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FULLY BIO-BASED EPOXY RESINS

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Abstract

Epoxy resins are mainly produced by reacting bisphenol A with epichlorohydrin. Growing concerns about the negative health effects of bisphenol A are urging researchers to find alternatives. In this work diphenolic acid is suggested, as it derives from levulinic acid, obtained from renewable resources. Nevertheless, it is also synthesized from phenol, from fossil resources, which, in the current paper has been substituted by plant-based phenols. Two interesting derivatives were identified: diphenolic acid from catechol and from resorcinol.

Epichlorohydrin on the other hand, is highly carcinogenic and volatile, leading to a tremendous risk of exposure. Thus, two approaches have been investigated and compared with epichlorohydrin.

The resulting resins have been characterized to find an appropriate application, as epoxy are commonly used for a wide range of products, ranging from composite materials for boats to films for food cans. Self-curing capacity was observed for the resin deriving from diphenolic acid from catechol.

The glycidyl ether of the diphenolic acid from resorcinol, a fully renewable compound, was cured in isothermal and non-isothermal tests tracked by DSC. Two aliphatic amines were used, namely 1,4-butanediamine and 1,6-hexamethylendiamine, in order to determine the effect of chain length on the curing of an epoxy-amine system and determine the kinetic parameters. The latter are crucial to plan any industrial application. Both diamines demonstrated superior properties compared to traditional bisphenol A-amine systems.

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Abbreviations

^{13}C-NMR: Carbon nuclear magnetic resonance spectroscopy

^{1}H-NMR: Proton nuclear magnetic resonance spectroscopy

BPA : bisphenol A

$CDCl_3$: Deuterated chloroform

$CDCN_3$: Deuterated acetonitrile

DEPT: Distortionless Enhancement by Polarization Transfer

DGEBA : diglycidyl ether of bisphenol A

DMSO-d_6: Deuterated dimethyl sulfoxide

DPA : Diphenolic acid

DPAC : Catecol diphenolic acid

DPAG : Guaiacol diphenolic acid

DPAM : m-Cresol diphenolic acid

DPAR : Resorcinol diphenolic acid

ECH : Epichlorohydrin

EEW : Epoxy equivalent weight

GEDPAC : Glycidyl ether of catecol diphenolic acid

GEDPAR : Glycidyl ether of resorcinol diphenolic acid

HMBC: Heteronuclear multiple bond correlation

NOE: Nuclear Overhauser effect

NOESY: Nuclear Overhauser effect spectroscopy

TMS: Tetramethylsilane

INTRODUCTION

1. Green chemistry

In view of the fast consumption of the petroleum stock and pressing demand for the use of polymeric materials to keep pace with the rate of growth of the world's population, the syntheses of chemical from bio-based products have achieved tremendous momentum at present all over the world. Indeed, climate change and other environmental problems are urging us to develop sustainable processes based on renewable resources.

In the recent years, due to heavy consequences of the climate change caused by our way of life, the awareness is rising that new alternative pathways of production and consumption need to be found. It becomes gradually clearer how our choices are not sustainable and chemistry plays an important role in it. Indeed, nowadays, no plant grows without a fertilizer and hardly any food is sold without using additives, or inert gases, used for transportation and storing. Chemistry is everywhere from the food, to transportation to medicine. Thus, these issues are also, to a huge extent, regarding chemistry. Chemists, all around the world are thus searching for better, more environmentally friendly solutions to everyday problems, to practically, reinvent chemistry. This is when the concept of "*green chemistry*" was born and consolidated by the eponymous book from Paul Anastas[1]. This book and several other works from the same author describe the guidelines and the basic methodology to adapt production procedures and the intrinsic properties of the products in order to make them less dangerous for humans and the environment.

The key points are summarized as the twelve principles of green chemistry. They are stated as follows in the book:

1. **Prevention**
   It's better to prevent waste than to treat or clean up waste afterwards.
2. **Atom Economy**
   Design synthetic methods to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Syntheses**
   Design synthetic methods to use and generate substances that minimize toxicity to human health and the environment.
4. **Designing Safer Chemicals**
   Design chemical products to affect their desired function while minimizing their toxicity.

5. **Safer Solvents and Auxiliaries**

   Minimize the use of auxiliary substances wherever possible make them innocuous when used.

6. **Design for Energy Efficiency**

   Minimize the energy requirements of chemical processes and conduct synthetic methods at ambient temperature and pressure if possible.

7. **Use of Renewable Feedstocks**

   Use renewable raw material or feedstock rather whenever practicable.

8. **Reduce Derivatives**

   Minimize or avoid unnecessary derivatization if possible, which requires additional reagents and generate waste.

9. **Catalysis**

   Catalytic reagents are superior to stoichiometric reagents.

10. **Design for Degradation**

    Design chemical products so they break down into innocuous products that do not persist in the environment.

11. **Real-time Analysis for Pollution Prevention**

    Develop analytical methodologies needed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. **Inherently Safer Chemistry for Accident Prevention** Choose substances and the form of a substance used in a chemical process to minimize the potential for chemical accidents, including releases, explosions, and fires.

These principles are thought as guidelines. Indeed, when developping a new chemical, we shall not only think of the finished product but also consider the whole procedure, the reagents, the production thereof and the waste as well as by-products. The major points being obviously renewable feedstock and reaction's conditions, by respecting these, a real green chemistry is not that far away.

In order to have an idea of the sustainability of the process, several indicators have been developed. The first was a simple count of the atom economy, defined by Barry Trost[2] as:

$$Atom\ economy = \frac{Molecular\ weight\ of\ the\ product}{\sum Molecular\ weight\ of\ the\ reagents}$$

This allowed to quickly identify wasteful reactions for example including protection/deprotection steps. The idea is that as many atoms as possible from the reagent should also be used in the final product.

However, this does not include waste generated by solvents for reaction and purification, as well as catalysts. Thus, the most popular indicator is the E-factor[3], which corresponds to the following:

$$E\ factor = \frac{Total\ mass\ of\ waste}{Mass\ of\ product}$$

Everything that has been put into the system or used for extracting the product has to be considered as waste. This gives a better indication about the actual sustainability of the process. However, it should not be overlooked that it does not give any indication about health hazards or environmental impact of the waste thereby generated.

Furthermore, also the energetic efficiency is another important factor when caring for the environmental impact. A "green" reaction should, indeed, be carried out in conditions close to room temperature and atmospheric pressure. This can be induced by using catalysts to reduce the activation energy of a reaction or by finding innovative reaction systems like biphasic reactions or "on water" reactions which often lead to surprising results.

Finally, also biotechnology is demonstrating more and more that enzyms and bacteria can carry out some complicated reactions, usually with satisfying yields and an outstanding selectivity.

2. Biomass

Over the last years, various researches allowed to develop a wide range of chemicals mainly from cellulose, starch and oil. Still, most of the polymeric material derives from reserves of fossils as they stay the cheaper choice. By continuing the development of new polymers and with the increase of the oil price, bio-based polymers are progressively more convenient.

When talking about biomass, the resources are not limited to cellulose but include all carbohydrates, lignin, oils, fats and proteins as well as all substances extracted from plants, for example flavonoids from tea.

Due to the rise of the oil price, another major issue the world is facing today is the competition between agriculture for food production and harvesting for industries. The biomasses are thus classified in three categories: The first generation biomass are deriving from cultures we would

as well eat. The second generation biomass uses waste products from the industrial food production or other products. Finally, the third generation biomass has been genetically engineered to increase the yield of the required feedstock.

Furthermore, it has to be mentioned that the use of renewable feedstock does not correlate with biodegradability. A polyethylene, even if produced from plant-based ethylene, will not be biodegradable. On the other hand, a poly(hydroxyalkanoate) is very prone for biodegradation, independently of whether it is produced by bacteria from renewable glycerol or from fossil feedstock. Indeed, the functional groups and not the source induce the biodegradability.

Each plant contains, in their cell walls a considerable amount of cellulose and lignin, as seen in figure 1. Depending on the final product, often only one of these is used and the other discarded. For example, in paper production only the cellulose is used and huge amounts of lignin are discarded.

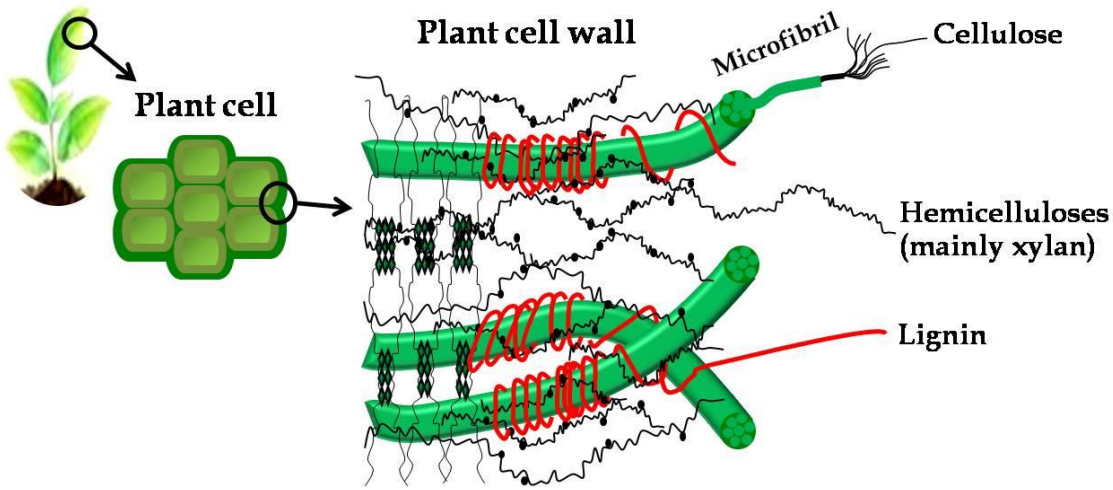

Figure 1: The composition of a plant cell wall[4]

Thus, enormous amounts of these products are discarded every day and uses for them need to be found urgently. In 2004, the US Department of energy has issued a full report about the most interesting value added chemicals from biomass[5], which has become a reference for scientists in the field. Starting from 300 substances of from natural resources, they identify 12 bio-based molecules that are the most appropriate as platform chemicals in order to provide, deriving from them, all chemicals needed for daily life. In the figure 2, extracted from the above-mentioned report, on the next page the diagram shows how these twelve platform chemicals and their derivatives could change all of the fossil-based chemistry into green chemistry. It is intended as an outlook for researchers, seeking to provide a hint in a global direction.

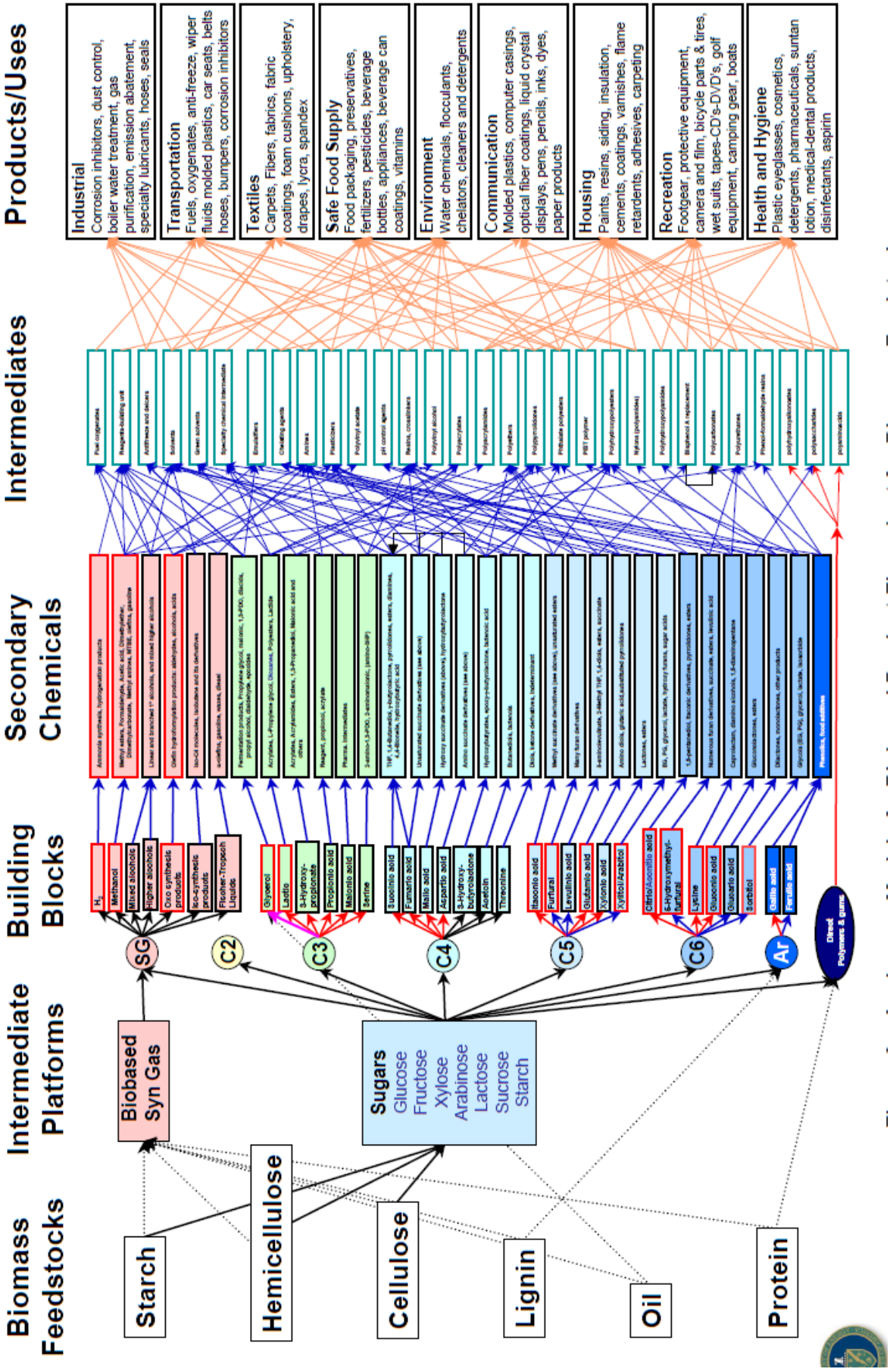

Figure 2: Flow chart of bio-based products from biomass

Their research focuses mainly on sugar, as carbohydrates are by far the most widespread category of biomass. Indeed, the 12 molecules identified are:

Building Blocks
1,4 diacids (succinic, fumaric and malic)
2,5 furan dicarboxylic acid
3 hydroxy propionic acid
aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol/arabinitol

In our research, we are going to focus mainly on levulinic acid and glycerol.

Levulinic acid

Levulinic acid is a particularly interesting molecule thanks to its structure containing one acid group and a ketone. Those are highly reactive groups and can potentially lead to a wide range of derivatives. Furthermore, thanks to the two methylene groups between the carbonyls, it readily undergoes heterocyclic reactions.

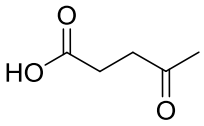

Figure 3: Structure of levulinic acid

Several approaches have been used for its synthesis but since the development of the Biofine[6,7] process, the production from biomass is also economically viable.

As shown in figure 3, the sugars are converted in hydroxymethylfurfural, which is then decarboxylated and the heterocyle opened to yield levulinic acid.

The maximum theoretical yield is 71,6% w/w, as formic acid is eliminated. Reaching this yield mainly depends on the continuous control of the degradation reactions. In the Biofine process,

the yield obtained is around 70-80% of this maximum yield owing to the high efficiency of the reactors and the use of polymerisation inhibitors.

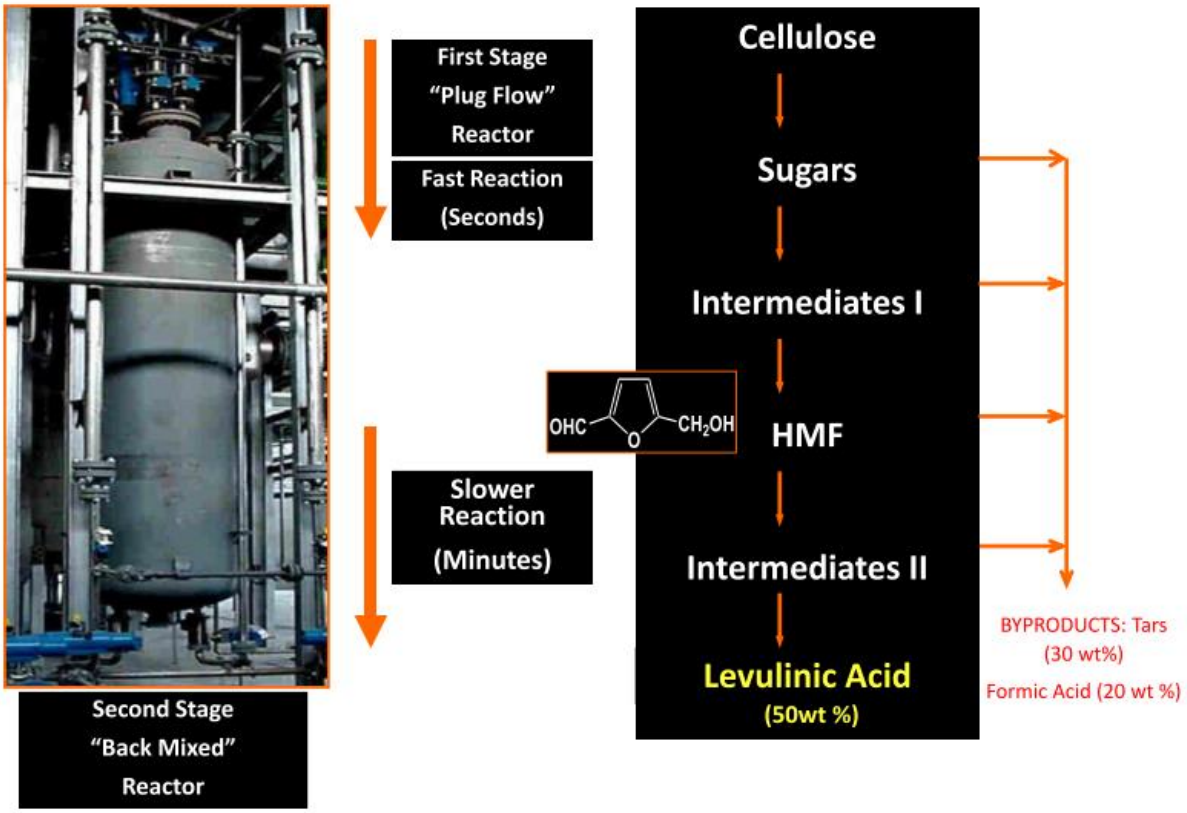

Figure 4: The Biofine process[7]

Glycerol

Also glycerol can potentially be synthesised from carbohydrates but it mainly derives from natural triglycerides as a by-product in the bio-diesel production[8]. With the rising profit of biodiesel caused by governmental subsidizing policy, a considerable amount of glycerol flooded the market[9], causing a substantial drop in price[10]. New applications are thus to be found urgently.

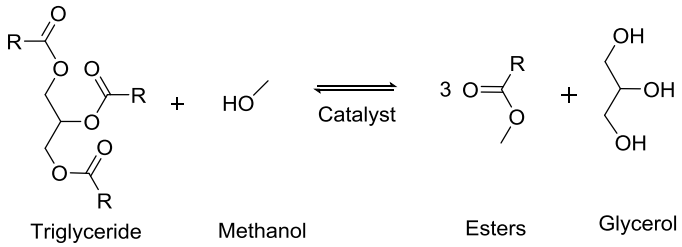

Figure 5: Production of biodiesel by transesterification of natural triglycerides

Glycerol reacts in a multitude of ways including oxidation, direct polymerisation or dehydration. It is also added as a pure substance into cosmetics, baking goods and drugs.

Allyl alcohol is one of its potential derivatives, which is currently obtained from fossil-sourced propene. Several ways exist to dehydrate glycerol in order to obtain allyl alcohol[11]. Amongst them, the dehydration via formic acid[12] is particularly interesting because formic acid is a by-product of many reactions, as for example the synthesis of levulinic acid described above.

Phenols

In addition to these platform chemicals, deriving from carbohydrates, lignin should also be mentioned as a feedstock. Indeed, many industrial processes like tobacco or cotton manufacturing use only the cellulosic part of the biomass, discarding the lignin.

Lignin is a valuable source of aromatic molecules, which have been entirely overlooked in the report[5], although they are essential, especially in polymer synthesis.

Indeed, lignin is an oligomer of aromatics, containing a variable amount and type of substituents. It can thus be decomposed by pyrolysis[13], hydrolysis[14] or enzymatic degradation.

The generated phenols strongly depend on the operating conditions[15]. For example, in pyrolysis, at the lower temperature the main products are guaiacol and syringol. These act, then, as significant precursors for the formation of derivatives such as cresol and catechol type aromatics. Also phenol is obtained at very high temperatures to a minimal extent.

Catechol, i.e. 1,2-dihydroxybenzene may as well be obtained from cellulose, more precisely from glucose as described by Frost et Al[16]. This synthesis uses a genetically modified strand of Escherichia Coli to yield an excellent selectivity on the catechol production. This new way makes catechol particularly interesting as a potential platform compound.

Similar to catechol, hydroquinone, i.e. 1,4-dihydroxybenzene, can be obtained by a biocatalytic conversion of glucose via chinic acid[17]. The yield of 87% is very good for a bio-based compound. Hydroquinone is an excellent platform chemical with a wide range of applications for example bisphenol A-free epoxy resins. In contrast to its original synthesis from benzene, a volatile carcinogenic fossil compound, glucose is neither volatile nor toxic and derives from renewable resources. Furthermore, the enzymatic catalysis leads to bland conditions, with a good practicality and simplicity. If this procedure spreads, hydroquinone could become fast one of the most important aromatic platform chemicals of the future.

Finally, resorcinol, i.e 1,3 dihydroxybenzene, is not synthesised but extracted from most types of vegetal resins. Indeed, especially in *Argania Spinosa* it is present in considerable quantities[18]. It would thus provide a revalorisation of the wastes form argan oil production.

3. Epoxy resins

General

Epoxy resin are thermosetting resins which means they are highly crosslinked materials. This structure is formed by reacting one or more polyfunctional molecules, usually enhanced by heat or UV. Highly crosslinked materials generally have good performances, with a high elastic modulus, and excellent thermal and chemical resitance compared to thermoplastics. These properties derive from the crosslinking density; indeed this structure makes thermosets insoluble and infusible. In particular, epoxy resins, have a huge number of applications due to the versatility depending on the cross-linker and filler used. Their name derives from the epoxide groups on their pre-polymer, that confers a high reactivity, allowing to use a wide range of cross-linkers.

Nowadays, 90% of the worldwide production of epoxy resins is based on bisphenol A (BPA) and epichlorohydrin (ECH), which form diglycidyl ether of bisphenol A (DGEBA). DGEBA might self-condensate in the reaction's conditions leading to an oligomer which, depending of the ratio between BPA and ECH, has typically 0 to 12 repetitive units: the so-called pre-polymer.

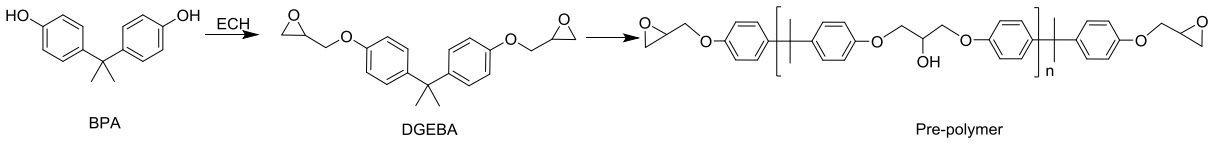

Figure 6: Synthesis of an epoxy pre-polymermeri

In general, a liquid pre-polymer, i.e with n = 0 (thus corresponding to the structure of simple DGEBA) or is preferred as solid prepolymers with more units tend to be very viscous and difficult to handle.

Furthermore, also epoxy resins deriving from bisphenol F or tri(hydroxyphenyl)methane are used for some specialty applications.

The formed prepolymers are then crosslinked, generally using a crosslinking agent. Homopolymerisation, i.e. self-curing without a hardener, is also possible in the case of a pre-

polymer with more than two epoxide groups but require the use of a catalyst to overcome the elevated activation energy.

Crosslinking agents are a more common way to cure the resin allowing also to modulate its properties. These hardeners consist of polyfunctional molecules with more than two groups that will react with epoxides. Epoxides are highly reactive and thus a huge number of cross-linkers exist, amongst which the most widespread are aliphatic and aromatic amines, anhydrides and phenols. It should also be mentioned that for the pre-polymers with n > 0 the hydroxyl generated by the epoxide ring opening, can react too, with a polyisocyanate, for example.

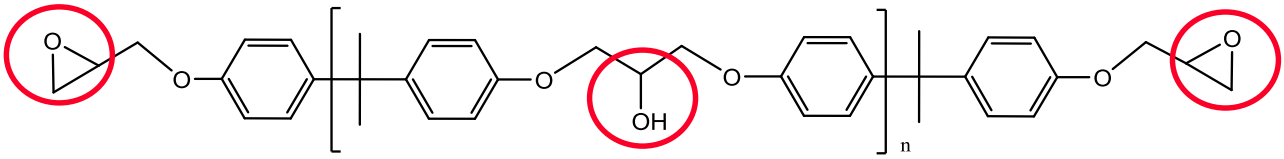

Figure 7: Functional groups on the epoxy pre-polymer

The crosslinking leads to the transformation of short pre-polymers into a solid of, in theory, infinite molecular weight. In the first stages, the reaction kinetics are in chemical control, dominated by the reactivity of the functional groups but at the later stages, the short chains bond together in longer chains with limited mobility. At this point, the reaction becomes diffusion controlled. When all the long chains link each other, the molecular weight is considered infinite.

In general, aliphatic amines offer higher reaction rates and cure even at room temperature, whereas aromatic amines require heat activation. Although curing agents are typically used in small quantities due to the difference in molecular eight compared to the per-polymer, they are in most cases toxic and lead to homogeneity issues during mixing.

Bisphenol A

Bisphenol A is one of the chemicals with the highest production volume in the world. It is manly used in the production of polycarbonates and epoxy resins.

It is synthesised from phenol and acetone, both being from fossil resources, following the reaction as follows:

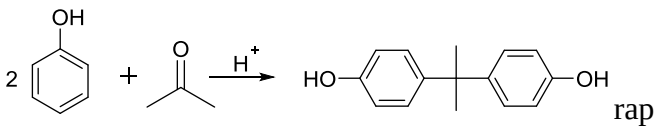

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Figure 8: Synthesis of bisphenol A

Athough, this reactions seems to pertain a high atom efficiency, usually it is carried out in a molecular ratio of 4:1 (phenol:acetone) with a continuous flow hydrochloric acid passing through the system for the whole 8 hours of reaction. The purity is not a critical parameter because epoxy resins typically derive form low molecular weight pre-polymers and the colour is not particularly important. Usually, a purity of 95-98% are satisfactory, the remainders being o-p' and o-o' isomers. This allows to produce at a very low price and in high volume, leading to a wide range of applications of the deriving thermosets as, for example, toys, pipes, water bottles and containers, optical lenses, monomers for dental use.

Due to this wide range of applications of items in everyday life, every consumer in industrialized countries is exposed to a certain amount of bisphenol A. Indeed, it has been found[19] in all fluids of our bodies, including in fetuses, leading to a range of negative health effects.[20,21,22,23,24] The most concerning is its pseudo-hormonal effect, due to its structural similarity with oestrogen causing issues especially in male foetuses and babies. In order to protect citizens from exposure and meet consumers demands, many countries have issued policies to forbid or limit the use of bisphenol A.[25,26] As an example, FDA banned its use in cans for infant formula packaging in July 2013.[27]

Epichlorohydrin

Epichlorohydrin is amongst the most important aliphatic epoxides from a commercial point of view as it represents an excellent platform chemical for countless chemical reactions. Epichlorohydrin is a volatile colourless liquid at room temperature. The combination of chlorine as an excellent exiting group and an epoxide makes it extremely reactive especially with certain metals like zinc and aluminium, strong acids and bases and in general all molecules containing hydroxyls.

Traditionally, it is produced from fossil propene in a multi-step procedure including chlorine gas. This synthesis is still practiced today but should be considered highly dangerous due to the hazardous reagents and the volatility and carcinogenicity of the produced epichlorohydrin.

In the recent years, combined efforts of big chemical companies led to the development of a new pathway to produce epichlorohydrin from glycerol, considered a waste product from their growing biodiesel production, needing re-valorization.

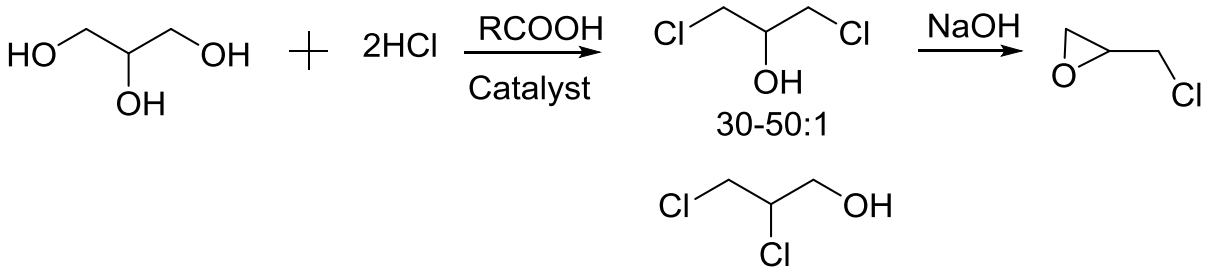


Figure 9: Chemical reactions included in the GTE process[28]

As shown in figure 9, GTE (*Glycerol To Epichlorohydrin*[2928]) is a process using hydrogen chloride, potentially from a waste stream, as a chlorine source, to chlorinate glycerol and yielding a high atomic efficiency. The subsequent elimination leads to the formation of the epoxidic cycle. It is, thus, considered in the most recent publications as the go-to renewable glycidylation agent for bio-based epoxy resins. Several small scale production plants of around 100,000 tons /year have been built, mainly in Asia, by DOW and Solvay (Epicerol©)[30].

However, the health concerns linked to epichlorohydrin cannot be overlooked, even if produced from renewable resources. Indeed, the data collected so far show that epichlorohydrin is extremely harmful to human health and therefore far away from the concepts of sustainable development. It is not only highly corrosive, toxic, flammable and carcinogenic but everybody handling it, undergoes an extremely high risk of exposure as it absorbs through the lungs, skin and gastrointestinal tract. In particular, at room temperature, the volatilized amount in the air at atmostpheric pressure is superior to the maximum safe level for breathing.[31] Adverse effects range from acute respiratory irritation with bleeding and severe edema[32] to neoplasm of the central nervous systems and lung cancer[33].

Recent developments

The health hazards correlated to these two reagents and increasing bans by policy makers led to a skyrocketing amount of alternative solutions for the production of epoxy resins, mainly substituting bisphenol A. Taking away projects using specialty reagents, with a low availability and high prices, like natural vanillin derivatives, the most common approaches are cardanol or epoxidized natural oils.

Vegetable oils[34,35] naturally contain unsaturated bonds which can be either be epoxidized and used directly or hydrolysed after epoxidation and glycidylized using epichlorohydrin. The latter leads to a higher crosslinking density. However, the long aliphatic side-chains work as internal

plasticizers to the material leading to low moduli. The selectivity of these processes being very low, naturally epoxidized oils are growingly interesting, as for example, vernolic acid deriving from *Vernonia Galamensis*[36]. If glycerol is used as a curing agent, these materials are even biodegradable, owing to the formed ester bond.

Cardanol is extracted from cashew nut shell liquid, deriving from the uneatable part of the cashew nut. Its valorisation is crucial as the shell is toxic and otherwise oftern discarded in nature. Cardanol is a phenol with a long aliphatic side chain in meta position, containing a certain amount of unsaturations, as seen in figure 10. These insaturations can be epoxidized and treated in the same way than vegetable oils to yield epoxies.

Figure 10: Cardanol and the typical composition of its side chains[37]

Another approach[37] is an O-glycidylation on the phenolic moiety followed by a polymerization of the double bonds, leading to a pre-polymer that can be cured with a hardener in the same way as DGEBA, as seen in figure 11. However, this epoxy coating is in rubbery state due to flexible side chains of the cardanol. Thus, a strategy[34] is to improve the mechanical properties by just blending a small amount of cardanol based resin (5-10% wt) into a commercial epoxy material as a modifier. Indeed the resulting blends showed higher tensile strength, energy absorption at break and water resistance compared to the unmodified resin.

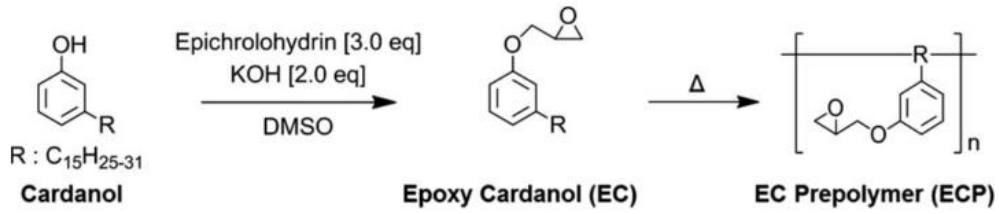


Figure 11: Pathway from cardanol to the epoxy-prepolymer[37]

The main issue with both strategies is that the composition of the side chains depend on the plant, the crop, the season and the growing conditions leading to a low predictability of the resulting resin.

4. Aim of the work

In the recent years, the approach to chemistry has fundamentally changed. Indeed, nowadays, in addition to the successful synthesis of the product, the environmental impact, source of the feedstock and waste management have become just as important. The rising awareness of the negative consequences of the traditional way of producing chemicals that we need to maintain our modern way of life, urged scientists to investigate solutions complying with the standards of chemistry. Also health hazards are not only being reassessed by R.E.A.C.H. but, for the first time, long-term health hazards are considered, in addition to the short-term toxicity. The subsequent rising awareness of the final consumers has increasingly led to consequences also on policy-making, inducing partial or complete bans of certain substances. Bisphenol A is amongst these chemicals that have been used without concern for a long time but after finding it in every body fluid in humans and the confirmation of its pseudo-hormonal effects, are progressively banned all around the globe.

One of its main applications are epoxy resins, 90% of which are composed by bisphenol A and epichlorohydrin, cured by a hardener. Both chemicals show severe health hazards, especially due to the severe carcinogenicity of epichlorohydrin. Furthermore, the generated prepolymers require cross-linkers, which are often toxic and leak from the material with time, to achieve curing. Thus, DGEBA-amine epoxy resins are clearly not adapted for modern chemistry anymore.

Whereas thermoplastic polymers have been widely explored and solutions from renewable resources are starting to flood the market, thermosets remain widely unexplored. This is surprising because they cover a huge range of applications, epoxy resins in particular. Indeed, by varying the crosslinking density or adding fillers their properties drastically change, enabling to use them in almost anything, from adhesives to boats, from boards for electric circuits to aluminum coatings in food cans.

The proposed alternatives are mainly epoxidized vegetable oils, which resins are in rubbery state because they do not contain aromatic cycles that induces the rigidity. They can thus not be used for the same high performance applications but merely added in small quantities in traditional resins, as plasticizers.

The most investigated aromatic solution so far is cardanol, which derives from the uneatable part of the cashew nut. This molecule, too, has a long polyunsaturated side chain that enables

curing but also induces plasticizing effects. Furthermore, carcinogenic epichlorohydrin is used to generate epoxide groups.

In the current work, the aim is to synthesize a fully renewable epoxy resin in a lower environmental impact pathway. Valid alternatives for the use of bisphenol A and epichlorohydrin shall be found and the solution shall comply as much as possible with the standards of green chemistry. These alternatives shall potentially derive from waste products because producing chemicals from plants cannot be ethically sustainable, if it causes famines of the local populations.

Obviously, the proposed solutions should be compared to a bisphenol A-epichlorohydrin based epoxy and demonstrate similar properties, to actually count as an alternative. This means that the chemical structure necessarily contains aromatic moieties, to induce rigidity and lead to comparable final properties.

Several natural phenols have been presented in this chapter but in order to successfully substitute bisphenol A, the structural similarity needed to be higher. Hence, diphenolic acid was investigated.

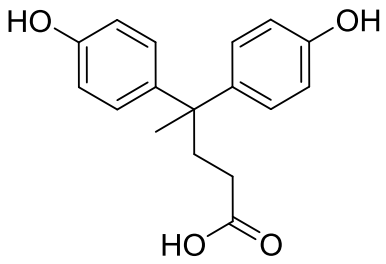


Figure 12: Diphenolic acid

Epichlorohydrin substitutes had not been investigated so far, since finding a renewable pathway for its synthesis from glycerol, leading to its green-washing. However, epichlorohydrin is highly carcinogenic and volatile, causing increased exposure. Thus, new approaches should be investigated in order to either substitute it with a less dangerous or a less volatile compound.

The final properties of the resin shall be thoroughly analysed, to allow a real comparison with the currently used systems. Only in this way, adequate applications can be proposed and the completely renewable epoxy resin can be used commercially.

CHAPTER 1:

Substituting Bisphenol A:

Synthesis of natural derivatives of diphenolic acid

1. Introduction

The first part of the work was to identify a suitable substitute for bisphenol A. The role of bisphenol-A in epoxy-resin is mainly to enhance resistance and confer rigidity to the final polymer due to the aromatic rings. The two hydroxyls are necessary for the further condensation with the epoxidic molecule. Thus, to replace bisphenol-A, a bibliographic research for molecules containing two hydroxyl groups and preferably a planar cycle has been carried out. A huge amount of researches for natural (or easily obtainable from natural resources) diols have already been made over the last years. The most common approach is epoxidizing unsaturated oils and then hydrolysing them.

As the presence of an aromatic cycle strongly increases the final properties, catechol and resorcinol (an aromatic cycle with two phenolic hydroxyls, respectively in ortho and meta positions) are particularly interesting as they can be synthesised from glucose present in large quantities in some biomass waste and are relatively cheap.

To create a molecule with a higher similarity to bisphenol-A, diphenolic acid is currently investigated. Indeed, it is synthesised by reacting levulinic acid, obtained from cellulose, with two equivalents of phenol. This molecule is interesting due to the excellent atom efficiency of its production of 95%. Furthermore, even the original reaction's conditions are bland, compared with oil-based reactions, and the solvent is water, the greenest solvent.

Diphenolic acid had been originally used in the first epoxy resins and was later on forgotten as it was substituted by the cheaper bisphenol A. But in the recent years major health concerns have been raised as bisphenol A has a pseudo-hormonal effect on the body, playing the role of oestrogen it can cause a severe impact on the organism, especially in males. Moreover, it is produced from acetone and phenol, both from fossil, and thus limited, resources.

The purpose of this first chapter is to study the possibility of replacing the phenol contained in the diphenolic acid with various phenols of natural origin such as catechol, resorcinol, m-cresol and guaiacol (i.e. 1,2-dihydroxybenzene, 1,3-dihydroxybenzene, 3-methylphenol and 2-methoxyphenol). As previously described, these phenols may be obtained by depolymerization [38] or pyrolysis of lignin that would otherwise be discarded.

Catechol, guaiacol and m-cresol can be obtain in various ways from lignin, which is a waste product from Tobacco and sludge from paper production. These phenols may in fact be obtained by depolymerization [38,39] or pyrolysis [40] of lignin that would otherwise be discarded. Catechol

may also be obtained from glucose, as well as resorcinol. However, resorcinol mainly derives from almost any kind of natural resins, with a particularly high content in *Argania Spinosa*,[18] *i.e.* natural argan oil.

These diphenolic acids were synthesized and thoroughly analysed in order to accurately determine their structure. In a second step, the DPAs were reacted with epichlorohydrin in order to obtain an idea about their reactivity.

2. Synthesis of the diphenolic acids

Theoretical considerations

To examine the possibility of using natural phenols instead of fossil phenol, diphenolic acids (DPA) were synthesised with four different natural phenols, namely m-cresol, guaiacol, catechol and resorcinol, in the same experimental conditions as in the original patent.[41] All the isomers were thoroughly analysed as the position of the aromatic hydroxyl strongly affects the properties of the final polymer.

Indeed, in order to yield a product leading to a polymer similar to the one deriving from bisphenol A, it is essential that the hydroxyls on the aromatic ring are at the outmost positions of the DPA derivatives, i.e. in para of the attached acid chain, deriving from levulinic acid. [For a better understanding, in the whole thesis, the denomination ortho, meta and para, will always be used referring to the position of bonding of the aliphatic acid chain on the aromatic].

As the natural phenols all have two substituents, several isomers are expected, depending on the most stable positions owing to mesomeric effects, as depicted by the mechanism, shown in figure 1.1.

As a reference, the original synthesis was carried out with phenol. Considering the strong electron-donating effect of the hydroxyl group, the ortho and para positions are activated leading to three potential isomers: p-p'DPA, o-o'DPA and p-o'DPA.

Bearing in mind that the other phenols present two substituents, a combination of the electronic effects can only give us a hint about the final product, as also steric effects play an important role.

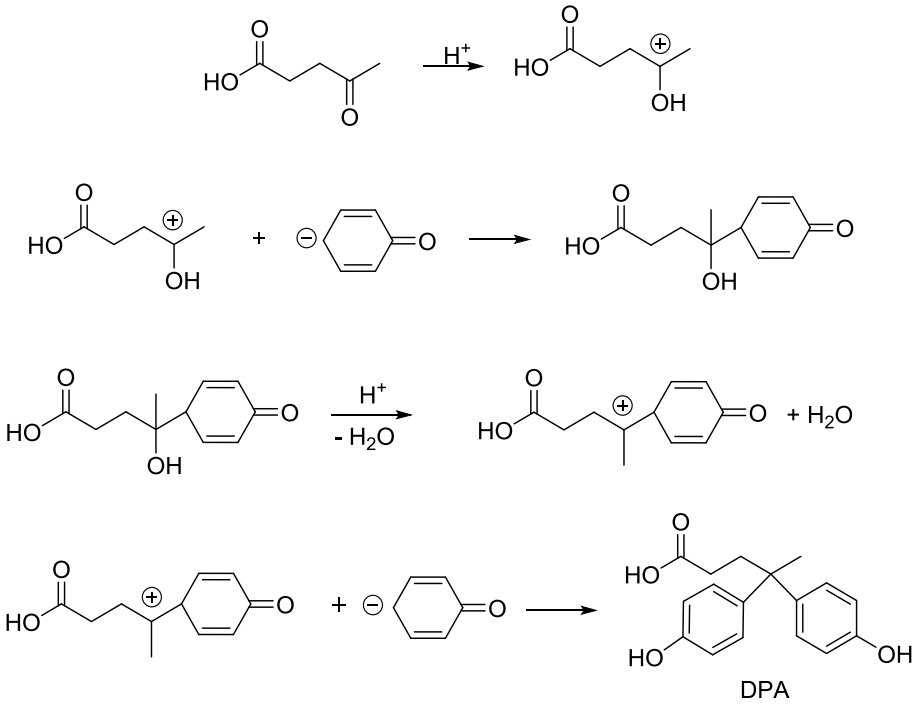


Figure 1.1: Mechanism of the DPA synthesis

Synthesis of the DPA from phenol

By carrying out the synthesis, we wanted to verify the experimental results of the synthesis from 1960s and determine the present isomers, as the state of technology at that time might not have allowed an unequivocal determination. The three potential isomers, as discussed previously, are represented in figure 1.2.

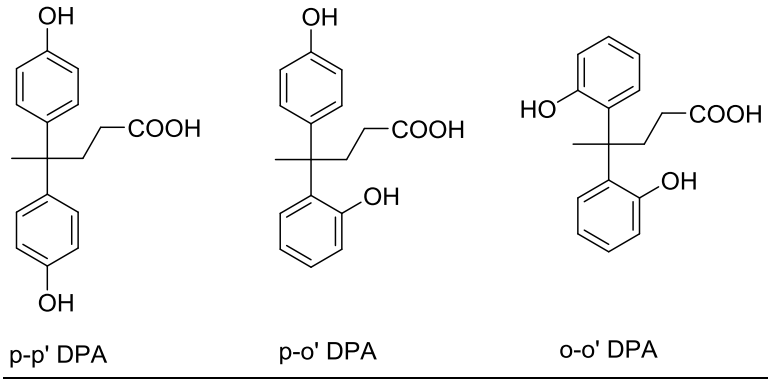
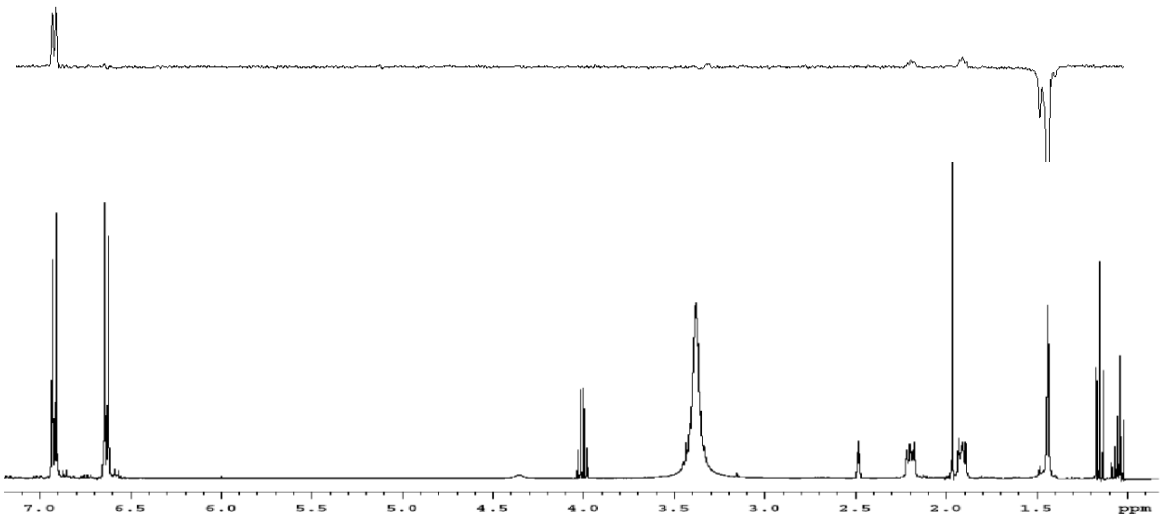


Figure 1.2: Potential isomers formed in the reaction between levulinic acid and phenol

^{1}H-NMR and the Nuclear Overhauser Effect (NOE), which correlates peaks which are close in space independently of chemical bonding, were used to thoroughly characterize the structure[42]. From the ^{1}H-NMR, it is obvious that the main product is the desired p-p' DPA, clearly indicated

by the distinctive pattern of the pair of doublets in the aromatic region (6.63 and 6.95 ppm) since ortho and meta di-substituted benzenes display much more complex patterns. Indeed, the o-o' DPA gives 4 complex aromatic signals, meanwhile the p-o' DPA having two different aryl group bonding to the central carbon gives 4 complex aromatic signals for the o'-hydroxy phenyl group and 2 doublets for the p-hydroxy phenyl group.

In order to determine the source of the residual peaks in the aromatic region, as seen in spectrum 1.1, the NOE effect was exploited, irradiating the methyl signal at 1.45 ppm. The hypothesis being twofold, either the presence of residual unreacted phenol or the presence of other isomers, with their methylic proton signals overlayed by the peak of the p-p'-isomer. Since the NOE effect reaches a spatial distance of up to about 4 Å from the irradiated atom for the p-p' DPA, the effect is expected to the doublet (d) of the ortho aromatic signal with a J coupling of 8.4 Hz. On the contrary, in the o-o' DPA, the only aromatic signals would be a dd signal with a big J coupling of around 8 Hz and a small J coupling of 1-2 Hz. At last, the p-o' DPA hypothetically shows two different ortho aromatic signals : a d and a dd in a 2:1 ratio. As only one doublet at 6,95 ppm, deriving from the p-p' isomer is detected, this allows to state that the reaction has a selectivity of 100% towards the p-p ' isomer, assigning the remaining peaks to residual unreacted phenol.



Spectrum 1.1: ^{1}H-NMR spectrum of DPA from phenol, in DMSO-d6 (TMS as reference) and NOE spectrum, proton at 1.45 ppm irradiated

Synthesis of the DPA from m-cresol (DPAM)

m-Cresol is a phenolic compound, substituted with a methyl group in meta of the hydroxyl. Both groups have an ortho/para activating effect leading to three potential positions for the condensation with levulinic acid, as shown in figure 1.3. Nevertheless, the position between the

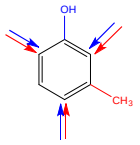


Figure 1.3: m-Cresol

two groups seems improbable, because of steric hindrance. Thus, three different isomers are expected: p-o'm-cresol DPA, p-p' m-cresol DPA e o-o' m-cresol DPA [referred to the position of the hydroxyl].

At the end of the reaction, the product was purified to yield 25% of a mixture of three isomers, which have been characterized by various NMR techniques namely ^{1}H-NMR and NOE NMR.

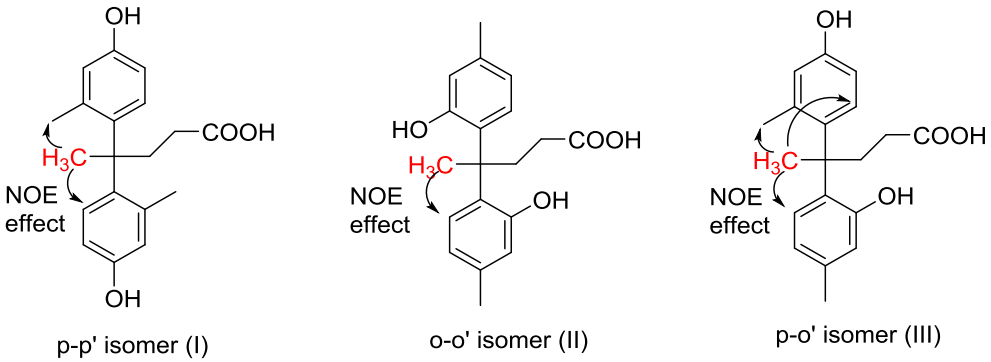


Figure 1.4: Potential isomers formed in the reaction between levulinic acid and m-cresol

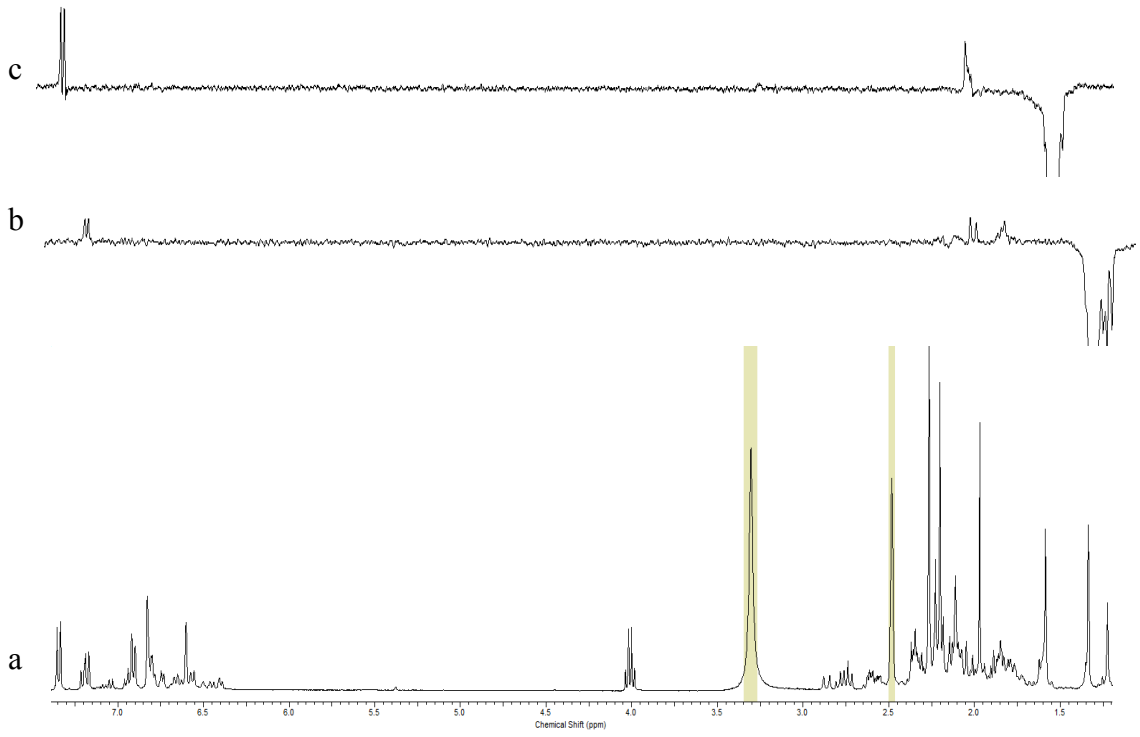
In the ^{1}H-NMR, three singlets are visible in the aliphatic zone at 1.23 ppm, 1.33 ppm and 1.58 ppm and can easily be assigned to the methyl group linked to the central quaternary carbon. Thanks to NOE, these peaks could be accurately assigned to the p-o', p-p' e o-o' isomers, respectively.

Indeed, when irradiating the peak at 1.58 ppm in a NOE experiment, only two peaks are observed, one at 2.10 ppm corresponding to a methylene group of the central aliphatic chain and one aromatic peak at 7.34 ppm. The absence of other peaks in the aliphatic region demonstrated that the peak at 1.58 ppm corresponds to compound o-o' m-cresol (II). As

depicted in figure 1.4, this compound is the only isomer that does not present an aromatic methyl group close enough to the irradiated methyl, to be reached by the NOE effect.

In order to distinguish between the two structures containing at least one methyl group in ortho, i.e. the p-p' and p-o' isomers, an additional NOE experiment was carried out, irradiating the peak at 1.33 ppm this time. The peaks observed are, in addition to the methylene of the central aliphatic chain, a peak at 1.87 of the aromatic methyl and an aromatic proton at 7.19 ppm. Excluding the non-symmetric p-o' isomer that gives two different aromatic protons in addition to the aromatic methyl signal, this compound was assigned to the p-p' m-cresol isomer. Hence, the singlet at 1.23 ppm corresponds to the p-o' isomer (III).

The proportions of the three isomers are thus 47% of compound (II), 34% of compound (I) and 19% of compound (III), from the integrals in the aliphatic region of the ^{1}H-NMR.



Spectrum 1.2: NOE spectra of m-cresol DPA, irradiating the protons at 1.58 (c) and 1.33(b) ppm respectively, altogether with its ^{1}H-NMR (a) in DMSO-d6 (Residual solvents are marked to avoid confusion)

Synthesis of the DPA from guaiacol (DPAG)

Guaiacol is a natural phenol, which is derived from lignin by depolymerisation or by bacterial degradation. Its extraction has been extensively studied[14,13,43] and can be obtained in very

"green"/bland reaction's conditions.[44] Indeed, in pyrolysis of lignin, guaiacol is often the first generated phenol[15], acting as a precursor to cresols and catechol.

Guaiacol presents a methoxy group in ortho of the hydroxyl and as both groups are ortho/para orienting, all of the available positions on the aromatic ring are activated, leading to 16 potential isomers.

However, from the ^{1}H-NMR, shown in spectrum 1.3, the condensation on the position in ortho of each substituent is immediately excluded due to the absence, in the aromatic region, of peaks with the typical multiplicity of three adjacent aromatic protons. Thus, three isomers have potentially formed, as shown in figure 1.5.

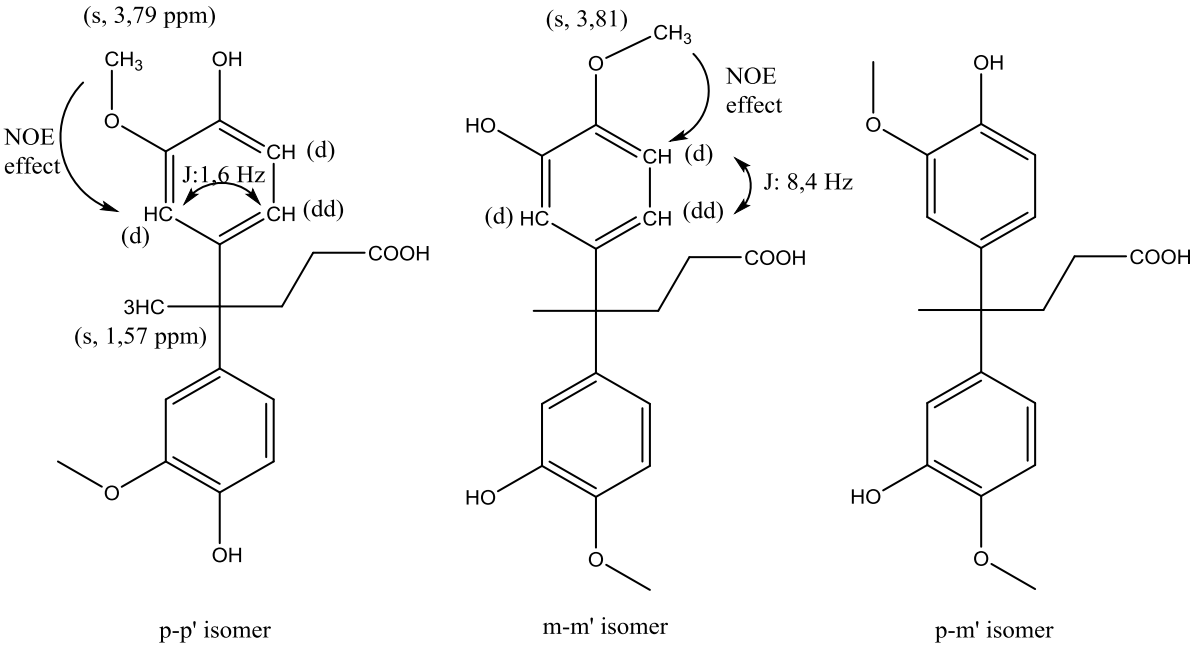


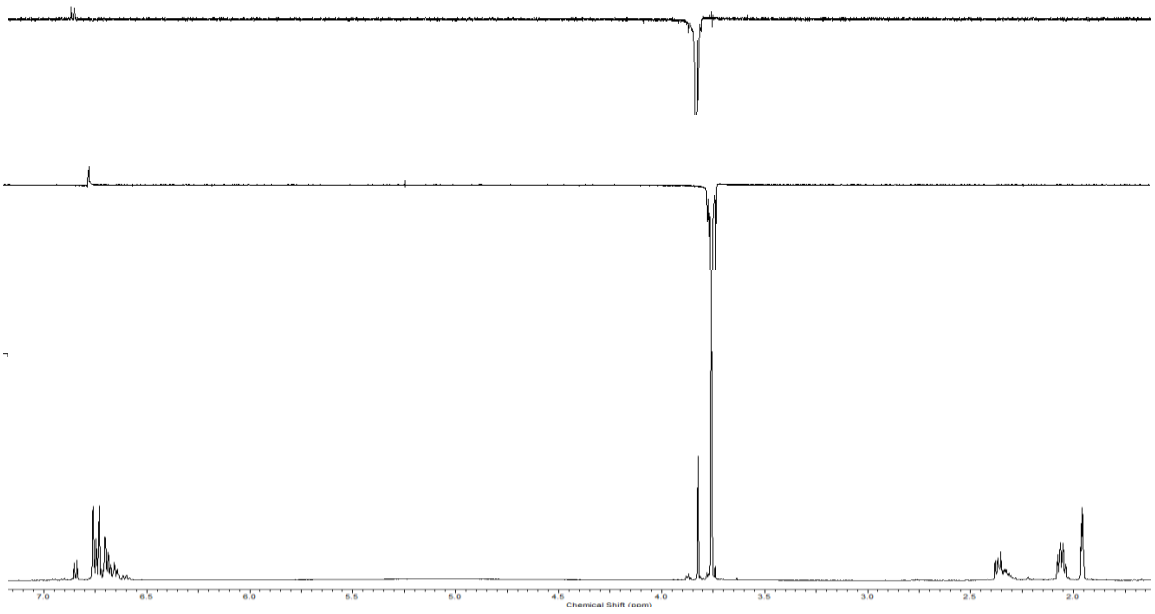
Figure 1.5: Isomers formed in the reaction between levulinic acid and guaiacol

Based on the spectrum of the previous compound, the three singlets at 1.53, 1.54 e 1.57 ppm, are potentially assignable to the methyl groups linked to the central quaternary carbon. Furthermore, the peaks at 3.79 and 3.81 ppm are assigned to the protons of the methoxy groups. This discrepancy between the number of methyl signals and the number of methoxy signal leaves broad space for interpretation. Indeed, the p-p' and m-m' isomers would both generate one signal from the methoxy whereas the p-m' isomer should give two signals of the same height. Thus, either this isomer is absent or the peaks are overlaid with one or both signals of the other isomers.

The main product with 64% of selectivity corresponds to the p-p' guaiacol DPA as determined by NOE spectroscopy, depicted in spectrum 1.3. Indeed, by irradiating the major methyl proton at 1.57 ppm the singularity of the response in the aromatic region demonstrates the symmetry of the molecule. Furthermore, by irradiating the methoxy proton at 3.79 ppm corresponding, to the methoxy group of this same molecule, a simple doublet with a coupling constant of 1.6 Hz, typical of the aromatic coupling of protons in meta is highlighted, demonstrating that the methoxy is in the meta position and the structure can be attributed to the p-p' isomer.

On the contrary, when irradiating the proton at 3.81 ppm, the sole adjacent aromatic has a coupling constant of 8.4 Hz, typical of an aromatic coupling of two aromatic protons in ortho, which is a situation present only in the m-m' isomer, as the p-m'isomer would give two aromatic signals, one for each aromatic cycle.

This confirms that the selectivity of the volitional p-p' isomer is 64% and the only othe isomer present is m-m'.



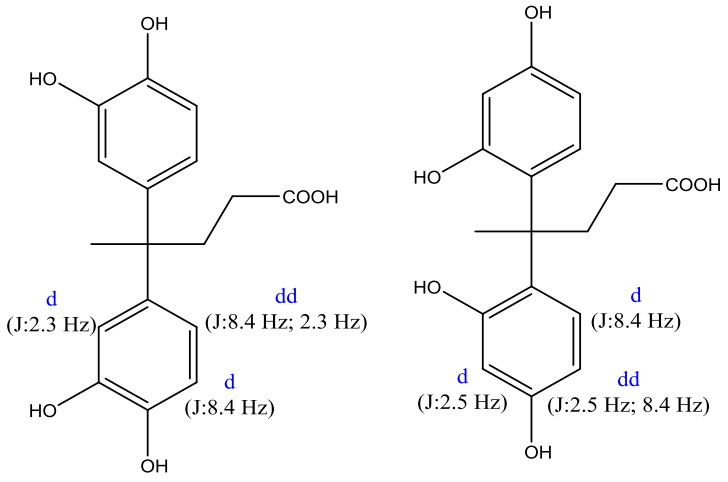
Spectrum 1.3: 1H-NMR spectrum of DPAG in CD_3CN and NOE spectra of guaiacol DPA, irradiating the protons at 3.81 and 3.79 ppm respectively

Synthesis of the DPA from catechol (DPAC) and resorcinol (DPAR)

1,2-dihydroxyphenol (catechol) is equally activated in all available positions of the aromatic ring by mesomeric effect, which are two by two equal by symmetry. Thus, potentially three isomers are generated. Nevertheless, the aromatic region of the ^{1}H-NMR demonstrates the presence of only one isomer, depicted in figure 1.6a.

Indeed, in spectrum 1.4, the two doublets (coupling constants: 2.3 Hz and 8.4 Hz) and one double doublet with the same coupling constants are easily attributed to the p-p'isomer as shown in figure 1.6a., as a condensation in the other position, adjacent to one hydroxyl, would generate three double doublets. The remaining peaks were assigned to unreacted catechol, by comparison with the pure reagent. This leads us to a yield of 55% of pure product.

In 1,3-dihydroxyphenol (resorcinol), on the contrary, the effects of the two hydroxyls sum up to strongly activate the ortho positions around the substituents. However, the position between the two substituents is potentially inhibited by steric hindrance. Indeed, based on our previous findings and the analysis of the aromatic region of the ^{1}H-NMR, the presence of only one isomer, the p-p' resorcinol DPA, was confirmed by the characteristic d, d, dd pattern, observed in spectrum 1.5, obtaining thus, the wanted compound with a yield of 83%



a) Catechol DPA b) Resorcinol DPA

Figure 1.6: DPA from catechol and resorcinol

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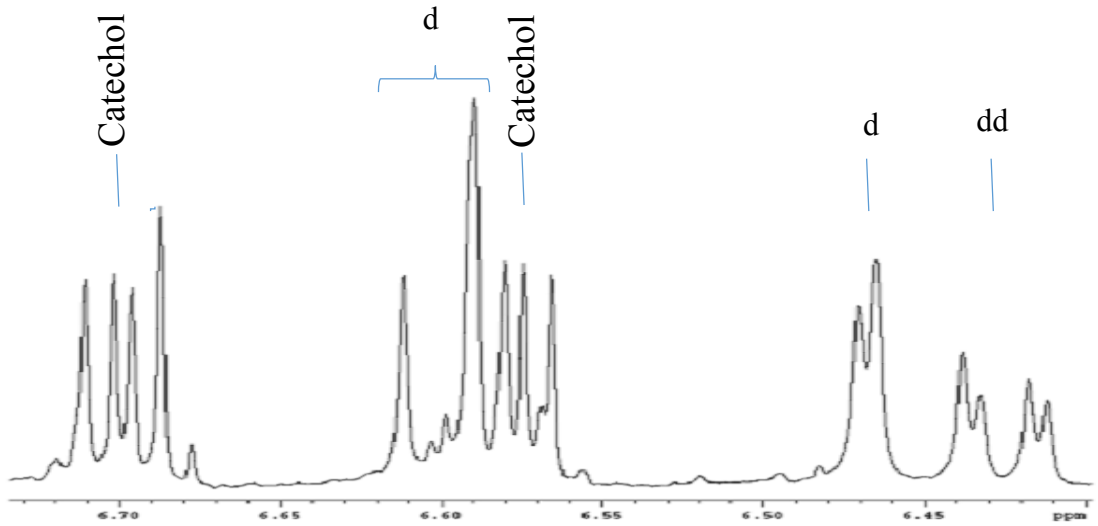
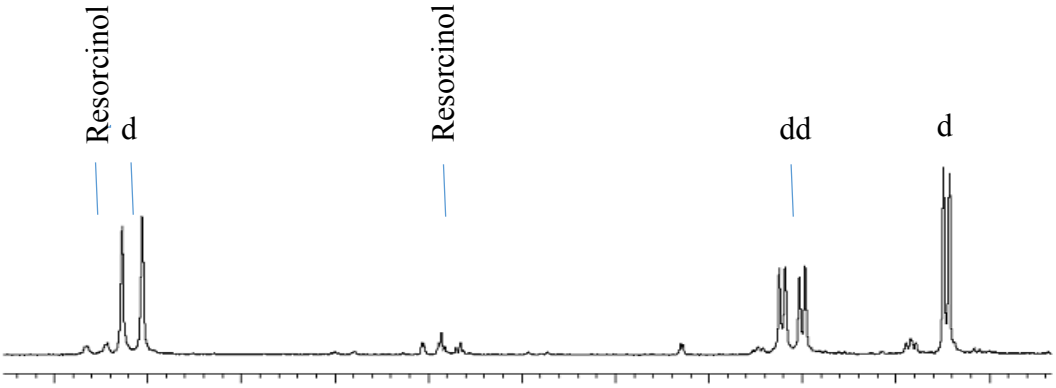


Spectrum 1.4: Detail of the aromatic region of the 1H-NMR spectrum of catechol DPA



Spectrum 1.5: Detail of the aromatic region of the 1H-NMR spectrum of resorcinol DPA

3. Optimisation of the purification

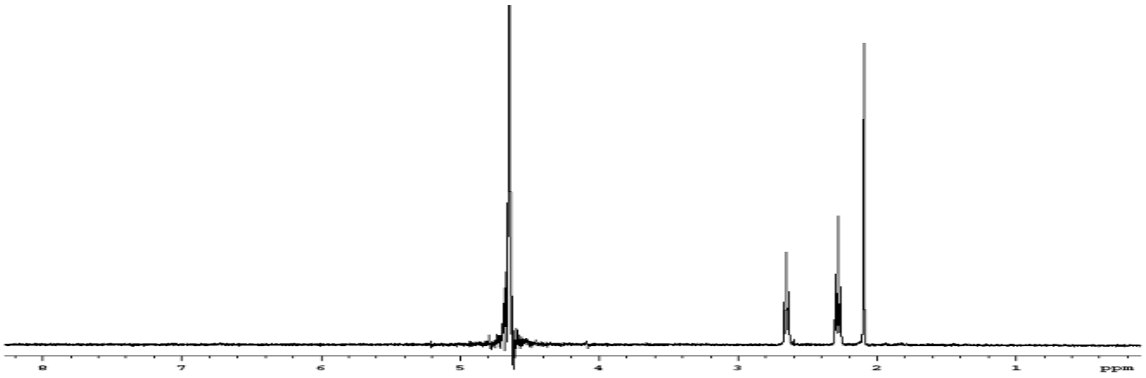
The obtained crude products were purified following the original patent of diphenolic acid from phenol[41], which suggest a sequence of extractions in acid and alkaline medium.

The reaction is carried out in highly acid water. By extracting in water and ethyl acetate several times, levulinic acid, which is highly soluble in water (657 g/L at 25 ^{o}C)[45] should be eliminated in the aqueous phase whereas phenolic compounds are expected to remain in the organic phase. After separation, a saturated solution of sodium bicarbonate is added, deprotonating the diphenolic acid making it thus water soluble; the phenol remaining in ethyl acetate. After

removing the organic phase, an acidification and extraction with diethyl ether allows to easily dry off the solvent and obtain a pure product.

Considering the requirements of industry, this sequence is longish and complicated, leading to a substantial loss in product. Especially for the diphenolic acid from resorcinol and catechol, purification represents a considerable problem as the reagents do not have the same solubility features as the original phenolic reagent and the resorcinol DPA shows scarce solubility in ethyl acetate, which leads to product crashing out during extraction and thus loss of yield.

First, we analysed all the different phases of extraction to test our assumptions. Indeed, in the waters of the first aqueous extraction of the DPA from phenol, the sole presence of levulinic acid is clearly visible in Spectrum 1.6 by the presence of two triplets at 2.58 ppm and 2.31 ppm and a singlet at 2.19 ppm on the ^{1}H-NMR.



Spectrum 1.6: ^{1}H-NMR spectrum of the first aqueous phase in D_2O

Also the organic phase, after adding the sodium bicarbonate, shows, as predicted, the presence of only phenol. This allows to consider that these two phases could be recycled into the process, as the separated chemical are the pure reagents.

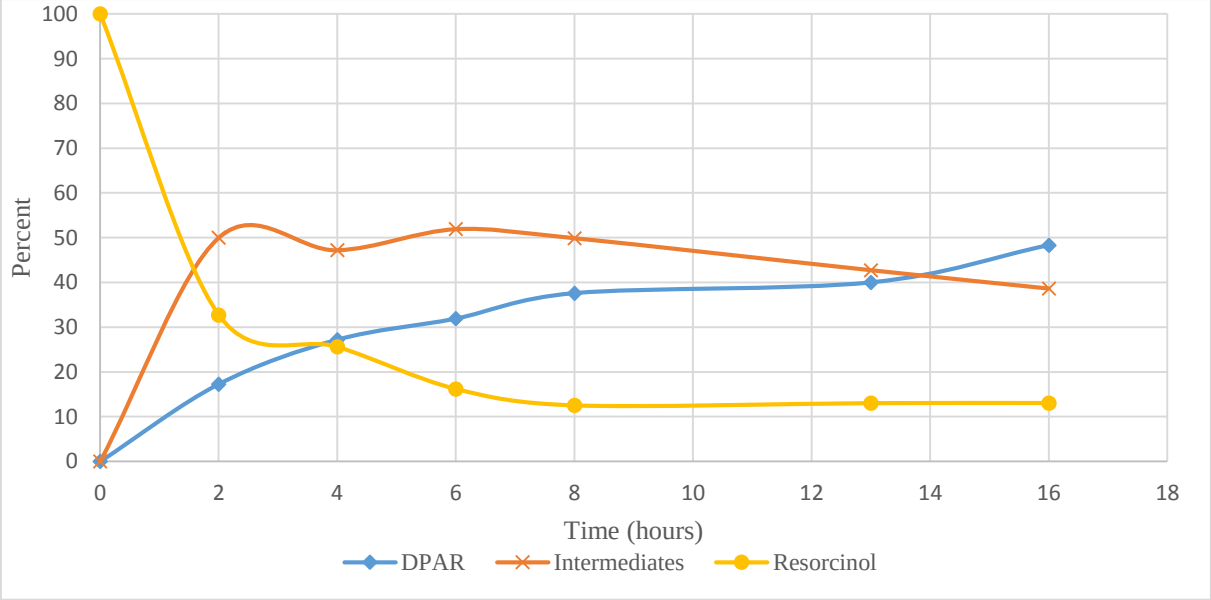
These considerations are valid for the synthesis of DPA with phenol but, as substituted natural phenols are used, their solubilities in water change. Whereas guaiacol and m-cresol are comparable with phenol with 15 g/L[46] and 23 g/L[46] against 84 g/L,[45] respectively, at 20 °C, catechol has a solubility in water of 450 g/L[45] and resorcinol even 1400 g/L[47].

For the latter two, it was thus considered to substitute the complete purification sequence by just extracting once in a sufficient amount of organic solvent and then washing with abundant water to remove the residual phenols as well as levulinic acid. This was of increased interest as these two presented the problem of substantial amounts of catechol and resorcinol remaining in the "purified" product. Indeed, the pKa of catechol (9,48) and resorcinol (9,44) are lower than

the one of phenol (9,96). Thus, during the deprotonation of the diphenolic acid with sodium bicarbonate, they are extracted in the aqueous phase, just like the product.

This approach, of washing with distilled water until clear, worked well for catechol, which was clearly visible on the ^{1}H-NMR along with the levulinic acid and allowed complete removal and a pure product.

For resorcinol on the other hand, the presence of a number of intermediates, along with strong inter-molecular bonds, leading to difficulties to fully remove the residual resorcinol, urged us to find a new solution. Indeed, on Graph 1.1, it is easy to observe that 65% of the present resorcinol reacts within the first two hours, mainly generating intermediates, which then, slowly become DPA.



Graph 1.1: Compounds present versus time (from ^{1}H-NMR)

Furthermore, during purification, due to hydrogen bonds and a multitude of steps, approximatively 25% of product was lost.

$FeCl_3$ is commonly used to prove the presence of phenolic compounds in solution[48]. It is a Lewis acid, which, in water, is able to form stable complexes with certain deprotonated phenolates, freeing a chlorine ion. This reaction usually is accompanied by a visible change in colour from transparent to dark green, which allows to assess the presence of resorcinol and some other phenolic compounds.

This phenomenon was exploited to completely purify the DPAR. Indeed, when adding $FeCl_3$ to the previously dried solution in n-butanol, the resorcinol and all intermediates chelate, whereas the DPAR remains in solution and can be extracted as a pure product.

The amount in $FeCl_3$ was accurately chosen to assure an excess to the resorcinol in the solution. Thus the stoichiometric amount (1:3 n $FeCl_3$: n_{ini} resorcinol) compared to the initial amount of resorcinol was added. After drying the reaction mixture, it was thus solubilized in the minimum amount of n-butanol and successively, $FeCl_3$ was added. After one hour at room temperature and one hour at 70°C, to make sure the activation energy of complexation is overcome, the mixture is extracted with a considerable amount of water and dichloromethane. ^{1}H-NMR analysis demonstrate that only pure DPAR is present in dichloromethane. Finally, this phase is washed three times with a saturated brine to remove potential residual $FeCl_3$ and then with distilled water. The yield of the extraction reaches 97% in this way.

We cannot overlook the fact that $FeCl_3$ exhibits certain health hazards, as most Lewis acids and is thus generally not appropriate for the use in "green" chemistry. However, in our case, the aqueous phase can be purified by adding NaCl, hence, safely regenerating the $FeCl_3$. Furthermore, the remaining aqueous phase contains only resorcinol and intermediates and can potentially be reintegrated into the next reaction batch, further increasing atom efficiency. This is thus the ideal purification for the DPAR.

4. Reactivity tests with epichlorohydrin

After the synthesis and characterization of the fully natural diphenolic acids, testing the similarity with bisphenol A was a major scope. Although the aim of this work includes also the substitution of epichlorohydrin, a carcinogen, tests were carried out with the latter to assess the etherification reaction in comparison with bisphenol A.

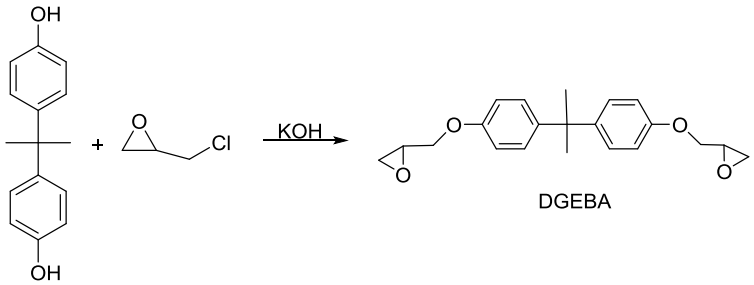


Figure 1.7: Reaction scheme of the glycidylation of bisphenol A with epichlorohydrin

On the contrary of bisphenol A, the natural diphenolic acids contain several substituents on the aromatic ring which, by their electronic and steric effects, inhibit or activate the etherification

of the aromatic hydroxyls. Furthermore, certain diphenolic acid derivatives, namely guaiacol DPA and m-cresol DPA, are a mixture of several isomers, making characterization complex. Finally, the outcome of the reaction between epichlorohydrin and bisphenol A strongly depends on the reaction conditions ranging from a barely glycidylized bisphenol A to a pre-polymeric chain with 10 or more repetitive units. Thus, we carried out two different glycidylations: one in rather bland conditions and the other one following the method of St. Clair[49]. For comparison, also bisphenol A was reacted in the same conditions as a reference.

First, the reaction was carried out with bisphenol A. The reaction takes place mainly at room temperature and 50ºC in alkaline water. At the end of the reaction, the product is a white rubbery compound, insoluble in water.

As the reaction is carried out in highly alkaline water, and epichlorohydrin readily hydrolises, especially at high temperatures, we can assume that all the epichlorohydrin was degraded. Indeed, epichlorohydrin has a half-life of 62 hours in alkaline medium[50] and the velocity of hydrolysis increases seven-fold at only 40ºC. As the reaction mixture was maintained at 50ºC for one hour and the NMR analysis was carried out 24 hours after the reaction, we can safely assume, that only a negligible amount of epichlorohydrin is present and that all the peaks in the epoxidic area can be assigned to glycidylized products. This was confirmed by the presence of several large multiplets at 3.4 and 4 ppm in the ^{1}H-NMR spectrum of the aqueous phase, which were assigned to glycerol, the degradation product of epichlorohydrin. These peaks were also present in the organic phase, to small extent.

Considering the complex characterisation and the fact that the products are mixtures of mono-, di-, tri- (tetra- and penta- for DPAR and DPAC) -glycidylized DPA derivatives as well as potentially dimers and oligomers, it was non-essential to separate all the products, and determine their precise structure. The important information is the percentage of the present hydroxyls on the molecule that had undergone glycidylation. In fact, in industry, for epoxy resins, the characteristic value is the epoxy equivalent weight (EEW), which corresponds to the weight of resin containing one mole of epoxide groups, independently of the composition of the single molecules. The epoxy equivalent weight is commonly determined by titration but can also be, in a precise way, be found by ^{1}H-NMR [51], by comparing the integrals of the peaks in the epoxidic region (2.5-3 ppm) with the ones in the aromatic region. This method is more precise, as residual salts from the etherification reactions are not mistakenly included, but requires the knowledge of the molecular mass of the product. Thus, in our case, we decided to compare the percentages of glycidylized hydroxyls and determine the EEW, assuming that no

dimerisation and oligomerisation had occurred, for information. In some cases, the differentiation between the external epoxidic methylene and the "internal" methanetriyl group of the epoxide was difficult due to superposition of several peaks. These issues were solved thanks to selectively irradiating certain peaks in a NOE experiment allowing to easily assigning certain peaks in case of doubt.

Furthermore, due to a huge number of peaks in the area, it was preferred to verify the success of the reaction by DEPT-NMR, which allows to easily assign primary, secondary and tertiary carbons. The presence of two negative methylene signals between 40 and 80 ppm, as for example at 44 and 69 ppm for the glycidylized resorcinol DPA, one assigned to the epoxidic methylene and one to the methylene adjacent to the aryl ether, are a clear sign that the product is an etherified DPA.

As seen in table 1.1, the yields of glycidylation of guaiacol, catechol and resorcinol were comparable to the ones obtained with bisphenol A in the same conditions, namely 32% of hydroxyls glycidylized.

Table 1.1 : Percentage of hydroxyls glycidylized in the bland conditions

PHENOLIC REAGENT	PERCENTAGE HYDROXYLS GLYCIDYLIZED (%)	EEW (g/mol)
m-Cresol	16	710
Guaiacol	63	239
Catechol	36	233
Resorcinol	30	404

The second glycidylation was carried out in conditions closer to industrial production, by following the method of St. Clair. The ratio between epichlorohydrin and DPA derivative is in large excess of epichlorohydrin (5:1 nECH : neqOH), which also works as the reaction medium. The temperature of 100°C for one hour strongly increases the reaction kinetics, leading to all kind of the above stated products and also a certain amount of dimers or oligomers, which were not generated in the bland conditions.

Table 1.2 : Percentage of hydroxyls glycidylized with the second method

PHENOLIC REAGENT	PERCENTAGE HYDROXYLS GLYCIDYLIZED (%)	EEW (g/mol)
m-Cresol	49	269
Guaiacol	70	220
Catechol	59	163
Resorcinol	54	174

In comparison with the percentage of 89% yielded with bisphenol A, all of these values seem low, but it should not be forgotten that the DPA from catechol and resorcinol present five reactive hydroxyls whereas bisphenol A contains only two. By comparing the EEW, it is clear that the resorcinol DPA has exactly the same EEW (174 g/mol) as the best grade of industrial diglycidyl ether of bisphenol A whereas catechol has even more available reactive groups.

Thus, these two seem the most interesting for substituting bisphenol A.

5. Experimental

General

All reagents and solvents were purchased from Sigma-Aldrich and used without purification. The reaction products were analysed by ^{1}H-NMR and ^{13}C-NMR spectra as well as bidimensional spectra acquired on Varian spectrometers, namely Varian *"Gemini 300",* Varian "Mercury 400" and Varian "Inova 600" operating at 300 MHz, 400 MHz and 600 MHz, respectively. Samples were prepared in appropriate deuterated solvents and the chemical shifts were calibrated to the internal TMS added as reference. This statement is valid for all the experimental work done for this thesis.

Synthesis of diphenolic acid derivatives

General procedure

Into a 100 mL three-necked round bottom flask provided with a magnetic stirrer, a reflux condenser and a thermometer was introduced 7.2 mL (0.085mol) of levulinic acid, 0.17mol of the desired phenol (phenol, m-cresol, guaiacol, resorcinol or catechol), 18 mL of hydrochloric acid (37%) and 13 mL of distilled water. The mixture reacted at 85-95 °C for 48 hours. It was then extracted with ethyl acetate. Then a solution of sodium bicarbonate was added and washed with several times with ethyl acetate until the latter was clear. The aqueous phase was neutralized using a 10% wt solution of hydrochloric acid and finally extracted with diethyl ether. The analysis were carried out after evaporation of the solvent under reduced pressure. In the case of the presence of more than one isomer, only the chemical shifts of the p-p'isomers are stated, as these isomers are the only potentially substituting DPA.

4,4-bis(4-hydroxyphenyl)pentanoic acid

The reaction was carried out in the above mentioned conditions using 16.5 g of phenol and yielded 57% of pure product.

^{1}H-NMR (400 MHz, in DMSO-d6) , δ (ppm): 1.45 (s, 3H, $-CH_3$); 1.90 (t, 2H, $-CH_2-$); 2.19 (t, 2H, $-CH_2-$); 6.63 (dd, 4H, Ar-H); 6.95 (dd, 4H,Ar-H)

4,4-bis(4-hydroxy-2-methylphenyl)pentanoic acid

The reaction was carried out in the above-mentioned conditions using 18 mL of m-cresol and yielded 25% of a mix of three isomers of which 34% corresponds to the above-stated p-p'isomer.

^{1}H-NMR (400 MHz, in DMSO-d_6) , δ (ppm): 1.58 (s, 3H, −CH_3); 2.10 (m, 2H, −CH_2−); 2.25 (m, 2H, −CH_2−); 2.26 (s, 6H, Ar−CH_3); 6.74 (d, 2H, Ar-H); 6.93 (dd, 2H, Ar-H); 7.34 (d, 2H, Ar-H)

4,4-bis(4-hydroxy-3-methoxyphenyl)pentanoic acid

The reaction was carried out in the above-mentioned conditions using 18.5 mL of guaiacol and yielded 19% of a mix of two isomers, of which 64% correspond to the above-stated p-p' isomer.

1H-NMR (600 MHz, in CD_3CN), δ (ppm): 1.57 (s, 3H, −CH_3); 2.07 (m, 2H, −CH_2−); 2.18 (m, 2H, −CH_2−); 3.79 (s, 6H, Ar−OCH_3); 6.53 (d, 2H, Ar-H); 6.56 (dd, 2H, Ar-H); 6.79 (d, 2H, Ar-H)

4,4-bis(3,4-dihydroxyphenyl)pentanoic acid

The reaction was carried out in the above mentioned conditions with 18.5 g of catechol. After 48 hours the yield obtained was 70%. The yield of the purified product (I) was 55%.

^{1}H-NMR (400 MHz, in DMSO-d_6) , δ (ppm): 1.38 (s, 3H, −CH_3); 1.92 (t, 2H, −CH_2−); 2.12 (t, 2H, −CH_2−); 6.43 (dd, 2H, Ar−H); 6.48 (d, 2H, Ar−H); 6.61 (d, 2H, Ar−H)

4,4-bis(2,4-dihydroxyphenyl)pentanoic acid

The reaction was carried out in the above mentioned conditions using 18.5 g of resorcinol, After purification the yield was 83% of pure product.

^{1}H-NMR (400 MHz, in DMSO-d_6) , δ (ppm): 1.53 (s, 3H, −CH_3); 1.60 (t, 2H, −CH_2−); 2.00 (t, 2H, −CH_2−); 6.53 (d, 2H, Ar−H); 6.51 (dd, 2H, Ar−H); 7.22 (d, 2H, Ar−H)

Synthesis of the glycidyl ethers

Glycidyl ethers have been prepared in two different ways from all the diphenolic products and from bisphenol A for comparison. The percentage of glycidylized hydroxyles is calculated from the 1H-NMR spectra by comparison between the integral of the aromatic protons and the characteristic signals of the methylenic protons of the epoxide group.

First preparation of the glycidyl ethers

In a 100 mL one-neck round bottom flask, diphenolic acid derivatives or bisphenol A were solubilized in ethanol with 1,1 equivalent for each hydroxyle of potassium hydroxide at room temperature. The salts were dried under reduced pressure for 3 hours at 40°C.

Thereafter, the latter were transferred in a three-neck round bottom flask fitted with a thermometer and a reflux condenser and 2,2 equivalent of epichlorohydrin for each hydroxyle were added. Solvent was water. The reaction mixture was maintained for 30 minutes at room temperature, then heated to 50°C for 1 hour and finally reached 80°C for 10 minutes. After letting it cool to room temperature the product is insoluble in the reaction mixture and is thus filtered and washed with distilled water. Remaining solvents and unreacted epichlorohydrin were evaporated under reduced pressure for several hours. It should be noticed, though, that this purification does not completely remove glycerol, a hydrolysis product of epichlorohydrin. As its peaks do not interfere with the analysis of the products, which only requires the integrals in the aromatic and epoxidic region, no attemps of further purification were made. However, the peaks of glycerol are partially overlaid on the ones of the methylenes adjacent to the epoxides, which will thus, for accuracy reasons, not be stated in the following section.

Glycidyl ether of diphenolic acid from phenol

The glycidyl ether is soluble in water, with a bright orange color. 25% of the hydroxyls are glycidylized.

^{1}H-NMR (600 MHz, in D_2O), δ (ppm): 1.45 (s, 3H, −CH_3); 1.90 (t, 2H, −CH2−); 2.19 (t, 2H, −CH_2−); 2.63 (2dd, 4H, −Epoxy−H_2); 2.81 (2dd, 2H, ester−Epoxy−H_2); 3.18 (m, 3H, H-Epoxy); 3.5 - 4.5 (m, 6H, O−CH_2−Epoxy); 6.63 (d, 4H, Ar−H); 6.95 (d, 4H, Ar−H)

Glycidyl ether of diphenolic acid from m-cresol

The glycidyl ether is soluble in water and dark brown in color. 16% of the hydroxyls are glycidylized.

^{1}H-NMR (400 MHz, in DMSO-d_6), δ (ppm): 1.58 (s, 3H, −CH_3); 2.10 (m, 2H, −CH_2−); 2.25 (m, 2H, −CH_2−); 2.26 (s, 6H, Ar−CH_3); 2.63 (2dd, 2H, ester−Epoxy−H_2); 2.98 (2dd, 4H, ether−Epoxy−H_2); 3.24 (m, 3H, H-Epoxy); 3.5 - 4.5 (m, 6H, O−CH_2−Epoxy); 6.74 (d, 2H, Ar−H); 6.93 (dd, 2H, Ar−H); 7.34 (d, 2H, Ar−H)

Glycidyl ether of diphenolic acid from guaiacol

The glycidyl ether is a dark green solid that is soluble in water. 63% of the hydroxyls are glycidylized.

^{1}H-NMR (600 MHz, in DMSO-d_6), δ (ppm): 1.57 (s, 3H, −CH_3); 2.07 (m, 2H, −CH_2−); 2.18 (m, 2H, −CH_2−); 2.63 (2dd, 2H, ester−Epoxy−H_2); 2.79 (2dd, 4H, ether−Epoxy−H_2); 3.25 (m, 3H, H-Epoxy); 3.79 (s, 6H, Ar-OCH_3); 3.5 - 4.5 (m, 6H, O−CH_2−Epoxy); 6.53 (d, 2H, Ar−H); 6.56 (dd, 2H, Ar−H); 6.79 (d, 2H, Ar−H)

Glycidyl ether of diphenolic acid from catechol

The glycidyl ether of DPAC is a dark green solid in which 36% of the hydroxyls are glycidylized.

^{1}H-NMR (600 MHz, in DMSO-d_6), δ (ppm): 1.38 (s, 3H, −CH_3); 1.92 (t, 2H, −CH_2−); 2.12 (t, 2H, −CH_2−); 2.65 (2dd, 2H, ester −Epoxy−H_2); 2.73 (m, 8H, ether−Epoxy−H_2); 3.25 (m, 5H, −H-Epoxy); 3.86 - 4.29 (m, 10H, O−CH_2−Epoxy); 6.43 (dd, 2H, Ar−H); 6.48 (d, 2H, Ar−H); 6.61 (d, 2H, Ar−H).

Glycidyl ether of diphenolic acid from resorcinol

The glycidyl ether of DPAR is a dark brown solid in which 30% of the hydroxyls are glycidylized.

^{1}H-NMR (600 MHz, in DMSO-d_6), δ (ppm): 1.53 (s, 3H, −CH_3); 1.60 (t, 2H, −CH_2−); 2.00 (t, 2H, −CH_2−); 2.79 (2dd, 2H, ester−Epoxy−H_2); 2.81 (m, 8H, ether−Epoxy−H_2); 3.29 (m, 5H, −H-Epoxy); 3.84 - 4.34 (m, 10H, O−CH2−Epoxy); 6.53 (d, 2H, Ar−H); 6.51 (dd, 2H, Ar−H); 7.22 (d, 2H, Ar−H).

Glycidylation of bisphenol A

The product of the reaction is a white rubber-like solid in which 32% of the hydroxyls are glycidylized.

^{1}H-NMR (600 MHz, in DMSO-d_6), δ (ppm): 1.62 (s, 6H, −CH_3); 2.73 (2H, −Epoxy−H); 2.88 (2H, −Epoxy−H'); 3.34 (2H, −H-Epoxy); 3.77 (dd, 2H, O−CH2−Epoxy); 4.24 (dd, 2H, O−CH’2−Epoxy); 6.81 (dd, 4H, Ar−H); 7.14 (dd, 4H, Ar−H).

Second preparation of the glycidyl ethers

General procedure

In a 50mL three-necked round bottom flask fitted with a thermometer and a reflux condenser, the diphenolic acid derivatives or bisphenol A were heated to 100°C with 5 molar equivalents of epichlorohydrin per hydroxyl. 0,05 equivalents of benzyltriethylammonium chloride per hydroxyl were solubilized in a minimum of water and added using a dropping funnel (in order to avoid contact with volatile and carcinogenic epichlorohydrin). The mixture was maintained under stirring at 100°C for one hour. Four equivalents per hydroxyl of sodium hydroxide were solubilized in water to obtain a solution at 20% wt and another 0,05 neq/hydroxyl of benzyltriethylammonium chloride were added. Using a dropping funnel, this solution was slowly introduced into the reaction mixture.

The emulsion formed was cooled to room temperature under continuous stirring. Distilled water was added and the result extracted 3 times with ethyl acetate. The solvent and remaining volatile reagents were evaporated under reduced pressure. The products are honey-like liquids. The ^{1}H-NMR clearly shows the presence of condensation products that were removed by filtration of the mixture previously solubilized in acetonitrile.

Glycidyl ether of the DPAR

From the ^{1}H-NMR, 54% of the hydroxyles are glycidylized (Chemical shifts as reported above).

Glycidyl ether of the DPAC

From the ^{1}H-NMR, 59% of the hydroxyles are glycidylized (Chemical shifts as reported above).

Glycidyl ether of the DPAG

From the ^{1}H-NMR, 70% of the hydroxyles are glycidylized (Chemical shifts as reported above).

Glycidyl ether of the DPAM

From the ^{1}H-NMR, 49% of the hydroxyles are glycidylized (Chemical shifts as reported above).

Glycidyl ether of bisphenol A

From the ^{1}H-NMR, 89% of the hydroxyles are glycidylized (Chemical shifts as reported above).

6. Conclusions

Several natural phenols were reacted with levulinic acid to evaluate their potential for substituting phenol in the synthesis of diphenolic acid, which could, eventually, replace bisphenol A. In each case the selectivity towards the isomer with both aromatic hydroxyls in para of the position of condensation, being the most similar to the "original" diphenolic acid was determined by various NMR techniques, leading to the results stated in table 1.3. Only the catechol and resorcinol derivative reach a sufficient yield to be comparable with phenol as a reagent, both also having the advantage of presenting only one isomer. The highest yields are obtained with resorcinol, with two hydroxyls in the same position as the "original" diphenolic acid and the other two hydroxyls expected to be strongly inhibited by steric hindrance. Its reactivity should thus be similar to the one of diphenolic acid and finally, bisphenol A.

Table 1.3 : Yields and selectivities of the DPA from different phenolic reagents

PHENOLIC REAGENT	YIELD	ISOMERS	SELECTIVITY P-P' ISOMER	FIRST GLYCIDYLATION	SECOND GLYCIDYLATION
Phenol	57%	p-p'	100%		
m-Cresol	25%	p-p'; o-o'; p-o'	34%	16%	49%
Guaiacol	19%	p-p'; o-o'	64%	63%	70%
Catechol	55%	p-p'	100%	36%	59%
Resorcinol	83%	p-p'	100%	30%	54%

Considering the low yields in the synthesis and glycidylation, for guaiacol and m-cresol respectively, we decided to focus on diphenolic acid derivatives from catechol and resorcinol.

These compounds also present the advantage of having five potentially reactive groups, which allows to potentially avoid the use of crosslinking agents at all.

CHAP. 2:

Substituting Epichlorohydrin: Two approaches

1. Introduction

Substantial efforts have been made in recent years to produce epichlorohydrin from biomass, namely glycerol, deriving from the growing bio-fuel production[8,9,10] , also due to increasingly competitive pricing. Amongst them, Dow Chemicals published a work[29] describing a sustainable process for producing epichlorohydrin through the GTE (*Glycerol To Epichlorohydrin*[28]) process using hydrogen chloride, potentially from a waste stream, as a chlorine source, and yielding a high atomic efficiency. It is, thus, considered in the most recent publications as the go-to renewable glycidylation agent for bio-based epoxy resins. However, the issue of the severe carcinogenicity of epichlorohydrin remains. The easiness of exposure combined with its high reactivity, as all small epoxide molecules, make it extremely dangerous to handle, store and use. Epichlorohydrin is readily absorbed by the skin and excessive vapour concentrations are attained even at room temperature. Indeed, at 25°C, its vapour pressure is 2,27 kPa which corresponds to 22 000 ppm by volume[31]. Considering the fact that the one hour LC-50 for rats is 3615 ppm for male and 2165 ppm for female, it is clear that this exposure will lead to long-term systemic effects.

These effects have been extensively studied and range from kidney[32] and liver injury to lung oedema and lung cancer, due to prolonged exposure. One particularly interesting study by *Barbone et Al.*[33] depicts the health effects of epichlorohydrin in a real-life situation: an epoxy resin production plant. This study demonstrates a link between epichlorohydrin and lung cancer in workers. Furthermore, a link between epichlorohydrin and tumours of the central nervous system was found.

In the USA, the Occupational Safety and Health Administration (OSHA) classifies it as a potential carcinogen and also in Europe, the Dangerous Substances Directive 67/548/EEC[50], as updated for the REACH directive, states epichlorohydrin as a Carcinogen class 1B (carcinogenic in animals) but adds " *The substance should be regarded as if it is carcinogenic to man. There is sufficient evidence to provide a strong presumption that human exposure to the substance may result in the development of cancer*."

The data collected so far on its acute toxicity and the long-term effects, show it is extremely harmful to human health and therefore far away from the concepts of sustainable development. The incredible likelihood of exposure, as it is rapidly absorbed through the skin, the gastrointestinal tract and due to its high volatility through the lungs, only increases the potential risk and can cause adverse effects ranging from acute respiratory irritation with bleeding and

severe edema to neoplasm of the central nervous systems and lung cancer. It thus had to be substituted by a safer molecule.

Two different pathways of epichlorohydrin substitution are presented, the first completely avoids the use of a highly reactive epoxides whereas the second aims to obtain glycidyl tosylate from glycerol and tosyl chloride.

2. Allylation – Epoxidation

Approach

Although the approach is obvious, the O-allylation should be reconsidered because it avoids the presence of small carcinogenic epoxide molecules. Furthermore, the studied procedure allows the O-allylation with a low environmental impact from renewable resources with no need of rare transition metals. This O-allylation has been studied using simple phenolic compounds, which are representative for the chosen diphenolic acids and bisphenol A. 1,2-dihydroxybenzene (catechol), 1,3-dihydroxybenzene (resorcinol) and 1,4-dihydroxybenzene (hydroquinone) could potentially be obtained from biomass and could thus also be directly used in other types of epoxy resins. Indeed, hydroquinone was used as a "model molecule" because the corresponding resins had been previously studied[52] and are described as yielding analogous properties to a bisphenol A resin. After, the study was extended to catechol and resorcinol. The three di-hydroxybenzenes are pyrolysis/extraction products[53,54,55] of lingo-cellulosic materials or biomass.

The allylation was carried out using allyl chloride, which can easily be obtained from glycerol via allyl alcohol[56,57,58] and the resulting precursors can lead to diepoxides, which are identical to the epichlorohydrin based ones. Allyl chloride is not a completely innocuous reagent, but it is far less reactive and thus harmful than epichlorohydrin. Furthermore, the experimental procedure allows full regeneration of the residual allyl chloride, avoiding chlorinated-waste generation. Allyl chloride was reacted with the natural phenols in a biphasic system. This ensured a very low environmental impact as it allows to use only water as solvent[59,60]. Indeed, the organic phase consisted merely in allyl chloride and the formed product. The aqueous phase contains, at the end of the reaction, only water, sodium hydroxide in barely changed concentration, unreacted phenolic reagents and the phase transfer catalyst. It could thus be recycled back into the process after separating the organic phase and without any further

purification. The reaction's conditions were purposely kept close to ambient temperature and pressure, for a maximum energy efficiency. The only by-product in the aqueous phase is sodium chloride. Only the phase transfer catalyst, tetrabutylammonium hydrogen sulfate (TBAHS), chosen for cost reasons, could be considered environmentally problematic as all tensioactives, but recent works on biodegradation of quaternary ammonium salts[61] have shown that these are probably the most ecological of all tensioactives.

O-allylation of hydroquinone: Influence of Temperature and Reaction time

The 1,4-bis(allyloxy)benzene was synthesised from hydroquinone and allyl chloride in stoichiometric ratio in a biphasic system at various temperatures and reaction times. It is easily identified by ^{1}H-NMR. Figure 1 displays the conversion of hydroquinone with temperature for various reaction times, namely 30, 60, 90 and 120 minutes. The maximum temperature was limited to 70°C, in order to ensure energy efficiency; indeed due to the low vapour pressure of the mixture, reaching higher temperatures would require a pressure vessel. It is clear that the conversion increases with temperature and time. Extended reaction times have been tested but did not lead to a significant increase in conversion.

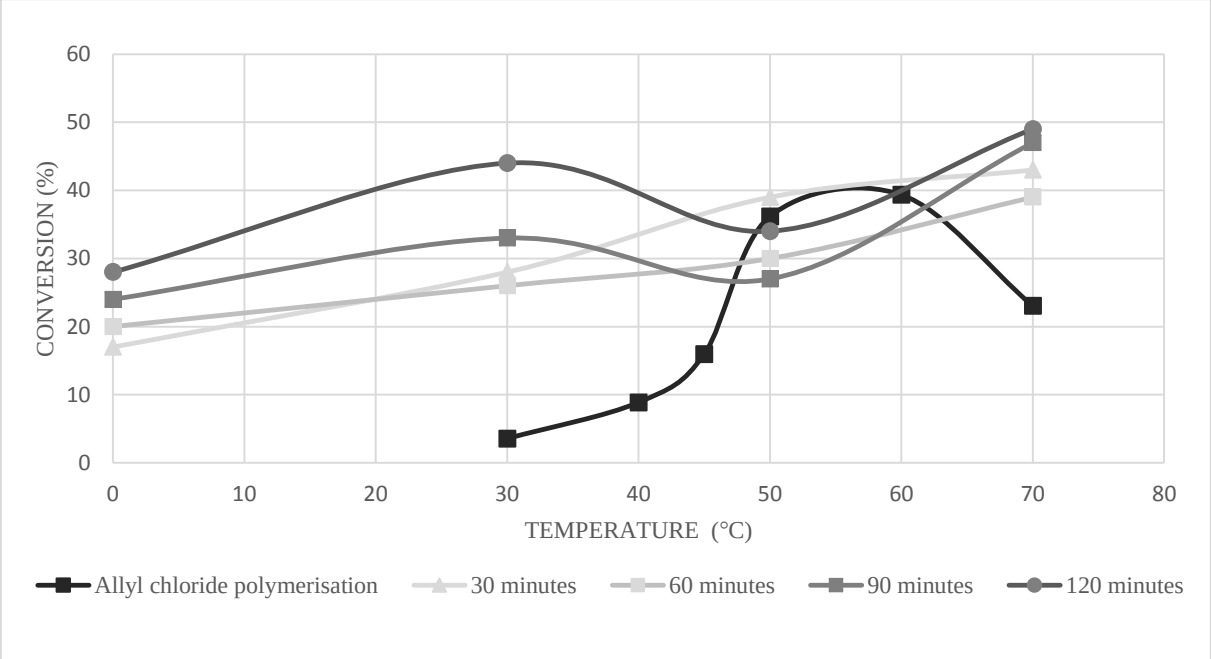


Figure 2.1: Conversion of hydroquinone as a function of temperature, for several reaction times as well as yields of allyl chloride polymerisation

The most unexpected result is the drop in conversions observed at 50°C. Indeed no obvious reason would lead to such an odd behaviour for just one particular set of temperatures, increasing with reaction times. At 30 and 60 minutes of reaction time, the behaviour is still almost linear with an asymptote towards a maximum conversion. After 90 minutes, the drop is clearly visible and increases further for 120 minutes of reaction time. This generates the hypothesis of a concurrent reaction. Thanks to the NMR, the broad peaks of the polymerised/oligomerised allyl chloride at 3,25 ppm are identified by comparison with pure allyl chloride polymer. Spontaneous polymerization of allyl chloride is well known and was used for numerous applications over the past years[62]. Still, a simple increase of polymerisation rate with temperature would be the expected behaviour.

Polymerisation test of allyl chloride in sodium hydroxide solution (50% w/w) at various temperatures, namely 30°C, 40°C, 45°C, 50°C, 60°C and 70°C,were carried out. As shown in figure 1, the polymerisation is strongly temperature dependent in these conditions with yields between 3% and 41%. Surprisingly the maximum conversion is reached between 50°C and 60°C and decreases for higher temperatures. Thus, we can assume that the drop in the conversion of O-allylation at this temperature is due to the competitive consumption of allyl chloride due to its polymerisation.

Claisen-rearrangement by-product

In addition to the allyl chloride polymer, another by-product was observed. Indeed, when studying O-allylation and thus the formation of allyl vinyl ethers, it is unavoidable to consider also the potential subsequent re-arrangement of the aromatic product. Claisen [3,3]-sigmatropic rearrangement is strongly favoured in polar and hydrogen bonding solvents[63], like water in our case but usually only occurs at high temperature.

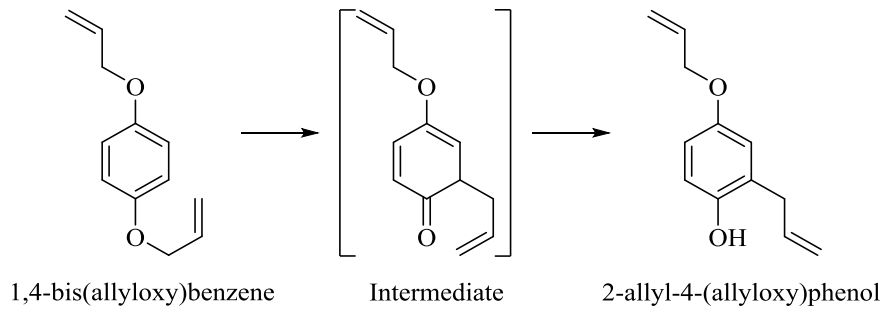


Figure 2.2: Claisen rearrangement of the allyloxybenzene moieties

On the NMR spectra, the rearrangement was clearly observed and not only at high temperature but even at 0°C. Surprisingly, as depicted on figure 3, the percentage of Claisen product decreases with temperature. This might be due to a difference in reaction rate between the O-allylation and the rearrangement. If the O-allylation is much faster at higher temperature compared to the Claisen rearrangement, the percentage of Claisen product will be lower at the end of the reaction time.

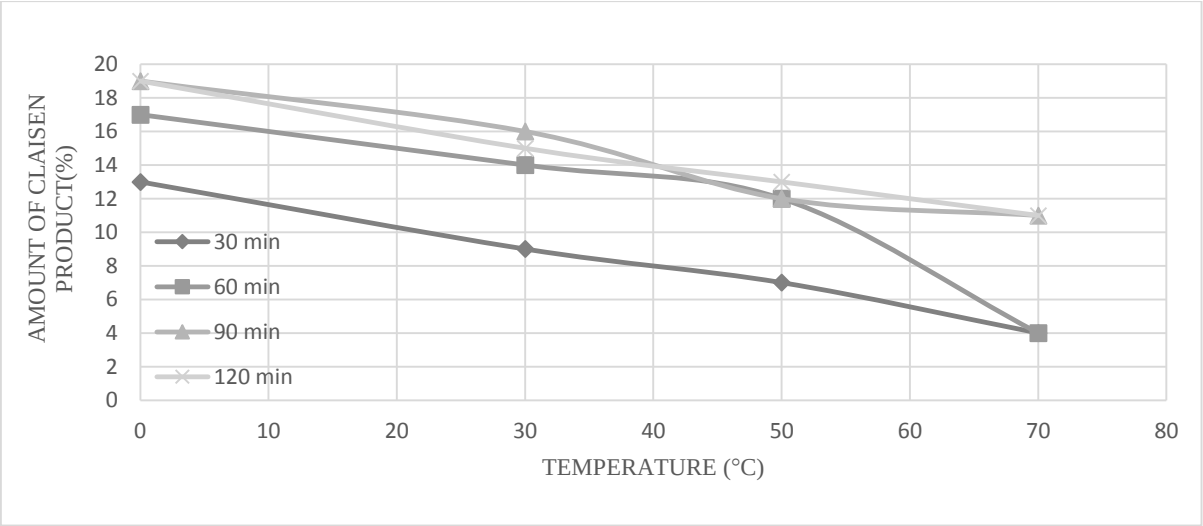


Figure 2.3: Amount of Claisen product as a function of temperature for several reaction times

Hence, the polymerisation with its maximum around 50°C and the Claisen rearrangement have opposite effects on the overall yield. As a consequence, the yields of the reactions at 70°C depicted in Figure 2.3 are overall superior to the other temperatures and that best yield (44%) is obtained for a reaction time of two hours.

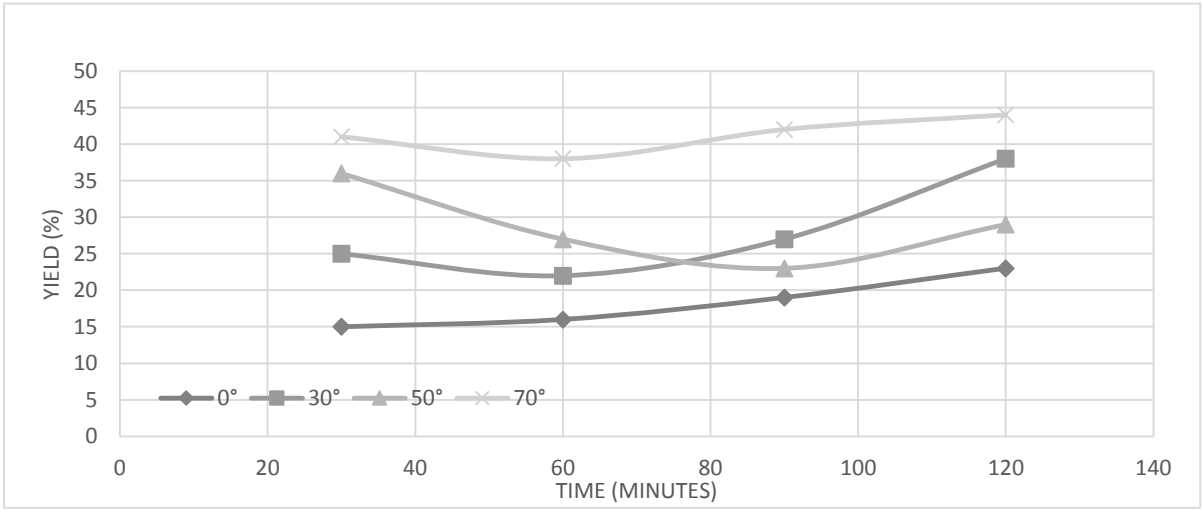


Figure 2.4: Overall yields in 1,4-(bisallyloxy)benzene as a function of time at different temperatures

This relatively low yield is mainly due to the fact that in a biphasic system, the reagents are in constant exchange between the two phases leading to equilibrium phenomena. As a lot of unreacted reagents remain, the system can easily be regenerated by simply removing the organic phase, which only consist of allyl chloride and product, and adding new organic reagents to the phenol containing aqueous phase, which is fully recyclable as is. Being very volatile, the removed allyl chloride can easily be distilled off and re-introduced in the system for a second reaction cycle. The same accounts for the extraction solvent, di-isopropyl ether, which can, thus, be reused without tremendous energy expenses. This high recyclability of all components compensates the low yield and can be interesting for an industrial application of the reaction.

O-allylation of catechol and resorcinol

After studying the O-allylation of 1,4-hydroxybenzene, the findings were extrapolated to catechol and resorcinol (1,2-dihydroxybenzene and 1,3-dihydroxibenzene, respectively). O-allylations were carried out in the same reaction set-up but for temperatures of 30°C, 50°C and 70°C and reaction times of 120 minutes, as these have shown to lead to the most significant results.

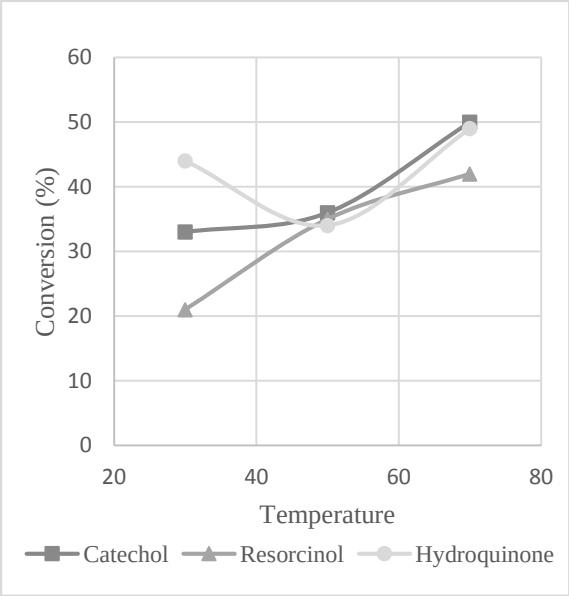


Figure 2.5: Conversion of the three di-hydroxybenzenes as function of temperature, at 120 minutes of reaction time

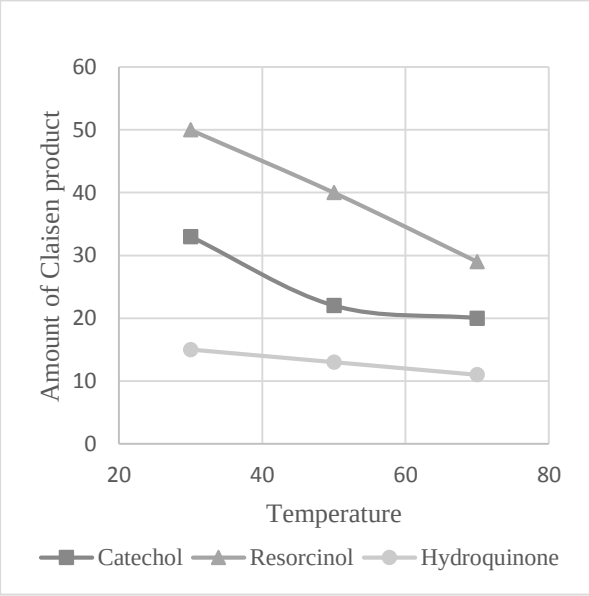


Figure 2.6: Percentage of Claisen rearrangement product of the three di-hydroxybenzenes as function of temperature, at 120 minutes of reaction time

At 70°C, the behaviour of catechol is similar to hydroquinone but with slightly lower yields whereas resorcinol leads to a substantial loss in conversion of 14%. The latter can easily be explained by the major stabilization of the generated phenolate due to delocalisation of the electrons on the aromatic ring causing a loss in reactivity.

Moreover, the effect of temperature on the kinetic behaviour between the two competitive reactions is very different for resorcinol compared to the other two dihydroxybenzenes. Indeed, although the yields are generally lower than with hydroquinone, as seen in figure 5, resorcinol does not show a drop in yield at 50°C, probably because the yield is so low that the concurrent consumption of allyl chloride in the polymerization reaction has no impact. On the contrary, as catechol and hydroquinone observe a drop in conversion for this temperature, at 50°C the three dihydroxybenzenes reach very similar conversions of around 35%.

Moreover, for the resorcinol diallyl derivative, as seen on figure 2.7, the very strong activation by mesomeric effect of the position in ortho of the ethereal moieties arising from the sum of both electron-donating effects, strongly favours the Claisen rearrangement on this position. As shown in figure 6, at 30°C, 50% of the molecules have rearranged, which is a 3 fold increase compared to hydroquinone. Combined with the generally lower conversion, 1,3-dihydroxybenzene reveals itself as the least prone to O-allylation with this method. Nevertheless, as the Claisen product leads to further epoxidisable terminal alkene groups, the rearrangement is not expected to have a great impact on the subsequent use in epoxy resins.

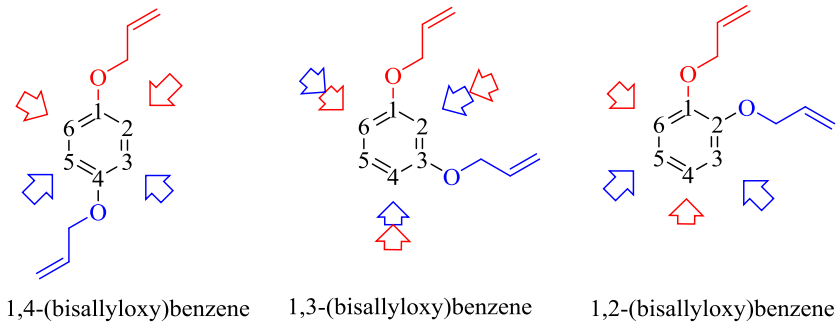


Figure 2.7: Activating mesomeric effects in Claisen rearrangement

Epoxidation of the bis-allyloxybenzenes

After identifying the optimum conditions for the allylation of the three model di-hydroxybenzenes, the most environmental friendly epoxidation was investigated. Indeed, epoxidations are commonly carried out using meta-chloroperoxybenzoic acid, a highly

flammable and explosive oxidizing agent, the reaction is typically carried out in dichloromethane and it has a very low atom efficiency. This was not acceptable in a procedure aiming to comply with the standards of green chemistry.

The alternative epoxidation proposed, found in litterature[64], uses an aqueous solution of hydrogen peroxide, a low environmental impact oxidizing agent. However, it requires activation for yielding epoxides and usually acids, leading to the formation of dangerous peracids, are added for this scope. In our case, bicarbonate was added for activation generating in situ the active species: peroxymonocarbonate ion via the following reaction:

$$H_2O_2 + HCO_3^- \rightleftharpoons H_2O + HCO_4^-$$

This type of reaction is adequate for our aims because it does not include toxic or hazardous reagents, the only by-product is water and it has a high atom efficiency. Furthermore, the reaction's conditions, at room temperature without stirring, are the blandest imaginable.

The reactions were carried out in a biphasic system H_2O/CH_3CN (3:2 v/v) with the three bisallyloxybenzenes, previously synthesised in a concentration of 0,05 M. The hydrogen peroxide was added in a concentration of 0,6 M and ammonium bicarbonate in a concentration of 0,4 M. The system is thus highly dilute, hence, safe. The yield of the reaction was calculated on the crude product, using the ^{1}H-NMR analysis by comparing the integral of the vinyl signals with the epoxidic signals. The double bonds having incurred Claisen-rearrangement were included in the calculation, as they potentially react, too.

In figure 2.8 , the yields of allyl groups that have epoxidised are stated altogether with a scheme of the theoretical products.

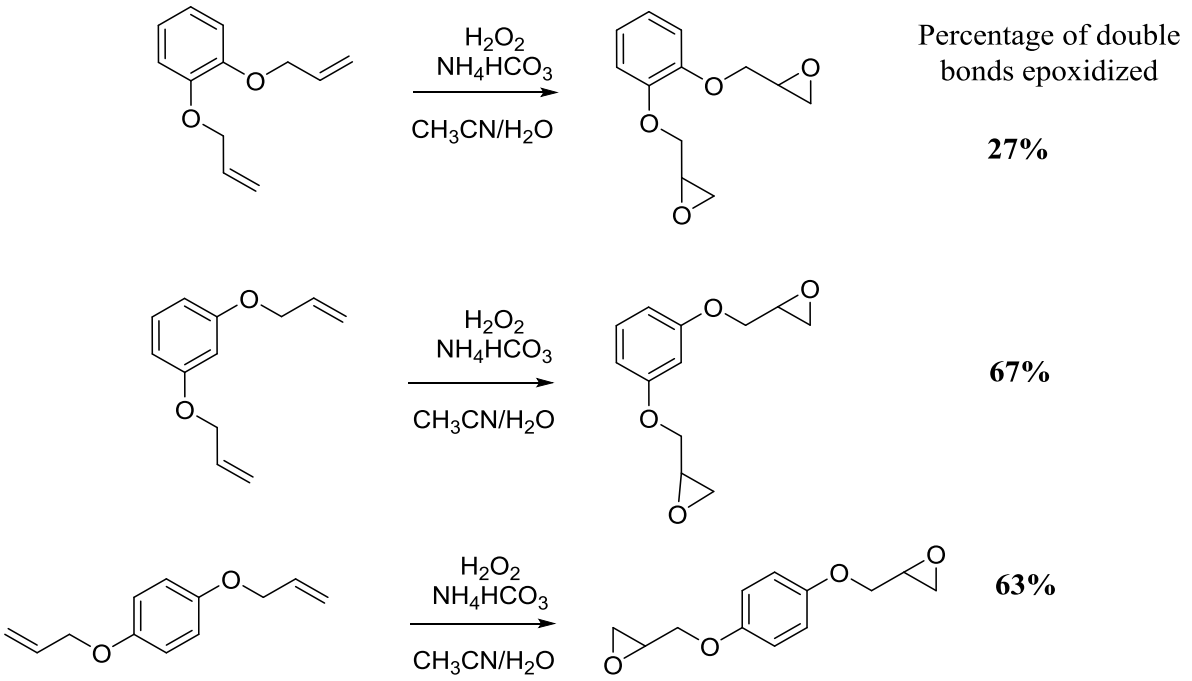


Figure 2.8: Reaction procedures and yields for the epoxidation of the bis-allyloxybenzenes

The yield of the compound deriving from catechol is only about half of the other two reagents.

As reported in the above-mentioned paper, the active species, peroxymonocarbonate reacts, by forming butterfly-like intermediates, as seen in figure 2.9. In the case of catechol, the formation of these intermediated is inhibited by sterical hinderance. As one intermediate has formed, there is no space for the formation of the second intermediate on the allyloxy group in ortho.

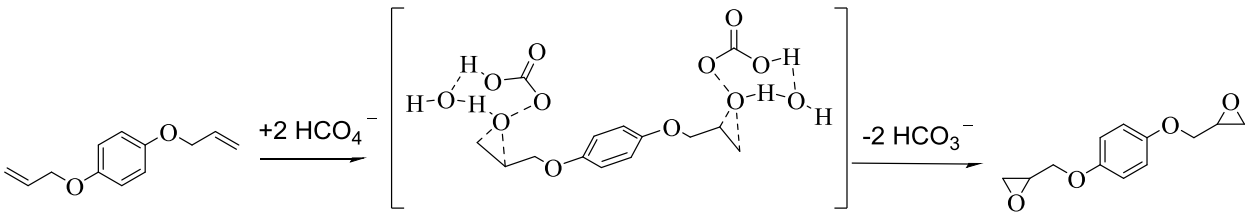


Figure 2.9: In situ formation of the butterfly-like intermediate on the hydroquinone derivative

Partial Conclusions

The first part of the study on the O-allylation of natural phenolic compounds led to conclude that, in the investigated biphasic system synthesis, three reactions take place, namely allylation of hydroquinone, homopolymerisation of allyl chloride and Claisen re-arrangement of the generated vinyl ethers. Both of the side reactions have an impact on the final yield of the product but are strongly dependent on temperature, and more heavily noticeable for longer reaction times. Indeed, the peak in polymerization of allyl chloride at 50°C drastically reduces the yield

in 1,4-bis(allyloxy)benzene whereas, Claisen rearrangement is, surprisingly, most favoured at lower temperature. The optimum conditions, in this "*green*" experimental procedure, are thus a temperature of 70°C for a reaction time of 2 hours. The yield of 44% remains low even for longer periods of time, not due to exhaustion of reagents (allyl chloride) but probably because of the constant equilibrium and phase transfer, the reagents find themselves in, in a biphasic system, especially the phase transfer catalyst. Thus, by removing the organic phase with the products, the aqueous phase, and the phenolic reagents herein could be directly re-used for a second cycle, by simply adding allyl chloride.

The investigations were then extended to 1,2-dihydroxybenzene and 1,3-dihydroxybenzene showing that the first has similar behaviour to hydroquinone whereas for the latter, the deactivating mesomeric effect of the aromatic side groups has a negative impact on O-allylation but strongly enhances Claisen rearrangement on the position in ortho to both hydroxyls. With a three-fold increase compared to hydroquinone, leading to as much as 50% re-arranged product at 30°C, this result is interesting for organic chemistry, as the first known evidence of low-temperature Claisen rearrangement and should be further investigated.

This work shows the feasibility of O-allylation of dihydroxybenzenes in a recyclable biphasic system with a very low environmental impact, as a first step towards substituting highly carcinogenic epichlorohydrin. The following epoxidation step should be chosen carefully in order to comply with the aims of "*green chemistry*". Environmentally friendly solutions such us hydrogen peroxide, in situ activated with innocuous sodium bicarbonate are readily available[64]. The combination of these two steps allows to completely avoid the use of highly carcinogenic epichlorohydrin.

3. Glycidyl tosylate

Approach

The second possibility is to use an epoxy bearing another leaving group instead of chlorine, chosen carefully with the aim to raise the boiling point and lower volatility (i.e. vapour pressure), maintaining its reactivity. Glycidyl tosylate is less problematic than epichlorohydrin because it is less volatile and thus the risk of exposure is drastically decreased.

Glycidyl tosylate is commercially available and industrially synthesised by reacting glycidol with tosyl chloride. Considering the fact that glycidol is carcinogenic and volatile, this pathway

presents no advantage compared to the use of epichlorohydrin. Thus, alternative routes were investigated.

We focused on two potential reaction pathways[65], one following a patent [66], in which it is produced starting from 3-chloro-1,2-propanediol and one directly from glycerol in a completely new procedure, unseen in literature.

3-Chloro-1,2-propanediol is obtained by catalytic chlorination of glycerol with HCl in the presence of a mixture of acid oxides, namely SiO2, TiO2, PbO2, and V2O5. In this first pathway, depicted in figure 2.10, 3-chloro-1,2-propanediol is transformed into glycidol, by the catalytic action of tribasic potassium phosphate, which is then tosylated with tosyl chloride in presence of triethylamine (TEA) and 4-diamethlaminopyridine (DMAP).

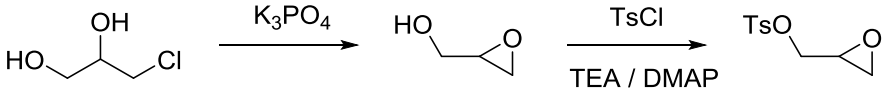


Figure 2.10: Synthesis of glycidyl tosylate from 3-chloro-1,2-propanediol

Although the yield was promising (48%) and the selectivity excellent (93%) it was clear that this reaction procedure was not the right path. As previously stated, glycidol as well as 3-chloro-1,2-propanediol are carcinogenic. Dichloromethane is amongst the most environmental unfriendly solvents and also the chosen catalysts are far from complying with green chemistry requirements.

Our synthesis of glycidyl tosylate from glycerol has been developed subsequently based on the idea to generate the epoxide ring through an intramolecular nucleophilic substitution mechanism, which consists in the attack of a deprotonated hydroxyl on a carbon next to the tosylate. This reasoning has led us to the following two possible pathways, as shown in figure 2.11.

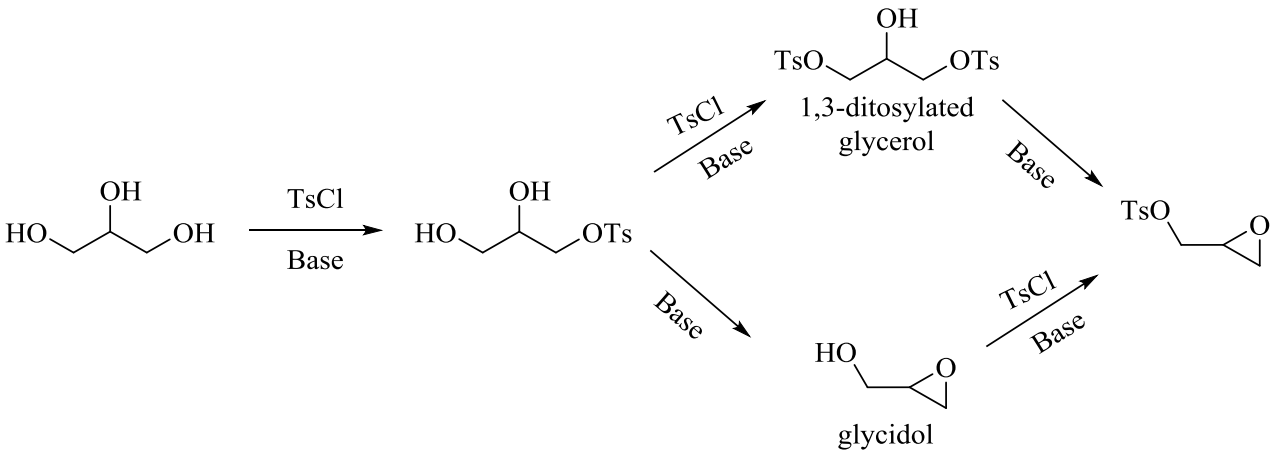


Figure 2.11: Potential reaction mechanisms of the formation of glycidyl tosylate from glycerol

The first reactions were performed with the same reaction setup as for the tosylation of glycidol, substituting it with glycerol to check whether even the slightest quantity of glycidyl tosylate was formed. Eventually, some l tosylate formed but the yield was low and a multitude of by-products were generated.

Optimisation

Thus, a series of reactions in different conditions were carried out in order to determine the critical parameters and optimise yield and selectivity, in the greenest possible way. The analysed variables were various reaction systems, solvents, bases and ratio between the reagents.

The best results were obtained in a biphasic system in which a solution of tosyl chloride in diethyl ether is slowly added to an alkaline aqueous solution of glycerol and reacted under intense stirring for 3 hours at 37°C. The most appropriate base was sodium hydroxide. A concentration of around 30% allows to deprotonate the middle hydroxyl on one hand, without creating parallel reactions with tosyl chloride or the generated tosylate. In order to safely avoid the production of glycidol, produced by the mechanism shown in the lower part of figure 2.11, the molar ratio between glycerol and tosyl chloride was not lower than 1:3, however, in these conditions the formation of glycerol tritosylate as a by-product is favoured.

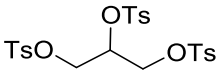


Figure 2.12: Glycerol tritosylate

A screening performed on the organic phase during the first two hours of reaction is shown in Figure 2.13

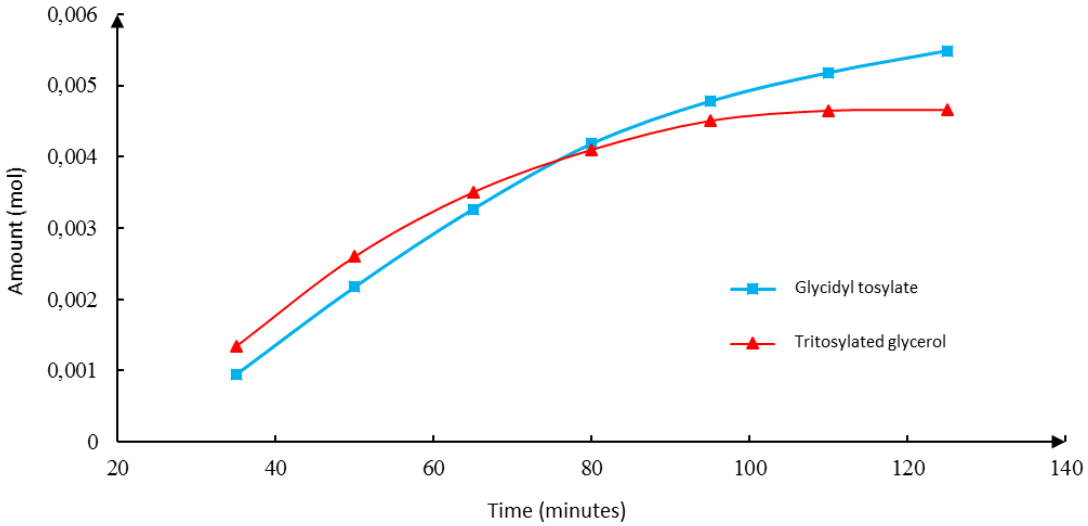


Figure 2.13 : Screening of the two major products of the reaction as a function of time

The graph shows that the two reactions follow a parallel trend at the beginning with a slightly higher conversion into glycerol tritosylate. Nevertheless, after 80 minutes the reaction speed of the tritosylate conversion strongly diminishes. This can be explained by the lower concentration of tosyl chloride present in the reaction mixture, which makes the third tosylation of the di-tosylated glycerol more difficult. Thus with time, after the first 80 minutes passed, the gap between glycidyl tosylate and glycerol tritosylate becomes always more important. The best results obtained with this type of reaction have led to a conversion equal to 60% of glycerol, of which 68% were glycidyl tosylate and 32% by-product. A typical problem of biphasic systems is that the conversion rarely reaches 100% because it is limited by several phase transfers of the reagents. Nevertheless, a phase transfer catalyst might have led to higher yields but was avoided to further decrease the, already quite low atom efficiency of this reaction. Furthermore, the aqueous phase can fully be reused as such and even the tosylate deriving from the epoxy ring formation can potentially be recycled back to tosyl chloride[67].

The glycidyl tosylate was subsequently tested with bisphenol A to synthesise diglycidyl ether of bisphenol-A, the best results were obtained using the same method of synthesis that is industrially used for the reaction with epichlorohydrin. The conversion of bisphenol-A was 97% and a yield in diglycidyl ether of bisphenol-A equal to 88%, being thus superior than the reaction with epichlorohydrin.

In a similar way as epichlorohydrin can potentially attach to bisphenol A in two ways,[68] reacting on the epoxide moiety followed by ring opening and elimination of the leaving group or directly

by nucleophilic substitution of the chlorine, we could hypothesized that two mechanisms could potentially take place in the reaction with glycidyl tosylate, as shown in Figure 2.14.

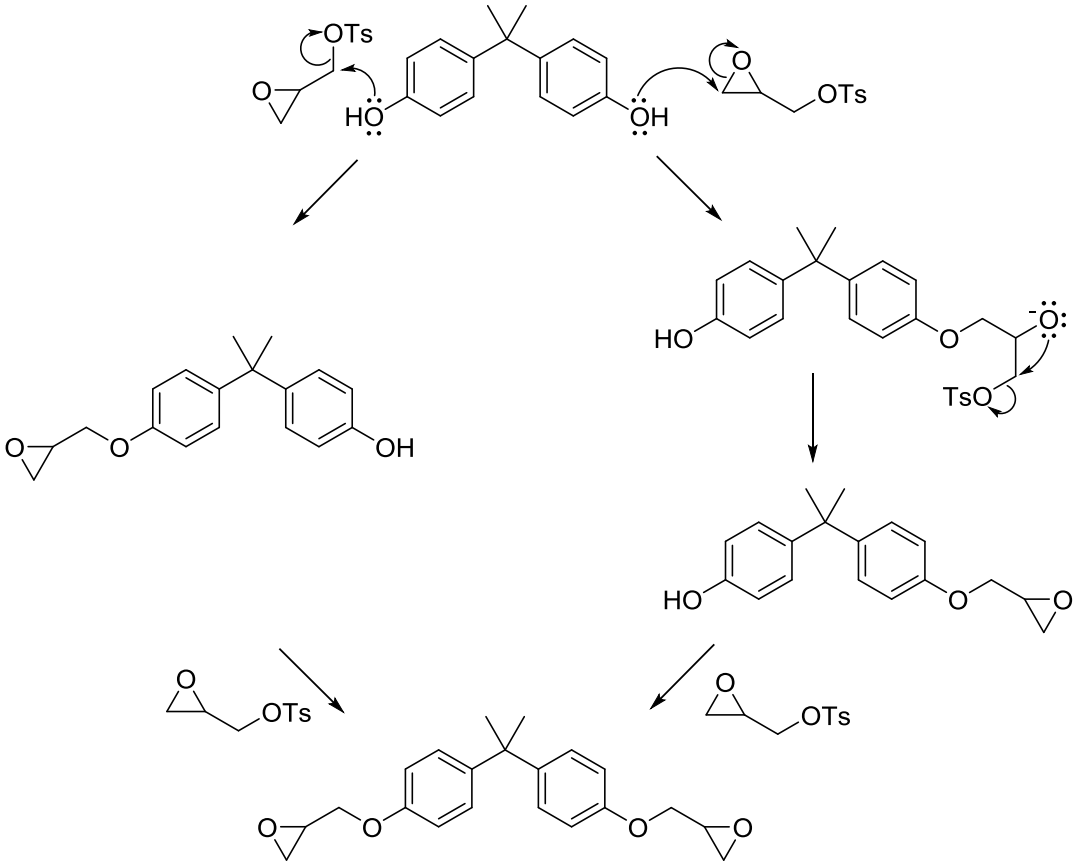


Figure 2.14: Potential mechanisms of etherification[65]

We thus aimed to check if glycerol tritosylate could also react with bisphenol A, potentially as a chain extender but in an ideal case even as a crosslinking agent, owing to the three exiting groups. However, the results clearly showed that the glycerol tritosylate does not react with bisphenol A, demonstrating that with glycidyl tosylate the reaction mechanism corresponds to the opening of the epoxide ring and subsequent elimination of the tosylate, probably due to the sterical hinderance of the tosylate group orienting the approach to the molecule.

Partial Conclusions

The best results were obtained with tosyl chloride that directly attaches to glycerol on the lateral hydroxyls and form the epoxide by internal nucleophilic substitution due to in-situ-generated heat.

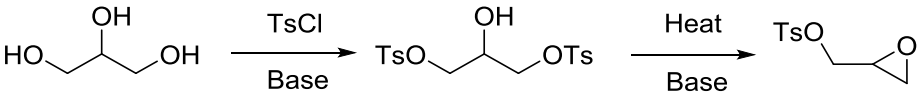


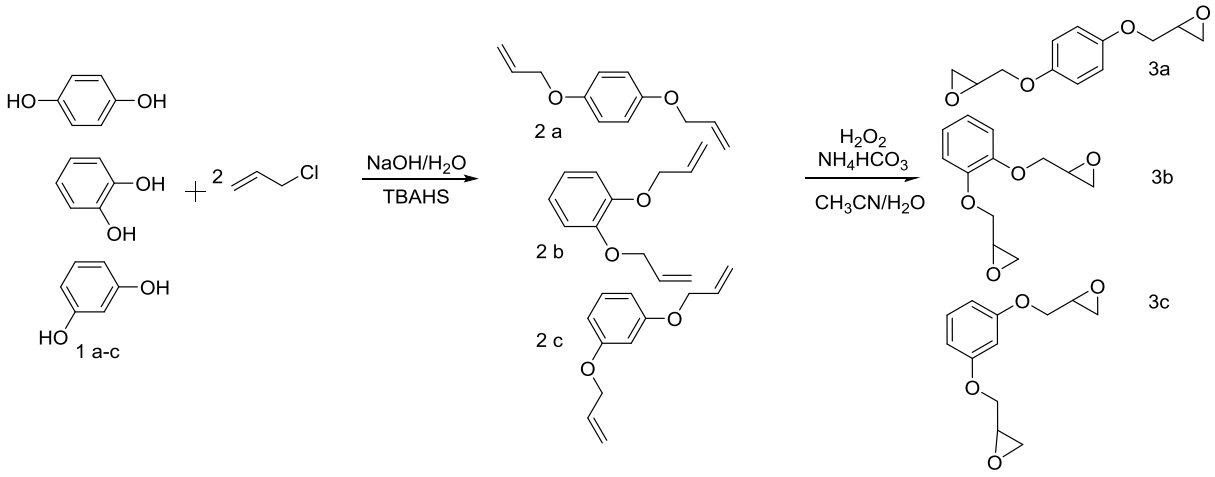
Figure 2.15: General glycidyl tosylate synthesis procedure

The described process, aiming to obtain glycidyl tosylate from glycerol through a biphasic system reaction, has an excellent practicality and an almost complete recyclability of all phases. The conversion in optimized conditions is 60%, with glycerol tritosylate as the major by-product (19%). Tests with bisphenol-A have demonstrated to give a higher yield of digylcidyl ether of bisphenol A, the epoxy prepolymer, than those obtained with epichlorohydrin under the same conditions. Finally, glycidyl tosylate is less problematic than epichlorohydrin because it is less volatile and thus the risk of exposure is drastically decreased.

4. Experimental

Allylation of the di-hydroxybenzenes

General procedure



A 50 mL round bottom flask fitted with a reflux condenser and magnetic stirring, was charged with a solution of the dihydroxybenzene compound (1 mmol, 0,110 g) in 10 mL of an acqueous solution of NaOH 50% w/w. Tetrabutyl ammonium hydrogen sulfate, TBAHS (5 mol%, 0,017 g) and allyl chloride (2 mmol, 0,163 mL) were added at room temperature. The mixture was reacted under vigorous stirring for various reaction times and temperatures as stated in the previous section. Subsequently, after cooling if applicable, the reaction mixture was extracted five times with 5 mL of isopropyl ether and, finally, dried under reduced pressure to yield a yellow-brown oil. Yields depend on the conditions and are stated in the previous section, based on integration of the corresponding ^{1}H-NMR. All experiments were repeated 3 times and the stated value is the average of the three resulting values.

Synthesis of 1,4-bis(allyloxy)benzene (2a)

The reaction was carried out following the general procedure using hydroquinone as a starting material**.**

^{1}H-NMR (400 MHz, $CDCl_3$) *δ (ppm)*: 4.48 (d, 4H, CH_2=CH-C$\underline{H}_2$), 5.26 (dd, 2H, C$\underline{H}_2$=CH-CH_2), 5.39 (dd, 2H, C$\underline{H}_2$=CH-CH_2), 6.04 (m, 2H, CH_2=C$\underline{H}$-CH_2), 6,84 (s, 4H, Ar-H).

Synthesis of 1,2-bis(allyloxy)benzene (2b)

The reaction was carried out following the general procedure using catechol as a starting material.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ (ppm)*: 4.51 (d, 4H, CH_2=CH-C$\underline{H}_2$), 5.28 (dd, 2H, C$\underline{H}_2$=CH-CH_2), 5.41 (dd, 2H C$\underline{H}_2$=CH-CH_2,), 6.05 (m, 2H, CH_2=C$\underline{H}$-CH_2), 6.85 (m, 4H, Ar-H)

Synthesis of 1,3-bis(allyloxy)benzene (2c)

The reaction was carried out following the general procedure using resorcinol as a starting material.

^{1}H-NMR (400 MHz, $CDCl_3$) *δ (ppm)*: 4.52 (m, 4H, CH_2=CH-C$\underline{H}_2$), 5.30 (m, 2H, C$\underline{H}_2$=CH-CH_2), 5.43 (m, 2H C$\underline{H}_2$=CH-CH_2,), 6.05 (m, 2H, CH_2=C$\underline{H}$-CH_2), 6.55 (m, 3H, Ar-H), 7.12 (m, 1H, Ar-H)

Epoxidation of the bis(allyloxy)benzenes

General procedure

In a closed vial, the compounds 2a-c (1mmol, 0,22g) were dissolved in a suspension of water (3,7mL) and acetonitrile (6,8mL) along with ammonium bicarbonate (2,25 mol) and hydrogen peroxide 30 wt %(10,3 mmol). This mixture was left to react in the darkness without stirring for 24 hours at room temperature. Subsequently, the mixture was diluted with 10 mL of water, extracted five times with dichloromethane and dried under vacuum to yield a yellow oil.

1,4-bis(oxiran-2-ylmethoxy)benzene

The reaction has been carried out as described using compound **2a** as reagent to yield 63% of pure product **3a.**

^{1}H NMR (400 MHz, $CDCl_3$) *δ (ppm)*: 2.77 (dd, 2H, Epoxy-H_2), 2.89 (dd, 2H, Epoxy-H'$_2$), 3.38 (m, 2H, H-Epoxy), 4.03 (dd, 2H, O-CH_2), 4.26 (dd, 2H, O-CH_2), 6.92 (m, 4H, Ar-H)

1,2-bis(oxiran-2-ylmethoxy)benzene

The reaction has been carried out as described using compound **2b** as reagent to yield 27% of pure product **3b.**

^{1}H NMR (400 MHz, $CDCl_3$) *δ (ppm)*: 2.77 (dd, 2H, Epoxy-H_2), 2.89 (dd, 2H, Epoxy-H'$_2$), 3.38 (m, 2H, H-Epoxy), 4.03 (dd, 2H, O-CH_2), 4.26 (dd, 2H, O-CH_2), 6.92 (m, 4H, Ar-H)

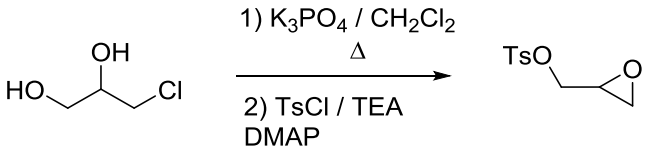
1,3-bis(oxiran-2-ylmethoxy)benzene

The reaction has been carried out as described using compound **2c** as reagent to yield 67% of pure product **3c.**

^{1}H NMR (400 MHz, $CDCl_3$) *δ (ppm)*: 2.76 (dd, 2H, Epoxy-H_2), 2.89 (dd, 2H, Epoxy-H_2), 3.34 (m, 2H, H-Epoxy), 3.93 (dd, 2H, O-CH_2), 4.21 (dd, 2H, O-CH_2), 7.17 (m, 4H, CH aryl)

Synthesis of glycidyl tosylate

Synthesis from 3-chloro-1,2-propanediol

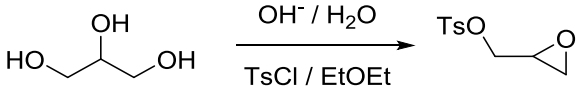


A 100 ml round bottom flask was loaded with 24 mL of dichloromethane, 3 mL of 3-chloro-1,2-propanediol and 10 g of tribasic potassium phosphate (K_3PO_4) and the obtained mixture was left for 3 hours at reflux. At the end, the mixture was cooled in an ice bath to a temperature of 0-1°C, to which were then added 5.5 mL of triethylamine (TEA), 0.08 g of dimethylamino pyridine (DMAP) and slowly 6.9 g of tosyl chloride and reacted for one hour at room temperature. Three washes were performed to remove unreacted reagents. The first with 40 mL of a 5% solution of potassium carbonate followed by 40 mL of a hydrochloric acid solution (1N) and finally with water. The residual solvent in the organic phase was evaporated to dryness at reduced pressure.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ (ppm)*: 2.45 (s, 3H, CH_3), 2.59 (dd, 1H, Epoxy-H_2), 2.81 (dd, 1H, Epoxy-H'$_2$), 3.19 (m, 1H, H-Epoxy), 3.94 (dd, 1H, O-CH_2), 4.26 (dd, 1H, O-CH_2), 7.36 (d, 2H, Ar-H), 7.80 (d, 2H, Ar-H).

Synthesis from glycerol

The synthesis carried out led to the obtaining of the glycidyl tosylate in a yield of 48% and a selectivity of 93%.



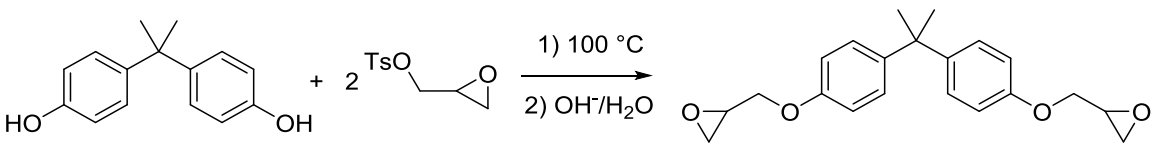
The synthesis has been performed with various organic solvents and various concentrations of NaOH, glycerol and tosyl chloride, as follows only the reaction setup leading to the highest yield is stated, but it can easily be adapted to other conditions as stated in the corresponding part.

A 100 mL three-necked round bottom flask in a cooling water bath, fitted with a bubble condenser and under stirring, was loaded with 2 g of glycerol, 20 mL of water and slowly 10 g of sodium hydroxide. At the end of the addition of the sodium hydroxide, the mixture is left under stirring for further 10 minutes until complete dissolution and returning to room temperature. Subsequently, an organic solution consisting of 12 grams of tosyl chloride dissolved in 50 mL of diethyl ether was added, using a dropping funnel. The biphasic mixture was reacted for 2 hours at reflux while maintaining a vigorous stirring. After the reaction, the two phases were separated after adding 50 mL of water and 50 mL of diethyl ether.

Finally, the organic phase was washed with water and dried with anhydrous sodium sulfate and the solvent evaporated under reduced pressure.

^{1}H-NMR (300 MHz, $CDCl_3$) *δ (ppm)*: 2.45 (s, 3H, CH_3), 2.59 (dd, 1H, Epoxy-H_2), 2.81 (dd, 1H, Epoxy-H'$_2$), 3.19 (m, 1H, H-Epoxy), 3.94 (dd, 1H, O-CH_2), 4.26 (dd, 1H, O-CH_2), 7.36 (d, 2H, Ar-H), 7.80 (d, 2H, Ar-H).

Reaction of glycidyl tosylate with bisphenol A



In a 50 mL round-bottom flask, were added 3 g of glycidyl tosylate, 0.375 g of bisphenol A and 0.037 g of benzyltriethylammonium chloride, dissolved in 1.5 mL of water. The flask was fitted with a bubble condenser and the mixture maintained under magnetic stirring and reacted for 1 hour at 100 °C.

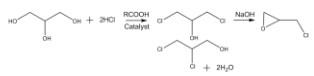
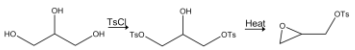
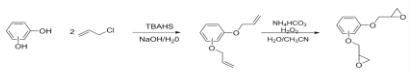
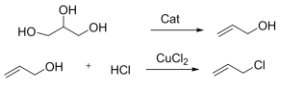
After the heating was turned off , a solution of 2.1 ml of water, 0.53 grams of sodium hydroxide and 0.037 grams of benzyltriethylammonium chloride was dripped in the mixture under vigorous stirring.

After cooling to room temperature, the mixture was extracted with 30 mL of ethyl acetate thrice. The organic phase obtained was then washed with 30 mL of water and finally evaporated to dryness by evaporation of the solvent under reduced pressure.

^{1}H-NMR (400 MHz, $CDCl_3$) ***δ (ppm):*** 1.63 (s, 6H, CH_3), 2.73 (dd, 2H, Epoxy-H_2), 2.88 (dd 2H, Epoxy-H'$_2$), 3.33 (m, 2H, H-Epoxy), 3.93 (dd, 2H, O-CH2), 4.18 (dd, 2H, O-CH2), 6.81 (d, 4H, Ar-H), 7.13 (d, 4H, Ar-H)

5. Conclusions

A thorough examination of the two possible pathways and their comparison with glycerol-based epichlorohydrin, allowed to state their respective characteristics regarding ecological parameters as follows.

	EPICHLOROHYDRIN[2]	GLYCIDYL TOSYLATE	ALLYLATION - EPOXIDATION
Procedure			
Reagents' source and safety	• Glycerol is a by-product of the transesterification of triglycerides from plant oils. • The data collected so far show that epichlorohydrin is extremely harmful to human health and therefore far away from the concepts of sustainable development. • Highly corrosive, toxic, flammable and carcinogenic (category 1a) • High risk of exposure: absorbs rapidly through, the gastrointestinal tract • Low vapor pressure: at room temperature the volatilized amount is higher than the maximum safe level for breathing. • Adverse effects ranging from acute respiratory irritation with bleeding and severe edema to neoplasm of the central nervous systems and lung cancer.	• Glycerol is a by-product of the transesterification of triglycerides from plant oils Glycidyl tosylate: • Causes serious eye damage • May cause respiratory sensitization if inhaled • May cause cancer (H350) But: not volatile (Stable crystals, mp= 45° C) ⇨ Risk of exposure radically reduced	• Allyl chloride can be derived from glycerol via allyl alcohol and then chlorinated in a well-known process:  • Solvent is water in both reactions • The epoxidation catalyst is mild with in-situ generated peroxymonocarbonate. • It is toxic and harmful to the environment but not a category 1 carcinogenic.
Waste generated and by-products	• 30-50:1 mixture of dichloropropan-2-ol and 2,3-dichloropropane-1-ol • Gas phase reaction in HCl • Carboxylic acid catalysts	• Tri-tosylate precipitates and is easy to remove • Best results (without rare metals or expensive catalysts): 19 % tritosylate • Recent papers have shown that p-toluensolfonic acid can be recycled back to p-toluensolfonyl chloride • Diethylether as solvent	Advantages of PTC: • Producing the solid by-products such as sodium chloride and sodium hydroxide which are easily removed by simple filtration, • Aqueous phase is fully recyclable thus saving reagents such as sodium hydroxyde, phase-transfer catalyst and phenolic reagent • Claisen rearrangement leads to by products – which can still be epoxidized to yield final oxiranes
Conclusions	• Renewable carbon sources • Glycerol is available in large quantities as a by-product of a thriving biodiesel production • Price • Already available on the market But:Carcinogenic, chlorinated organic by-products	• Renewable carbon sources • Glycerol is available in large quantities as a by-product of a thriving biodiesel production •Risk of exposure by breathing drastically reduced •p-toluene sulfonic acid is recyclable and by-products are easily removed by filtration But: Atom efficiency low due to substantial by-products	• Renewable carbon sources • Small, highly reactive epoxides are avoided • Glycerol is available in large quantities as a by-product of a thriving biodiesel production •Reaction in water as solvent – "green" •Most by-products can be recycled But: yield to be improved

Comparing epichlorohydrin with the two potential substituting pathways, both including a recyclable biphasic reaction medium, makes it clear that, although the two-step process including the allylation of aromatic hydroxyls followed and epoxidation has the low yields, it is the safest and most environmentally friendly. Its high recyclability and practicality compensate the losses in conversion.

CHAPTER 3:

Synthesis of the fully renewable prepolymer

1. Introduction

In the first chapter, we identified an appropriate substitute for bisphenol A : diphenolic acids. Amongst the fully natural diphenolic acids synthesized and the reactivity tested, DPAC and DPAR were identified as the most interesting. In the second chapter, epichlorohydrin was compared with two potential alternatives. The sequence consisting in the allylation of the hydroxyl in a biphasic system and subsequent epoxidation of the double bond was determined as the "greenest" solution, owing to its full recyclability and bland conditions. This pathway has been optimized with regard to temperature and reaction time and a biphasic reaction set-up at 70°C for two hours led to the best results. This optimization was carried out with simple resorcinol and catechol, as models for the resorcinol and catechol moiety in DPAR and DPAC, respectively. After having assessed the potentially best conditions for the model molecules, the glycidylation is performed on the DPAs.

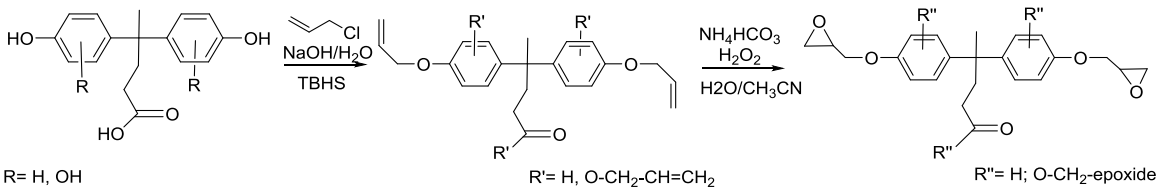


Figure 3.1: Overall reaction scheme of glycidylation of the DPAs

Owing to their five hydroxyls, which can all potentially react in allylation and epoxidation, the characterization of DPAR and DPAC derivatives is expected to be relatively complex. In addition to a mixture of several products, after partial allylation, the Claisen re-arrangement also has to be taken into consideration.

Thus, in order to have a simplified model and obtain an idea of the values of the chemical shifts of the new molecules, in a first step DPA from phenol was reacted in the same conditions and thoroughly characterized. Subsequently, the knowledge obtained was used for DPAR and DPAC derivatives analysis, which was, indeed, relatively complex.

2. DPA

Allylation of DPA

In order to have a simplified model for the more complex molecules, deriving from resorcinol and catechol, the reactions were first carried out with the previously synthesized DPA from phenol. As determined in chapter 2, the reaction was performed at 70°C, for two hours with a molar ratio of one mole of allyl chloride for each molar equivalent of hydroxyl. The reaction scheme is represented in figure 3.2. As we expect the acid to react too, in this case, three reactive hydroxyls are considered. Using the same conditions also allows to gain a first idea of the reactivity of the DPAs in the allylation, in particular, of the possible effect of the acid group.

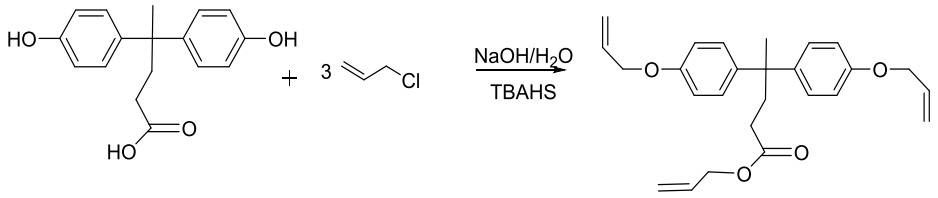


Figure3.2: Reaction scheme of the allylation of DPA from phenol

By comparing the spectra of DPA and of the product, the allylation is obvious, as shown in figure 3.3. Whereas the spectrum of DPA (3.3.a) is rather simple with 5 peaks, in the allylation product, a multitude of peaks appeared in the vinyl and allyl region. Indeed, in the spectrum of the unreacted DPA, two symmetric double doublets (dd) between 6.5-7 ppm are assigned to the aromatic protons, two multiplets, at 1.93 ppm and 2.23 ppm to the methylene groups of the central aliphatic chain and a singlet at 1.46 ppm to the methyl deriving from the levulinic acid and linked to the central quaternary carbon. The other peaks correspond to residual solvents. After allylation, these same peaks are visible, slightly shifted and a certain number of other peaks have appeared, between 4-6 ppm. Indeed, in the detail shown in figure 3.4, at around 4.4 we can observe the allylic proton, linked to the ether. These protons are diastereotopic and thus, the peak is a result of two overlayed 2dd signals for each type of allyl ether generated. This coupling is generated as one doublet from the geminal proton and one from the vicinal vinyl proton.

At around 5.2 ppm, the terminal vinyl protons depict this same type of coupling, but with higher coupling constants and a much more noticeable difference in chemical shift between the two protons. Indeed, at 5.32 ppm a clear dd signal is visible, with its geminal counterpart at around 5.2 ppm, partially covered by the residual solvent's peak. A second smaller series of peaks with the same type of coupling is visible at 5.13 ppm; the second dd signal also covered by the

solvent. The small coupling constant J is identical for all, whereas the big J are two by two equal.

Finally, at 5.8 and 6 ppm, the vinyl CH is visible. The multitude of peaks derives from its coupling with the two diasterotopic vinyl protons, in addition to the two terminal vinylic protons, each of them generating a doublet coupling with a different J.

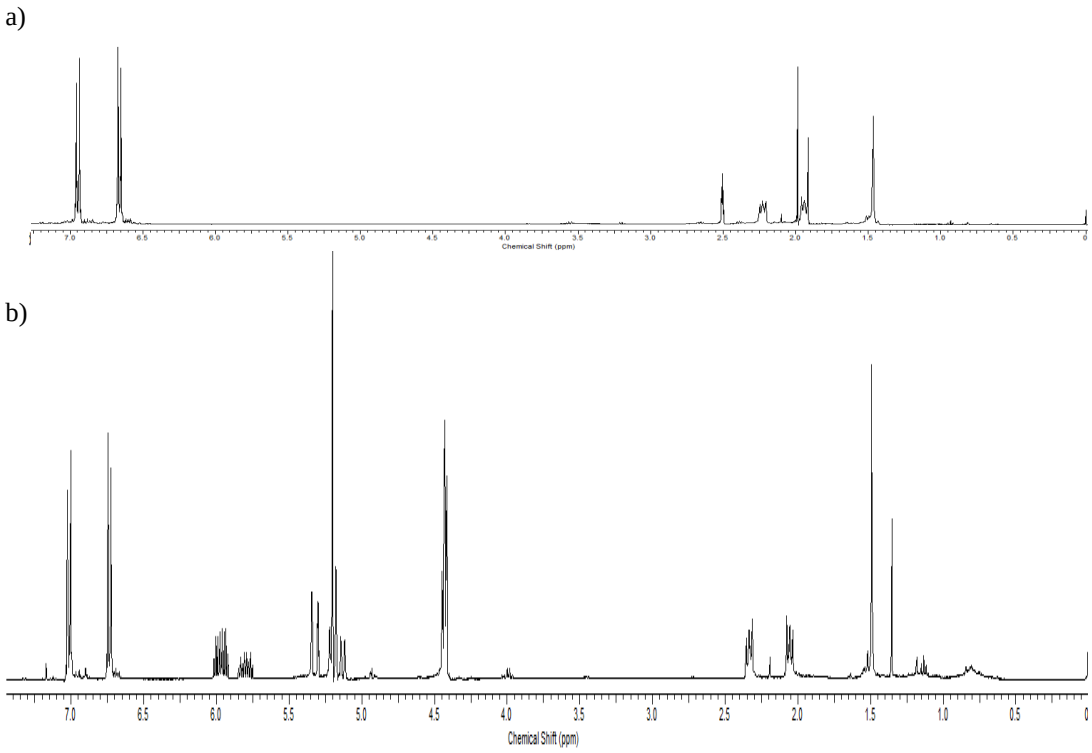


Figure 3.3: ^{1}H-NMR of DPA (a) an the product of its etherification with allyl chloride (b) in DMSO-d_6

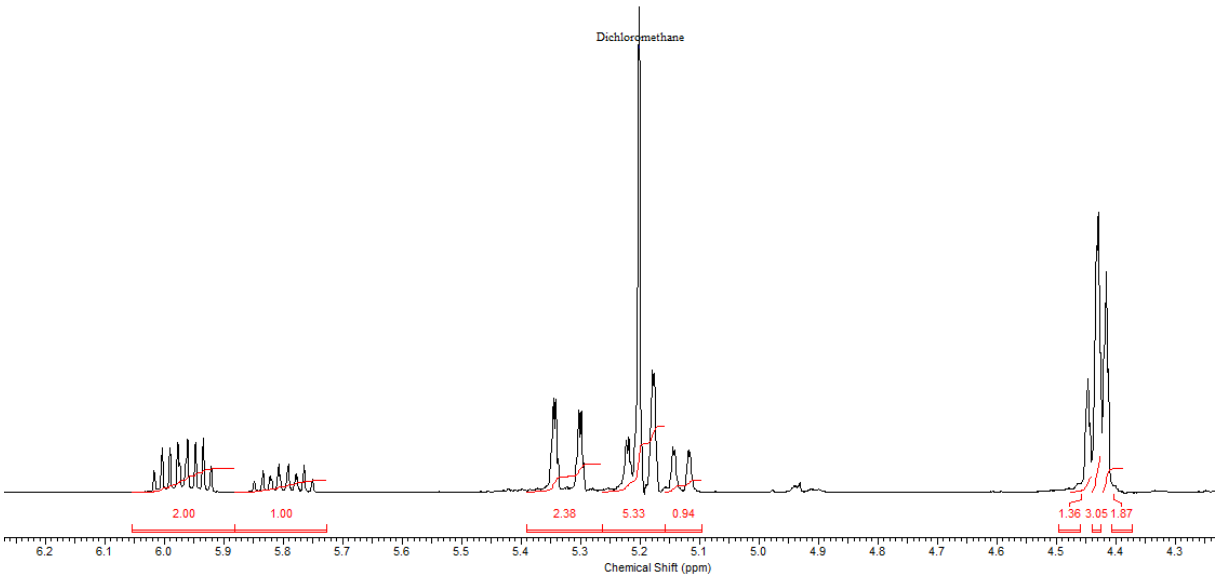


Figure 3.4: Detail of the ^{1}H-NMR of allylated DPA

As briefly stated before, all of these signals present two series of peaks, one big and one smaller. The more intense signals are assumed to correspond to the allyl ether's protons and the small

ones to the allyl ester deriving from the acid group. In the case of the signal at 4.4 ppm, these peaks are overlapped and cannot be defined as precisely as for the other signals. Indeed, when comparing the integrals of the two vinylic CH signals at 5.8 and 5.97 ppm, the integral of the latter is the double of the small one. This is due to the fact, that the signals of both allyl ethers add up owing to the intrinsic molecular symmetry. Also for the other peaks in the region, this phenomenon is visible, even though the residual solvent affects the value of the integrals and covers a part of the peaks. But if we consider the peak at 5.13 ppm, which corresponds to one proton out of the two terminal ester protons, its integral (0.94, 1H) is in agreement with the value found for the allylic peaks (2 for the intense signal, 1 for the lower signal).

We can thus say that the DPA react equally on all its positions, including the acid, with allyl chloride.

In order to confirm this finding, a HMBC NMR experiment was performed. This experiment correlates carbons with protons using long range coupling, at a distance of 2 to 4 chemical bonds.

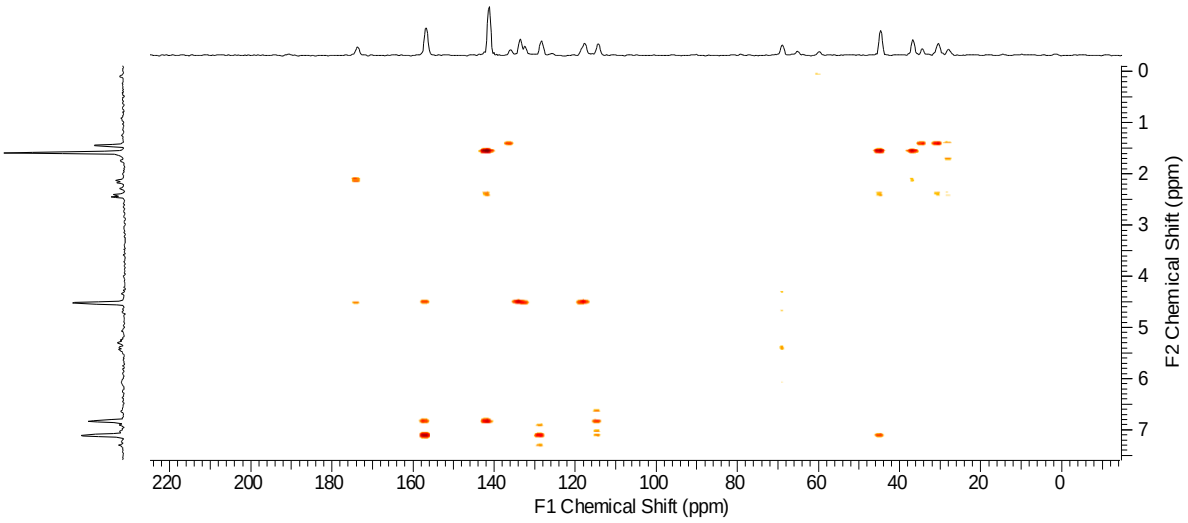


Figure 3.5: HMBC Spectrum of DPA from phenol in DMSO-d_6

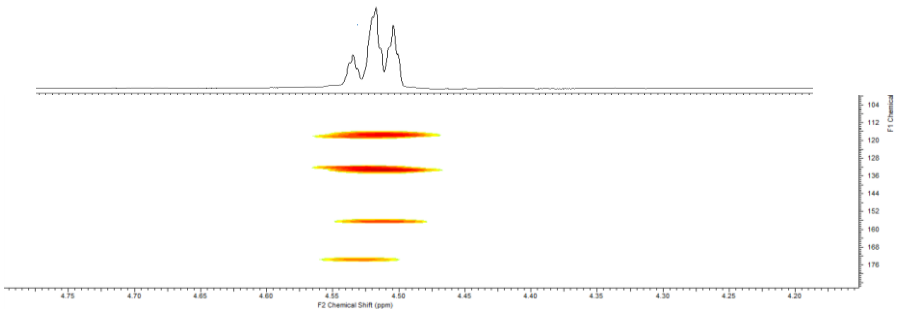


Figure 3.6: Detail of the HMBC spectrum of DPA from phenol and the corresponding ^{1}H-NMR

When focusing on the peaks of the carbons that correlate in long range with the allylic protons visible at around 4.5 ppm, four signals are present, shown in figure 3.6. In particular, we notice two signals at 157 and 174 ppm. They are slightly shifted horizontally and thus correspond to two separate overlaid peaks. Indeed, the latter is in the typical range of ester carbons, which is around 175-185 ppm. Hence, this signal corresponds to the carbonyl, and the correlated proton peak is assigned to the proton of the allyl ester. The carbon at 157 ppm, on the other hand, can easily be assigned to the aromatic carbon vicinal to the ether group, because it also correlates with aromatic protons. This proton signal does thus correspond to the allyl ether.

By comparison with the integrals of the methylenes on the aliphatic chain around 2 ppm, it becomes clear that the DPA is allylated to 100% on all these three positions.

Epoxidation of the DPA

The epoxidation of the generated double bonds is the next step towards synthesizing a fully renewable pre-polymer for epoxy resins. The reaction was carried out following exactly the same set-up as described in chapter 2, for comparison with the model compounds and understanding the effect of the presence of an ester group on the epoxidation mechanism. Indeed, this mechanism includes complex intermediates, which are strongly influenced by the surrounding molecules and the solvent.

In the case of an epoxidation, we would expect, like in the case of epichlorohydrin, our paradigm, several peaks appearing in the epoxidic region, between 2.5 and 3 ppm for the terminal methylenes and between 3 and 4 ppm for the methanetriyl proton. Simultaneously, the allyl and vinyl protons are assumed to disappear or at least, gradually reduce.

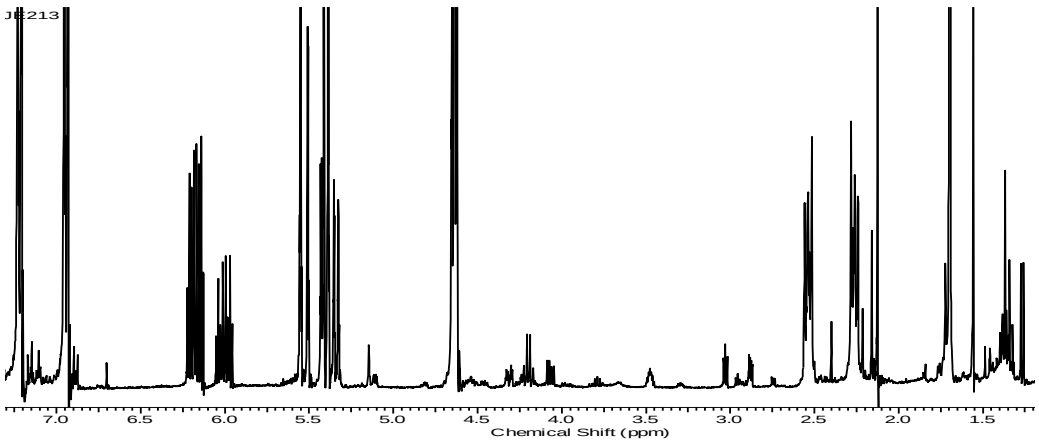


Figure 3.7: ^{1}H-NMR of DPA after epoxidation, in $CDCl_3$

In addition to the peaks deriving from DPA and its allylation, that have been already thoroughly discussed, in the epoxidic regions some peaks are visible, although of low intensity, as

highlighted in figure 3.7. Indeed, two identical series of peaks are observed between 2.75 and 3 ppm, of which one corresponds to the ester epoxide and the other to the ether epoxide group. The intensity of the peaks makes them easy to assign. Moreover, the terminal epoxidic protons are diastereotopic due to the rigidity of the cycle, and a separate peak with a dd coupling (with the geminal and vicinal) for each one of the four protons (two of the ether epoxy and two from the ester epoxy) is visible.

Two multiplets at about 3.5 ppm are assigned, as predicted, to the methanetriyl group, using their integrals to attribute them to their respective epoxide group.

Finally, at around 4 ppm, two more series of multiplets correspond to the methylene between the epoxide and the ether or ester. These protons are bonded to an asymmetric carbon, induced by the epoxide group.

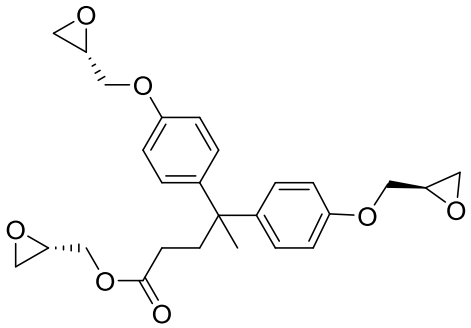


Figure 3.8: Theoretical structure of one fully epoxidized DPA

Considering the presence of three chiral carbons on the molecule, they potentially generate 8 diastereoisomers; one of them being represented in figure 3.8. Each of the diastereotopic methylenes generates two dd coupled peaks, which are slightly shifted leading to a lot of overlaps in the spectrum. It is clear from the ^{1}H-NMR that the peaks of the allyl groups are much more intense than the epoxidic proton peaks. Thus, only a very small part has epoxidized with this method, namely 7.7%, calculated by comparison of the integrals of the aromatic and epoxidic peaks.

As 93% of the groups remained unepoxidized and thus do not react with a crosslinker to form a resin, for the sake of creating a useable pre-polmer, the epoxidation was reapeated, using m-CPBA a commercial and very strong oxidizing agent.

As seen in figure 3.9, in this case, the quantity of epoxide is considerably higher, still, some allyl groups remain. Indeed, 35% of the double bonds have been epoxidized.

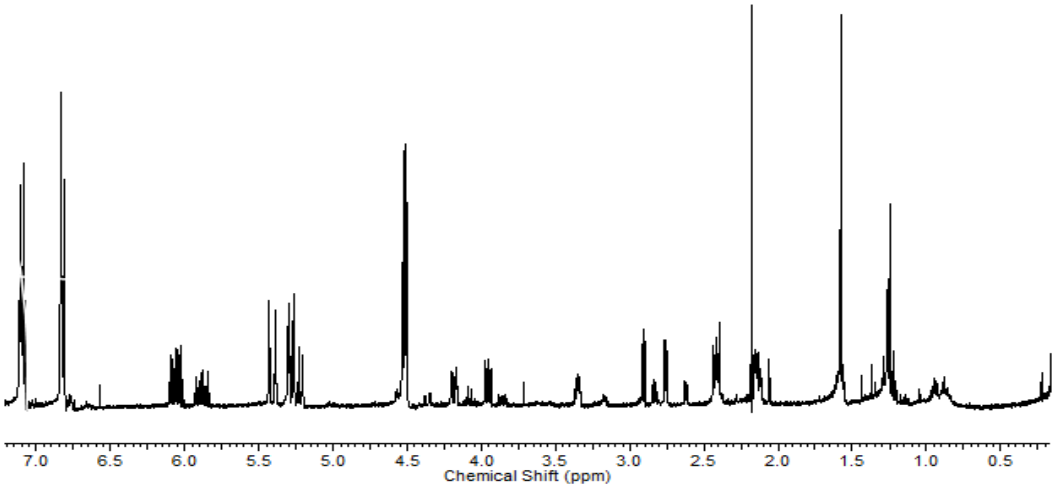


Figure 3.9: ^{1}H-NMR of DPA epoxidized with m-CPBA

3. DPAR

Allylation of DPAR

The results of allylation and esterification are particularly interesting in the case of DPAR. Indeed, on one hand, the synthesis of DPAR has the highest yield, on the other hand, the allylation tests carried out with resorcinol lead to much lower yields than the other two model reagents. The mutual deactivation of the hydroxyls that inhibited the resorcinol etherification, is present also in the corresponding DPAR.

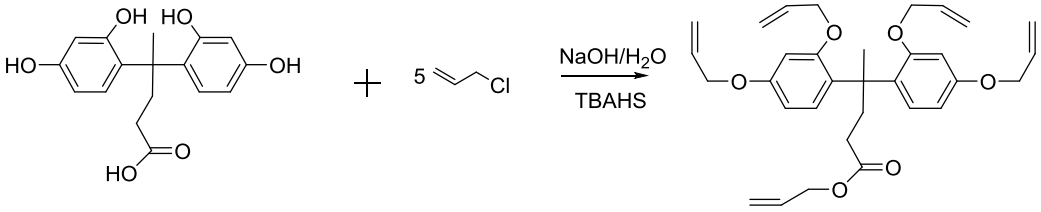


Figure 3.10: Reaction scheme of the allylation of DPAR

When carrying out the reaction and assigning the NMR peaks based on findings previously described for DPA, a very low yield of 6.5% is obtained.

In order to be able to use DPAR it was thus crucial to understand the underlying phenomena and further optimize the reaction[69].

The etherification reaction of the hydroxyl groups is a nucleophilic substitution whose speed depends on the steric hindrance of the carbon on which replacement occurs, the nucleophilicity of the anion and the stabilization of the leaving group.

The reaction is conducted in aqueous two-phase system without the use of organic solvents and is enhanced by a phase-transfer catalyst such as TBAHS, available at low cost. TBAHS is an ammonium salt whose cations pair with the phenolic substrate and migrates into the organic phase enabling the reaction with allyl chloride. The cation of the catalyst returns to the aqueous phase at the end of the cycle to begin another one. This contributes positively in the calculation of the E-factor, which gives an indication about the environmental friendliness of a reaction, as the mixture can be recycled after extraction of the product with organic solvent. The reaction is conducted in a basic environment thus allowing the deprotonation of the hydroxyl groups that in the case of the resorcinol have a pKa = 9 while in the case of DPA the pKa is about 5.

As previously noted, in the reaction, the formation of by-products of the homopolymerisation/oligomerisation of allyl chloride plays an important role. It was, therefore, considered that the exhaustion of the allyl chloride due to the parallel reaction is a major factor in the low yield of the reaction in the case of resorcinol. Indeed, as the resorcinol's hydroxyls are strongly deactivated, and thus the reaction rate slow, the homopolymerisation is taking the overhand in the competition for the reagent. In the case of catechol and DPAC that have strongly activated hydroxyls, the reaction rate is high enough to successfully compete with homopolymerisation. To check the hypothesis if the amount of allyl chloride was the limiting factor of the reaction, we decided to carry out further tests with resorcinol, changing the ratio of the reagents. Comparing with the values stated in chapter 2, the aim was to increase the yield of 42% in bisallyloxybenzene in the same conditions of time and temperature, increasing the amount of allyl chloride. The screening reaction was tested with an excess of 1.5 moles of allyl chloride per hydroxyl equivalent and then with an excess of 2. Increasing the amount of allyl chloride does not have negative consequences on the green policy pursued in this work because, being very volatile, the excess amount is recovered and recycled in the process by simple evaporation.

The tests carried out with a ratio of 1: 1.5 (molar equivalent of hydroxyls: mol allyl chloride) demonstrate a clear improvement in the yield of the previous work, obtaining a yield of 53%, as an average of three experiments performed. From the results obtained in these tests becomes clear that the allyl chloride is the limiting reagent in the reaction and its decrease during the course of the reaction adversely affects the yield. However, an even higher ratio, like 1:2 (molar

equivalent of hydroxyls: mol allyl chloride) have not led to a significant increase in yield with 54% on average. This shows that only these 12% of difference accounted for the exhaustion of reagents due to side reactions. The remaining 46% of missing yield are mainly due to the fact that in a biphasic system, the reagents are in constant exchange between the two phases leading to equilibrium phenomena. Thus, by recycling the system, these 46% are not actually lost but will react in the next cycle. However, with this yield, the allylation of resorcinol becomes comparable with catechol again.

Thus, the 1: 1.5 ratio (OH: allyl chloride) was found to be the most adequate and was used for the subsequent allylation of the DPAR.

The etherification reaction of the DPAR was thus conducted again with an excess of 1.5 equivalents of allyl chloride per equivalent of hydroxyl, with all the other conditions unchanged. The etherified DPAR was characterized using several NMR techniques.

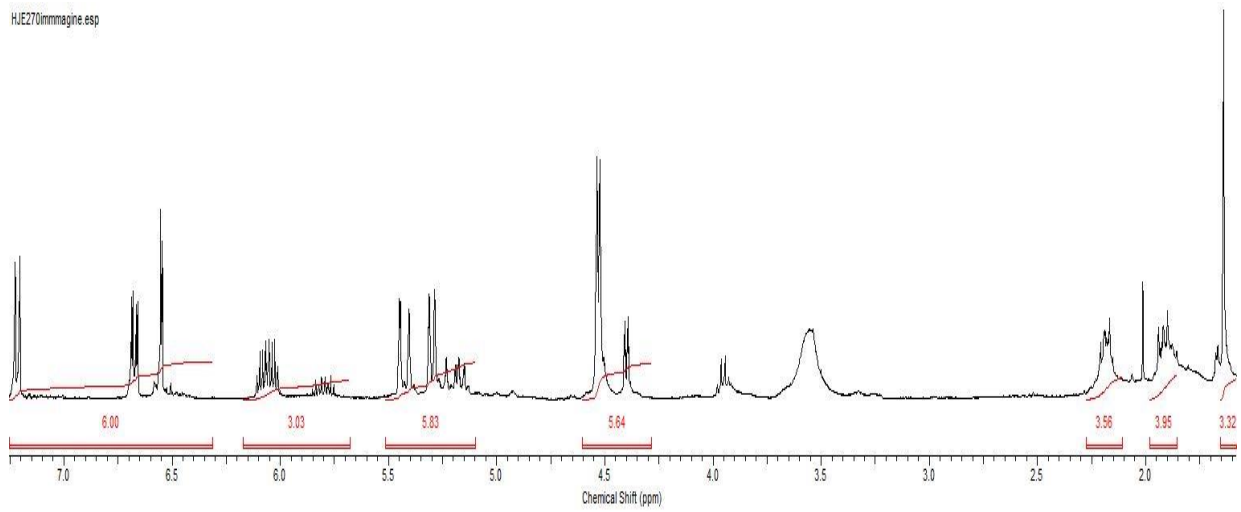


Figure 3.11: ^{1}H-NMR of the DPAR after allylation, in $CDCl_3$

In the proton spectrum we recognise peaks in the same areas as in the case of DPA from phenol. The peaks in the aromatic part of the molecule, similar to those of DPAR, the allyl signals around 4.5 ppm and a series of peaks corresponding to the different vinylic hydrogens in the range between 5 and 6 ppm. We already know from chapter 2 that the resorcinol and thus also DPAR is particular prone to Claisen-rearrangement, which is visible with peaks at around 3.6 ppm for the hydrogens in position a, 5.8 ppm for those in position b finally 5.4 ppm for c, in figure 3.12.

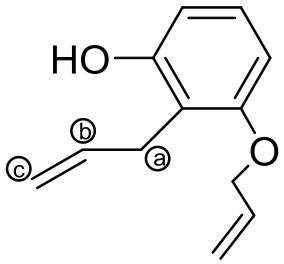


Figure 3.12: Claisen-rearrangement product on the resorcinol moiety

By comparing the peaks of the protons corresponding to the vinyl with the aromatics, the amount of allylated hydroxyls was calculated as 60% (including the acid), of which 11% have undergone Claisen-rearrangement.

Interestingly, on the spectrum, only 2 series are visible for each type of proton, one intense and one small. If the allyl groups were distributed randomly to an extent of 60%, at least three peaks should be visible, one for the allyl ester, one for the allyl ether in para and one for the allyl ether in ortho to the central aliphatic chain. Most probably the combination of two aromatic cycles, that have undergone allylation on different positions would give a multitude of peaks. Assuming the perfect superposition of the two allyl ethers is a hypothesis, although the integrals do not match.

Thus, NOE experiments were carried out to determine the precise structure. NOE (Nuclear Overhauser Effect) allows to determine the spatial proximity between two hydrogen atoms of the same molecule. The maximum distance at which the effect is observed, is 4.0 Å, as it decreases with the distance by r^6. In addition, HMBC (Heteronuclear Multiple-Bond Correlation) spectroscopy was used for further insight.

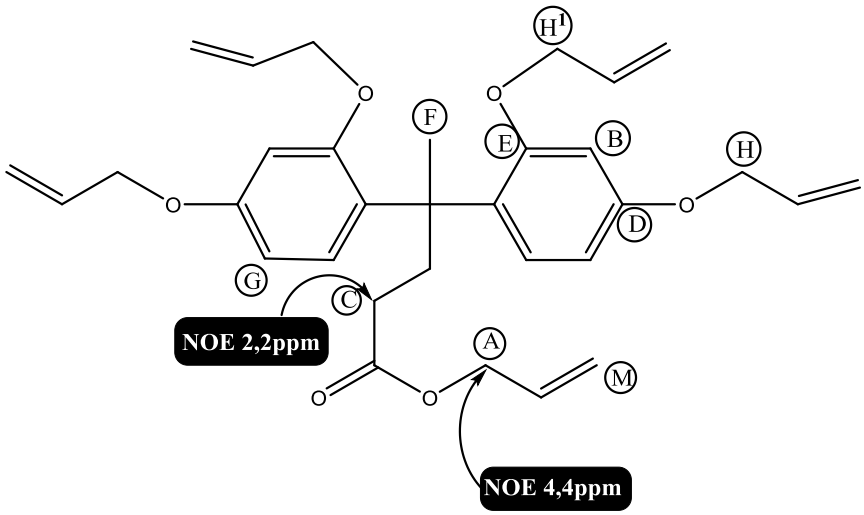


Figure 3.13: Assumed structure of the DPAR

The aim was to understand on which positions the etherification had taken place. Two peaks of clearly different intensity are visible at 4.6 ppm and 4.4 ppm on the ^{1}H-NMR in figure 3.11. Based on the findings for DPA from phenol, these peaks are assumed to correspond to the allylic methylenes (H, H1 and A). But from the integral, these peaks are in a ratio of 2:1 and not as expected, 4:1 (assuming the extreme case that H and H1 are overlapped).

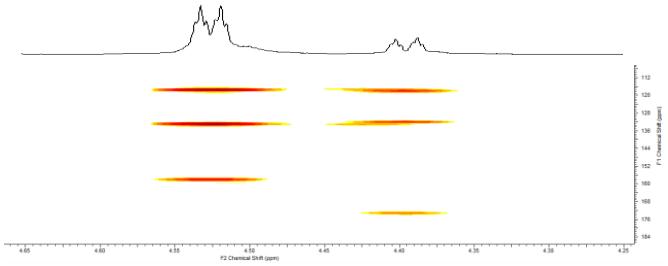


Figure3.14: Detail at around 4.5ppm of the HMBC of allylated DPAR, with the corresponding ^{1}H-NMR

The HMBC experiment in this area shows that the more intense peak, as well as the lower one, only correlate with one proton signal, eliminating the hypothesis that the peaks from H ad H1 are overlapped. The singularity of the correlation demonstrates that one of the two positions has not reacted. Moreover, the peak at 4.4 ppm only correlates with one carbon, at 173 ppm, which clearly corresponds to the ester carbon. Thus it is clear that this peak shall be assigned to the allylation of the acid. This was confirmed by a NOE, irradiating this same peak at 4.4 ppm, which generates a signal at 2.2 ppm, assigned to the methylene of the central aliphatic chain (C). It is thus demonstrated that this smaller peak corresponds to the allyl ester methylene (A).

To identify which position has been etherified, a second NOE was performed, irradiating the methylene group at 2.2 ppm corresponding to (C). Indeed, if the allylation had taken place in the ortho position, an allylic or vinylic peak should be visible. The absence of this peak in the NOE demonstrates that the etherification has taken place in the para position only, assigning the peak at 4.6 ppm to H (figure 3.13).

This allowed us to conclude that the two hydroxyls in ortho of the main chain don't participate in the allylation reaction at all, whereas the other three hydroxyls (including the acid) are fully allylated. It is assumed that the hydroxyls in ortho to the main chain (which will be called the "internal" hydroxyls from this point) are strongly sterically hindered and thus much less accessible for reactions.

Moreover, these positions are electronically deactivated owing to the presence of the allyl ether group in meta. The reactive hydroxyls are therefore those that occupy the outer positions. This allows to obtain a molecule, that is very similar to BPA and therefore we expect similar properties.

The product was purified from its by-product, the oligomer of allyl chloride, by precipitation in hexane, using the different polarity of the etherified DPA and by-product.

The total yield in etherified product (seen in figure 3.15) is 26%, all of it being allylated to its maximum potential. This is an enormous progress compared to the 6% obtained in the first case. These findings show that the reaction rate of allylation of the DPAR is even lower than in the case of resorcinol. Thus, a huge part of allyl chloride had probably undergone oligomerisation making it unavailable for condensation with DPAR.

As the yield is not very high, the extraction with isopropyl ether is very efficient because it extracts only the DPAR that is allylated to its full potential, and leaves intermediates like mono- and di-allyl ethers/esters in the aqueous phase. This aqueous phase can be immediately be reused as is, and contains all reagents except allyl chloride. Indeed, this is the big advantage of biphasic systems; the aqueous phase can potentially be recycled by just adding allyl chloride, until exhaustion of the DPAR therein. This reduces the loss of reagents, allowing to create a completely recyclable system.

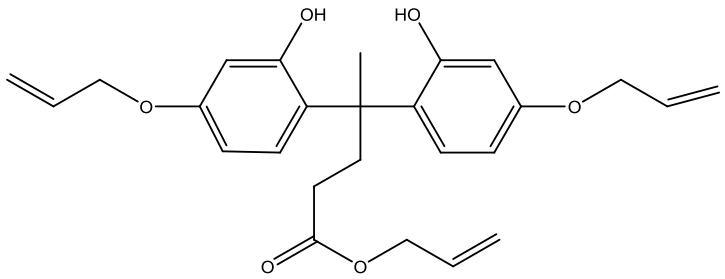


Figure 3.15: Real structure of the etherified DPAR

Epoxidation of DPAR

The last step of the procedure to synthesise a fully renewable pre-polymer from DPAR is generating the terminal epoxide groups by epoxidation of the double bonds. This step has shown satisfactory yields with the model molecule, resorcinol, in which 67% of the double bonds were epoxidized.

As previously mentioned, the selected procedure is very interesting due to its very low environmental impact. Thanks to peroxymonocarbonate ions, which are generated in situ from

"household chemicals", namely hydrogen peroxide and ammonium bicarbonate, the epoxidation takes place in very bland conditions, at room temperature and without stirring in a dilute solution. Without activation, this reaction does not take place to an extent of more than 2-3 %.

Nevertheless, the result of this reaction is uncertain as the epoxidation of DPA from phenol led to an extremely low yield of only 7%. As discussed in chapter 2, the steric hinderance has a tremendous impact on this reaction because it inhibits the formation of the butterfly-like intermediate. Thus, one hypothesis is that the conformation of DPA, with the presence of a second geminal aromatic cycle and an aliphatic chain, impedes the formation of the bulky intermediate, even in the outmost positions. The idea was thus to investigate several solvents, leading to different types of solvatation of the compound and thus maybe to a conformation that is susceptible to allow the reaction with the intermediate.

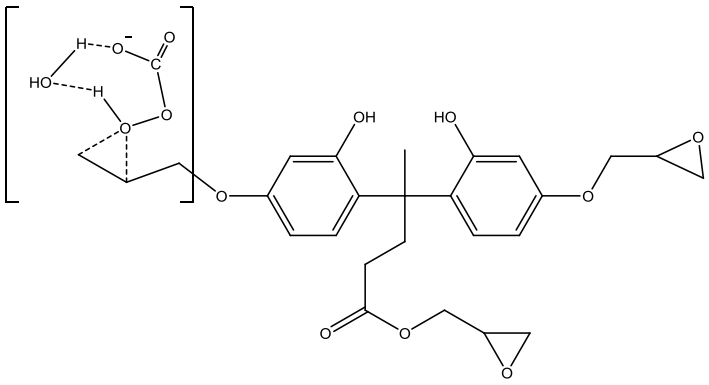


Figure 3.16: Butterfly-like intermediate epoxidizing the allylated DPAR

It was mentioned in the paper[64], that an increase of the amount of water was favourable to the epoxidation reaction rate. This is probably due to the essential contribution that water has in the formation of the active species and the stabilisation of the intermediate. Thus, this system was tested in several homogeneous and non-homogeneous conditions in order to identify, amongst various solvents, the most appropriate for the epoxidation of DPAR.

First, only water was used as a solvent, to enhance to the maximum its positive effects on the reaction. However, due to the scarce solubility of the allylated DPAR in water, as well as its glycidyl ether, this reaction did not produce a significant amount of epoxides.

Thus, a mixture of acetonitrile and water in a ratio 3:2 (V:V) was used, in analogy to the epoxidation of the resorcinol derivative described in chapter 2. The acetonitrile solubilizes the reagent and maintains the polarity of the solution high. This enhances the formation of the peroxymonocarbonate ion, as in this conditions, the k_{eq} of the reaction is 35 at 25°C. The

mixture was reacted for 24 hours in darkness, to avoid generating radicals. The final conversion of the product was calculated by comparing the integral of the vinyl groups with the groups in the epoxidic region; 41% of the double bonds had been epoxidized.

This result demonstrates that our hypothesis of steric hindrance is not the crucial factor in the reaction.

Nevertheless, in order to improve the yield, a series of solvents was tested. First, the idea was to solve the reagent in a small amount of methanol and mix it with a significantly higher amount of water, in order to reach a ratio of the double of water compared to the original reaction. But the quantity of methanol was not sufficient to maintain the reagent solubilized after adding the water. Thus, methanol was used in the same quantity as the acetonitrile in the previous reaction, namely 3:2 (V:V, methanol: water). Methanol is only slightly less polar than acetonitrile, as its polarity index is 5.1 against 5.8 for acetonitrile but the reagent is much more soluble therein, which would allow to reduce the amount of methanol in further steps. Furthermore, methanol is much more environmental friendly and is potentially produced from biomass. After 24 hours, the reaction did not show any results, making it clear that methanol is not polar enough for the scope.

As the amount of acetonitrile is already at the limit of the solubility of the DPAR derivative, adding more water to enhance the reaction would only lead to crashing out of the product, hence, inactivity.

On the other hand 41% of the double bonds epoxidized on a DPAR molecule are not sufficient for yielding a three-dimensional resin upon reaction with a curing agent, as each DPAR molecule, statistically, contains only the equivalent of 1.23 epoxide groups.

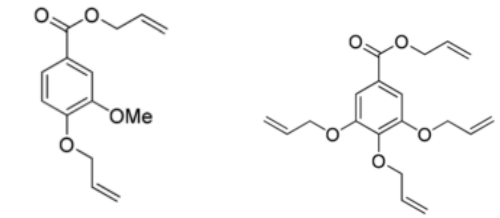


Figure 3.17: Examples of compounds, epoxidized by lipase[64]

In literature, a number of epoxidation systems have been published, often including catalysis, which makes the step more efficient but more expensive and frequently hazardous or rare metals are used. Particularly interesting and very environmental friendly is the use of lipases[70] for epoxidation. Unfortunately, this method could not be investigated in our lab for technical

reasons. However, it is reported that lipase successfully epoxidizes natural phenolic compounds like diallylated vanilic acid and tetraallylated gallic acid, represented in figure 3.17. As these molecules are aromatics, containing allyl ethers and one allyl ester, the structures are very similar to the allylated DPAs we used. We can thus assume that our allylated DPAs are able to react in the same way, leading to a fully glycidylized DPAR

4. DPAC

Finally, the method was applied to DPAC. Catechol had shown a satisfactory yield in the allylation, similar to hydroquinone.

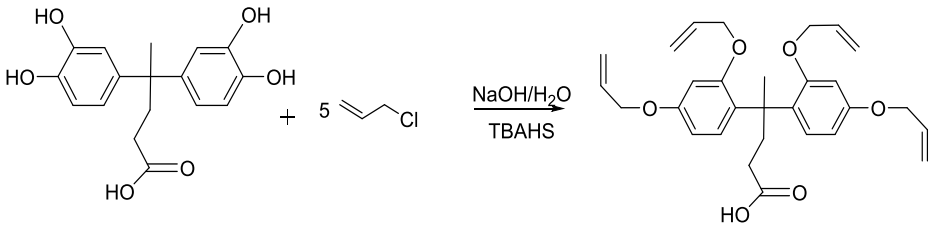


Figure 3.18: Reaction scheme of the allylation of DPAC

Especially, in this case, the extraction was crucial. Indeed, in the first extraction, with di-isopropyl ether, the phases were both very dark in colour, making separation difficult. Furthermore, this meant that a considerable amount of the product had remained in the aqueous phase and was subsequently removed by acidifying the latter and extracting with diethyl ether.

Furthermore, this product is prone to oligomerisation. Indeed, a viscous oil formed in the flask and was not soluble in any of the used solvents. Its ^{1}H-NMR displays an enormous amount of peaks, making it clear that the product is an oligomer. A possible hypothesis is that the acid moiety, deriving from the levulinic acid, has esterified with one of the phenolic hydroxyls. Such esterification is enhanced by the temperature - as the reaction was carried out at 70°C - and the strongly alkaline medium for activation. However, this phenomenon had not occurred for DPAs from phenol and resorcinol. Indeed, the hydroxyls on DPAC are mutually strongly activating. This activation leads to strong reactivity, leading us to the idea that the hydroxyls which did not incur glycidylation, might potentially be reactive enough to also react with an epoxide group, maybe even inducing self-reticulating, i.e. forming a three dimensional resin without using a curing agent.

The resulting NMR analyses are comparable to the ones of the products from in DPA from phenol and DPAR and will thus not be explained in detail. The first extraction with di-isopropyl ether leads to a fully allylated DPAC, with all five hydroxyls etherified/esterified. The yield is

40%. This yield not being particularly high, the second extraction was highly interesting and showed that in the aqueous phase, 55% of the hydroxyls had randomly allylated. Furthermore, all the diphenolic compounds were extracted by this method. This is highly interesting because it means that the choice is open to, either recycle the aqueous phase and react further by adding only simple allyl chloride until all of the DPAC is fully allylated or mixing the two products, obtaining a product that is allylated to an extend of 74% with a yield of almost 100% in weight. This is particularly interesting for the reasons described in the previous paragraph, requiring unreacted hydroxyl groups.

The epoxidation with bicarbonate-activated hydrogen peroxide yielded 51% of epoxidized groups, which, although it is the highest yield amongst the three investigated compounds, leads to a considerable amount of remaining double bonds, which are dead chain ends in the curing reaction.

5. Experimental

Allylation of the DPAs

General procedure

For this reaction, the previously synthetized DPAs were used. Their synthesis has been carried out following the procedure described in chapter one.

This reaction has been carried out changing several parameters, which are stated. The described procedure corresponds to the procedure used as the starting point, and performed with all three DPAs at least once.

A 100 mL three-necked round bottom flask, equipped with magnetic stirring and a cooling system on an oil bath heating system fitted with a thermometer, was loaded with a solution of 50% NaOH in water, tetrabutylammonium hydrogen sulfate (TBAHS) and a stoichiometric amount of allyl chloride. The oil bath was preheated and the mixture was reacted for 2 hours at 70°C under vigorous stirring.

After reaching room temperature again, the mixture was extracted five times with di-isopropyl ether. It was observed that the partially allylated DPAC and DPAR compounds tend to remain in the aqueous phase. The latter was thus acidified with dilute hydrochloric acid until pH 4-5 and extracted with diethyl ether, to recover as much product as possible. After removal of the solvent with a rotary evaporator the compounds were analysed by NMR.

The generated oligomers of allyl chloride were removed by a plug on silica gel, with dichloromethane as eluent.

Allylation of DPA

Since DPA contains 3 potentially reactive hydroxyls, were used 52.4 mL of water, 26.2 g of NaOH, 1.5 g of DPA (0.0052 mol), 0.0889 g of TBHS (0.26 mmol) and 1.27 mL of allyl chloride (0.0157 mol).

The yield obtained after purification was of 26%.

^{1}H-NMR (600 MHz, in DMSO-d$_6$), *δ (ppm)*: 1.50 (s, 3H, -CH_3); 2.06 (m, 2H, -CH_2-); 2.33 (m, 2H, -CH_2-); 4.41 (m, 2H, COO-CH_2); 4.43 (m, 4H, -O-CH_2); 5.21 (2dd, 2H, = CH_2 vinyl ester); 5.32 (2dd, 4H, = CH_2 vinyl ether); 5.80 (m, 1H, -CH = vinyl ester); 5.97 (m, 2H, -CH = vinyl ether); 6.74 (dd, 4H, Ar-H); 7.02 (dd, 4H, Ar-H).

Allylation of DPA derived from resorcinol

Since the DPA contains 5 potentially reactive hydroxyls, were used 65 ml of water, 32.5 g NaOH, 2.055 g of DPA (0.0065 mol), 0.1103 g of TBHS (0.32 mmol) and 2.63 ml of allyl chloride (0.0325 mol).

The yield obtained after purification was 6.5%

^{1}H-NMR (600 MHz, in DMSO-d$_6$), *δ (ppm)*: 1.53 (s, 3H, -CH_3); 1.62 (m, 2H, -CH_2-); 2.01 (m, 2H, -CH_2-); 4.40 (m, 2H, COO-CH_2-); 4.60 (m, 4H, Ar-O-CH_2-); 5.22 (2dd, 4H, = CH_2 vinyl ether); 5.36 (2dd, 2H, = CH_2 vinyl ester); 5.80 (m, 1H, -CH = vinyl ester); 6.06 (m, 2H, -CH = vinyl ether); 6.56 (d, 2H, Ar-H); 6.68 (dd, 2H, Ar-H); 7.23 (d, 2H, Ar-H)

Allylation of DPA derived from catechol

Since the DPA contains 5 potentially reactive hydroxyls were used 63 ml of water, 31.5 g NaOH, 1.3477 g of DPA (0.0042 mol), 0.1064 g of TBHS (0.29 mmol) and 1.797 ml of allyl chloride (0.0292 mol).

The yield obtained after purification is of 40%

^{1}H-NMR (600 MHz, in DMSO-d$_6$), *δ (ppm)*: 1.33 (s, 3H, -CH_3); 1.44 (m, 2H, -CH_2-); 1.55 (m, 2H, -CH_2-); 4.53 (m,10H, O-CH_2-); 5.37 (2dd, 10H, = CH_2); 5.97 (m, 1H, -CH= vinyl ester); 6.07 (m, 4H, -CH= vinyl ether); 6.74 (dd, 2H, Ar-H); 6.78 (d, 2H, Ar-H); 6.86 (d, 2H, Ar-H)

Epoxidation of the double bonds

General procedure

This reaction has been carried out changing several parameters, which are stated. The described procedure corresponds to the procedure with the highest yields.

A one-necked 100 mL flask was loaded with 0.17 mmol of the DPA (0.1 g) and 0.43 g of NH4HCO3 (5.7 mmol), 10.4 mL of water and 19.2 mL of acetonitrile. Finally, 5 mL of hydrogen peroxide at 22% (w/w) was added. The reaction was carried out at room temperature for 24 hours without stirring.

At the end of the reaction the product was extracted with dichloromethane and dried at the rotary evaporator.

Epoxidation of the etherified DPA from phenol

The reaction was carried out in the above-stated conditions, leading to 8% of the double bonds getting epoxidized.

^{1}H-NMR (600 MHz, in D_2O), δ (ppm): 1.45 (s, 3H, −CH_3); 1.90 (t, 2H, −CH2−); 2.19 (t, 2H, −CH_2−); 2.63 (2dd, 4H, −Epoxy−H_2); 2.81 (2dd, 2H, ester−Epoxy−H_2); 3.18 (m, 3H, H-Epoxy); 3.5 - 4.5 (m, 6H, O−CH_2−Epoxy); 6.63 (d, 4H, Ar−H); 6.95 (d, 4H, Ar−H)

Epoxidation of the etherified DPAC

The reaction was carried out in the above mentioned conditions, leading to 51% of the double bonds getting epoxidized.

^{1}H-NMR (600 MHz, in DMSO-d_6), δ (ppm): 1.38 (s, 3H, −CH_3); 1.92 (t, 2H, −CH_2−); 2.12 (t, 2H, −CH_2−); 2.65 (2dd, 2H, ester −Epoxy−H_2); 2.73 (m, 8H, ether−Epoxy−H_2); 3.25 (m, 5H, −H-Epoxy); 3.86 - 4.29 (m, 10H, O−CH_2−Epoxy); 6.43 (dd, 2H, Ar−H); 6.48 (d, 2H, Ar−H); 6.61 (d, 2H, Ar−H).

Epoxidation of the etherified DPAR

The reaction was carried out in the above mentioned conditions, leading to 41% of the double bonds getting epoxidized.

^{1}H-NMR (600 MHz, in DMSO-d_6), δ (ppm): 1.53 (s, 3H, −CH_3); 1.60 (t, 2H, −CH_2−); 2.00 (t, 2H, −CH_2−); 2.79 (2dd, 2H, ester−Epoxy−H_2); 2.81 (m, 4H, ether−Epoxy−H_2); 3.29 (m, 3H, −H-Epoxy); 3.84 - 4.34 (m, 6H, O−CH2−Epoxy); 6.53 (d, 2H, Ar−H); 6.51 (dd, 2H, Ar−H); 7.22 (d, 2H, Ar−H).

Epoxidizing with m-CPBA

As m-CPBA is a highly reactive and explosive chemical, for safety, we followed a procedure suggested in literature[71] that used relatively bland conditions.

In a 50 mL round bottom flask, fitted with a thermometer and magnetic stirring, we dissolved the allylated DPA in chloroform. Separately, we dissolved m-CPBA in a ratio of 1:2 (molar equivalents of allyl groups: mol m-CPBA) in chloroform. While stirring, the acid was slowly added with a dropping funnel, cautiously controlling the temperature. After two hours of mixing at room temperature, the mixture was filter and dried under vacuum.

This procedure was used only for the DPA from phenol and lead to 35% of epoxidized double bonds. The chemical shifts are similar to the ones stated above but slightly shifted because of variation in the surrounding groups caused by the low yield.

6. Conclusion

In this chapter, the synthetized DPAs were allylated and subsequently the generated double bonds epoxidized, following a glycidylation procedure identified as the "greenest" amongst three in the previous chapter.

The allylation was carried out in a biphasic system, in which only allyl chloride, the reagent, was used as the organic phase. The maximum yields obtained in reactions with resorcinol and catechol, representing the corresponding moiety on the DPAs, were around 50%.

The same conditions were, thus, used for the allylation of DPAR and DPAC. Furthermore, the reaction was carried out with DPA from phenol, for comparison and to simplify the interpretation of the ^{1}H-NMR analyses. The yield was particularly low for DPAR, with only 6%. Also resorcinol had demonstrated lower yields in this reaction, due to electronic effects in which the hydroxyls have a mutually deactivating action. The reaction rate is thus significantly slower than the one of the competitive reaction, the spontaneous homo-polymerisation of allyl chloride. Several tests on resorcinol with different ratios of allyl chloride have shown that the exhaustion of the allyl chloride due to the parallel reaction accounts for as much as 20% in yield, in the allylation of DPAR. For DPAC, with the hydroxyls in ortho to each other, they are both strongly mutually activating, thus the parallel reaction presents a negligible issue.

Although the yields, stated in table 3.4, still seems low, it should not be forgotten that in this biphasic system, the organic phase contains all the fully allylated product whereas partially allylated and unreacted DPA derivatives remain in the aqueous phase. The latter can thus easily be recycled after removal of the organic phase by just adding allyl chloride, without further treatment. In this way, the reaction can potentially by continued until all the DPA has reacted to 100%.

Table 3.4: Results of allylation and epoxidation in the best conditions

	Allylation		Epoxidation
	Yields	Extent of allylation (% hydroxyls allylated)	Percentage of double bonds epoxidized (%)
DPA from phenol	25%	100	35 (with m-CPBA)
DPAR	26%	60	41
DPAC	40%	100	51

A further interesting finding was the complete inactivity of the hydroxyls in ortho to the central chain, in DPAR. Indeed the "internal" hydroxyls do not react with allyl chloride, leading to a

product, in which only the outmost hydroxyl and the acid group are active, causing it to be equivalent to diphenolic acid from phenol from the structural point of view. In addition, this reactivity in the outmost positions, makes it very similar to bisphenol A, thus, analogous properties are expected.

Finally, DPAC not only demonstrates an allylation to 100% of all the five hydroxyls (including the acid) to an extent of 40% but also the DPAC remaining in the aqueous solution is allylated to 55%, which is comparable with the yield of glycidylation with epichlorohydrin (59%), described in chapter 1. Furthermore, spontaneous esterification generating oligomers clearly depicts the particularly strong mutual activation of the hydroxyls. This could potentially give rise to self-reticulating behaviour, hence avoiding the use of curing agents, which are often toxic and can cause homogeneity issues.

Regarding the epoxidation, this step is crucial, as allylated and not oxidized groups lead to dead ends during curing. The proposed epoxidation uses peroxymonocarbonate ions as the active species, generated in situ from household chemicals, namely hydrogen peroxide and ammonium bicarbonate. The yields are around 50% of double bonds epoxidized, which is not enough to form a three-dimensional network during curing, especially in DPAR that has only three active sites. A highly environmentally friendly solution for epoxidation is, in recent publications, the use of lipases[70]. Indeed, some natural compounds with a similar chemical structure have been successfully epoxidized by this mean. Unfortunately, the technical capabilities did not allow to perform this kind of biotechnological reaction in our laboratory. However, the results are expected to be analogous.

CHAPTER 4:

Curing and characterization of the cured resins

1. Introduction

Epoxy resins have a wide range of applications, amongst which is the use as coatings for metals. A particular interesting one is can coatings for food applications. Indeed most of the BPA absorbed by the human body in adults, derive from this source and from the dissolution into the foods therein. Nevertheless, their excellent adhesion to the aluminium surface due to the presence of a significant amount of polar hydroxyls still makes them the best choice. An effective coating prevents corrosion thus avoiding food safety issues, i.e. bacteria penetrating the can and spoiling its content.

Thus, several tests were carried out to evaluate the characteristics of the resins, including the properties required for the application as food-contact coating. In order to be used as a coating for food applications, the most important factor is the absence of leaking, during the storage, but also during sterilisation. The latter is particularly crucial, as the can is usually sealed after filling and heated in an autoclave for a certain period of time, in order to reach an internal temperature of 100°C. This procedure increases potential solubilisation of low molar mass compounds in the food content. Furthermore, it could also cause degradation of the resin. This is the reason why thermogravimetric analysis, used to determine the thermal resistance of the materials is also performed. Finally, the measurement of the swelling capacity and hardness are additional properties of the resin, which are typically checked. Indeed, for thermosetting resins, in general a soft material is not very well cured and will not adhere properly, creating corrosion issues and increased leakage. The swelling allows to determine the cure density , further indicators of a successful curing.

The interesting feature noticed in diphenolic acids is the presence of up to five reactive groups that, in part, have an activating or deactivating effect on each other. These five reactive groups may make the use of a curing agent unnecessary, as the molecule has enough functionalities to generate a three-dimensional network. In the best case, these functional groups would even react with each other spontaneously without even needing a “bridging” molecule. This “bridging” molecule, for example a linear secondary diamine with only two reactive positions, allows to bond in a linear way two functional group of diphenolic acids, like a bridge; it reacts only with two molecules, without causing cross-linking.

Finally, the two selected diphenolic acid resins were compared with a standard bisphenol A resin, cured with an aliphatic diamine: 1,6 hexamethylenediamine.

2. Self-curing of diphenolic acid derivatives

The DPA derivative from resorcinol and catechol offer another advantage in addition to their interesting yields: As they feature up to five functional groups, potentially no cross-linking agent is necessary.

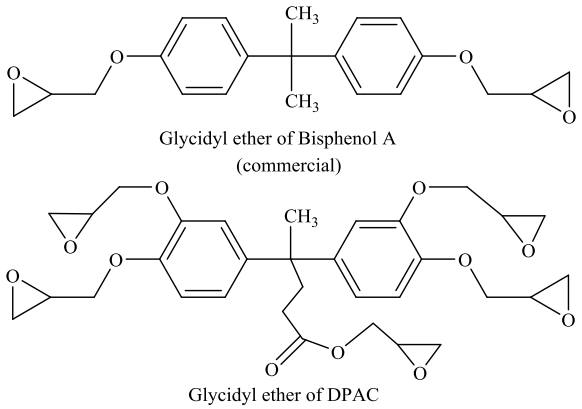


Figure 4.1: Glycidyl ethers of bisphenol A and of the DPA derivatives from catechol and resorcinol

More surprisingly, it has been found that the DPAC derivative holds self-curing properties i.e. it cures into a three-dimensional network even without a hardener. It has been demonstrated in several curing tests that a sample self-cures at 200°C into a hard brittle material, insoluble in all the major laboratory solvents, like acetone, dimethyl sulfoxide, DMF, THF, chloroform and water. Obtaining a highly cross-linked resin is only possible due to the presence of the ester group as an internal initiator. Indeed, bisphenol A will not yield a polymer in similar condition. The hypothesis is that the ester works as a Lewis base, catalysing the curing reaction between the unreacted hydroxyls and the epoxide groups.

Furthermore, the curing cycle carried out with the derivative of DPA from phenol, which thus contains only two glycidyl ethers and a glycidyl ester, yielded a fully cross-linked resin instead

of the expected linear polymer. This demonstrates that the glycidyl ester deriving from the acid is included in the cross-linking mechanism.

There is an enormous difference between the DPAC and DPAR derivative. Indeed, although it was thought at the beginning that DPAR self-cures as well, even leaving it in the oven for 6 hours does yield only short oligomers, which hydrolyse in boiling acid water. This means that only the ester bond had reacted and it had not fulfilled its role as a catalyst of the reaction between the hydroxyls and the other epoxides. Although the yield of glycidylation is comparable to the one of DPAC, with 54% of total hydroxyls glycidylized for DPAR compared to 56% for DPAC, GEDPAR is not able to self cure. Furthermore, as two hydroxyls are inactive, the yield of glycidylation on the remaining three hydroxyls is 88%. This higher amount of terminal epoxides should theoretically enhance curing.

As discussed in chapter 3, in which the allylation of DPAR is described, the aromatic hydroxyls on the resorcinol moieties are strongly mutually deactivating, due to their respective positions, in meta to each other. This leads to lower yields in allylation. Furthermore, it was observed that the "internal" hydroxyls are completely inactive in the allylation. This applies as well in the glycidylation with epichlorohydrin. As shown in figure 4.1, the DPAR derivative presents, thus, two inactive hydroxyls and potentially (almost) three epoxides.

Calculations with Gaussian G09 allow to optimise the conformation in gas phase. These calculations demonstrate that the conformation, shown in figure 4.2, in which both "internal" hydroxyls are bent inwards, has the lowest energy. This is probably due to hydrogen bonding between these two hydroxyls, which inhibits their reactivity. Furthermore, in the generated conformation, stabilized by hydrogen bonding, the molecule approaching the hydroxyls is strongly sterically hindered by the aromatic rings and the aliphatic acid chain. It is thus almost impossible to access these sites.

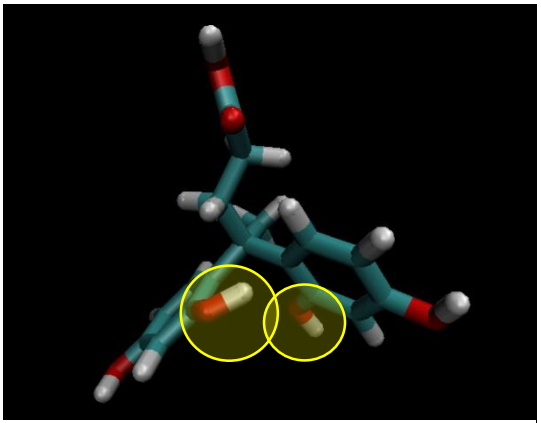


Figure 4.2: Most stable conformation of DPAR, from Gaussian G09

Nevertheless 12% of hydroxyls remain in the active positions, the "internal" hydroxyls, although not reactive with other molecules, maintain their electronic effect, strongly deactivating these outmost hydroxyls. Another hypothesis is that 12 % of hydroxyls might simply not be enough to react with 88% of epoxides and form a three-dimensional network.

3. Curing of GEDPAR

In order to find an adequate way of curing the glycidyl ether of DPAR (GEDPAR), a series of tests were performed, namely:

1) GEDPAR without any curing agent, at 200°C for 6 hours,

2) GEDPAR with a secondary diamine, for "bridging" the molecules only,

3) GEDPAR with a primary diamine curing agent.

Indeed, the GEDPAR has three active groups and should thus crosslink, even without a curing agent, just by adding a "bridging" molecule which will generate a linear bond. The last setup, on the other hand, was chosen, in analogy to the curing of DGEBA, using 1,6-diaminobutane as a curing agent. The resulting materials of the three curing conditions were fully analysed, where possible, and some showed interesting features. Indeed, even not fully crosslinked but polymerised epoxy have a wide range of applications, other than in food contact, due to expected leaking.

As an initial test, GEDPAR was put in the oven at 200°C for 4 and later for 6 hours. The result is a hard material, with a pencil hardness of H and a scratch hardness of HB (ASTM-D3363). These are acceptable values for an organic coating and it seems cured from its appearance but dissolves in THF. This is a clear evidence that curing did not take place.

In order to compensate this loss in reactivity compared to DPAC, a linear secondary diamine was used to "bridge" between the epoxide groups of GEDPAR. N,N'-diethylethylendiamine was used as a "bridging" molecule, reacting it in stoichiometric ratio for 2 hours at 100°C and for another 2 hours at 200°C after checking the characteristic bands via FT-IR. Although the characteristic peaks of the N-H stretching at around 3300 cm^{-1} and the elongation of the epoxide cycle at 916 cm^{-1} had disappeared at this point, the compound was still partially soluble in THF, demonstrating an oligomerisation only. On the ^{1}H-NMR the reaction between the epoxide and the amines is clearly visible but apparently the amount of present epoxides was not sufficient to lead to a three-dimensional resin. Indeed, GEDPAR has an EEW of 174 g/mol, which corresponds to the value of DGEBA. Thus the combination of the deactivated 12% of hydroxyls

with the two completely inhibited hydroxyls impedes the curing into a three-dimensional resin even with a "bridging" molecule.

Finally, the resin was cured with a stoichiometric amount of the primary 1,6-hexamethylendiamine, a tetrafunctional curing agent, for 2 hours at 100°C to yield a cured resin. The nice gloss and insolubility in all major solvents confirms the successful curing. In table 4.1, the main features of the three materials are compared, also stating the values for commercial DGEBA, cured with the same curing agent. The tests reported are, at this point, only used to get an indication about the state of the material and they are thoroughly described in the fourth part of this chapter. All the values are averages over three repetitions of the same experiment.

Table 4.1: Comparison of three experimental set-ups

	Pencil hardness (scratch hardness)	Leaking(5% brine, mg/dm^2)	Leaking (3% acid, mg/dm^2)	Swelling (%)
DGEBA (reference)	3H(H)	8.8	61.7	88
GEDPAR	H(HB)	5.1	8.4	dissolved
GEDPAR + "bridge"	4H(H)	-16.9	-1.6	41
GEDPAR + hexamethylendiamine	7H(HB)	2.0	15.7	21

This table clearly shows that GEDPAR has not cured spontaneaously upon simple heating as it dissolves in THF during the swelling test. Also the GEDPAR with the "bridging agent" breaks into pieces during swelling, which were then filtered and weighted. The number is thus not representative, as part of the compound has probably dissolved. The hardness obviously increases from:

oligomerised GEDPAR < GEDPAR reacted with "bridging agent" < GEDPAR reacted with curing agent,

indicating the increase in the formation of bonds. Interestingly, the hardness of GEDPAR with the 'bridging agent" is superior to the hardness of a fully cure BPA epoxy resin, used as a reference.

Furthermore, the leaking of oligomerised GEDPAR, shown in mg/dm^2 for two different solutions after two hours at boiling point, is lower than the one of the reference BPA resin. This demonstrates that the compound, although it is not fully crosslinked, is not soluble in water or dilute solutions and could thus be interesting as a natural organic coating for surfaces that are not in contact with organic solvents or as a structural material.

The GEDPAR reacted with ‘bridging agent” shows a widespread issue in epoxies: water uptake. Indeed the negative numbers show that up to 16.9 mg/dm^2 of water were absorbed by the film in a diluted 5% brine. Although the samples have been washed and dried after the migration tests, the compound is so hydrophilic, that it absorbs the humidity from the air, even before weighting. This is probably due to the presence of a lot of unreacted polar groups.

Thus, the DPAR derivative needs a curing agent in order to yield a full crosslinked epoxy resin. Its structure, with only the outmost hydroxyls and the glycidyl ester reacting combined with its EEW of 174 g/mol and finally, its reactivity, makes it very similar to a bisphenol A epoxy resin.

It is important to note that it is not the low amount of epoxides, which in fact is comparable to the one of DPAC (EEW=163 g/mol) that impeded the self-curing.

These findings also allow us to get a deeper insight into the self-curing of DPAC. Indeed, the main factor of the self-curing is not the presence of aromatic hydroxyls activated by resonance only but the combination of several factors:

1. The presence of the ester group acting as a Lewis base, catalysing homopolymerisation.
2. Five reactive groups, epoxides or hydroxyls.
3. The electronical effects of the substituents on the aromatic cycle, not deactivating the hydroxyls.

For the sel-curing of DPAC the hydroxyls play the leading role in the reaction: After activation by the Lewis base, they form a phenolate that is highly active due to mesomeric effects, attacking the epoxide and thus forming an intermolecular bond.

4. Characterization

During characterization, the resin from DPAC and DPAR were compared with commercial DGEBA. The latter two were cured with 1,6-hexamethylenediamine for two hours at 100^{o}C. The samples were prepared on aluminium plates by drop casting or as pellets, for the various tests, as shown in figure 4.3. The values always correspond to the average of three repetitions. Several commonly used tests for films were carried out.

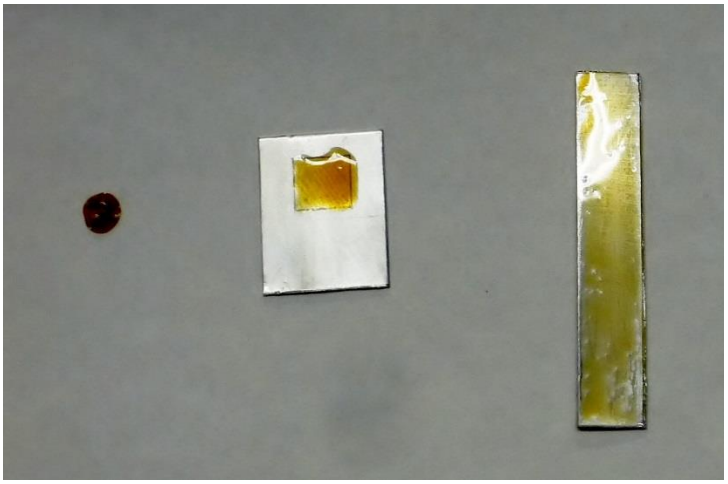


Figure 4.313: Samples of self-cured DPAC

Pencil hardness

Pencil hardness is an easy and widespread way to test coatings. The hardness is determined using pencil lead as comparison. The hardness of pencil lead is determined using designations consisting of letters and numbers according to the current ASTM standard (ASTM D3363). A high number of H designates a very hard compound, a high value of B designates a soft material.

The values range from 6B to 9H, the latter being the hardest. HB is considered an acceptable hardness for a coating that is not exposed to particular stresses. The scratch hardness designates the value until which no scratches are visible in the material whereas the pencil hardness corresponds to the resistance against actual scoring, until the aluminium plate is visible.

The pencil hardness, shown in table 4.2 was determined on samples prepared on aluminium plates and is outstanding for the resin from DPAC, considering that it derives form self-curing, without any curing agent. Indeed, after 2 hours at 200°C, the pencil hardness of its film on aluminium plate was 5H. Also the resin deriving from DPAR is harder than the BPA based one but this is less surprising due to the difference between two molecules, namely trifunctional against bifunctional. This leads potentially to an increase in crosslinking, as GEDPAR itself crosslinks too, and thus a greater hardness.

From the table it is clear that the crosslinking is completed after 2 hours, except for DPAC, which slightly changes in scratch hardness.

Table 4.2: Pencil Hardness (Scratch hardness in parenthesis)

Curing time	DPAC	DPAR	BPA
2 hours	5H (H)	7H (HB)	3H (H)
5 hours	5H (2H)	7H(HB)	3H(H)

These outstanding hardnesses are greatly superior to the one necessary for an efficient can coating (around HB). Thus it could potentially even be appropriate for some high performance applications like aerospace, given the condition that the heat resistance is sufficient.

Swelling

Thermosetting resins are not soluble in organic solvents due to crosslinking. However, their solvatation is visible due to swelling of the material. The swelling capacity is directly linked to the distance between the nodes, hence, the crosslinking density. The more solvent penetrates the material, the longer the distance between the nodes and the lower the crosslinking density. A small sample of material is thus immersed in a solvent for one hour. After drying the superficial solvent with a paper towel, the sample is weighted. The difference in mass divided by the original mass, leads to the swelling of the material in percent.

$$Swelling = \frac{Final\ mass - Initial\ mass}{Initial\ mass} \times 100$$

Obviously, the choice of the right solvent is crucial as a good solvatation of the linear parts of the resin is necessary. In our case, THF was appropriate, as the most common solvent for epoxy resins. Furthermore, the results are not absolute values but strongly depend on the solvent and should thus only be analysed by comparison.

Table 4.3: Comparison of DPAR and DPAC with Bisphenol A

Phenolic compound	Percentage of hydroxyles glycidylized	Epoxy equivalent weight	Pencil hardness (scratch hardness)	Swelling Solvent:THF)
Bisphenol A	100%	174 g/mol	3H(H)	88%
DPAC	59%	163 g/mol	5H(H)	21%
DPAR	54%	174 g/mol	7H(HB)	21%

As mentioned above, GEDPAR is a trifunctionally reactive molecule, which works also as a crosslinker itself, whereas DGEBA is a bifunctional molecule which only forms linear links.

This is particularly visible in the swelling capacity, which is four times lower for the resin from DPAR than from bisphenol A and correlates with the crosslinking density. It thus confirms the hypothesis erected previously.

Interestingly, also the swelling of the self-cured DPAC resin is substantially lower than the reference and comparable with DPAR. Although the precise parity is assumed as a mere coincidence, in both resins, all molecules have a role as a cross-linker, leading to very short linear parts and thus a higher crosslinking density. However, this result is surprising because intramolecular reactions in DPAC account for as much as the inactivity of the "internal" hydroxyls for DPAR. Indeed, the reaction of catechol with epichlorohydrin is described as generating substantial amounts of cyclisation[68], as highlighted in figure 4.4.

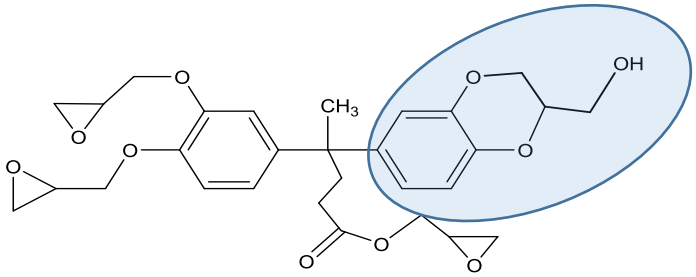


Figure 4.4: Potential intra-molecular reaction on GEDPAC

This cyclisation is assumed to reduce the number of nodes in the resin. However, the combination of the different effects leading to self-curing seem to have partially avoided this reaction.

Furthermore, the direct correlation between the swelling and the hardness is observed. Indeed, the lower the swelling the higher the crosslinking density and the harder the material. However, this counts only to a certain extent, if all the molecules are performing their role as a crosslinker, the swelling is theoretically equal, independently of the number of "arms". But a penta-functional cross-linker yields a harder resin, like DPAC.

Chemical resistance

These tests were designed to screen the material for a potential food-contact application. Can coatings are a potential application for the synthesised renewable epoxy resins and leaking into the food content is a crucial factor. In particular during sterilisation, during which the cans are heated under pressure for up to two hours, the kinetics are enhanced and thus also degradation

and solubilisation. As the cans are sealed before this treatment, we can assume that heat has a much stronger effect on the inside coating than the outside pressure.

For these tests, the samples were deposited on aluminium plates by drop casting and cured in the appropriate way (as stated above). Subsequently, they were separately immersed in two solutions:

- A solution at 5% of NaCl, to investigate the leaking into foods preserved in brine, like olives or tuna,
- A solution of 3% of acetic acid, representing slightly acid foods, as most of them are, for example beans or tomatoes.

In both cases, the aluminium plates were immersed in a separate container of the solution and kept at 100°C for two hours. After, the sample was washed with distilled water and dried at 110 °C for one hour. The difference in weight shows the leakage of material into the solution.

It should be mentioned that this procedure can only give us an indication about leakage because we are not following exactly the industrial conditions in an autoclave. However, we can evaluate our coating compared to the legal limit of 10 mg/dm^2.

The results, stated in table 4.4, show that especially the resins containing cross-linker are prone to leaking in acid conditions. The only resin that complies with the limits of the law is the epoxy deriving from DPAC. This is also the reason why in general self-curing resins were preferred in this work. In addition to leaking, cross-linking agents are often toxic and induce issues during homogenisation.

Table 4.4: Results of the migration tests

	Leaking (mg/dm^2)	
	5% NaCl	3% acid
BPA	8.8	61.7
DPAC	6.9	5.9
DPAR	2.0	15.7

As stated above, the testing conditions, were slightly different from the operating conditions in the factory, and are only used as an indication. The value obtained for BPA should thus not be considered as an actual value corresponding to industrial canning conditions. Hence, it should only be used as a reference and, in this case, also the DPAR derived resin has a lower leaking than BPA. Finally, in chapter 5, we will notice that in these curing conditions, only a degree of

cure of around 22% is reached for DPAR. However, the DPAC-derived resin's leaking is considerable lower and can be considered as safe for food contact use.

Thermogravimetric analysis

Thermogravimetric analysis is mainly used to determine the thermal resistance[72] of materials, commonly in experiments from room temperature to 800°C, at 10°C/min. It can be used in air or nitrogen, but nitrogen leads to higher reproducibilities. It allows to identify unreacted material evaporate as well as water. Furthermore, the TGA we used also had the additional feature of heat flow measurement, which provides a further insight into the curing reaction.

In our case, TGA is also very interesting for determining the water uptake of the resins[73]. Epoxies are very prone to hydrogen bonding with water vapour from air, even second order hydrogen bonding[74], as described in detail later. Water bonded to the epoxy in the three different possible ways of hydrogen bond should be visible as weight loss.

TGA of GEDPAC

In order to evaluate the self-curing and degradation of GEDPAC, two experiments were carried out, as shown in figure 4.5. The starting material was uncured glycidyl ether of diphenolic acid of catecol (GEDPAC) with an EEW of 163 (59% of hydroxyls epoxidized).

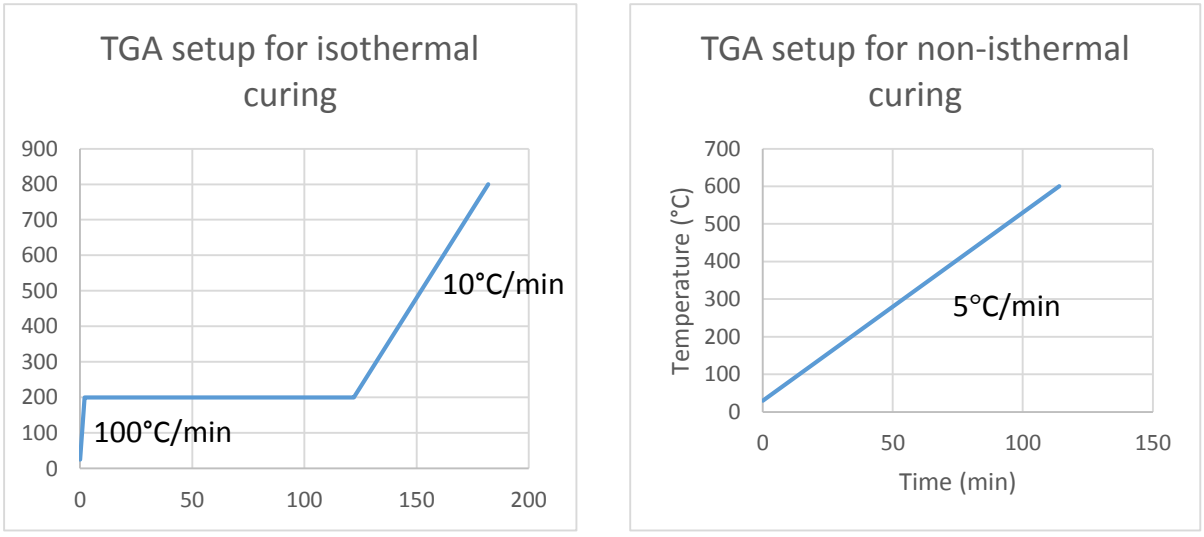


Figure 4.5: Experimental set-up of the TGA

First, a set-up comparable to the experimental curing conditions was carried out, in which the temperature was launched to 200°C as fast as possible (100°C/min), followed by an isothermal at 200°C for 2 hours (corresponding to the curing in the lab oven) to finish with the degradation study, at the typical heating rate of 10°C/min until 800°C.

During this experiment, the most important observation was that during the first 2 minutes, i.e. before it even reached 200°C, a weight loss of 13,74% is registered, as shown in figure 4.7 and the heat flow presents three peaks, as seen in zoom in figure 4.6. On the contrary, during the two hours, the weight loss is minimal and no further peaks in heat flow are visible.

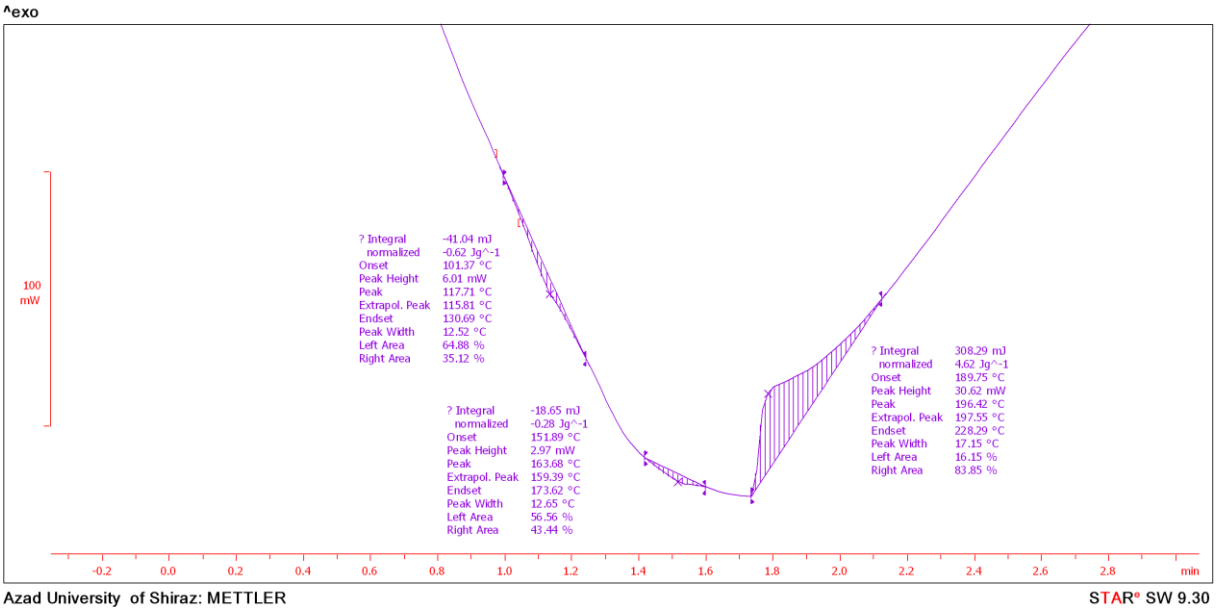


Figure 4.6: Detail of the heat flow measurement during experimental set-up 1

The first two peaks are endothermic and thus probably correspond to the evaporation of remaining water (with or without hydrogen bond) because volatiles had been previously removed with a vacuum pump. The temperatures of 117ºC and 163ºC are quite elevated for water evaporation but the very high heating rate make these values less reliable.

The third peak is exothermic, which lead to the hypothesis that it may correspond to a chemical reaction of curing.

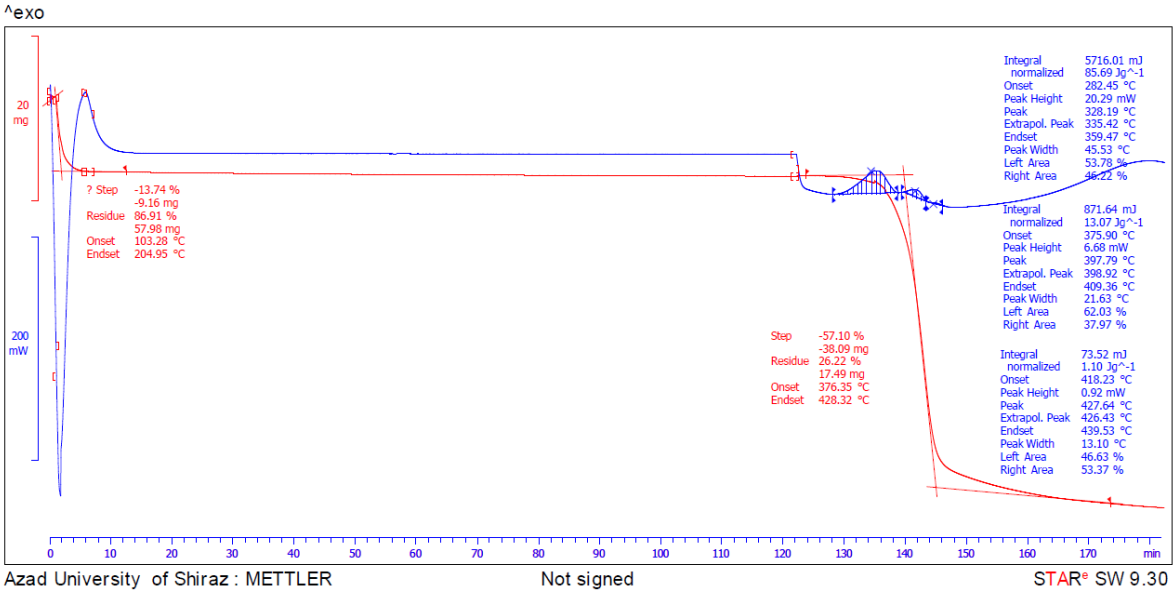


Figure 4.7: Full thermogravimetric analysis in set-up 1

This, and the absence of further peaks during the 2 hours of " curing time", as seen in figure 4.6, leads to the conclusion that the chemical reaction of curing takes place even before reaching 200°C. Thus, in order to obtain more reliable peaks, a second, non-isothermal, experiment was carried out at a constant heating rate of 5°C/min.

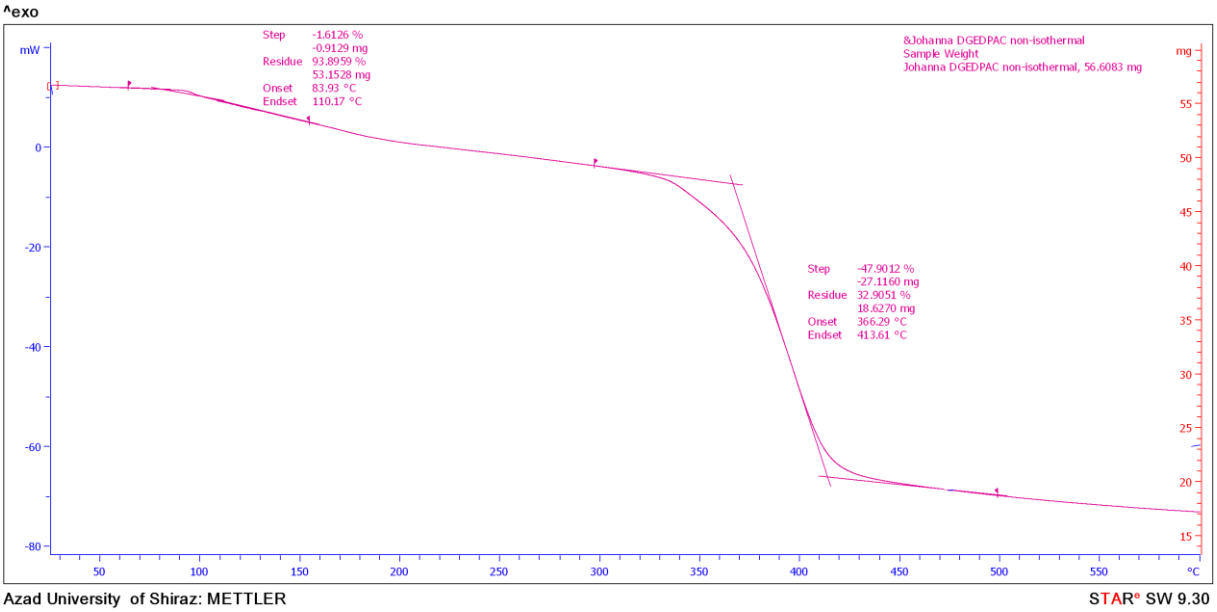


Figure 4.8: Thermogravimetric analysis in experimental set-up 2

As seen in figure 4.7, the mass loss, starts at 100°C approximatively and levels out, before the degradation drop. The endothermic peak of water evaporation in observed at 99°C and the ΔH is very similar to the one of the isothermal curing. For curing, one exothermic peak is observed. Due to a technical problem, the sample was extracted at 360°C for another test and it was clearly

visible that it was fully cured. Thus even without the 2 hours of waiting time, a fully cured resin is obtained. This confirms that the observed exothermic peak corresponds to curing and probably an opening of the epoxy rings. Indeed, epoxy rings have a very high strain energy that leads to exothermicity when opening. As the heating rate is lower, the peak is wider and much less defined for the second experiment than in the fast curing at 100°C/min.

The conditions of degradation are similar in both experiments, with only different heating rates of 5°C /min and 10°C/min and so are the results for the degradation.

As the curing reaction substantially does not include elimination reaction, all the weight loss of 13,74% can be attributed to water evaporation. Thus, after one month at 90% humidity , the GEDPAC has absorbed roughly 14% in weight of water meaning that GEDPAC is thus very prone to water absorption. Water can potentially link in different states. Amongst the three possible states, namely free water, type I hydrogen bonded water and type II hydrogen bonded water, which are depicted in figure 4.9, free water has the lowest energy requirement for vaporization.

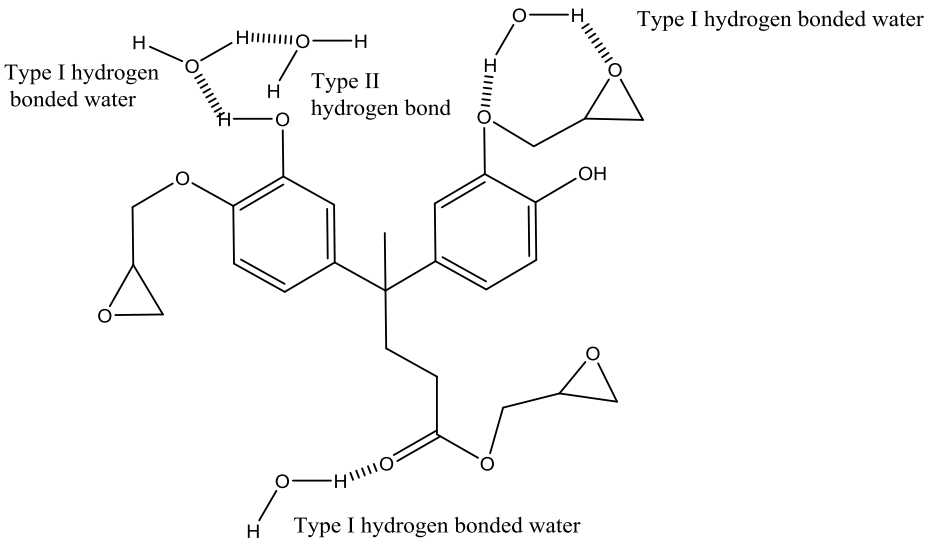


Figure 4.9: Hydrogen bonding on GEDPAC

TGA of GEDPAR

The TGA of GEDPAR was carried out on sample, previously cured with 1,6-hexamethylenediamine.

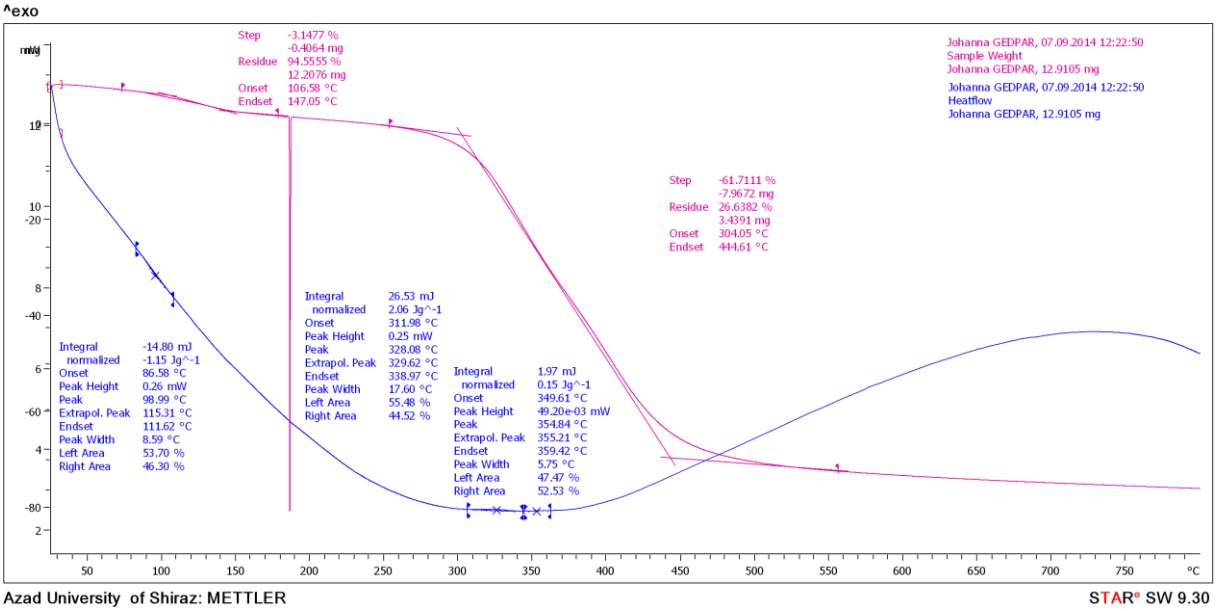


Figure 4.10: Thermogravimetric analysis of the cured DPAR resin

The heating rate was 10°C/min from 25°C to 800°C. The result observed is typical for an epoxy resin with a degradation at about 350°C. The residue at 800°C is 20%. This result is comparable to commercial amine-cured epoxy resins. Indeed the degradation starts at the weakest bond: in the case of the DPAR resin, the C-N bond from the reaction with the crosslinker. As the crosslinking reaction involves the same functional groups for any amine-cured epoxy resin, the results are analogous also for the BPA resin.

Moreover, a water uptake experiment was carried out. We observe the loss of 3.3% in mass of water, after leaving it in 90% humidity for a month. The resin is thus slightly hydrophilic, owing to the presence of many polar groups.

5. Conclusion

In this chapter, the curing and the characteristics of the cured resin were thoroughly described. Indeed, whereas DPAC withholds self-curing capacity, i.e. it cures upon heating without adding catalysts of hardeners, DPAR requires the use of a crosslinker. So called homopolymerisation, i.e. the crosslinking without a curing agent, is possible in most epoxy resins upon addition of a catalyst. In the case of diphenolic acids, the ester moiety, in its role as a Lewis base, is potentially able to activate the hydroxyls and generate their intermolecular reaction with epoxides leading to a crosslinked resin without the need of adding a catalyst.

As in DPAC the hydroxyls are also strongly activated by mesomeric effect, this reaction occurs spontaneously upon heating. In DPAR on the other hand, not only two positions out of five are inhibited by a combination of steric hindrance and deactivating electronic effects but these same hydroxyls deactivate the remaining aromatic hydroxyls by mesomeric effect. This compensates the activating effect of the ester and inhibits self-curing.

In order to find an adequate application, several tests have been carried out demonstrating that, in general, the results for both resins, shown in table 4.4, are superior than the commercial DGEBA resin, cured with 1,6–hexamethylendiamine. Leaking was also examined for a potential application as a can coating for food containers. Both resins containing crosslinkers showed poorer results, probably due to a not-perfect homogenisation leading to not fully crosslinked sectors, releasing unreacted material. This is a general problem of using a hardener, existing even at industrial level.

Table 4.6: Summary of the characterization results for the diphenolic acid resins compared with BPA

	Hardness (4 hours)	Leaking (5% NaCl, mg/dm^2)	Leaking (3% acid, mg/dm^2)	Swelling (%)	Onset point (^{o}C)
DGEBA, cured	3H(H)	8,8	61,7	88	295[75]
DPAR, cured	7H(HB)	2,0	15,7	21	304
DPAC	5H(2H)	6,9	5,9	21	366

The resin from DPAC is the only with values inferior to the legal limit and also depicts outstanding hardness and excellent heat resistance. High performance and structural applications should thus be taken into consideration.

CHAPTER 5:

Curing kinetics of glycidyl ether of DPAR with two amine curing agents

1. Introduction

As GEDPAR has been identified as the most similar to bisphenol A, it was cured with two curing agents. Several tests have already been carried out with 1,6 hexamethylendiamine-cured GEDPAR. Its epoxy equivalent weight is 174 g/mol. This derives from the fact that, except the two internal hydroxyls whose reactivity is strongly inhibited and who are thus not to be considered, the other three available hydroxyls (including acid) had been glycidylized to an extent of 88%. Thus, still 12% of reactive hydroxyls are available, although not represented in the figure. They demonstrate mainly that the synthesized glycidyl ether of diphenolic acid from

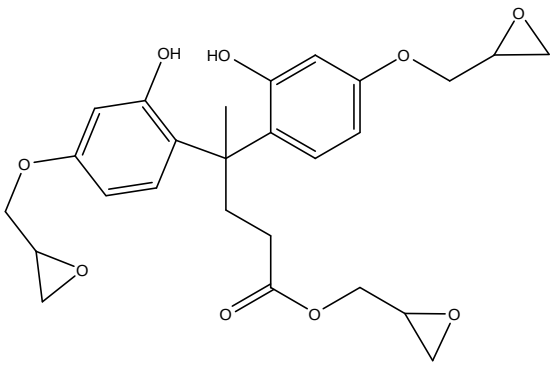


Figure 5.1: Chemical structure of GEDPAR

resorcinol (GEDPAR), as shown in figure 5.1, has the advantage of having highly inhibited hydroxyl groups in the ortho position to the central aliphatic chain. This leads to three reactive epoxide groups, and thus the reactivity is comparable with BPA. GEDPAR was reacted with two different curing agents, 1,4-butanediamine and 1,6-hexamethylendiamine. Their only difference is composed of two methylene groups on the aliphatic chain, allowing to evaluate the effect of chain length on the curing of an epoxy-amine system. Especially, 1,4-butanediamine is particularly interesting as it could potentially derive from renewable itaconic acid.[5]

Differential Scanning calorimetry (DSC) measurements were used to accurately determine the cure kinetics, necessary for choosing the appropriate cure cycle. Indeed, many other mechanical and thermal properties,[76] as , for example, the elastic modulus,[77] depend on the degree of cure. Amine-epoxy systems are generally modelled by the Kamal[78] model which is also successfully applied in our case, for low degrees of cure. The substantial viscosity of the sample in addition to the presence of three reactive epoxide groups lets us anticipate a strong effect of diffusion due to fast gelation. This phenomenon will be modelled thanks to Chlern's and Poehlein's corrective term,[79] which introduces the critical degree of cure, i.e. the moment when kinetic

control is taken over by diffusion control. It will also allow predicting the very low final degrees of cure for the lower temperatures. The temperatures were chosen in order to characterize a full range of degrees of cure (from approx. 0.2 to 1) and is thus different for each curing agent leading to fully assessing the effect of diffusion in both cases.

2. Theoretical considerations

Non- isothermal curing

In order to determine the cure kinetics, several non-isothermal experiments were carried out at heating rates of 5 K/min, 10 K/min, 20 K/min, 25 K/min and 50 K/min. T_{exo} was determined as the maximum of the exothermic peak.

Subsequently, the Kissinger and Ozawa's methods[80,81] were applied to determine the activation energy of the curing reaction. Kissinger's equation can be expressed as follows:

$$ln\left(\frac{\beta}{\mathrm{Texo}^2}\right) = -\frac{\mathrm{Ea}}{R\mathrm{Texo}} + ln\left(\frac{AR}{Ea}\right) \qquad (1)$$

In which ß is the heating rate, T_{exo}, the temperature at the exotherm's maximum, A the frequency factor, and R the gas constant. Hence, the activation energy is determined from the slope of the $\ln(ß/T_{exo}^2)$ vs $1/T_{exo}$ curve defined as the Arrhenius plot.

Whereas Ozawa's equation is:

$$Ea = -\frac{R}{1.052} \times \frac{d\ln\beta}{d(\frac{1}{Texo})} \qquad (2)$$

Thus the activation energy can be directly calculated from the slope of the ln(ß) vs $1/T_{exo}$ curve.

Isothermal curing

Isothermal curing experiments were conducted at 40, 60, 80, 100 and 200°C for 1,4-butanediamine and 80, 100, 120, 140, 160 and 180°C for 1,6-hexamethylendiammine. The total heat of reaction ΔH_0 was calculated as the area under the exothermic peak at full cure, determined from the DSCs at 200 and 180°C respectively for butanediamine and hexamethylenediamine. Thus, the degree of cure α was derived from the enthalpy released as heat at a certain point in time, allowing to estimate the fractional degree of cure by integration, as shown in (3). Also the maximum degree of cure for each isothermal temperature is deducted, as described in equation (4), corresponding to the ratio of the heat of reaction for one temperature on the total heat of reaction

$$\alpha = \frac{1}{\Delta H_0} \int_0^t \left(\frac{dH}{dt}\right) dt \qquad (3)$$

$$\alpha_{max} = \frac{\Delta H}{\Delta H_0} \qquad (4)$$

The Kamal and Sourour equation was developed to describe the autocatalytic nth order curing of the stepwise reactions of epoxy resins with amine curing agents and can be expressed as follows:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (5)$$

In equation (5), k_1 and k_2 are the temperature-dependent reaction's rate coefficients and m and n are the reaction orders, which are found to be temperature-dependent as well. The temperature dependence of the rate constants is given by the Arrhenius expressions[80] in equation 6. i represents the number of the amine-epoxy reaction (primary or secondary), E is the apparent activation energy for each reaction, A is the pre-exponential factor, R is the Universal gas constant and T the temperature.

$$k_i = A_i e^{-\frac{E_i}{RT}} \qquad i = 1, 2 \qquad (6)$$

During an epoxy–amine curing reaction the system undergoes a range of processes such as gelation, vitrification and changing from a chemical controlled to a diffusion controlled progress of the conversion. Thus, for describing the latter phenomenon, a corrective term, based on the works of Chern and Poehlein,[79] allows to adapt the original equation, adequately describing the diffusion controlled progression after vitrification.

The equation can thus be expressed as follow:

$$\frac{d\alpha}{dt} = \frac{(k_1 + k_2\alpha^m)(1-\alpha)^n}{1+exp[C(\alpha-\alpha_c)]} \qquad (7)$$

in which α_c corresponds to the critical degree of cure, at which the reaction starts to get diffusion controlled, and C is the diffusion control parameter.

3. Results and discussion

Non-isothermal curing

The curing reaction of the studied epoxy resins in presence of 1,4-butanediamine and 1,6-hexamtehylenediamine was investigated by DSC at five different heating rates. The maximum values of exothermic peaks were determined and the most significant were selected to apply it to Kissinger's and Ozawa's methods.

One major difference to be noticed, is that GEDAR cured with 1,4-butanediamine presents two exothermic peaks, which probably correspond to the primary and secondary amine reactions, typical for aliphatic amine curing agents. For 1,6-hexamethylendiamine, on the other hand, these peaks are superposed and only one peak is visible. In figure 5.2, the DSC thermograms for a heating rate of 20 K/min clearly show this difference.

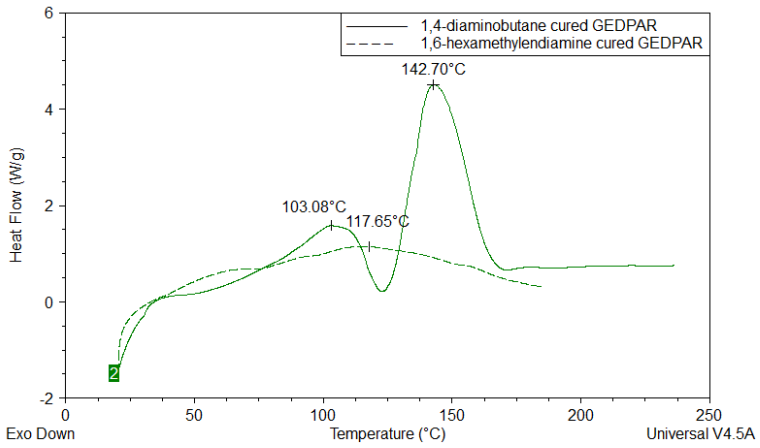
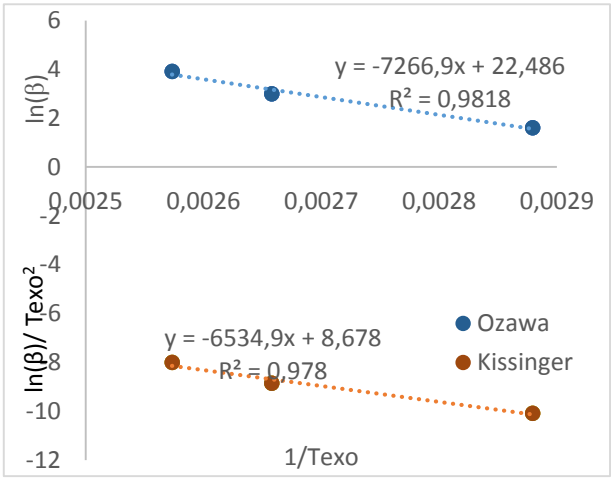


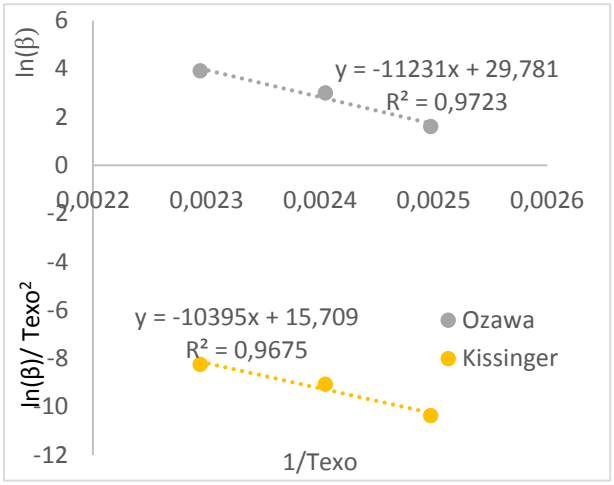
Figure 5.2: Thermograms of non-isothermal cure of GEDPAR at a heating rate of 20K.min^{-1}

For the 1,4-butanediamine cured GEDPAR, the two peaks were thus analysed separately and their activation energies for the first and secondary amine reaction was determined. Graph 5.1 and 5.2 depict the plots used for the determination of the activation energies, with the Ozawa and Kissinger methods. The activation energies associated to the first and second exotherm were 51.87 kJ/mol and 86.71 kJ/mol, respectively, with Kissinger and 55.09 kJ/mol and 89.03

kJ/mol, respectively, with Ozawa's method. Regarding the curing of GEDPAR with 1,6-hexamethylenediamine, the associated activation energies amount to 122.16 kJ/mol and 122.22 kJ/mol respectively with Kissinger's and Ozawa's method.



Graph 5.1: Plots of the determination of Ea by Ozawa and Kissinger method for the first exothermic peak with 1,4-butanediamine



Graph 5.2: Plots of the determination of Ea by Ozawa and Kissinger method for the second exothermic peak with 1,6-hexamethylenediamine

The total activation energy for curing with 1,4-butanediamine, 138.58 kJ/mol and 144.12 kJ/mol, respectively with Kissinger's and Ozawa's method, is higher than with 1,6-hexamethylendiamine. It can be assumed that this increase in activation energy is due to the shorter length of the aliphatic chain. Indeed, the steric hindrance for the approach to the second amine rises more, once one amine has reacted with GEDPAR or already formed macromolecules, if the cross-linker is shorter.

Isothermal curing

A series of isothermal cure tests were performed using DSC in order to evaluate the autocatalytic kinetic parameters in equation 5. Figure 5.3 shows the time-dependent heat of reaction for the tested temperatures between 100 and 180°C for the reaction between the epoxy and the 1,6-hexamethylene curing agent. The experimental results for the epoxy-1,4-butanediamine system, cured at temperatures between 40 and 200°C, are similar and thus not represented. In general, due to the strong similarity between the results of the two curing agents, only one will be reproduced graphically, and the other accurately described.

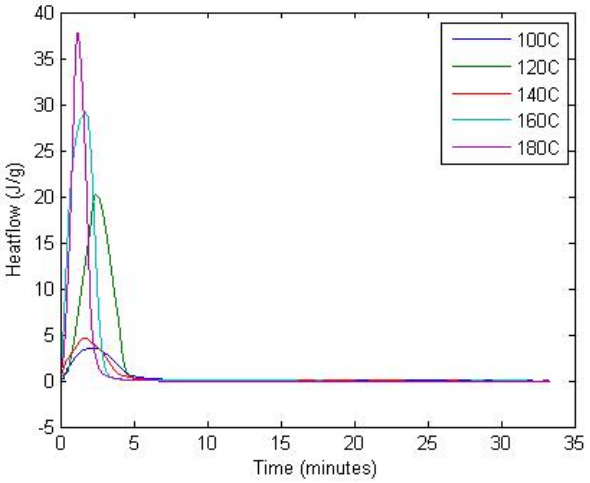


Figure 5.3: Time dependent heat of reaction for each temperature, for curing with 1,6-hexamethylenediamine

Table 5.1: Heat of reaction and maximum degree of cure for a) 1,4-diaminubutane and b)1,6-hexamethylendiamine

a)

	Isothermal temperature (°C)				
	40	60	80	100	200
ΔH(J/g)	508	626	667	867	1335
α_{max}	0.38	0.47	0.50	0.65	1

b)

	100	120	140	160	180
ΔH(J/g)	667	744.2	2183	2813	3101
α_{max}	0.22	0.24	0.70	0.91	1.00

The reaction heat at any time of cure was determined using these standard DSC heat flow measurements and calculated by the integration of each isothermal heat flow curve. The temperatures for the isothermal experiments were purposely chosen to assure full cure of the sample. Indeed, to the series of temperatures for diaminobutane, 40, 60, 80 and 100°C, a run at 200°C was added to have a reference at full cure. The heat of cure for all temperatures are stated in table 5.1 altogether with the degree of cure, derived from equation 4. It is noticeable, that the degrees of cure remain low, for the lower temperatures, probably due to the high viscosity of GEDPAR at low temperatures. Furthermore, due to three reactive functional groups on each GEDPAR, in addition to the four reactive groups of the curing agent, the mobility of the system is strongly inhibited.

The curves of the degree of cure and the cure rate, derived from equation 3 and 5 represented in figure 5.4a and 5.4b follow a typical path of an isothermal epoxy amine-cure with a drastic increase in reaction rate for the high temperatures. The reaction progress is fast at the beginning

due to low viscosity and a good availability of reactive groups with its maximum at the middle of the reaction. This is typical for auto-catalytic reactions and confirms our choice of the Kamal model. Finally, it decreases and, especially for low temperatures, levels off before reaching full cure, due to reduced chain mobility caused by early vitrification. This demonstrates the significant effect of diffusion, hence, the necessity of a corrective term in equation 7.

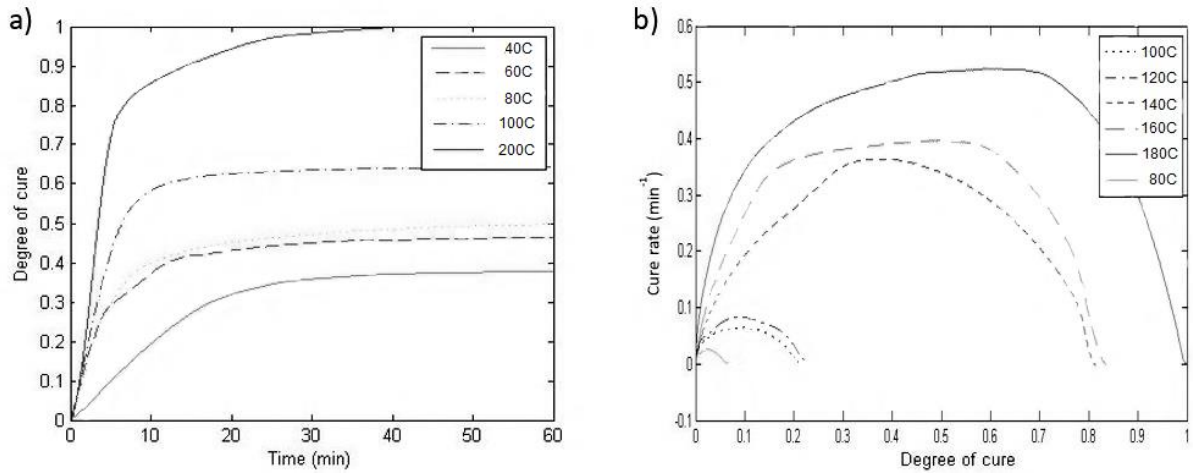
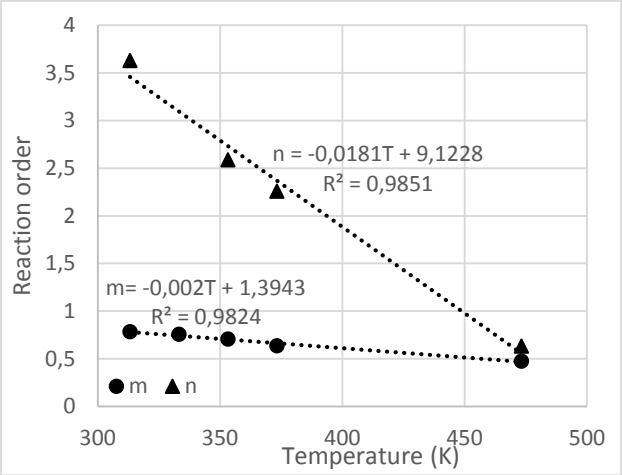


Figure 5.4: Degree of cure versus time for 1,4 diaminobutane(a) and curing rate versus degree of cure for 1,6-hexamethylenediamine (b)

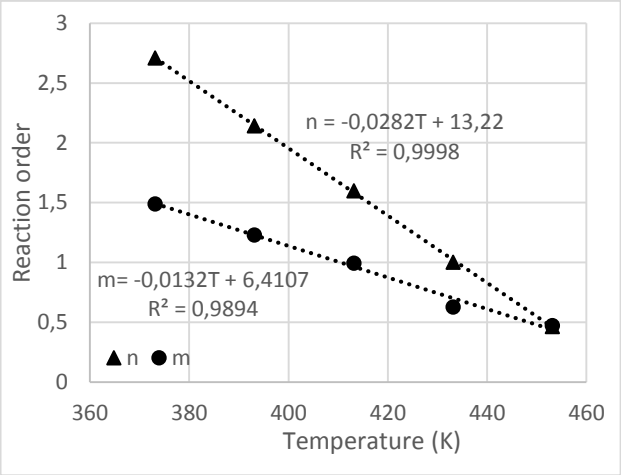
The model parameters for the autocatalytic model were generated by robust least square approximation of the curves and the results are stated in table 5.2. The reaction orders, m and n, are strongly temperature-dependent, as seen in the graph 5.3 and 5.4, indicating the complexity of the mechanism, as opposed to a simple n^{th} order reaction.

Table 5.2: Kinetic parameters for the isothermal model

Temperature	k_1	k_2	m	n	α_c	C	R^2
1,4-diaminobutane							
40	0.011	0.062	0.498	3.630	0.328	50.5	0.995
60	0.036	0.793	0.758	7.240	0.375	105.7	0.998
80	0.016	0.150	0.289	2.590	0.357	23.2	0.997
100	0.054	0.293	0.638	2.260	0.555	39.5	0.997
200	0.014	0.387	0.478	0.640	0.732	16.0	0.993
1,6-hexamethylenediamine							
100	0.007	0.551	1.491	2.711	0.191	120.0	0.999
120	0.009	1.000	1.231	2.143	0.206	158.0	0.994
140	0.024	1.967	0.995	1.599	0.789	179.4	0.997
160	0.000	2.794	0.629	1.002	0.794	107.0	0.996
180	0.000	4.363	0.474	0.464	0.960	55.0	0.998



Graph 5.3 : Reaction orders m and n as dependent on temperature for 1,4-diaminobutane



Graph 5,3: Reaction orders m and n as dependent on temperature for 1,6-hexamethylendiamine

Also the critical degree of conversion increases linearly with temperature at a rate of α_c=0,0025T-0.4476 for 1,4-butanediamine and α_c=0.0094T-3.2553 for 1,6-hexamethylendiamine. The reason for this decreasing effect of diffusion control is that at higher temperatures, the mobility of the chains is maintained, leading to higher αc as well as higher total degrees of cure. This finding demonstrates once again that the modified and not the original Kamal model equation will best describe our situation, which is heavily diffusion controlled.

In figure 5.5 and 5.6, the experimental and theoretical curing rate, calculated with the modified Kamal model is represented for each temperature and curing agent, depicting their good fit, also confirmed by the R^2 previously stated in table 5.2. In these curves it is clearly visible, that in fact, the peaks we are observing are the overlay of several types of exothermic and endothermic phenomena occurring in the system upon heating, due to the structure of GEDPAR, amongst which the most significant are:

- Primary amine reacting with aromatic ether attached epoxy
- Primary amine reacting with aliphatic ester attached epoxy
- Secondary amine reacting with aromatic ether attached epoxy
- Secondary amine reacting with aliphatic ester attached epoxy
- Dissociation of the hydrogen bond between the two hydroxyls in ortho to the central aliphatic chain (Endothermic)

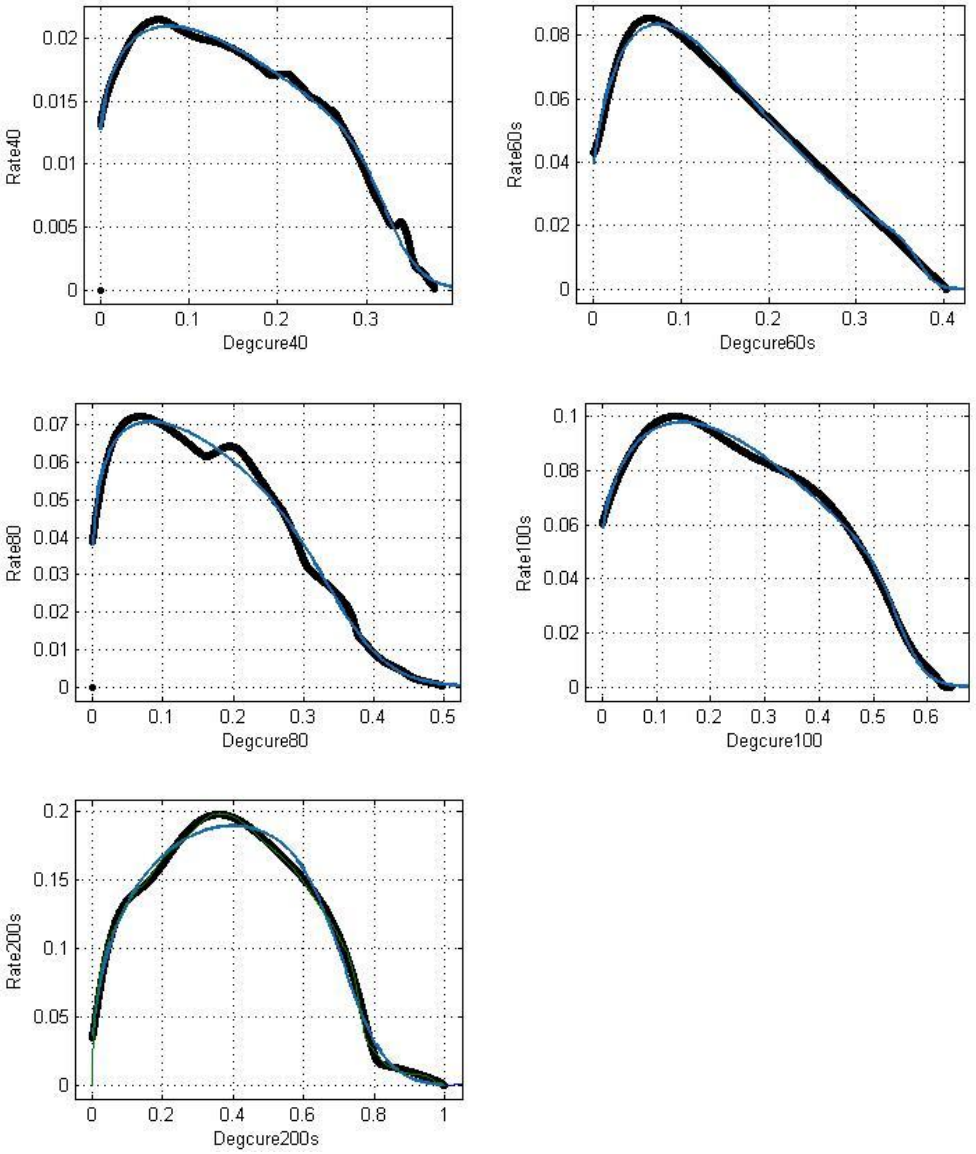


Figure 5.5: Calculated and experimental Curing rate versus degree of cure for 1,4-butanediamine

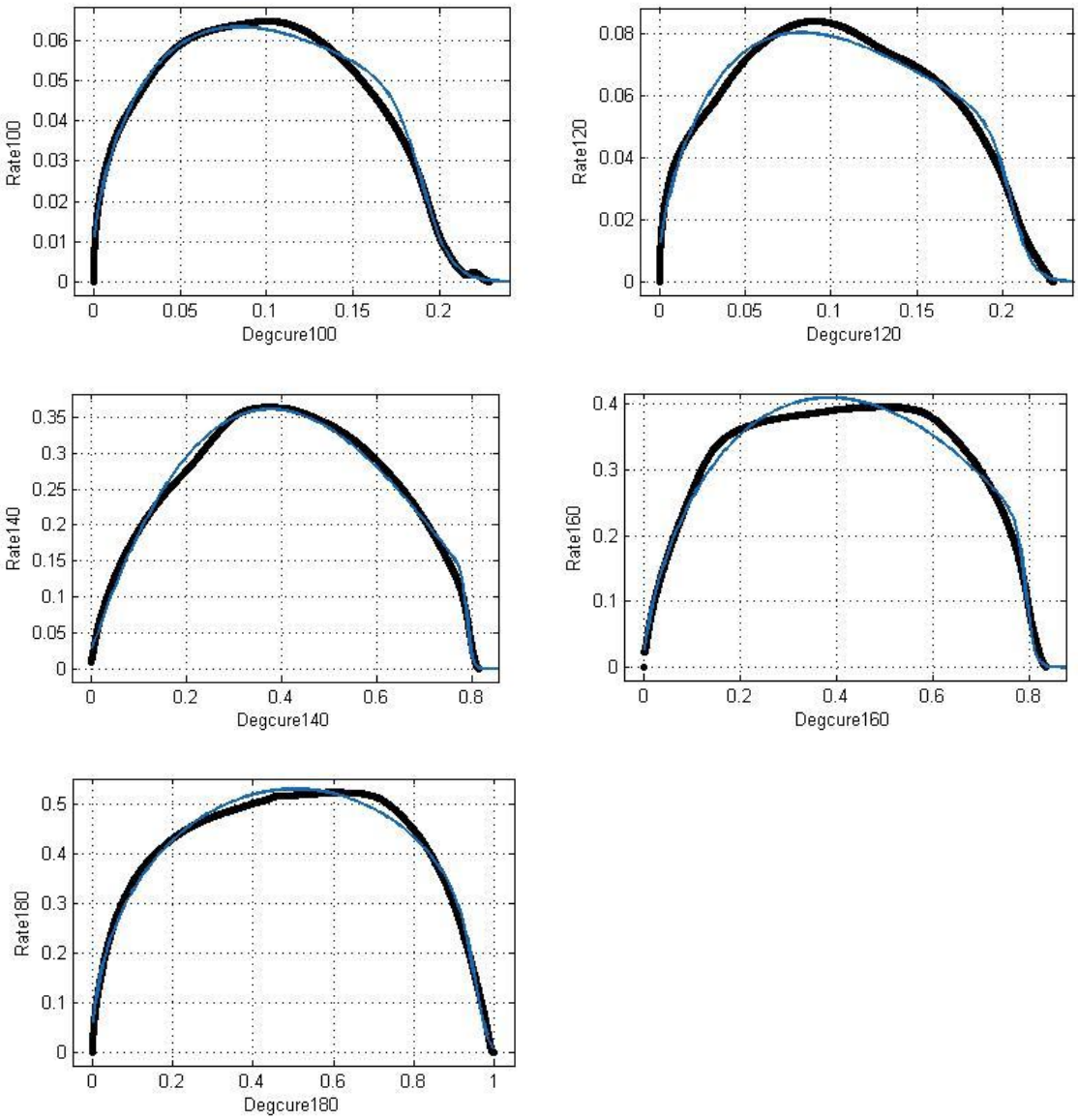
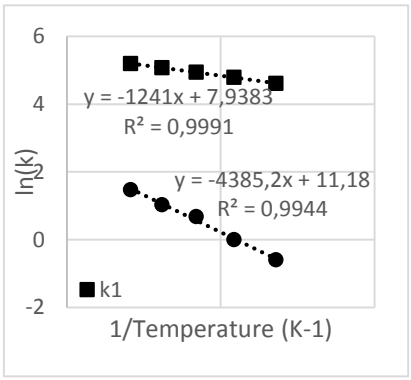


Figure 5.6 : Calculated and experimental Curing rate versus degree of cure for 1,6-hexamethylendiamine

Table 5.3: Activation energies (isothermal)

	1,4-butanediamine	1,6-hexamethylendiamine
E1(kJ/mol)	24.45	10.31
E2(kJ/mol)	24.30	36.35
Total activation energy	48.76	46.67



Graph 5.4: Arrhenius plot of 1,6-hexamethylendiamine

As mentioned above, also the fact that m and n are not a single value but temperature-dependent underlines that the reaction kinetics is highly complex. Therefore, the kinetic parameters k_1 and k_2 as well as the calculated activation energies are apparent ones and should not be considered as the real values but give information about the total energy. The activation energies corresponding to k_1 and k_2 have been calculated from the Arrhenius plots (graph 5.5) using equation 6 and are stated in table 5.3. Hence, the total activation energies, as the sum of the energies relative to k_1 and k_2 are 46.66 kJ/mol for 1,6-hexamethylene diamine and 48.75 kJ/mol for 1,4 diaminobutane.

Like in non-isothermal curing, the activation energy is slightly higher (4%) for 1,4-butanediamine. As stated above, this difference can only be explained by the shorter chain length of butanediamine, everything else being identical. It can be assumed that after diaminobutane has bonded with an epoxide, the approach of the next molecule of GEDPAR is more inhibited, if the aliphatic chain of the crosslinker, is shorter.

4. Experimental

Materials

The reagent, GEDPAR was synthesized reacting diphenolic acid from resorcinol with epichlorohydrin following the method of St. Clair[49]. The GEDPAR was thoroughly mixed with a stoichiometric amount of 1,6-hexamethylenediamine and 1,4-butanediamine , respectively, as cross-linkers and degassed before the experiments. The cross-linkers were purchased from Sigma-Aldrich and used without further purification.

Measurements

The differential scanning calorimetry (DSC) measurements were performed with a TA Q10 DSC Instrument. All experiments were conducted under nitrogen flow, at a rate of about 50 mL/min as purge gas. Approximatively 5 mg samples were accurately weighed into DSC aluminium pans. Runs were carried out using an empty cell as reference.

5. Conclusions

The reaction kinetics of glycidyl ether of diphenolic acid from resorcinol (GEDPAR) curing with aliphatic amine curing agents were determined in non-isothermal as well as isothermal mode. Two different linear aliphatic amines, namely 1,4-butanediamine and 1,6-hexamethylenediamine were compared in order to evaluate the effect of chain length on the curing reaction. A modified Kamal model was used to provide a satisfactory fit of the experimental data, in which several visibly overlaid reactions and strongly temperature-dependent reaction orders indicate a highly complex reaction mechanism. The diffusion effect was greatly visible especially for low temperatures, significantly decreasing the final curing degree. This phenomenon is mainly due to the presence of 3 reactive epoxides on GEDPAR, which leads to gelation and vitrification even at low degrees of cure if this effect is not sufficiently compensated by decreasing the viscosity with high temperatures. In general, 1,4-butanediamine showed slightly higher total activation energies in both cases, owing to the increased sterical hindrance after the first condensation with GEDPAR due to shorter chain length.

CONCLUSIONS

In the recent years, the awareness about the depletion of the natural resources and damaging effect of our current lifestyle on the environment has skyrocketed due to recurrent natural disasters. The consequence was a shift of focus of research turning away from simple profit towards finding a more sustainable way of production, maintaining the economic viability. "Green chemistry" is the new paradigm.

Our lifestyle as a throw-away society is only possible due to the presence of polymers in vast parts of our everyday life. From plastic bags to nail polish, from electric boards to airplanes, most of the modern day commodities have been only been possible due to the progress in polymer science.

Polymers are so anchored in our daily lives that, although not being aware of it, many people could not imagine a life without them. In particular plastic bags, for many consumers a symbol of the waste producing society, have been in the focus, and new "greener" approaches have been found.

However, thermosettings remain widely unexplored. Epoxy resins are of great interest because they are used in an incredibly wide range of applications, from wind power mills to adhesives. However their main components are highly carcinogenic epichlorohydrin and hazardous bisphenol A. The latter has been demonstrated to have pseudo-hormonal effect due to its similarity with estrogen. The consequence are bans, emitted in a rising number of countries, especially in applications with food contact.

In this thesis a fully renewable epoxy resin was developed, starting from molecules deriving from biomass, as seen in figure C.1.

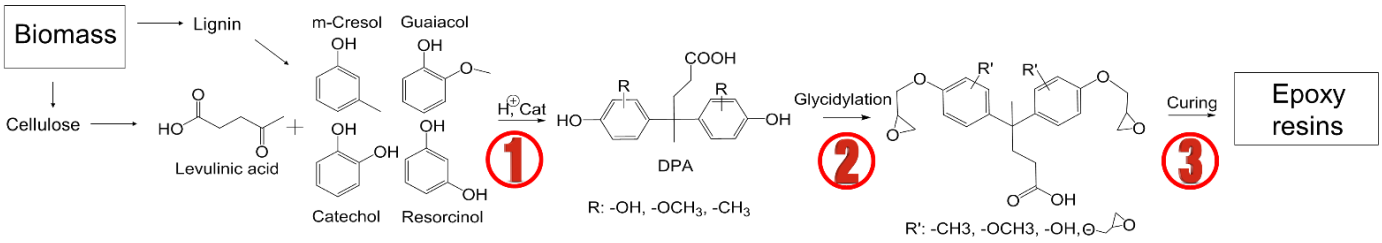


Figure C.1: Pathway of synthesis of a fully bio-based epoxy resin

Regarding Bisphenol A (BPA), the major alternatives proposed are epoxidized plant oils and cardanol. Both lead to materials with a low mechanical resistance due to the plasticizing effect of the long side chains. Furthermore, severe repeatability problems occur owing to the strong dependence of the chemical structure of these products on environmental factors.

In the first chapter, corresponding to the reaction number 1 in the figure, diphenolic acid (DPA) derivatives have been presented as a potential alternative to BPA. Indeed, DPA is structurally similar and was originally used for epoxy resins. It is produced from levulinic acid, a potentially renewable resource. However, in the original synthesis, the phenol moieties are introduced by phenol, from fossil feedstock. Thus, experiments have been carried out to synthesize DPA derivatives from potentially natural phenols, namely m-cresol, guaiacol, catechol and resorcinol. The yields are promising for the catechol and resorcinol derivative. As these phenols have two substituents on the aromatic ring, not only several isomers could form but also the reactivity in subsequent reactions is expected to be different from the original DPA and also from one another. Thus, the DPAs were reacted with epichlorohydrin (ECH) in two different ways in order to study their capacity of forming the epoxy pre-polymer, in the same way that in industrial production. The results show that DPAG (DPA from guaiacol) has a particularly high nucleophilic activity with epichlorohydrin. Also DPAC (DPA from cathecol) and DPAR (DPA from resorcinol) have acceptable reactivities, comparable to BPA's, in the same conditions. After a careful evaluation of both the yields and selectivities of their synthesis as well as their nucleophilic activity in the glycidylation reaction, DPAR and DPAC can be considered interesting substitutes for BPA in epoxy resins. In this thesis, only their use for epoxy resins was investigated but obviously, these derivatives could also potentially be used for other applications of BPA, for example polycarbonates. This would allow to produce a new generation of BPA-free polycarbonate for bottles, an item for which at the moment the public resistance is particularly high.

In the second chapter, potential ways of avoiding the use of highly carcinogenic epichlorohydrin were investigated. Indeed, substantial efforts have been made in recent years to produce epichlorohydrin from biomass, namely glycerol deriving from the growing bio-fuel production, also due to increasingly competitive pricing. Still, nowadays epichlorohydrin is mainly produced from oil. However, the main problem remains the epichlorohydrin itself. The data collected so far on its acute toxicity and the long-term effects, show it is extremely harmful to human health and therefore far away from the concepts of sustainable development. The incredible likelihood of exposure, as it is rapidly absorbed through the skin, the gastrointestinal tract and due to its high volatility through the lungs, only increases the potential risk. It thus had to be substituted by a safer molecule.

Two different possibilities of epichlorohydrin substitution were investigated; the first completely avoids the use of a highly reactive epoxide whereas the second aims to obtain glycidyl tosylate from glycerol and tosyl chloride.

Comparing epichlorohydrin with the two potential substituting pathways, both including a recyclable biphasic reaction medium, makes it clear that, although the two-step process including the allylation of aromatic hydroxyls by allyl chloride followed by an epoxidation has the lowest yields, it is the safest and most environmentally friendly. Its high recyclability and practicality compensates the losses in conversion.

Allyl chloride is a derivative of glycerol. Furthermore, the reaction is carried out in phase transfer catalysis with no organic solvent. This means that the only solvent is highly alkaline water that can easily be recycled. The organic phase only consists of the product and the reagent, allyl chloride. After an optimization of the reaction time and temperature using hydroquinone as a pilot molecule, the maximum yield was 44%. The epoxidation is very green using in situ generated peroxymonocarbonate.

After having assessed the potentially best conditions for the model molecules, the glycidylation is conducted on the DPAs, in the third chapter.

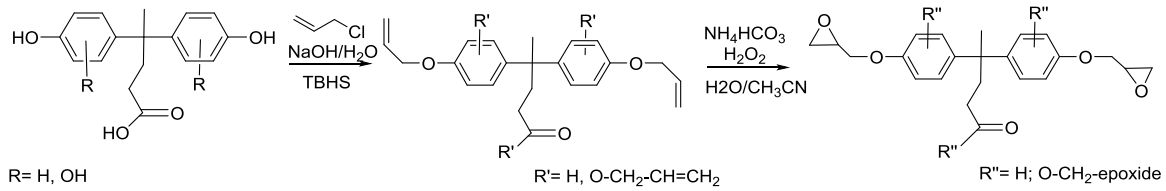


Figure C.2: Overall reaction scheme of glycidylation of the DPAs

Owing to their five hydroxyls, which can all potentially react in allylation and epoxidation, the characterization of DPAR and DPAC derivatives is expected to be relatively complex. In addition to a mixture of several products, after partial allylation, the Claisen re-arrangement also has to be taken into consideration.

The yield was particularly low for DPAR, with only 6% due to electronic effects, indeed the hydroxyls have a mutually deactivating action. The reaction rate is thus significantly slower than the one of the competitive reaction, the spontaneous homo-polymerisation of allyl chloride. Several tests on resorcinol with different ratios of allyl chloride have shown that the exhaustion of the allyl chloride due to the parallel reaction accounts for as much as 20% in yield, in the

allylation of DPAR. A further interesting finding was the complete inactivity of the hydroxyls in ortho to the central chain, in DPAR. Indeed the "internal" hydroxyls do not react with allyl chloride, leading to a product, in which only the outmost hydroxyl and the acid group are active, causing it to be equivalent to diphenolic acid from phenol from the structural point of view. In addition, this reactivity in the outmost positions, makes it very similar to bisphenol A, thus, analogous properties are expected.

DPAC, on the other hand, not only demonstrates an allylation to 100% of all the five hydroxyls (including the acid) with a yield of 40% but also the DPAC remaining in the aqueous solution is allylated to 55%. This is comparable with the yield of glycidylation with epichlorohydrin (59%), described in chapter 1.

The epoxidation, in both cases, did not reach sufficient yield to be used industrially but lipase-catalysed epoxidation on analogous compounds is reported in literature and gives satisfactory yields[70].

In the fourth chapter, corresponding to step number 3 on the figure C.1, the curing and the characteristics of the cured resin were thoroughly described. Indeed, whereas DPAC withholds self-curing capacity, i.e. it cures upon heating without adding catalysts of hardeners, DPAR requires the use of a crosslinker. Homopolymerisation is possible in most epoxy resins upon addition of a catalyst. In the case of diphenolic acids, the ester moiety, in its role as a Lewis base, is potentially able to activate the hydroxyls and generate their intermolecular reaction with epoxides leading to a crosslinked resin.

As in DPAC the hydroxyls are also strongly activated by mesomeric effect, this reaction occurs spontaneously upon heating. In DPAR on the other hand, not only two positions out of five are inhibited by a combination of steric hindrance and deactivating electronic effects, but these same hydroxyls deactivate the remaining aromatic hydroxyls by mesomeric effect. This compensates the activating effect of the ester and inhibits self-curing.

In order to find an adequate application, several tests have been carried out demonstrating that, in general, the results for both resins, are superior than the commercial DGEBA resin, cured with 1,6–hexamethylendiamine. Leaking was also examined for a potential application as a can coating for food containers. Both resins containing crosslinkers showed poorer results, probably due to a not-perfect homogenisation leading to not fully crosslinked sectors, releasing unreacted material. This is a general problem of using a hardener, existing even at industrial level.

In the last chapter, a model was developed to allow the simulation of the curing process. This is a fundamental step to using the newly developed resin in industrial applications. The reaction kinetics of glycidyl ether of diphenolic acid from resorcinol (GEDPAR) cured with aliphatic amine were determined in non-isothermal as well as isothermal mode. Two different linear aliphatic diamines, namely 1,4-butanediamine and 1,6-hexamethylenediamine were compared in order to evaluate the effect of chain length on the curing reaction. A modified Kamal model was used to provide a satisfactory fit of the experimental data, in which several visibly overlaid reactions and strongly temperature-dependent reaction orders indicate a highly complex reaction mechanism. The diffusion effect was greatly visible especially for low temperatures, significantly decreasing the final curing degree. This phenomenon is mainly due to the presence of 3 reactive epoxides on GEDPAR, which leads to gelation and vitrification even at low degrees of cure if this effect is not sufficiently compensated by decreasing the viscosity with high temperatures. In general, 1,4-diaminobutane showed slightly higher total activation energies in both cases, owing to the increased sterical hindrance after the first condensation with GEDPAR due to shorter chain length. In a future research, rheological test could also be of great interest.

Thus, in the course of this thesis, a fully renewable epoxy resin was developed. Although some further research could have been done, especially regarding the testing of the final properties, the groundwork has been done, from the first synthesis to the preparation of the industrialisation. Optimisation of the glycidylation has been stopped because of the lack of time however, allylation of phenols is currently studied all around the world and seems like the green go-to method. This pathway is thus very interesting leading to a brighter future with BPA-free epoxy resins, without needing to use of highly carcinogenic epichlorohydrin.

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