hz, 0.2H, HA PER-OH), 7.12, 6.97, 6.88, 6.71, 6.65 (s, 3H, NH), 4.59 (bt, 0.1 H, terminal OH), 4.41 (t, 0.4 H, J = 4.7 Hz, terminal OH), 4.37 (t, 0.4 H, J = 5.1 Hz, terminal OH), 4.28 (t, 0.2 H, J = 6.6 Hz, terminal OH), from 4.11 to 3.83 (m, 6H, OCH₂ PEG chain and butandiol chain, perilene chain), from 3.79 - 3.36 (m, 168H, PEG chain, perilene chain), 3.24 - 3.09 (m, 1H, CHN), from 1.87 - 0.77 (m, 44H, HMDI, CH₂CH₂ butandiol).

Film Preparation. The synthesized PU (i.e., PolyPer1 and PolyPer5) were blended with commercial TPU (poly[4,4'-methylenebis(phenylisocyanate)-alt-1,4-butanediol/di(propylene glycol)/poly caprolactone], purchased from Merck) to produce flexible and highly deformable films. Each synthesized PU was dissolved in THF (4% w v⁻¹ solution) with commercial TPU (30:70 w/w) and cast in a petri dish. After 24 h, the films were removed from the petri dish and pressed in a compression molding apparatus (laboratory press, Carver C12, Carver Inc., Indiana USA) at 150 °C and 40 Bar. The film produced using PolyPer1 and PolyPer5 contained a final concentration of covalently linked Per-OH of 0.15 wt.% and 0.78 wt.%, respectively. These films were labeled MC-0.15 and MC-0.78, where MC stands for "main chain" and refers to the covalent dye insertion in the synthesized PU main chain. Unfunctionalized Poly, TPU, and Per

samples were also prepared by physical blending. Poly and TPU (30:70 w/w) were dissolved in THF (4% w v⁻¹ solution), and proper amounts of Per were added to gain a final concentration of 0.15 wt.% and 0.78 wt.%. Films were obtained by solvent casting and hot pressing, as previously described. These films were labeled D-x, where D is the abbreviation of dispersed dye and x (x = 0.15, 0.78) refers to the dye weight content. Films were stored at room temperature (RT) for at least two weeks before characterization to attain equilibrium crystallinity.

3.3. In situ monitoring of mechanofluorescent polymeric nanofibers made with excimer-forming telechelic Macromolecule

3.3.1. Introduction

The studies presented so far in the field of aggregachromic dyes have involved both the use of traditional dye molecules included in the matrix by simple dispersion and by functionalization of the main chains. However, this latest work introduces a third form of inclusion, made possible by a new formulation developed by Prof. Weder's group at the University of Fribourg. They reported the fabrication of mechanoluminochromic materials by using, as an additive of the polymeric formulation, a telechelic molecule carrying two excimer-forming OPV dyes at the termini (tOPV).[8,30] Due to its structure, the tOPV dispersed in the polymer can form entanglements with the polymer chains, and as it disperses, it keeps the dye units close together, increasing the likelihood of aggregation. In one of their recently works they used two different thermoplastic polyurethanes elastomers as matrices, one highly amorphous containing poly(tetrahydrofuran) (PUTHF) as a soft segment, and one semicrystalline due to the PBA segments (PBA-PUTHF).[30] These blends were transformed into films by solvent casting and subsequent compression molding, which allowed the formation of tOPV-based entangled micro-inclusions in the polymer matrices. The formation of the entanglements facilitates the mechanical stress-induced dissociation of dye aggregates in the matrix. This process leads to the generation of OPV monomers, which are responsible for the emission change and thus the mechanoluminochromic response of the sample. The fluorescence response results to be highly sensitive to the deformation and relaxation processes that occur in both TPU matrices, regardless of their crystallinity. The advantage of using telechelic additives is associated with their ability to prevent excessive aggregation and the formation of hard-to-break aggregates without the need for special treatments or covalent bonding. The photophysical behavior of tOPV appears to be intricately linked to mechanically induced rearrangements within the surrounding matrix. Consequently, these additives should offer insights into the type and

magnitude of even very subtle deformations experienced by any elastomeric material in advance.[30] It is, therefore, interesting to expand the use of these materials, not only in terms of the types of matrices but also in the variety of shapes and processing methods possible. The possibility is given by the adaptability of polymers in acquiring different morphologies and shapes. In particular, fibers have the attractive feature of an exceptional surface-to-volume ratio with tunable diameters. The outcome is a material that can sense environmental changes effectively. In the context of mechanoluminochromism, numerous examples abound. Of course the most simple method to produce mechanoluminochromic fibrous materials is to coat an already and commercially available yarn.[31,32] Moving forward, some researchers have manufactured the fibers themselves from oligomer solutions as Lagerwall et al. who developed cholesteric liquid crystal elastomer filaments able to give a progressive and reversible mechanoluminochromic responses.[33] Alternatively, as already tested in bulk films, it is possible to use chemically-modify polymers. A striking example is the spiropyran-doped polymers, where the spiropyran are included in the backbone. The structure of these molecules can be easily modified through the elongation of polymer chains, and the transition from spiropyran to merocyanine acts as a probe of the applied force on the material.[34,35] In these studies the most relevant feature is given by the alignment of the mechanoluminochromic probes and polymeric chains along the fiber, which is essentially the direction in which the force will subsequently be applied.

The methods of obtaining polymer fibers are diverse, from the electrophoretic deposition to centrifugal spinning. Among them, electrospinning represent the main method to obtain polymeric nanofibers. Electrospinning employs electrostatic forces to elongate a viscoelastic polymer solution, resulting in the formation of fibers with diameters ranging from a few tenths of nanometers to a few micrometers. Fibers are deposited onto a collector, forming non-woven structures characterized by a typical mesh porosity exceeding 80% with pore diameters varying from a few to tens of micrometers.

In fact, compared with others, this technique allows for precise control over the morphology and alignment of fibers within a material, by simply varying a few basic parameters: the composition of the electrospun solution (e.g., polymer molecular weight, concentration, electrical conductivity, viscosity), processing parameters (e.g., applied voltage, tip to collector distance, solution flow rate), or environmental conditions (e.g., temperature and relative humidity).[36] Thus, because of its versatility, electrospinning technique has enabled the production of nanofibrous materials for a wide range of applications, such as water filtration,[37] sensors,[35] catalytic systems, energy harvesting/conversion/storage, structural composites, and biomedical applications.[36,38,39]

In order to shed light on the structure-property relationships that govern the mechanical behavior of this versatile class of materials, we fabricated mechanoluminescent nanofibrous materials made by the electrospinning of polymer solutions that contain small amounts of the tOPV mechanoluminochromic additive. The resulting electrospun mats exhibit two distinct fiber orientations, determined by the type of collector used during electrospinning. They can be either randomly oriented or aligned in parallel (Figure 3.42). Upon applying mechanical stress, it is observed that both specimens display MLC behavior. However, the nature of this behavior varies depending on the orientation of the fibers relative to the applied stress. An in-depth analysis of single fibers within the mats via fluorescence microscopy reveals that fibers aligned along the direction of the applied strain deform significantly more than perpendicularly aligned fibers. The results reported herein offer valuable insights into how mechanical force is transferred within microfibrillar mats, thus improving one's ability to rationally tune the mechanical properties of electrospun fiber mats to fit a wide range of potential applications.

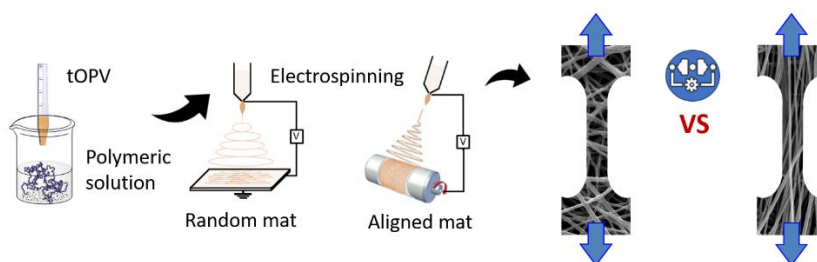


Figure 3.42 Scheme of the preparation of electrospun nanofiber materials obtained by blending the polymer solution with tOPV and electrospinning it onto different collectors.

3.3.2. Results and discussion

In this work desmopan 2795A (PBA-PUTHF, Figure 3.43a) was used as polymeric matrix to produce electrospun nanofibers containing different amounts of tOPV (Figure 3.43b) as an additive in the starting solution.

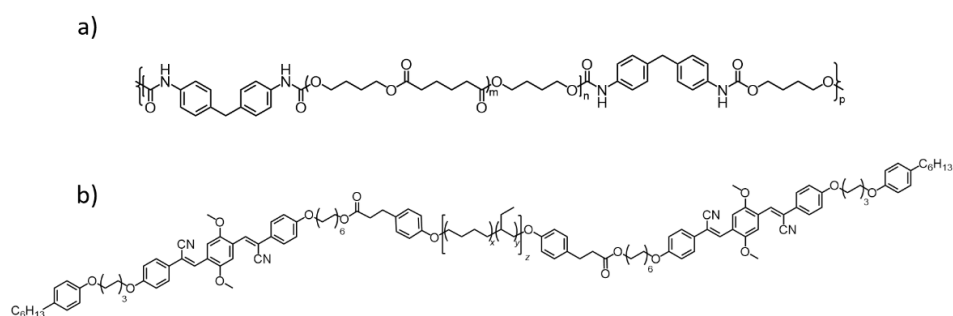


Figure 3.43 a) Chemical structure of the PBA-PUYHF used as polymeric matrix. b) Chemical structure of the tOPV dye.

Either 1 or 2 wt.% tOPV yielded fiber mats were obtained, comprised of homogeneous, bead-free nanofibers (Figure 3.44a-d). Fibers comprising PBA-PUTHF/tOPV 1 wt.% mats exhibited a mean diameter of ca. 400 nm, whereas PBA-PUTHF/tOPV 2 wt.% mats contained much larger nanofibers with a mean diameter of ca. 700 nm (Figure 3.44e-h).

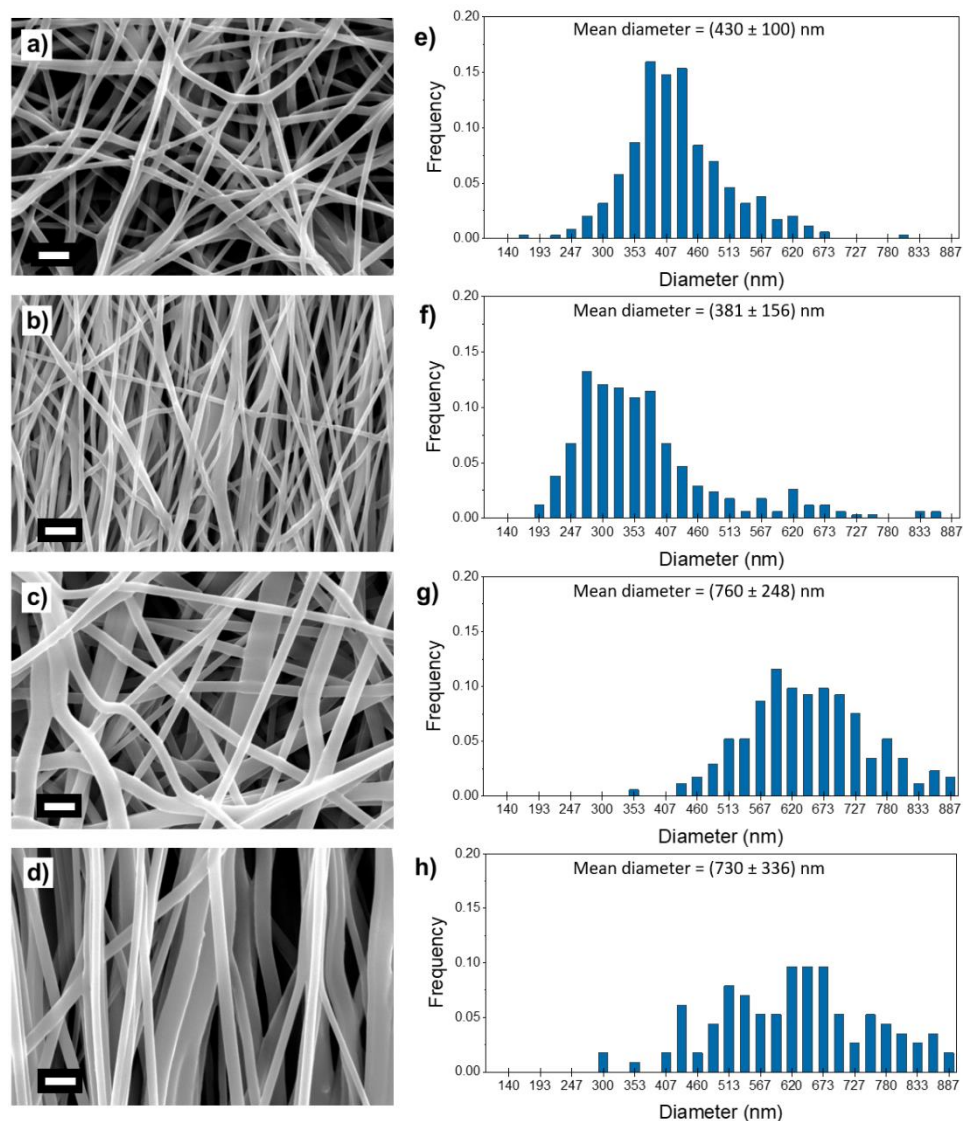


Figure 3.41 SEM images of mats of random (a, c) and aligned (b, d) fibers containing 1 wt.% (a, b) and 2 wt.% (c, d) tOPV (scale bar: 2 μm) with the corresponding size distributions (e-h).

SEM image orientation analysis (Figure 3.45) revealed that samples electrospun on flat collectors produced randomly oriented fibers (Figure 3.44a,c and 3.45a,c), while those electrospun on a rotating drum produced fibers aligned primarily in the same direction (Figure 3.44b,d and 3.45b,d).

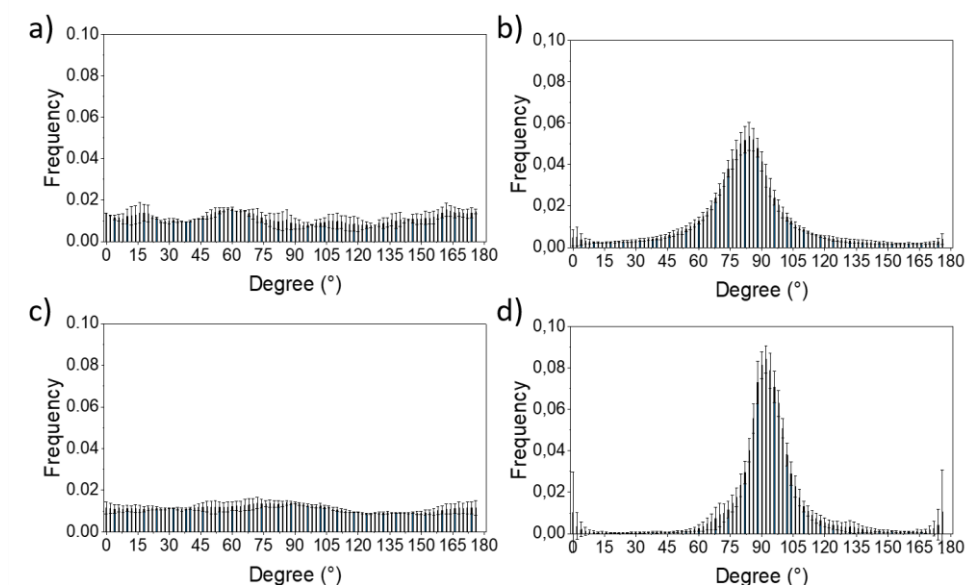


Figure 3.45 Orientation distribution of the fibers in random (a, c) and aligned (b, d) mats, containing 1 wt.% (a, b) and 2 wt.% (c, d) tOPV.

DSC measurements revealed that the glass transition of the mats occurs at the same temperature as in bulk PBA-PUTHF, i.e., much lower than room temperature (Figure 3.46, Table 3.9). Nonetheless, the presence of a PBA crystalline phase ($T_m = 50\text{ }^{\circ}\text{C}$) preserves the morphology of the polymer nanofibers under ambient conditions.[40] Notably, both random and aligned fiber mats electrospun with the same concentration of tOPV exhibit the same glass transition temperature (T_g), while the amount of crystal phase, as determined by the melting peak enthalpy, is greater for the aligned samples (Table 3.9).[41–44]

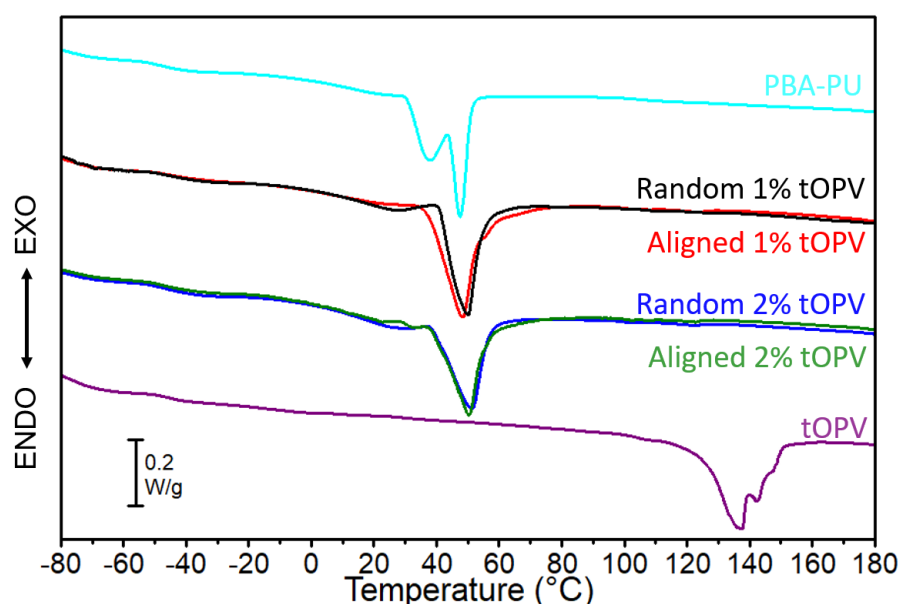


Figure 3.46 DSC first heating scans of the polymer (cyan) and the tOPV additive (purple) used to electrospin random mats with 1 wt.% (black) and 2 wt.% (blue) tOPV, as well as aligned mats with 1 wt.% (red) and 2 wt.% (green) tOPV.

Table 3.9 Thermal data of the 1st and 2nd heating scan of undoped and doped polymers (T_g is determined at the mid-point at the half height).

Sample	T_g (°C)	ΔC_p (J g ⁻¹ °C ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)
PBA-PUTHF	-46	-46	43	25.5
Random 1% tOPV	-43	-38	41	18.5
Aligned 1% tOPV	-43	-37	37	25.3
Random 2% tOPV	-46	-40	40	20.4
Aligned 2% tOPV	-45	-39	41	26.3
tOPV	-46	-47	125	28.3

Next, the fiber mats were subjected to uniaxial tensile deformation to probe the influence of fiber orientation on the mechanical properties of the mats. The results show that the aligned fiber mats exhibit significantly higher stiffness and stress at break, as

well as consistently lower strain at break, than randomly oriented mats (Figure 3.47 and Table 3.10). While the Young's modulus of the aligned mats is four-fold lower than that of bulk PBA-PUTHF,[30] the rise in mechanical stress observed for the mats during strain hardening is significantly steeper than for bulk films.[30] Namely, the aligned mats reach their maximum stress of ca. 18 MPa during the test between 35-50% strain (Figure 3.47), whereas bulk PBA-PUTHF experiences only ca. 8 MPa stress at 50% strain.[30] Taken together, these data suggest that mechanical stress is more effectively concentrated along the backbone of individual polymer chains that are pre-aligned along the stretching axis. In contrast, when random mats are stretched, only a fraction of the fibers are deformed along their main axis resulting in a more gradual, linear rise in mechanical stress for random mats (Figure 3.45).The former exhibits higher stiffness and brittleness compared with the latter which displays increased ductility and elasticity (Table 3.10).

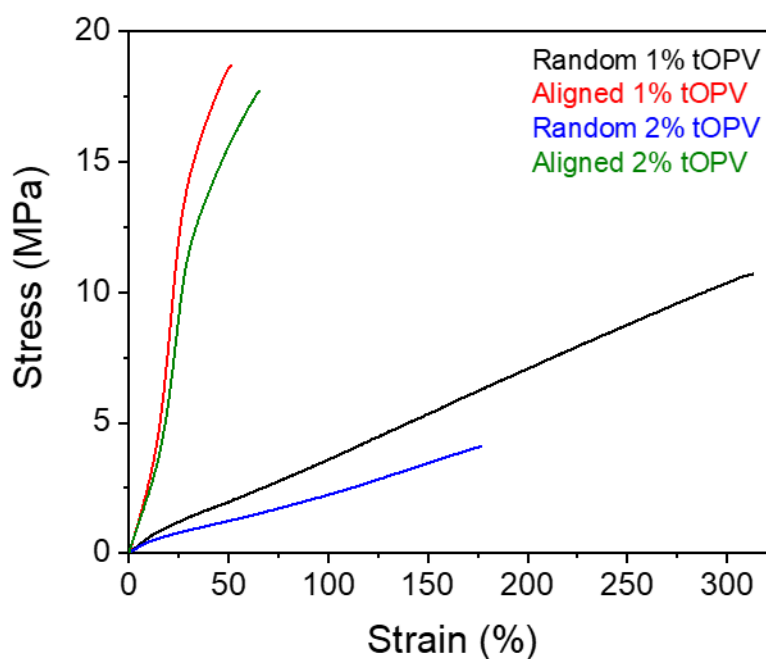


Figure 3.47 Strain-stress curves of all the samples obtained during uniaxial tensile testing (strain rate = 30% min⁻¹).

Table 3.10 E, ϵ_b , σ_b and tensile toughness (U_T) of electrospun samples with different fiber orientations and tOPV concentrations. Mechanical data are reported as the average of three samples.

Sample	E [MPa]	ϵ_b [%]	σ_b [MPa]	U_T [MPa]
Random 1% tOPV	8.3 ± 1.6	318 ± 4	9.6 ± 1.6	15.8 ± 2.5
Random 2% tOPV	5.4 ± 0.4	228 ± 46	6 ± 2	4.9 ± 2.3
Aligned 1% tOPV	26.1 ± 0.5	51 ± 14	17 ± 3	7.0 ± 3.0
Aligned 2% tOPV	25.5 ± 3.3	63 ± 3	17 ± 1	6.4 ± 0.5

Having established the morphology and mechanical properties of the microfiber mats, we examined their fluorescence in both the presence and absence of applied force. Both random and aligned mats blended with tOPV display the characteristic emission bands of the tOPV monomer ($\lambda_{\max} = 520$ nm) and the corresponding excimer ($\lambda_{\max} = 630$ nm) (Figure 3.48 and 3.49, red traces),[30] the latter of which dominates the emission color of the as-prepared mats. The mats were then subjected to uniaxial tensile deformation, while this time simultaneously monitoring their fluorescence via the ratio between tOPV monomer and excimer emission intensities (*i.e.*, the monomer-to-excimer intensity ratio, henceforth referred to as I_M/I_E). Notably, all mats show a strain-dependent increase in I_M/I_E that persists until sample failure (Figure 3.48 and 3.49). The most pronounced mechanofluorescence was detected for randomly aligned PBA-PUTHF/tOPV 1 wt.% mats (Figure 3.48a), for which an increase in I_M/I_E from 0.7 to 1.5 was observed when stretching from 0–300% strain. Above ca. 150% strain, the predominant emission color becomes that of the tOPV monomer, as is also readily apparent when observing the fiber mats under the fluorescence microscope (Figure 3.50a). In contrast, the considerably less noticeable fluorescence change in the randomly aligned PBA-PU/tOPV 2 wt.% mat (Figure 3.48b) can be

ascribed to the minimal tOPV monomer emission initially observed in the sample as-prepared. Possibly, this phenomenon may be in part due to rapid re-formation of excimers at such a high additive loading or due to their big dimensions, more difficult to break and disaggregate.

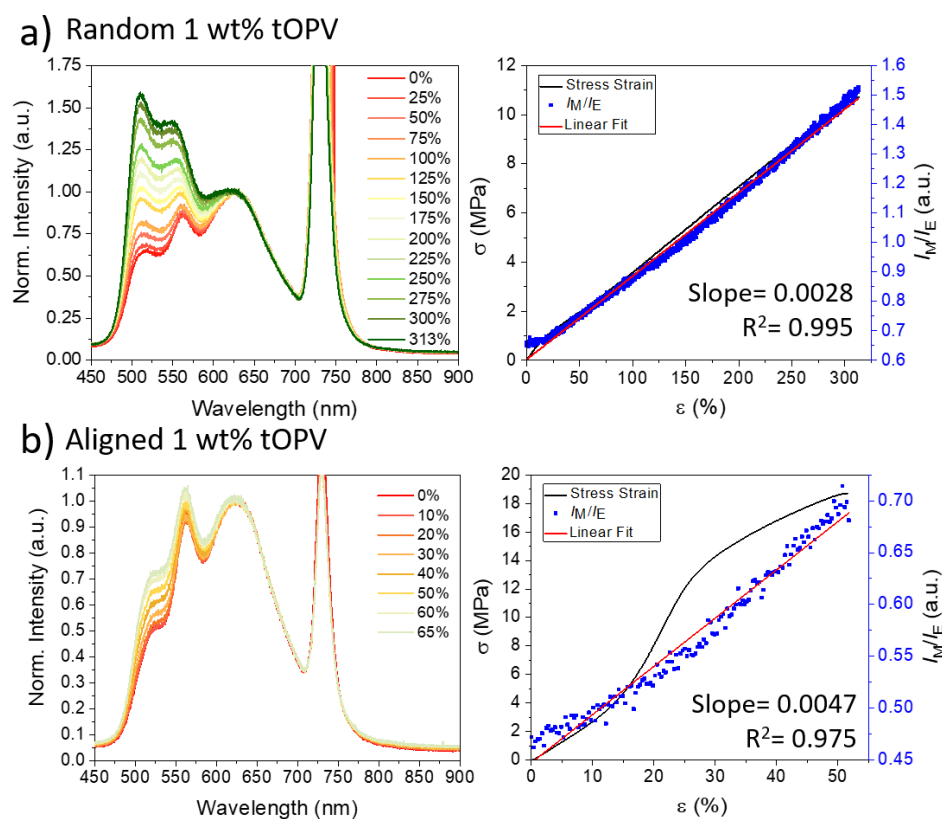


Figure 3.48 Left side: emission spectra of random (a) and aligned (b) microfibrillar mats containing 1 wt.% of tOPV at the indicated applied strains. Spectra are normalized to the excimer emission band at 630 nm. Right side: plots of the corresponding I_M/I_E ratio (right y-axis) and mechanical stress (left y-axis) of the samples as a function of strain determined from in situ mechanofluorescence testing.

As the random samples, also aligned fiber mats with 1–2 wt.% tOPV (Figure 3.49) demonstrate a strain-dependent increase in I_M/I_E . A great change in the emission color of the fibers was not visible since the achieved levels of deformation before failure are only about 50% (Figure 3.50b). Finally, while the I_{522}/I_{630} ratios of the aligned PBA-PUTHF/tOPV 1–2 wt.% mats are nearly identical, the emission band at $\lambda_{\max} = 562$ nm is much more pronounced for aligned PBA-PUTHF/tOPV 2 wt.% tOPV emission at this wavelength has been shown to

correspond to “Y-form” excimers,[45] suggesting that this type of tOPV excimer is favored at high additive loadings in aligned polymer mats.

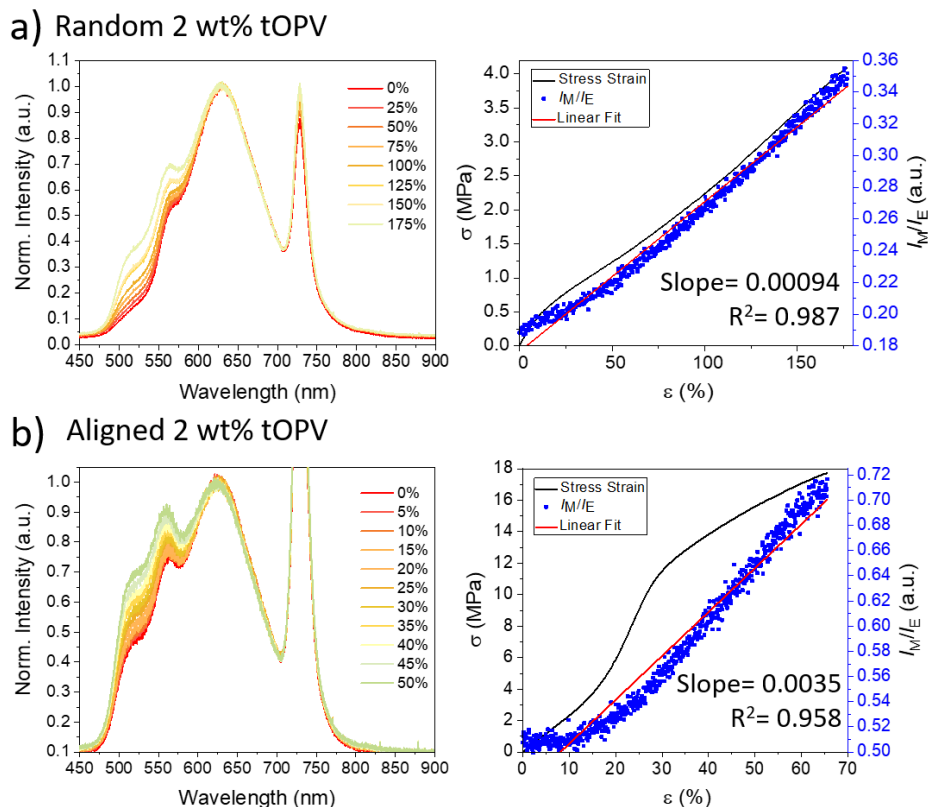


Figure 3.49 Left side: emission spectra of random (a) and aligned (b) microfibrillar mats containing 2 wt.% of tOPV at the indicated applied strains. Spectra are normalized to the excimer emission band at 630 nm. Right side: plots of the corresponding I_M/I_E ratio (right y-axis) and mechanical stress (left y-axis) of the samples as a function of strain determined from in situ mechanofluorescence testing.

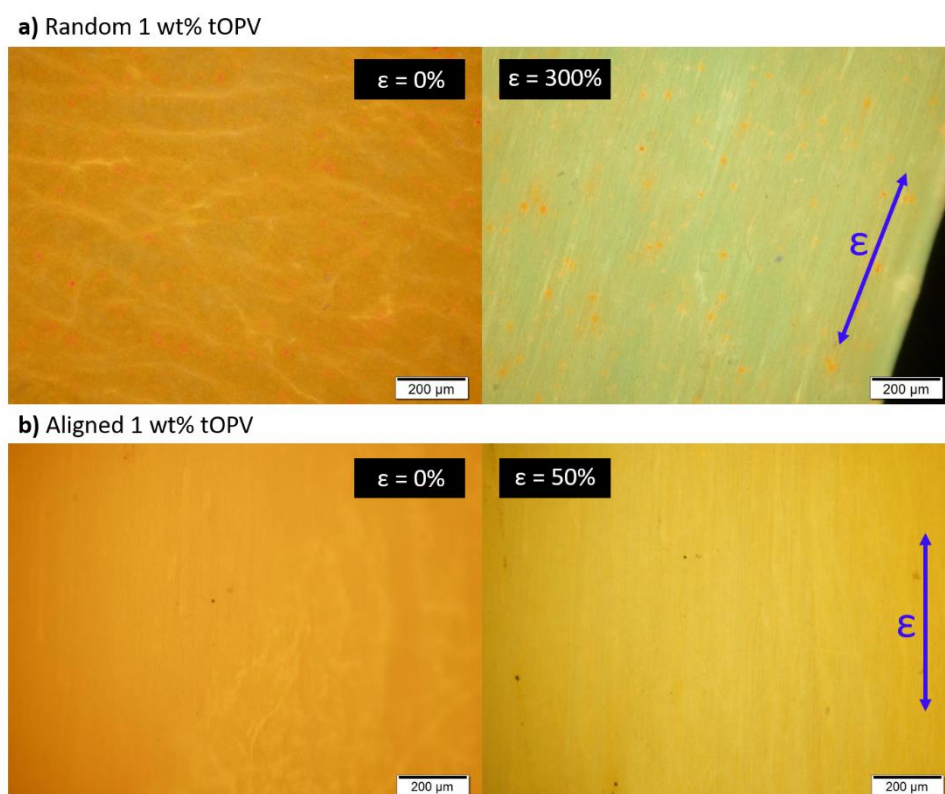


Figure 3.50 Images of the random (a) and aligned (b) mats containing 1 wt.% of tOPV stretched under the fluorescence microscope (10x magnification). Both the direction and strain values are displayed.

On the other hand, when considering the slope of the curve depicting the I_M/I_E ratio as a function of strain (Figure 3.48 and Figure 3.49, right side), a notable trend related to fiber orientation becomes evident. Specifically, aligned samples exhibit a significantly steeper slope compared to random ones. Therefore, despite achieving overall lower elongations, the signal variation is substantially greater at an equivalent strain value. This provides a crucial indication that in a sample where all fibers are aligned in the same direction as the applied stress, it exhibits higher sensitivity in mechanoluminescence response at low deformations. Beyond the mechanofluorescence of the ensemble of fibers that comprise the PBA-PUTHF mats, we sought to probe the mechanoluminescence of individual fibers themselves. Leveraging the versatility of the electrospinning technique, we spun ultra-low density fiber mats onto a two different devices that enabled the study of individual or small quantities of fibers under elongation. In Figure 3.51 the support used to prepare

this samples are depicted, while the procedure is described in detail in the experimental section.

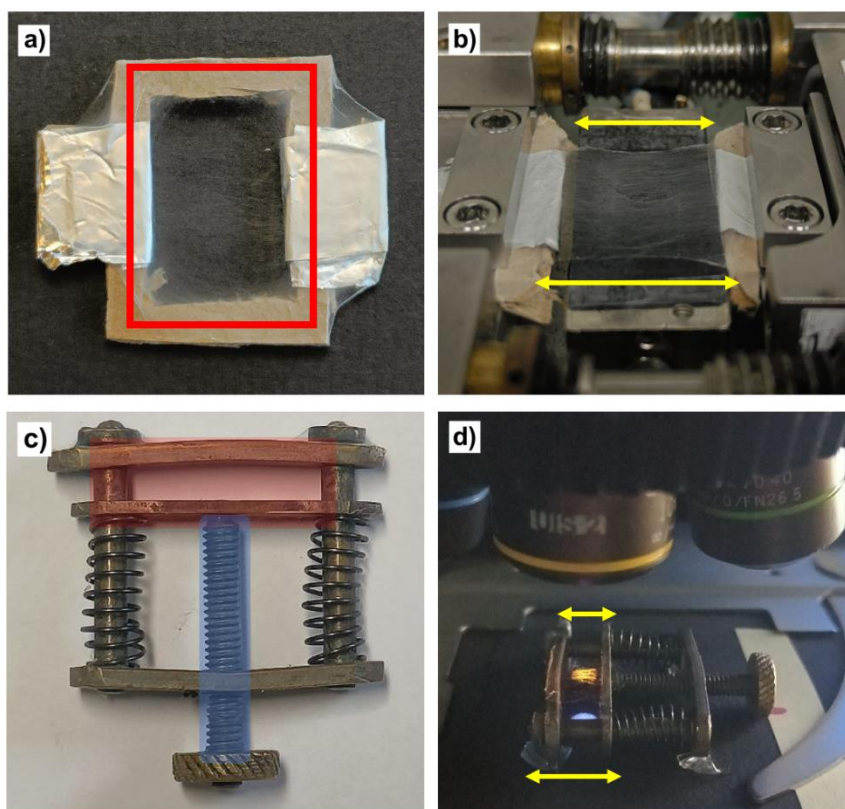


Figure 3.51 a) Cardboard mask covered with a ultra-thin layer of electrospun fibers collected in the red area. b) cardboard mask fixed at the clamps of the tensile stage, the sides of the mask along the stretching direction (yellow arrows) have been cut to elongate the collected fibers. c) Metal brackets where the red area highlights the zone where the fibers are collected, the screw (indicated in blue) allows to increase the distance between the brackets, thus elongating the fibers. d) Bracket placed under the microscope, indicating the direction of elongation (yellow arrows)

Fluorescence microscopy images of these fibers during stretching show that the fibers aligned parallel to the stretching axis are the first to change their emission color from orange to green (Figure 3.52). Then, as the fibers are continuously stretched, more fibers are forced into alignment with the stretching axis and subsequently exhibit the same change in fluorescence color (Figure 3.52).

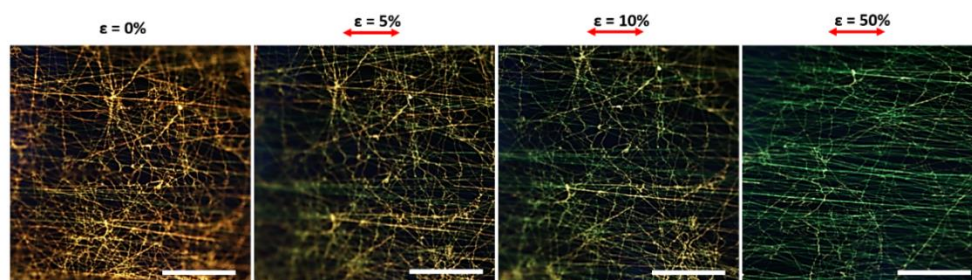


Figure 3.52 Fluorescence microscopy images at 20x magnification of a thin layer of random fibers at increasing strain values. The indicated strain values are calculated based on the initial distance between the clamps and their progressive stretching. Scale bar = 200 μm .

Thus, these microscopy images provide unambiguous proof that mechanical strain is first directed towards fibers pre-aligned along the stretching axis, and that force transfer to non-parallel fibers induces re-alignment of the latter. Finally, these observations were corroborated by acquiring high-magnification fluorescence microscopy images of individual fibers (Figure 3.53). As observed with the thin layer of random fibers, the most prominent mechanofluorescence is observed for individual fibers oriented along the direction of stretching. Moreover, a change from orange to yellow fluorescence is observed for fibers that have begun to re-orient along the stretching direction, which ultimately change to green once nearly parallel to the stretching axis (Figure 3.53).

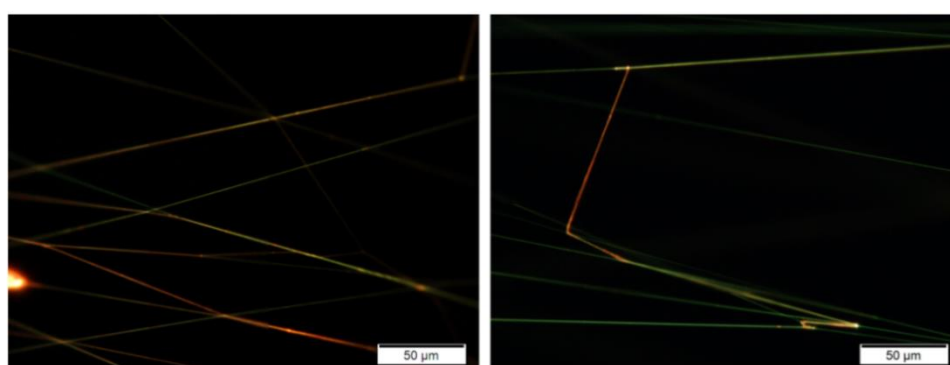


Figure 3.53 Fluorescence microscopy images at 50x magnification of electrospun random fibers at applied strains of approximately (left) 30% and (right) 60% applied strain (see Supporting Information for details).

3.3.3. Conclusions

In conclusion, the investigation into mechanoluminescent properties of electrospun materials has provided valuable insights into their potential applications in strain sensing and responsive systems. Through a series of comprehensive experiments and analyses, it has been demonstrated that the arrangement and orientation of fibers significantly impact the mechanical and optical properties of the materials. The random and aligned fiber structures exhibit distinct mechanical behaviors, with the former displaying greater elasticity and ductility, while the latter showcasing stiffness and brittleness. Importantly, the mechanoluminescent responses of the materials are closely linked to their mechanical deformation, as evidenced by the variations in emission spectra and color changes during stretching. By testing various doping levels of tOPV, no significant differences in mechanoluminescence were observed. Only in the case of the highly concentrated aligned sample did we observe a greater formation of the “Y-form” excimers, which, however, does not compromise the measurement. Additionally, the investigation of individual fibers has revealed the anisotropic effect of fiber orientation, where only the fibers aligned with the applied force undergo significant color changes. Overall, these findings highlight the potential of electrospun materials as versatile and sensitive strain sensors, opening pathways for further research and development in the field of functional materials.

3.3.4. Experimental section

Materials. The tOPV (Figure 3.43b) was synthesized by Prof. Weder’s group at the Adolphe Merkle Institute of Fribourg, as reported by Calvino *et al.*, [8] (with $M_n = 4500 \text{ g mol}^{-1}$; $m \approx 0.36$, $n \approx 0.64$, $p \approx 44$). Desmopan 2795A (PBA-PUTHF, Covestro, $M_n = 93 \text{ kDa}$, $D = 2.1$) (Figure 3.43a) was employed to produce the electrospun microfibers. DMF ($\geq 99.8\%$ GC) and THF ($\geq 99.9\%$) solvents were purchased from Sigma Aldrich and used without further purification.

Samples preparation. The electrospun nanofiber materials were fabricated using an in-house electrospinning apparatus consisting of

a high-voltage power supply (Spellman SL b50 P 10/CE/230), a syringe pump (KD Scientific 200 series) and a glass syringe filled with the polymer solution. The syringe was connected to a blunt, stainless-steel needle (inner diameter = 0.51 mm) through a PTFE tube. To obtain aligned fiber mats, a high-speed rotating collector (length = 120 mm, diameter = 60 mm) with a rotation speed of 5400 rpm (peripheral speed = 17.1 m s^{-1}) was employed. This collector facilitated preferential alignment of the fibers along the direction of drum rotation. Conversely, random samples were obtained using a static plate collector. Electrospinning was carried out at room temperature with a relative humidity of 40-50%. The polymer was dissolved in a solvent mixture of THF : DMF (70 : 30 v/v) at a concentration of 9% w v^{-1} . The polymer solution was electrospun using an applied voltage of 18-20 kV, a feed rate of 1.0 mL h^{-1} , and a needle-to-collector distance of 20 cm. The solutions with different tOPV amounts, used for electrospinning, will henceforth be referred to as PBA-PUTHF/tOPV X wt.%.

Characterization methods. SEM analysis was carried out using a Philips 515 SEM at an accelerating voltage of 17 kV, on samples sputter-coated with gold. Average fiber dimensions and orientation were determined by SEM image analysis of individual fibers ($n = 300$) using ImageJ. The ImageJ Directionality plug-in, which exploits the local gradient orientation method, was used to determine the orientation of the fibers. For a given fiber mat, fiber orientation was averaged across images acquired at four different spots in the sample to accurately determine the overall orientation of fibers in the sample. DSC analysis was carried out using a Q2000 DSC apparatus (TA instruments) equipped with a refrigerated cooling system (RCS90). Under nitrogen atmosphere, approximately 6 mg of sample were placed in a T-Zero[®] aluminum pan and heated at $10 \text{ }^{\circ}\text{C min}^{-1}$ from $-90 \text{ }^{\circ}\text{C}$ to $215 \text{ }^{\circ}\text{C}$. Then, the sample was rapidly cooled to $-90 \text{ }^{\circ}\text{C}$ and subsequently heated to $215 \text{ }^{\circ}\text{C}$ at $10 \text{ }^{\circ}\text{C min}^{-1}$, after which it was cooled at $10 \text{ }^{\circ}\text{C min}^{-1}$ to $-90 \text{ }^{\circ}\text{C}$ and heated again to $215 \text{ }^{\circ}\text{C}$ at the same rate. T_g were determined from the second DSC heating scan at the midpoint of the glass transition. T_m were determined at the minimum of the

most prominent endothermic melting peak of the second heating scans. Mechanical tests were carried out using a Linkam TST350 microtensile stage equipped with a 20 N load cell, controlled by the accompanying Linksys32 software. Dog bone-shaped specimens were first produced using a die-cutter (Zwick/Roell, gauge length = 16 mm, width = 5 mm, thickness = 0.05-0.15 mm) and then subjected to uniaxial deformation with a strain rate of 30% min⁻¹. Solid-state fluorescence measurements were made using an Ocean Optics USB 4000 spectrometer connected to an Ocean Optics LS-365 LED light source with an excitation wavelength of $\lambda_{\text{ex}} = 365$ nm and an Ocean Optics QR230-7-XSR SMA 905 optical fiber. Samples were placed on top of a piece of black paper and the optical fiber was positioned at an angle of approximately 35° to the surface of the film at a distance of approximately 2 mm away from the film. In situ fluorescence data were acquired using Stream Basic software in real time while the sample was deformed in the manner described above. Fluorescence microscopy images were acquired at 20x and 50x magnification using an Olympus BX51 microscope equipped with an Olympus DP72 high-resolution camera. The samples were imaged in reflectance mode using an X-Cite Series 120-Q Mercury vapor short arc lamp as the excitation source ($\lambda_{\text{ex}} = 345$ nm). Birefringence images were obtained with an optical microscope with polarized light at 32x magnification, at different degrees of rotation with respect to the polarization direction.

3.4. References

- [1] Löwe, C. and Weder, C. (2002). Oligo(p-phenylene vinylene) excimers as molecular probes: Deformation-induced color changes in photoluminescent polymer blends. *Advanced Materials*. DOI: 10.1002/1521-4095(20021118)14:22<1625::AID-ADMA1625>3.0.CO;2-Q.
- [2] Crenshaw, B.R. and Weder, C. (2006). Self-assessing photoluminescent polyurethanes. *Macromolecules*. DOI: 10.1021/ma061685b.
- [3] Crenshaw, B.R. and Weder, C. (2003). Deformation-Induced Color Changes in Melt-Processed Photoluminescent Polymer Blends. *Chemistry of Materials*. DOI: 10.1021/cm034447t.
- [4] Crowe, W.E. (1929). Institutes of Radiology. *The Lancet*. DOI: 10.1016/S0140-6736(01)03014-8.
- [5] Rossi, N.A.A. et al. (2009). Synthesis and characterisation of pyrene-labelled polydimethylsiloxane networks: Towards the in situ detection of strain in silicone elastomers. *Journal of Materials Chemistry*. DOI: 10.1039/b908708g.
- [6] Pucci, A. et al. (2005). Luminescent bis(benzoxazoly)stilbene as a molecular probe for poly(propylene) film deformation. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.200500227.
- [7] Calvino, C. et al. (2017). Approaches to polymeric mechanochromic materials. *Journal of Polymer Science, Part A: Polymer Chemistry*. DOI: 10.1002/pola.28445.
- [8] Calvino, C. et al. (2019). Mechanoresponsive, Luminescent Polymer Blends Based on an Excimer-Forming Telechelic Macromolecule. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.201800705.
- [9] Micheletti, C. et al. (2023). Blending or Bonding? Mechanochromism of an Aggregachromic Mechanophore in a Thermoplastic Elastomer. *ACS Applied Polymer Materials*. DOI: 10.1021/acsapm.2c02037.
- [10] Winnik, F. (1993). Photophysics of Preassociated Pyrenes in Aqueous Polymer Solutions and in Other Organized Media. *Chemical Reviews*. DOI: 10.1021/cr00018a001.
- [11] Basu, B.J. et al. (2005). Optical oxygen sensor coating based on the fluorescence quenching of a new pyrene derivative. *Sensors and Actuators, B: Chemical*. DOI: 10.1016/j.snb.2004.04.092.
- [12] Coleman, L.E. et al. (1959). Reaction of Primary Aliphatic Amines with Maleic Anhydride. *Journal of Organic Chemistry*. DOI: 10.1021/jo01083a626.
- [13] Hu, G.H. and Lindt, J.T. (1992). Amidification of poly(styrene-co-maleic

- anhydride) with amines in tetrahydrofuran solution: A kinetic study. *Polymer Bulletin*. DOI: 10.1007/BF00944831.
- [14] Bauers, F. et al. (1999). Melt Modification of Poly (styrene-co-maleic anhydride) with Alcohols in the Presence of 1 , 3-Oxazolines.
 - [15] Van Der Mee, M.A.J. et al. (2008). Thermoreversible Covalent Crosslinking of Maleated Ethylene/Propylene Copolymers with Diols. *Journal of Polymer Science: Part A: Polymer Chemistry*. DOI: 10.1002/pola.
 - [16] Polgar, L.M. et al. (2015). Use of Diels-Alder Chemistry for Thermoreversible Cross-Linking of Rubbers: The Next Step toward Recycling of Rubber Products? *Macromolecules*. DOI: 10.1021/acs.macromol.5b01422.
 - [17] Zych, A. et al. (2019). Strain-reporting pyrene-grafted polyethylene. *European Polymer Journal*. DOI: 10.1016/j.eurpolymj.2018.12.016.
 - [18] Johnson, G.E. (1980). Effect of Concentration on the Fluorescence Spectra and Lifetimes of Pyrene in Polystyrene Films. *Macromolecules*. DOI: 10.1021/ma60076a013.
 - [19] Gucciardi, P.G. et al. (1997). Versatile scanning near-field optical microscope for material science applications. *Review of Scientific Instruments*. DOI: 10.1063/1.1148246.
 - [20] Otsu, N. et al. (1979). Otsu 1979 Otsu Method. *IEEE Transactions on Systems, Man, and Cybernetics*.
 - [21] Nečas, D. and Klapetek, P. (2012). Gwyddion: An open-source software for SPM data analysis. *Central European Journal of Physics*. DOI: 10.2478/s11534-011-0096-2.
 - [22] Traeger, H. et al. (2021). Folded Perylene Diimide Loops as Mechanoresponsive Motifs. *Angewandte Chemie - International Edition*. DOI: 10.1002/anie.202105219.
 - [23] Traeger, H. et al. (2022). Strain-correlated mechanochromism in different polyurethanes featuring a supramolecular mechanophore. *Polymer Chemistry*. DOI: 10.1039/d2py00218c.
 - [24] Rigodanza, F. et al. (2015). Fast and Efficient Microwave-Assisted Synthesis of Perylenebisimides. *European Journal of Organic Chemistry*. DOI: 10.1002/ejoc.201500670.
 - [25] Hamad, F.A. et al. (2017). Investigation of the melting process of polyethylene glycol 1500 (PEG 1500) in a rectangular enclosure. *International Journal of Heat and Mass Transfer*. DOI: 10.1016/j.ijheatmasstransfer.2017.07.014.
 - [26] Mauck, C.M. et al. (2017). Characterization of excimer relaxation via femtosecond shortwaveand mid-infrared spectroscopy. *Journal of Physical*

Chemistry A. DOI: 10.1021/acs.jpca.6b11388.

- [27] Margulies, E.A. et al. (2014). Excimer formation in cofacial and slip-stacked perylene-3,4: 9,10-bis(dicarboximide) dimers on a redox-inactive triptycene scaffold. *Physical Chemistry Chemical Physics*. DOI: 10.1039/c4cp03107e.
- [28] Gotti, C. et al. (2020). Biomimetic Hierarchically Arranged Nanofibrous Structures Resembling the Architecture and the Passive Mechanical Properties of Skeletal Muscles: A Step Forward Toward Artificial Muscle. *Frontiers in Bioengineering and Biotechnology*. DOI: 10.3389/fbioe.2020.00767.
- [29] Bergström, J.S. and Boyce, M.C. (1998). Constitutive modeling of the large strain time-dependent behavior of elastomers. *Journal of the Mechanics and Physics of Solids*. DOI: 10.1016/S0022-5096(97)00075-6.
- [30] Kiebala, D.J. et al. (2020). Mechanoresponsive Elastomers Made with Excimer-Forming Telechelics. *Organic Materials*. DOI: 10.1055/s-0040-1721052.
- [31] Zhang, J. et al. (2016). The continuous fabrication of mechanochromic fibers. *Journal of Materials Chemistry C*. DOI: 10.1039/c5tc04073f.
- [32] Zhao, R. et al. (2023). Mechanochromic photonic fibers composed of strain responsive colloidal crystals and spandex yarns. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. DOI: 10.1016/j.colsurfa.2023.131689.
- [33] Geng, Y. et al. (2022). Robust cholesteric liquid crystal elastomer fibres for mechanochromic textiles. *Nature Materials*. DOI: 10.1038/s41563-022-01355-6.
- [34] Colaco, R. et al. (2020). Mechanochromic Microfibers Stabilized by Polymer Blending. *ACS Applied Polymer Materials*. DOI: 10.1021/acsapm.0c00213.
- [35] Raisch, M. et al. (2018). Highly Sensitive, Anisotropic, and Reversible Stress/Strain-Sensors from Mechanochromic Nanofiber Composites. *Advanced Materials*. DOI: 10.1002/ADMA.201802813.
- [36] Montanari, U. et al. (2021). Functionalisable epoxy-rich electrospun fibres based on renewable terpene for multi-purpose applications. *Polymers*. DOI: 10.3390/polym13111804.
- [37] Amorini, M. et al. (2022). Reusable Cavitand-Based Electrospun Membranes for the Removal of Polycyclic Aromatic Hydrocarbons from Water. *Small*. DOI: 10.1002/sml.202104946.
- [38] Liguori, A. et al. (2022). Thermoactive Smart Electrospun Nanofibers. *Macromolecular Rapid Communications*. DOI: 10.1002/marc.202100694.
- [39] Iregui, A. et al. (2017). Electrospinning of cationically polymerized

- epoxy/polycaprolactone blends to obtain shape memory fibers (SMF). *European Polymer Journal*. DOI: 10.1016/j.eurpolymj.2017.07.026.
- [40] Shirole, A. et al. (2018). Tailoring the Shape Memory Properties of Segmented Poly(ester urethanes) via Blending. *ACS Applied Materials and Interfaces*. DOI: 10.1021/acsami.8b07083.
- [41] Gazzano, M. et al. (2015). Structure-morphology correlation in electrospun fibers of semicrystalline polymers by simultaneous synchrotron SAXS-WAXD. *Polymer*. DOI: 10.1016/j.polymer.2015.03.002.
- [42] Kakade, M. V. et al. (2007). Electric field induced orientation of polymer chains in macroscopically aligned electrospun polymer nanofibers. *Journal of the American Chemical Society*. DOI: 10.1021/ja065043f.
- [43] Liu, J. et al. (2017). Single electrospun PLLA and PCL polymer nanofibers: Increased molecular orientation with decreased fiber diameter. *Polymer*. DOI: 10.1016/j.polymer.2017.04.070.
- [44] Ma, X. et al. (2012). Molecular orientation in electrospun poly(vinylidene fluoride) fibers. *ACS Macro Letters*. DOI: 10.1021/mz3000122.
- [45] Sagara, Y. et al. (2016). A Thermo- and Mechanoresponsive Cyano-Substituted Oligo(p-phenylene vinylene) Derivative with Five Emissive States. *Chemistry - A European Journal*. DOI: 10.1002/chem.201600272.

4. Overall conclusions

In this work, various luminescent molecules, belonging to the category of molecular rotors and aggregachromic dyes, were incorporated into polymer matrices and comprehensively explored, to develop self-diagnostic and smart polymers. The research conducted spanned different areas of polymer science, including mechanoluminochromism, temperature-dependent behavior, and sensitivity to changes in free volume and chain mobility. The results offer new insights into the dynamic interaction between polymer matrices and luminescent additives when exposed to various environmental factors, such as temperature, mechanical deformation, and aging.

In the framework of molecular rotors, these studies have advanced our understanding of how dye's emission properties can be intrinsically linked to the mobility and free volume within polymer matrices. In the examination of AIE-doped polymers under both thermal and mechanical stress, our research led to a reconsideration of conventional assumptions regarding changes in emission intensity. The findings unveiled that previously underappreciated alterations of matrix properties, including changes in transparency and the formation of microfractures, massively affect the emission intensity. Specifically, the results highlighted the critical roles of altered optical transparency and waveguide effects on the variation of the emission intensity. Consequently, fluorescence lifetime measurements emerged as a powerful tool to differentiate between intrinsic changes in the AIE dye's photophysical properties due to the RIM effect and extrinsic fluctuations in the matrix's optical characteristics. These findings hold fundamental importance for future studies, further solidifying the value of lifetime measurements over intensity-based assessments.

Building upon this approach, the presented methodology was successfully applied to analyze the response of various molecular rotors, aiming to precisely identify fluorophores demonstrably sensitive to their polymer environment. Within this framework, by measuring the fluorescence lifetime of diverse rotors embedded in polymers exhibiting distinct chain mobilities, an AIE probe displaying unique responsiveness to the glass transition temperature through the RIM effect was identified. Furthermore, the lifetime of this dye correlates with a common polymer property solely dependent on T_g - namely, the mobility of polymer chains. This temperature-independent

AIE probe (TPE-MRh), when combined with advanced imaging techniques, exhibits the potential for quantitative visualization of chain mobility with high spatial and temporal resolution.

Further insights into the processes occurring during stress-strain tests and physical aging in polymers, particularly at the free-volume level, were gained by harnessing the unique attributes of a phosphorescent AIE probe. Thanks to its extended lifetimes, the development of materials capable of autonomously monitoring physical aging and mechanical stresses in real-time with exceptional precision and sensitivity became achievable, all while minimizing the impact of instrumental errors.

This initial study demonstrates the responsiveness of the probes to different polymer processes. Further investigation is needed to understand why these luminophores react differently. By combining additional experiments, computational analysis, and theoretical models, it would be possible to determine the significance of the RIM effect on the probe sensitivity. A reasonable hypothesis is that the dye exhibits sensitivity to a particular polymer process when the timescale of the process, and in turn the polymer chain relaxation time, closely aligns with the emission timescale (lifetime) of the luminophore.

On the other hand, aggregachromic dyes were integrated into polymer matrices for the creation of mechanoluminochromic materials, being extraordinarily sensitive to changes in intermolecular distances and orientation of chromophores. The research was focused on ascertaining whether the bonding of the dye to the polymer chain provides noticeable advantages over the simple blending, thus justifying the synthetic efforts of linking the fluorophore to the macromolecules. In this framework, a commercial thermoplastic elastomer (SEBS) was functionalized through both covalent bonding and physical dispersion with pyrene derivatives. The comparative analysis of mechanochromic performance highlighted the crucial role of covalent bonding in achieving a detectable and reversible mechanoluminochromic response. In this type of polymer, mechanoresponsiveness, indeed, arises from the strategic confinement of pyrene chromophores within the soft SEBS block, a feature unattainable in a dispersed dye system.

Subsequently, to streamline the synthetic process and explore its scalability, we delved into thermoplastic polyurethanes containing perylene

diimide derivative. This new approach shed light on the advantages of both covalent and physically dispersed methods, highlighting their respective potentials. On one hand, the covalent approach enhances the alignment between stress relaxation and the mechanochromic response. However, it does not significantly enhance mechanoluminescence under uniaxial stress, at least within the examined dye's low concentration regime. In contrast, the simpler and more convenient blending approach yields excellent results. This underscores the value of both methodologies in the pursuit of mechanoluminochromic materials.

A further investigation employed a telechelic aggregachromic dye incorporated into electrospun materials to demonstrate that fiber orientation significantly influenced the mechanoluminochromic responses, with interesting implications in the field of strain sensors and responsive systems.

In conclusion, this second part highlights the impact of the processing and the morphology of mechanoluminescent materials that must be tailored to match a specific application. In this regard, the most straightforward and versatile way to simplify the material preparation avoiding complex synthesis, is to incorporate the dye in a short polymer chain. This approach limits the dispersion of chromophores while simultaneously enhancing the impact of the polymer chain movements through entanglements between the dye and the matrix. In this thesis, this strategy has enabled the study of mechanoluminescence with submicrometer spatial resolution.

To summarize, the collective findings from these studies provide a rich overview in the realm of luminescent materials within polymer matrices. This research deepens our understanding of these materials and offers practical applications across various fields, from damage detection and load-bearing devices to wearable technology and mechanochromic textiles. The versatility and sensitivity of these materials make them invaluable for a wide range of real-world applications, paving the way for exciting developments in the future.