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POLYMERIC AND INORGANIC MATERIALS BEARING TRIPHENYLTIN CARBOXYLATE MOIETIES HAVING CATALYTIC ACTIVITY IN TRANSESTERIFICATION REACTIONS

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INTRODUCTION

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1.1 - Tin and organotin compounds[1]

Tin is one of the oldest metals known to mankind. The main reason of the importance of this chemical elementl in early times was the discovery of its hardening effect on copper to form bronze. Since the beginning of the Bronze Age, indeed, metallic tin and its alloys have been widespread[2]. Tin itself was important in early civilization and was mentioned in the Old Testament and in the Iliad.

Tin does not occur naturally as metal. By far the most economically important tin mineral is cassiterite, a naturally occurring oxide of tin having the chemical formula SnO_2. However, organotin compounds have been known for just the past 150 years. First systematic studies have been done by Sir Edward Frankland who, in the second half of the nineteenth century, synthesized diethyltin-diiodide[3], the first organotin compound reported in literature, and then tetraethyltin-diiodide[4]. Other investigations followed and today has been estimated that more than 800 organotins are known. For nearly 100 years the organotins have not been utilized, mainly due to the absence of any commercial application[5]. This changed in the 1940s, when the plastics industries began to expand[6]. Organotin compounds, indeed, were used as heat and light stabilizer additives in PVC processing and, even nowadays, this is their major application. Therefore, tin played a full part in the great increase of activity in organometallic chemistry, which started in about 1949. During the past 50 years the commercial applications of organotin compounds have spread out into other important industrial commodities and they have found a variety of applications in industry, agriculture and medicine, even if in recent years their uses have been limited by environmental considerations, due to their toxic effects. In industry they are used not only for the PVC stabilization, but also for the catalysis of the formation of polyurethanes, for the cold vulcanization of silicone polymers and, finally, as transesterification catalysts. Their biological properties are made use of in antifouling paints on ships, in wood preservatives and as agricultural fungicides and insecticides. Today the biocidic products make up about 20% of the total annual production.. In addition, in medicine they are showing promise in cancer teraphy[7,8] and in treatment of fungal infections.

The various commercial applications gave rise to a drastic increase in the worldwide production of organotin chemicals, in particular between the 1950s and 1990s, when their production increased from less than 5000 tons up to 50000 tons[9].

Due to the widespread use of the organotins considerable amounts of these compounds have entered various ecosystems.

Leaching from soils and landfills[10,] weathering of plastics[11] and dissolution of ship paints lead to the release of OTC into aquatic systems. Sediments of rivers, estuaries and marine systems have been identified as the major sinks of organotin compounds. As a consequence, there is abundant literature on input, distribution and toxicity of organotins mainly focused on the aquatic environment [12,13]. For example, so far attention has mainly been given to tributyltin pollution in water and sediments, because of its high toxic effect to aquatic life even at low concentrations[14].

1.2 - Chemical and physical properties of tin and organotin compounds

Tin belongs to the IV B group in the periodic table, together with C, Si, Ge and Pb and its electronic configuration is [Kr] $4d^{10}$ $5s^2$ $5p^2$. Since the metallic nature increase down to the group, its elements show different properties, passing from non-metallic C, through semi-metallic Si and Ge and finally to Sn and Pb, which actually can be considered as metal. As a consequence organotin compounds, term which refers to all chemical compounds bearing at least one C-Sn bond, are real organometallic compounds[15].

The Sn-C bonds are stable in presence of water, atmospheric O_2 and heat. They are also reported to be stable at temperatures up to 200°C[16], so thermal decomposition has no significance under environmental conditions.

The typical oxidation states for tin are Sn(II) and Sn (IV), but it has to be underlined that the first one is very unstable in organotin compounds.

Among the organotins having the metal in its lower oxydation state, an important example is the dicyclopentadienyltin (II). It is actually the only one which do not owe its stability to steric hindrance: as it can be seen in **Figure 1**, in this case the tin is hybridised *sp*^{2} with two of the hybrid orbitals interacting with ligands π systems, while the third one contains the unshared electron pair[17].

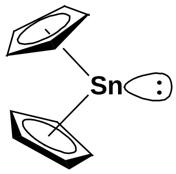


Figure 1. Structure of di-cyclopentadienyl-tin(II).

However, the organotin (II) compounds are of low interest since they have no practical use.

Concerning the common organotin (IV) compounds, their features, as hybridisation and coordination number, are highly influenced by the kind of ligand present on the metal centre. In fact the tetrahedral four coordinated arrangement (**Figure 2**), typical of *sp*^{3} hybridisation, is present in case of electron donor tin substituents, as tetralkyltins R_4Sn and hexalkylditins R_6Sn_2, in the alkyltin hydrides R_3SnH or in compounds like R_3SnX, where X could be either OH or Cl, if only R is a bulky alkylic ligand as, for instance, the 2,2-dimethyl-2-ethylphenyl moiety.

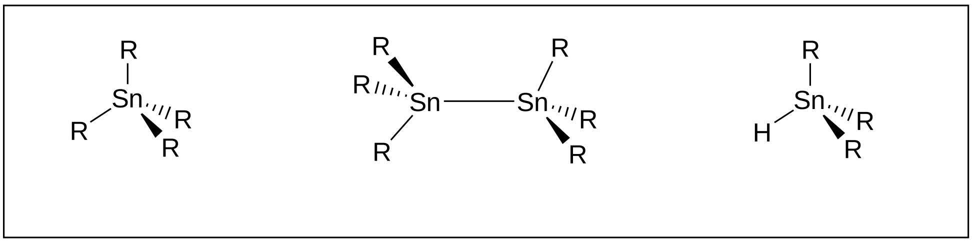


Figure 2. Structure of tin compounds having coordination number 4

When tin subtituents have electron withdrawing character as, for example, the chlorine, they increase the Lewis acidity of the metal centre, favouring its tendency to expand its coordination number from four to five, six, until seven through complex formation with any possible Lewis base present[18]. When tin raises its coordination number from 4 to 5 is hybridised sp^3d and usually has a trigonal bipyramidal geometry (**Figure 3**). This is the case of R_3SnX, where X can be OH, OR’, OCOR’, F. This kind of compounds can present three different isomeric forms: *trans*, *cis* and *mer*. The *trans* form is the most common: in this case oligomeric chains have been formed, having the planar R_3Sn units bridged by the X groups placed in axial position.

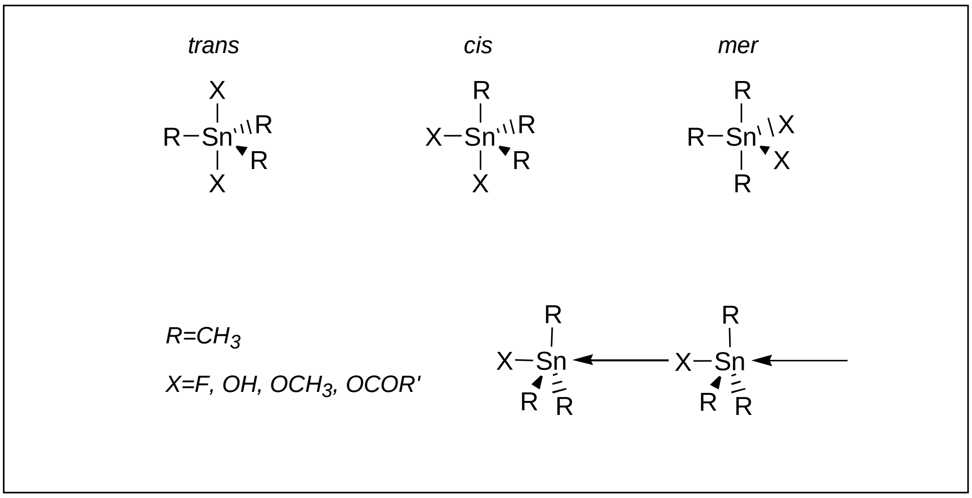


Figure 3. Bipyramidal trigonal structure for compounds having coordination number 5 and their supramolecular arrangement.

Organotin compounds can assume a pseudo-octahedral arrangement around the metal centre when more than one electron-withdrawing substituent is present on tin (**Figure 4**). In this case the metal is hybridised *sp*^{3}*d*^{2} and increases its coordination number up to 6. An important example of these molecules is provided by dialkyltin (IV) di-halides R_2SnX_2 and monoalkyltin(IV) tri-halides $RSnX_3$: these derivatives, due to their Lewis acidity, show an higher tendency to assume associated form. For instance, in $(CH_3)_2SnF_2$ the strong Lewis acidity, derived from the presence of the two electronegative fluorine atoms, makes each tin atom linearly linked to its four neighbours by the simmetrically placed halogen atoms: in this way an infinite two-dimensional sheet-like structure is formed, with the two trans methyl groups lying perpendicularly out of this plane[19].

When X is a chlorine or a bromine atom[20,21], instead, the intermolecular association is weaker and an infinite chain is formed, presenting the tin aton still hexacoordinated, while the halogen atoms are coupled in pair to the same metal centre.

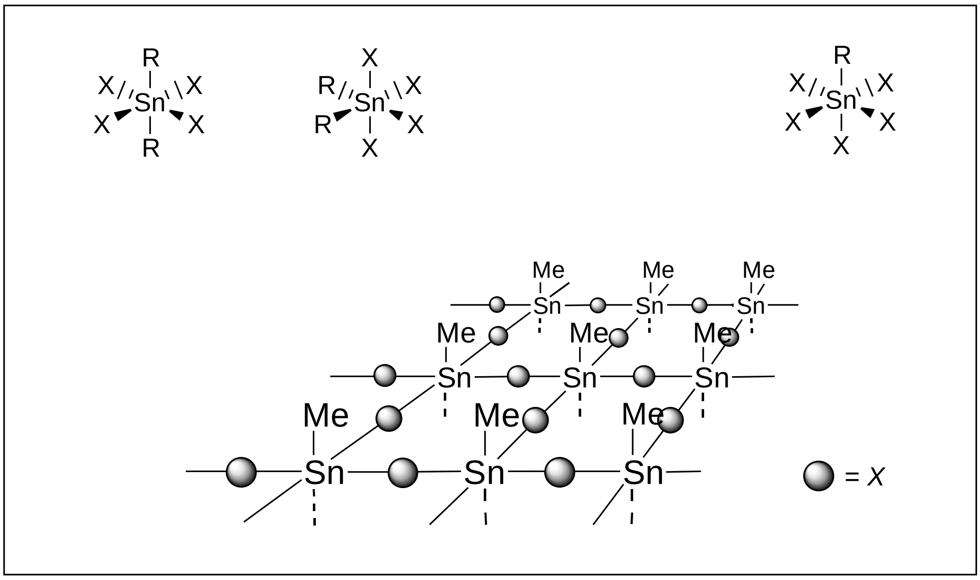


Figure 4. Octahedral structure for tin compounds having coordination number 6.

As it has been previously reported, tin can also reach coordination number 7, as in $(CH_3)_2Sn(NCS)_2$ compound, where the tin atom assumes a pentagonal bipyramidal geometry, having the two methylic groups in *trans* position.

Finally, it can be added that the very unusual Sn(III) oxydation state is present mainly in compound bearing a Sn-Sn single bond.

1.3 - Organotin Carboxylates

1.3.1 - Synthesis of organotin carboxylates

A common way to achieve organotin esters is the reaction of the carboxylic acid with the bis(triorganotin)oxide[22,23], as well as with the convenient triorganotin hydroxide[24] or diorganotin oxide[25, 26]. The water formed as co-product can be easily removed from the reaction mixture by azeotropic distillation in toluene, in order to shift the equilibrium towards the desired products. In the laboratory practise to this goal a Dean-Stark apparatus can be conveniently used.

$$R_3SnOSnR_3 \quad + \quad 2\,R'CO_2H \xrightarrow[-H_2O]{toluene} 2\,R_3SnOCOR' \qquad \textbf{Eq. 1}$$

$$R_3SnOH \quad + \quad R'CO_2H \xrightarrow[-H_2O]{toluene} R_3SnOCOR' \qquad \textbf{Eq. 2}$$

Organotin halides also can successfully converted in the corresponding organometallic esters reacting with a metal carboxylate[27] instead of with the carboxylic acid, using a suitable solvent, like acetone or carbon tetrachloride and heating.

$$R_nSnCl_{4-n} \quad + \quad (4-n)\,MOCOR' \longrightarrow R_nSn(OCOR')_{4-n} \quad + \quad (4-n)\,MCl \qquad \textbf{Eq. 3}$$

In addition the diorganotin dihalides can also be used in the transesterification of triorganotin carboxylates, carring out the reaction at room temperature[27].

The organotin esters can be prepared, moreover, by the cleavage of one or more Sn-C bond in tetraorganotin derivatives SnR_4 using a carboxylic acid (**Eq.4**) or, less frequentely, by mercury carboxylates (**Eq.5**).

$$R_4Sn \quad + \quad n\,R'CO_2H \longrightarrow R_{4-n}Sn(OCOR')_n \quad + \quad n\,RH \qquad \textbf{Eq. 4}$$

$$2Me_4Sn + Hg_2(OCOMe)_2 \longrightarrow 2Me_3SnOCOMe + 2Hg + C_2H_6 \qquad \textbf{Eq. 5}$$

In order to obtain organotin carboxylates another possible synthetic pathway consists on the reaction between organotin hydrides with carboxylic acids[28,29], although it is generally not used extensively (**Eq.6**).

$$Bu_2SnH_2 \quad + \quad 2\,MeCO_2H \longrightarrow Bu_2Sn(OCOMe)_2 \quad + \quad 2\,H_2 \qquad \textbf{Eq. 6}$$

1.3.2 - Chemical and physical properties of organotin carboxylates

The organotin carboxylates $R_nSn(OCOR')_{4-n}$ generally show low solubility in the common organic solvents, due to the strong Lewis acidity of the metal centre substitued with one or more electron-withdrawing groups such as, at least, one carboxylate.

However, the Lewis acidity depends also on the other tin substituents R. In previous studies[30] it has been observed that the organotin carboxylates are stronger Lewis acids than their relative chlorides and that the Lewis acidity of tin increase with raise of acid strenght of the carboxylic acid R'COOH[31].

As it has been already described, all organotin carboxylates can expand the tin coordination number, thus assuming different arrangements around the central metal atom.

In particular, the tin arrangements in triorganotin esters $R_3SnOCOR'$ can be referred to three structures, as shown in **Figure 5**. In the solid state the infinite polymeric chain structure (**a**) with bridging carboxylate and planar, or almost planar, triorganotin groups is the most likely, as demonstred by X-ray crystallography for different compounds, such as $Me_3SnOCOMe32$, $Me_3SnOCOCF_3$[32], $Me_3SnOCHO$[33], $Bz_3SnOCOMe$[34] and $(CH2{=}CH)_3SnOCOCCl_3$[35]. When the organic residue, both on the metal and on the carboxylate, are bulky, but the tin Lewis acidity is particularly strong, as in the case of triphenyltin(*o*-2-hydroxy-5-methylphenylazo)benzoate, the molecule is in the monomeric form **b**[35, 36].

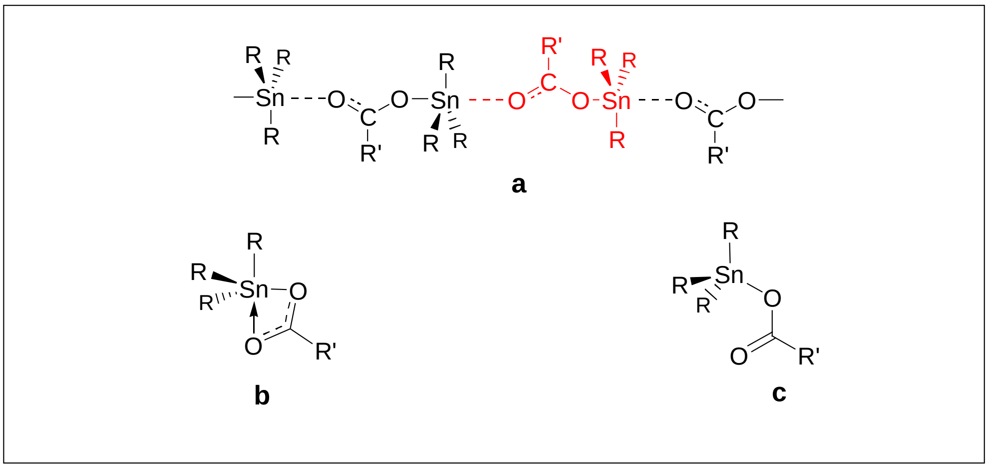
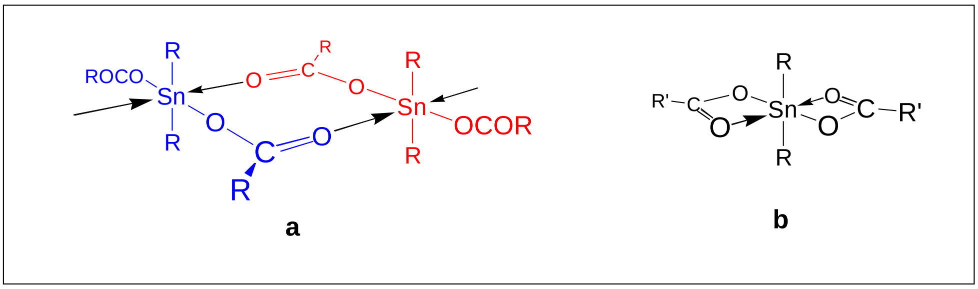


Figure 5. Possibile structures for triorganotin carboxylates.

Triorganotin carboxylates are generally scarcely soluble in organic solvents. A high dilution of these associated forms leads first to oligomers and finally, to monomeric tetrahedral species (**Figure 5**, **c**), in which the carbonyl oxygen is free from any interaction. The same structure can also be observed in the solid state only when the metal or carboxylate substituents are bulky enough to prevent the formation of any interaction, both inter- and intramolecular[37].

The tiorganotin carboxylates are usually more stable with respect to hydrolysis reaction, although organotin esters are generally more quickly hydrolysed than the corresponding halides: the ease of hydrolysis increases as *n* decreases in the general formula $R_nSn(OCOR')_{4-n}$.

The diorganotin dicarboxylates (**Figure 6**) are known to exist in the solid state both as monomeric form (**a**), with the two carboxylic moieties acting as intramolecular chelating groups, and polymeric infinite chains (**b**): in both cases the tin-oxygen bond length is different for the covalent and the chelating carbonyl oxygens, thus resulting in a overall distorted octahedral structure.



a **b**

Figure 6. Structure of diorganotin dicarboxylates in the solid state and in solution.

In solution these compounds are believed to be in the monomeric intramolecularly chelated form **b**[38, 39].

1.4 - Organotin Polymers

The pollution problems raising from tin leaching durino organotins employment can be opportunely overcome by grafting covalently the organometallic moiety onto a macromolecular support, thus preventing its release in the environment and leading to the so-called “clean organotin derivatives”. For this reason, among the great veriety of organotin compounds avaiable, those bearing also a polymerizable moiety are of outstanding importance.

Depending on the type of conjugation and the mutual location of the tin atom and reactive functional group, organotin monomers can be divided in the following major groups[40]:

- monomers with d_π-p_π conjugation;
- monomers with d_π-σ-π conjugation;
- monomers containing electron-rich group, or atoms, located between tin atoms and polymerizable moieties.

A great number of organotin compounds containing functional groups able to polymerize have been described in the literature so far, but only the monomers in last group show a reasonable reactivity towards homo- and co-polymerization reactions. As it is well-known, vinyltin compounds undergo no free radical homopolymerization, as well as no copolymerization reaction with different vinyl monomers[41]. This can be due to the inhibiting effect of the organotin moiety towards radical reactions as underlined by copolymerization of both trimethyl- and tributylvinyltin with styrene or methyl methacrilate, that results in low yields, decreasing with high contents of tin monomers in the starting mixture. In addition, the reactivity of vinylstannane evaluated in the copolymerization with ethylene, initiated by dibutyl peroxide, resulted to be almost suppressed, owing to the conjugation within the molecule itself[42]. On the other hand, vinyltin monomers are readily homo- and co-polymerized with butyllithium at 0 and 20°C respectively by an anionic mechanism[43].

It has been noted, however, that the inhibiting action of the unsaturated organotin compounds is strongly dependent on the arrangement of the double bond within the molecule. Indeed, as previously stated, the strongest effect occurs when the vinyl group is directly connected to the metal atom. Thus it has been found that molecules such as the tributyltin methacrilate, and di(tributyltin) itaconate (**Figure 7**, **a** and **b**) can be homo- and co-polymerized with styrene, methyl methacrilate and acrylonitrile, even if leading to low yields[44]. Better results can be achieved in the homopolymerization of 3-tributylstannylstyrene (**Figure 7**, **c**) and in its copolymerization with styrene, vinyl acetate or other acrylic monomers (yields around 35-45%)[45]. Anyway, when the monomer bears a carboxylic and a phenylic group at the same time, such as in the case of tributyltin 3-(4-styryl)-propionate (**d**), yields of 73% in the homopolymerization and arouond 25-70% for its copolymerization with styrene, depending on the composition, can also be achieved[46].

Epoxytin compounds are also been investigated: the introduction of organotin residues into an epoxide resin improves the dielectric properties and thermal stability of the final products[47].

Carbon chain polymeric tin compounds have found increasing interst in the last few years, since the introduction of alkyltin residues in polymers or copolymers provides specific properties to the products, favouring their applications as plastic stabilizers, in particular for PVC, biocides, antioxidants or catalysts.

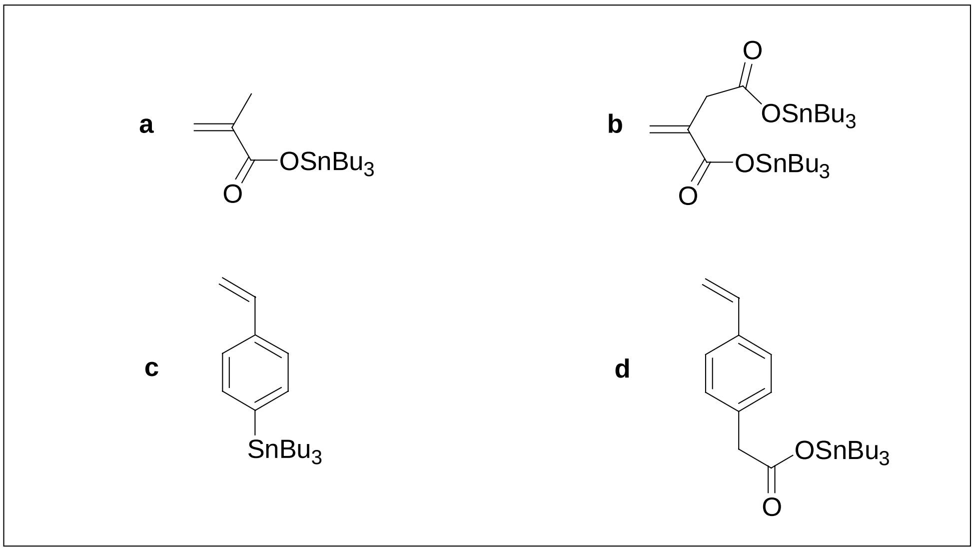


Figure 7. Some polymerizable organotin monomers.

2 - Characterization of Organotin Compounds

2.1 - Tin NMR Spectroscopy[1]

Tin has ten naturally occurring isotopes, as it can be seen in **Table 1,** the largest number observable for every known element. Among these, however, only ^{115}Sn, ^{117}Sn and ^{119}Sn have a nuclear spin I = ½ and are, therefore, magnetically active. Indeed they are suitable for nuclear Magnetic Resonance detection (NMR).

Table 1. **Natural abundance, gyromagnetic ratio and NMR sensivity for the ten tin isotopes.**

Isotope	*Natural Abundance (%)*	*Gyromagnet ratio γ ($10^7 radT^{-1}s^{-1}$)*	*Relative NMR sensivity$^{(a)}$*
^{112}Sn	1.01	-	-
^{114}Sn	0.68	-	-
^{115}Sn	***0.35***	***-8.792***	***3.5×10^{-2}***
^{116}Sn	14.28	-	-
^{117}Sn	***7.67***	***-9.578***	***4.5×10^{-2}***
^{118}Sn	23.84	-	-
^{119}Sn	***8.68***	***-10.021***	***5.2×10^{-2}***
^{120}Sn	32.75	-	-
^{122}Sn	4.74	-	-
^{124}Sn	6.01	-	-

Nevertheless, ^{115}Sn isotope can not be used extensively in tin NMR analysis, because of its very small natural abundance and its lower relative NMR sensivity. On the other hand, the ^{119}Sn nucleus is the most employed[48], since it has higher natural abudance and gyromagnetic ratio, that leads to a receptivity 25 times higher than ^{13}C. However, ^{117}Sn is equally suitable for NMR detection and it is generally used when external circumstances, such as radio frequency interferences, modify the signal-noise ratio for ^{119}Sn nucleus[49], or when one wants to study coupling by tin atoms.

The development of FT-NMR techniques have allowed to record high quality and better sensivity spectra also for complex molecules when ^{119}Sn-^{1}H or ^{11}9Sn-^{13}C couplings are present.

2.1.1 - Tin chemical shifts (δ)

Organotin compounds are characterised by a very wide range of chemical shifts δ(^{119}Sn), thus covering a spectral window of more than 6500 ppm. However, the most common classes of these compounds show resonaces between + 200 and -300 ppm[50, 51], value referred to tetramethyltin (**Figure 8**).

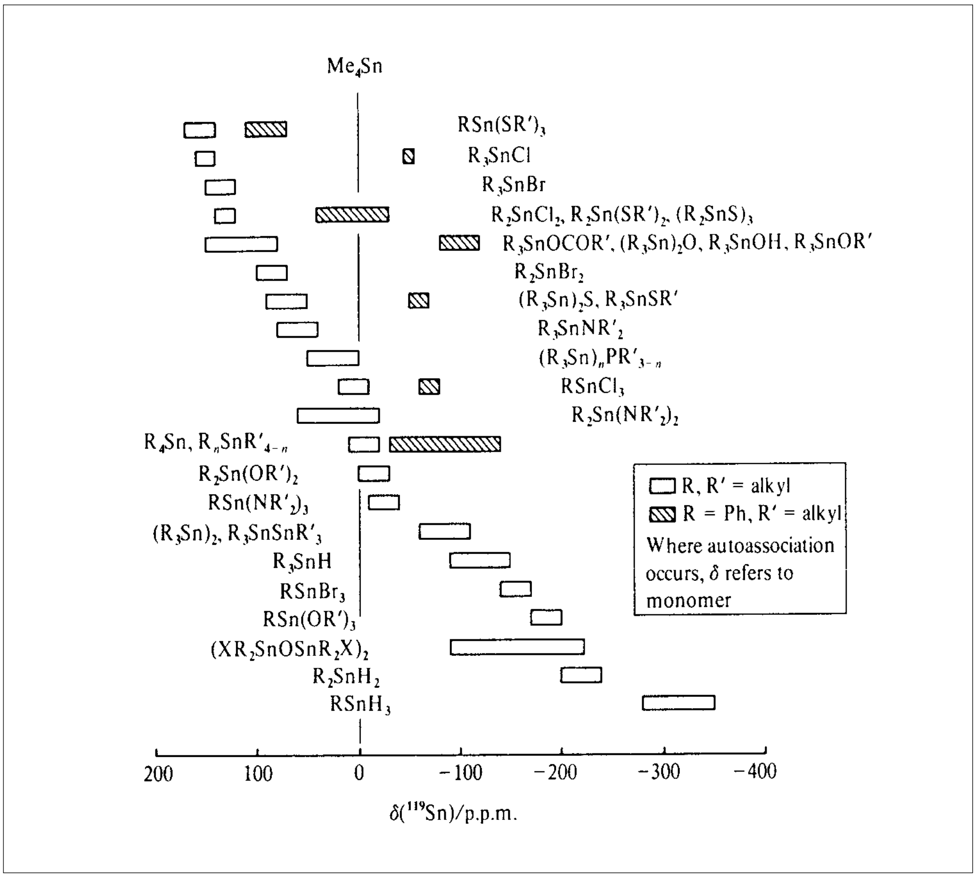


Figure 8. ^{119}Sn chemical shifts of organotin compounds.

It has to be said, moreover, that the tin chemical shift is sensitive to a number of competing factors, so this allows NMR spectroscopy to be a powerful tool in structural characterisation of organotin compounds. Indeed, in a series of general formula R_nSnX_{4-n}, increasing the electron donor effect of the organic alkylic group, the tin atom becomes progressively more shielded, thus shifting the chemical shift towards higher field, showing a correlation between these two parameters[52] (**Table 2**).

Table 2. Effect of organic substituent R on $\delta(^{119}Sn)$ for the R_nSnCl_{4-n} compounds.

R substituent	*$RSnCl_3$*	*R_2SnCl_2*	*R_3SnCl*
Me (CH_3)	+20	+141	+164
Et (C_2H_5)	+6.5	+126	+155
Bu (C_4H_{10})	+6.0	+122	+141
Bu^t (C_4H_{10})	-	+52	-
Ph (C_6H_5)	-63	-32	-48

If the alkyl groups are replaced by phenyl moiety, the ^{119}Sn resonance moves to lower frequencies, although the huge electron-withdrawing effect this substituent has. The same beaviour is also observed in presence of vinyl or allyl residues, probably due to the higher polarizability typical of the unsatured groups[53]. The same consideration can be made about the inorganic radical X, since the ^{119}Sn chemical shift moves accordingly with the increased inductive electron-withdrawing power of the substituent. This is rather evident plotting $\delta(^{119}Sn)$ vs. Pauling electronegativity χ of X group in different Me_3SnX compounds, resulting in a good linear correlation[54], as depicted in the figure below (**Figure 9**).

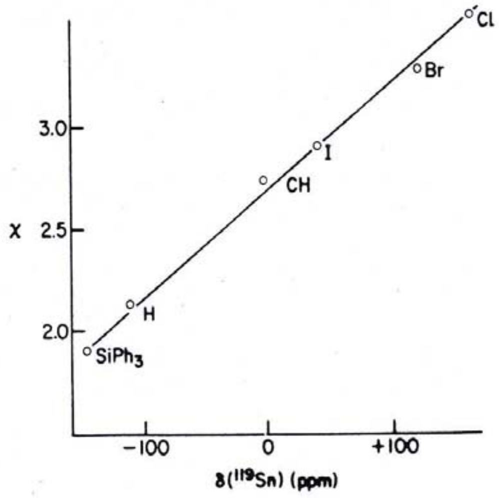


Figure 9. Relation between δ(^{119}Sn) and Pauling electronegativity χ for some Me_3SnX compounds.

A very important aspect of the ^{117}Sn/^{119}Sn spectroscopy is the dependence of tin resonance upon the coordination number of the metal itself. It has been observed that δ moves upfield by at least 40 ppm as the tin coordination increases from 4 to 5, 6 and 7, either by interaction with external ligands or intramolecular autoassociation[55]. This feature is very important for a structural analysis of the organotin compounds, since it allows a quite easy determination of the spatial arrangement around the metal centre. It is clear how the choice of the solvent in preparing samples for NMR can deeply affect tin chemical shift: in fact it has been noticed that the dilution of some trimethyltin halides in non-coordinating solvent, such as benzene o CCl_4, causes negligible shifts of δ (^{119}Sn), while polar coorinating solvents, such as acetone, DMSO or pyridine produce relevant changes of the chemical shift. In this latter case, changing the molar ratio Me_3SnCl/ pyridine from 1/0 to 1/12 the chemical shift moves from + 159 down to -9 ppm, while the greatest variation of δ (^{119}Sn) occurs passing a Me_3SnCl/ pyridine ratio 1/0 to 1/1, due to the formation of a 1:1 adduct of the tin compound and pyridine[52] (**Figure 10**).

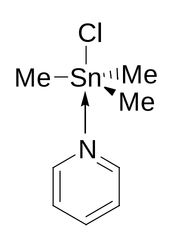


Figure 10. Pentacoordinated adduct of Me_3SnCl with pyridine.

Since tin can achieve the coordination expansion also by self-association, ^{119}Sn chemical shift can be even affected by concentration of sample in non-coordinating solvents: indeed, an investigation[56] of the relationship between δ (^{119}Sn) and the concentration for trimethyltin formate in $CDCl_3$ shows, in fact, that upon passing from 0.05 M solution up to 3.0 M the chemical shift moves from +152 down to +2.5 ppm. This difference can be explained by passing from a tetracoordinated tin present in diluted solution to a pentacoordination in the more concentrated one (**Figure 11**, **a** and **b** respectively).

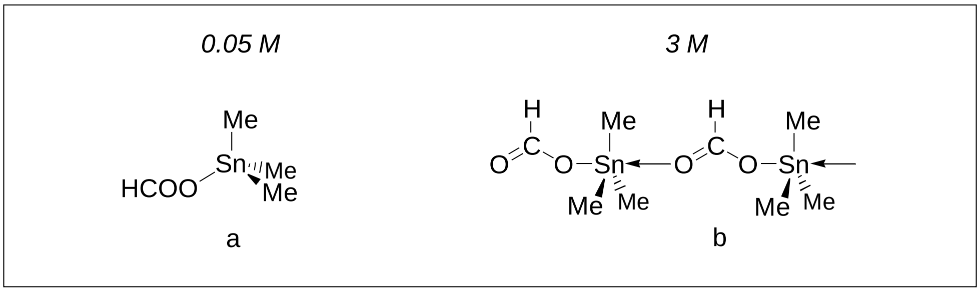


Figure 11. Structure of the trimethyltin formate in diluted (a) and concentrate (b) solution.

2.1.2 - *Coupling costants*

A lot of detailed investigations on the coupling costants of tin have been performed. Some of the obtained results are shown in **Table 3**.

Table 3. **Tin coupling costants for R_nSnCl_{4-n} compounds in non-coordinating solvents**

Compound	*$^nJ(^{119}Sn\text{-}X)$ (Hz)*	*X*	*n*
Me_3SnH	1744	^1H	1
Me_4Sn	54	^1H	2
$MeSnCl_3$	100	^1H	2
Me_2SnCl_2	69	^1H	2
Me_3SnCl	58.5	^1H	2
R_3SnX (tetracoord.)	330-390	^{13}C	1
R_3SnX (pentacoord.)	450-480	^{13}C	1
R_2SnX_2 (tetracoord.)	370-480	^{13}C	1
R_2SnX_2 (esacoord.)	900-970	^{13}C	1
$R_3SnOCOCH_2(C_6H_4)Et$	174	^{13}C	1
$R_3SnOCOCH_2(C_6H_4)Et$	10	^{13}C	2
$R_3SnOCOCH_2(C_6H_4)Et$	31	^{13}C	3
$(PhMe_2CCH_2)_3SnF$	2298	^{19}F	2
$MeSnCF_2CF_2H$	265.5	^{19}F	2
Me_3SnPPh_2	596	^{31}P	1
$(Me_3Sn)_2PPh$	724	^{31}P	1
$(Me_3Sn)_3P$	832.5	^{31}P	1
$Me_3SnB(NMe_2)_2$	953	^{11}B	1
R_3SnSnR_3	700-4500	^{119}Sn	1
$R_3SnSnR_2SnR_3$	400-3000	^{119}Sn	1
$R_3SnSnR_2SnR_3$	200-800	^{119}Sn	2

Among NMR parameters, the scalar coupling constant of type $^nJ(^{119}Sn, X)$, with n=1-5 and X any atom having a spin $I \neq 0$, can give useful information. In fact, as generally no decoupling with tin atom is applied, $^nJ(^{119}Sn, X)$ can be detected either by the ^{119}Sn or the X-NMR spectrum. Satellites bands due to coupling by both ^{117}Sn and ^{119}Sn isotopes can be thus observed in ^1H and ^{13}C-NMR spectra.

Accordingly to Holecek and co-workers[57,58], the tin chemical shift is sensitive towards its geometry and, moreover, depends on this parameter. It has been proposed, in fact, a linear empirical correlation between this value and the dihedral bond angle C-Sn-C, that actually is a key parameter in the evaluation of the ligands arrangement around the central metal centre. Furthermore it has to be said that $^{1}J(^{119}\text{Sn-}^{13}\text{C})$ increases with the *s*-character of the tin-carbon bond.

It is also weel-established that $^{n}J(^{117/119}\text{Sn-}^{13}\text{C})$ follows the general rule $|^{1}J(^{117/119}\text{Sn-}^{13}\text{C})| \gg |^{3}J(^{117/119}\text{Sn-}^{13}\text{C})| > |^{2}J(^{117/119}\text{Sn-}^{13}\text{C})|$[48] and this statement is very useful for assigning the ^{13}C resonances of the tin substituents.

Another important application of tin coupling is the possibility of recording Heteronuclear Multiple Quantum Coherence (HMQC) $^{1}\text{H-}^{119}\text{Sn}$ spectra: this is a particular kind of bi-dimesional spectroscopy that is able to correlate protons and tin nucleus through $^{n}J(^{119}\text{Sn- }^{1}\text{H})$ coupling. This technique, firstly used by Bax ans Summers[59], and then developed for the pair $^{119}\text{Sn-}^{1}\text{H}$ by Willem and co-workers[60, 61], shows only the protons coupled to ^{119}Sn, appearing as multiplets, since $^{1}\text{H-}^{1}\text{H}$ is kept; the main proton signal is suppressed, as well as the contribution rising from the coupling with ^{117}Sn. This technique can provide very useful information in the determination of organotin structures, in particular in order to understand if the coordination expansion occurs inter- or intramolecularly[60, 61].

2.1.3 - *Solid state NMR spectroscopy*

Upon passing from solution to the solid state the molecular mobility is strongly lowered and the existence of some nuclear interactions, such as the dipole-dipole coupling interactions and the chemical shift anisotropy, can influence the NMR resonace bandwidth, causing its expansion over several kHz. On the other hand, this problem is quite negligible in solution, as a consequence of the fast molecular motions[62].

Moreover, it has been observed that the molecular orientation is linearly correlated to the magnitude of the nuclear interaction effects on the nuclear spin energy levels[63]. In fact the dipole-dipole effect bertween two spins can be considered similar to the scalar coupling in the solution state, but in this case, the transition frequencies depend on the molecular orientation, whose value can be represented in the equation expressing the dipolar interactions and the chemical shift anisotropy as a factor of the form ($3\cos^2\theta$-1), where θ is the angle between the interaction axis and the magnetic field B_0[62]. With the aim of removing those contributions to the NMR resonance, the so-called Magic Angle Spinning (MAS) technique has been introduced[63]. It consist on spinning the sample around an axis forming an angle θ with the external magnetic field B_0. When the spinning angle $\theta = 54.7°$, i.e. the so-called Magic Angle, the factor ($3\cos^2\theta$-1) is nullified, so that the dipolar , as well as chemical shift anisotropy, can be averaged to zero, thus resulting in high resolution solid state spectra.

When the complete removal of the chemical shift anisotropy is not possible, the solid state $^{117/119}$Sn-NMR provides two types of resonances: those related to the isotropic chemical shift and the ones raising from the spinning side bands. The intensity of the latter can be lowered rising the angular spinning rate of the sample ω_r, , sice they are nullified when $\omega_r = 2\pi\Delta\nu$, being $\Delta\nu$ the bandwidth generated by dipolar interactions and chemical shift anisotropy. If that contribution is not completely removed, spinning side bands appear at either sides of the isotropic chemical shift, at a distance equal to (or multiple of) the rotation frequency of the sample itself. This is the reason because the solid state spectra must be recorded, at lest, at two different spinning rate: the final overlap of the spectra can easily point out the isotropic chemical shifts, being the only signals unchanged upon spinning rate modifications[63].

In order to improve the signal-noise performance of the MAS spectra the Cross-Polarization (CP) technique can be also applied. It consist of the transformation of the magnetization of an abundant and sensitive nucleus (typically ^{1}H or ^{19}F) to lesse sensitive and abudant nuclei (^{13}C, ^{15}N, ^{29}Si, $^{117/119}$Sn). Unlike NOE transfer in solution, which occurs with longitudinale megnetization, Cross-Polarization occurs in the transverse plane of the rotating reference frame.

2.2 - FT-IR Spectroscopy of Organotin Compounds

2.2.1 - General properties

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the presence of chemical functional groups in the sample: indeed different functional groups absorb characteristic frequencies of IR radiation. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification[64].

Infrared radiation spans a section of the electromagnetic spectrum having wavenumbers from roughly 13.000 to 10 cm^{-1}, or wavelengths from 0.78 to 1000 μm. It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies.

The IR region is commonly divided into three smaller areas: near IR, mid IR, and far IR.

2.2.2 - Theory of Infrared Absorption[65]

At temperatures above absolute zero, all the atoms in molecules are in continuous vibration with respect to each other. When the frequency of a specific vibration is equal to the frequency of the IR radiation directed on the molecule, the molecule absorbs the radiation.

Each atom has three degrees of freedom, corresponding to motions along any of the three Cartesian coordinate axes (x, y, z). A polyatomic molecule of n atoms has $3n$ total degrees of freedom. However, 3 degrees of them are required to describe translation, the motion of the entire molecule through space. Additionally, 3 degrees of freedom correspond to rotation of the entire molecule. Therefore, the remaining $3n - 6$ degrees of freedom are true, fundamental vibrations for nonlinear molecules. Linear molecules possess $3n - 5$ fundamental vibrational modes because only 2 degrees of freedom are sufficient to describe rotation. The total number of observed absorption bands is generally different from the total number of fundamental vibrations. It is reduced because some modes are not IR active and a single frequency can cause more than one mode of motion to occur. Conversely, additional bands are generated by the appearance of overtones (integral multiples of the fundamental absorption frequencies), combinations of fundamental frequencies, differences of fundamental frequencies, coupling interactions of two fundamental absorption frequencies, and coupling interactions between fundamental vibrations and overtones or combination bands (Fermi resonance). The intensities of overtone, combination, and difference bands are less than those of the fundamental bands. The combination and blending of all the factors thus create a unique IR spectrum for each compound.

The major types of molecular vibrations are stretching and bending. The various types of vibrations are illustrated in **Figure 12**.

In particular, stretching vibrations are divided in symmetrical (movement in the same direction) and asymmetrical (movement in opposite directions). Bending vibrations are classified as scissoring, rocking, twisting, or wagging.

Figure 12. Different types of stretching and bending vibrations.

Infrared radiation is absorbed and the associated energy is converted into these type of motions. The absorption involves discrete, quantized energy levels. However, the individual vibrational motion is usually accompanied by other rotational motions. These combinations lead to the absorption bands, not to the discrete lines, commonly observed in the mid IR region.

The stretching frequency of a bond can be approximated by Hooke's Law. In this approximation, two atoms and the connecting bond are treated as a simple harmonic oscillator composed of 2 masses (atoms) joined by a spring:

According to Hooke's law, the spring vibration frequency is related to the mass and the force constant of the spring, ***k***, by the following formula:

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where ***k*** is the force constant, $\boldsymbol{\mu}$ is the reduced mass and ν is the frequency of the vibration. In the classical harmonic oscillator:

$$E = h\nu$$

Thus, the energy or frequency is dependent on how far one stretches or compresses the spring, which can be any value. If this simple model were true, a molecule could absorb energy of any wavelength.

However, vibrational motion is *quantized*: it must follow the rules of quantum mechanics and only particular transition are thus allowed

2.2.3 - FT-IR spectroscopy of organotin compounds[1]

FT-IR spectroscopy is particularly useful in order to characterized all the organic or organometallis compounds. Analyses of the spectral region between 4000 and 600 cm^{-1} usually provides interesting information about the structure and, moreover, the functional groups present in the compound. As regard organotin compounds, their absorption frequencies have been studied for a long time in order to understand the typical regions where the vibrations related to tin involving bonds are located. Typical vibrational frequencies were tabulated by Neumann[66], Poller[67], Omae[68], Harrison[69] and Nakamoto[70]. Some important examples of Sn-X bonds stretching frequencies are reported in **Table 4**.

Table 4. Absorption frequencies of some organotin compounds

Compound	ν Sn-X (cm^{-1})	***Compound***	ν Sn-X (cm^{-1})
R_3SnH (monom.)	1777-1846	Me_3SnOH (5-coord.)	531-576
R_2SnH_2 (monom.)	1820-1863	$(Bu_3Sn)_2O$ (5-coord.)	770
$RSnH_3$ (monom.)	1855-1880	$(Ph_3Sn)_2O$ (5-coord.)	770
R_3SnF (5-coord.)	340-377	R_2SnNR_2	520-620
R_3SnCl (5-coord.)	318-336	R_2SnSR'	320-370
R_3SnBr	222-234	$Me_3SnSnMe_3$	192
R_3SnI	176-204	$Ph_3SnSnPh_3$	138
$Me_3SnCl_2^-$ (5-coord.)	227	$(Me_3Sn)_4Sn$	159, 198
$Me_3SnBr_2^-$ (5-coord.)	140	(2,4,6 $Et_3C_6H_2)_6Sn_2$	92
$Me_3SnI_2^-$ (5-coord.)	134		

It has been noticed that all the tin derivatives that are not prone to increase their coordination number, such as tetraalkyltin, organotin hydrides or hexalkyl-ditin derivatives, provide both in solid state and in diluted or concentrated solution the same IR spectra. On the other hand, all the compounds undergoing coordination expansion show modification in the frequency absorption, passing from diluted solution to the solid state.

In many types of triorganotin compounds like R_3SnH, self association is able to give an oligomeric structure placing the tin in a trigonal bipyramidal arrangment. The consequently symmetrical vibration of the R_3Sn moiety is infrared inactive: the absence of the stretching band at about 510 cm^{-1} can be used therefore as evidence for the presence of oligomeric structures.

Accordingly, infrared spectroscopy due to these properties and, in addition, to the easiness of recording spectra, represents an important technique for the structure determination of organotin compounds and, at the same time, a convenient tool for monitoring the reactions progress.

2.2.4 - FT-IR spectroscopy of triorganotin carboxylatess

Due to the strong absorption of the carbonylic residue and to the presence of a directly linked organotin moiety, FT-IR spectroscopy has become an important instrument for the characterization of triorganotin carboxylates, because it can give, as we have seen, important structural informations. The IR spectral regions mainly involved in the the organotin carboxylates characterization are from 1700 to 1400 cm^{-1}, where the carbonyl asymmetric and symmetric stretching can be found, and the region 600-500 cm^{-1}, related to the Sn-C bond absorption band.

As regards to the carbonyl moiety, the systematic investigation carried out on some alkyltin acetates, mainly focused on the carboxylic moiety, has assessed important feautures that can be extended to all the organotin carboxylates[71]. In particular it has been concluded that the absorption of the carbonyl stretching is not affected by the size of the tin alkyl substituents, as it has been underlined in **Table 5**.

Table 5. Vibrational frequencies of some trialkyltin carboxylates in solid state (on KBr) and in CCl_4 solution

Compound	***υ R_3-Sn (cm^{-1})***		***υ COO (cm^{-1})***	
	Solid State	***CCl_4 Solution***	***Solid State***	***CCl_4 Solution***
Trimethyltin acetate	547	-	1565, 1412	-
Triethyltin acetate	-	-	1572, 1412	1655, 1302
Tributhyltin acetate	-	-	1572, 1410	1647, 1300
Triexyltin acetate	-	-	1570, 1408	1650, 1304
Trimethyltin laurate	548	548, 516	1567, 1410	1642, 1302

It is however important to consider that, on the contrary, the carbonyl absorption frequencies are affected by the physical state of the compound. In fact a considerable shift in both asymmetrical and symmetrical stretching frequencies, passing from the solid state to a solution in non-coordinating solvent, for example CCl_4, has been observed. In particular the solid state values are rather close to the ones related to the carboxylate in its anionic form, as for CH_3COONa[72], characterized by ν_{asym} =1582 cm^{-1} and ν_{sym} = 1425 cm^{-1} , while in diluted solution are closer to the usual organic esters[73] (ν_{asym} =1750-1735 cm^{-1} and ν_{sym} = 1225 cm^{-1} respectively).

The solid state behaviour of organotin carboxylates has been explained on the basis of the tin coordination expansion, leading to the hypothesis of a bridging carboxylate lying between two SnR_3 residues in an almost anionic form[74].

When dissolved in excess of CCl_4 the organotin ester looses its supramolecular structure: free carboxylate molecules are generated, assuming a structure very close to the other esters. Nevertheless, the vibrational absorptions in the latter case is different from those reported for the organometallic derivatives: in fact, the presence of a heavy metal atom is actually considered as reducing the frequencies to value lower than those of the common esters.

When the polymeric chain is not completely interrupted, although the concentration is high enough, some oligomers remain.

As we have previously said, another interesting part of the infrared spectra of trialkyltin carboxylates is the tin-carbon bond stretching region, which is an important tool for the invetsigation of their structure.

It has been observed that the $Sn(CH_3)_3$ moiety in diluted solution, in the presence of a tetrahedral tin arrangment, shows two different stretching vibrations (ν_{asym} = 548 cm^{-1} and ν_{sym} = 516 cm^{-1}), while in the solid state one of these two absorptions disappears, due to the tin pentacoordination. In fact, as previously stated, when in the solid state the tin atom configuration is pentacoordinated with a trigonal bipyramidal geometry, the trimethyltin residue is assumed to be planar, lying between two bridging carboxylate groups: in these condition, as known, the Sn-C symmetric stretching becomes infrared inactive[75], experimentally confirmed by the disappearance of the corresponding absorption band. This is a smart approach for evaluating the geometry around the tin atom: in fact, the appearance of a band related to the symmetric absorption, whenever tin pentacoordination is established, suggests a relevant distortion of the trigonal bipyramidal arrangment[76], leading to a non planar conformation of the R_3Sn residue and, therefore, to the infrared activity of this vibration.

2.3 - Mass Spectrometry of Organotin Compounds[76]

As it has been previously said, tin has ten naturally occurring isotopes, more than any other element. In the mass spectrum, these isotopes give rise to the characteristic pattern of peaks depicted in **Figure 13**.

Figure 13. Naturally occurring isotopes of tin

Rather limited use has been made of mass spectrometry in the study of organotin compounds, although MS linked to GC is now being used for the identification of organotin compounds, expecially in environmental studies. Typical modes of fragmentation have been elucidated for Me_4Sn and Bu_4Sn. Very little of the molecular ion $R_4Sn^{\bullet+}$ is usually detected by EI MS at 70 eV. It decays by progressive loss of $Me^{\bullet}$ and MeMe, while the hydrides Bu_2SnH^+ and $BuSnH_2^+$ and Sn are the major products from Bu_4Sn.

R_3Sn^+ is usually the principal ion fragment in the spectra of R_4Sn compounds. Distannanes show rather more of the molecular ion under EI at 70 eV and can fragment to give $R^\bullet$ and $R_3SnSnR_2^+$ or R_3Sn^+ and $R_3Sn^\bullet$.

3 - Toxicity of Organotin Compounds

Tin has a larger number of its organometallic derivatives having commercial use than any other element, thus considerable amounts of organotin compounds have entered various ecosystems.

Commonly tin in its inorganic forms is considered as being no-toxic or, at least, low toxic, in particular when compared to their analogues as Pb and Hg derivatives.

As regards to organotin compounds, instead, their toxicological pattern is still not completely clear and, moreover, very complex. In fact these compounds differ each other in the degree of their toxic effects as well as in the target organs depending not only on the nature, but also on the number of the organic groups bound to the Sn atom. In products of general formula R_nSnX_{4-n} it can be said that the hazard raises as the *n* value increases; while as regard to the R substituent the toxicity enhances when alkylic chain lenght decreases, owing to the higher volatility of the final product[77].

Usually trialkyltins are considered the most toxic tin compounds in every R_nSnX_{4-n} series, followed by the di- and monoalkyltins; tetraorganotins show a delayed toxic activity in organism, since they are metabolized to their trialkyltin analogues[78] (**Table 6**). Their toxic effect in fact is related to the latter compounds, depending mainly on the rate of their metabolic conversion.

Table 6. Acute oral toxicity of several organotin compounds to rats[79]

Organotin Compound	***LD_{50} (mg/kg)***	***Organotin Compound***	***LD_{50} (mg/kg)***
Et_3SnOAc	4	Hex_3SnOAc	1000
Me_3SnOAc	9	$(Bu_3Sn)_2O$	150-234
Me_3SnCl	13	Bu_3SnOAc	380

Me_3SnOH	540	Bu_3SnOCl_2	100
Me_2SnCl_2	74	Bu_3SnOCl_3	2140
$MeSnCl_3$	1370	Bu_4Sn	> 4000
Ph_3SnOH	125	Oct_4Sn	50000

However, many microorganisms exhibit resistence to organotins, a phenomenon of relevance to their environmental cycling and also to novel biological methods of treatement. Finally it has been noticed that the group X usually has little or not effects on the biocide activity, except when X itself is a toxic component: in this case it increases drammatically the overall toxicity of the compound. On the other hand, the nature of the R organic substituent determines the toxicological and, often, selective target, as briefly summarized in the **Table 7**.

Table 7. Specific effects on species of the *R_3SnX* compounds[77]

Organotin Compounds of R_3SnX series	
Substituent	***Target***
$-CH_3$	Insects
$-C_2H_5$	Mammals
$-C_3H_7$	Gram-negative bacteria
$-C_4H_9$	Gram-positive bacteria, Fishes, Algae, Mussels, Molluscs, Fungi,
$-C_6H_5$	Fungi, Molluscs, Fishes
$-C_6H_{11}$	Mites, Fishes

It has to be underlined, moreover, that an increase in the *n*-alkyl chain lenght produces a sharp drop in biocide activity to all living species: this makes the long-chain species, like *n*-octyltin derivatives, essentially non-toxic to all organisms. In fact they are allowed to be used as stabilizers in PVC food packaging materials.

The toxic triorganotin compounds are able to inhibit mitochondrial oxidative phosphorylation[80] and their biological activity pattern is probably due to their ability to bind to certain proteins[81]. Although the exact nature of the bindings sites is not yet known, in haemoglobin has been observed that both cysteine and histidine residues are associated with the R_3Sn moiety[82].
Tributyltin is supposed to be the agent having the highest toxic effect towards aquatic life. Even at nanomolar aqueous concentration it can cause chronic and acute poisoning of the most sensitive aquatic organisms, such as algae, zooplankton, molluscs and fishes in their larval state[83]. Lethal concentrations are in the range of 0.04-16 mg l^{-1}, depending on the specific aquatic species. As previously underlined, among the butyltins, the highest toxicity is provided by the trisubstituted species, although the less toxic derivatives are both of a relevant environmental concern. So far, the occurrence of these less alkylated compounds in the environment have been related to degradation of tributyltin operated by microbial activity or photochemical reactions[84].
Triphenyltin is also hazardous to aquatic life, in particular when fishes are in their early life form, for instance larvae.
Anyway, tributyl- and triphenyltin pollution of aquatic systems may cause on the affected organism characteristic symptoms, such as thickening of shell in oysters, impotence in gastropods, retardation of growth in mussels and immunological dysfunctions in fishes[85, 86, 87].
In addition di- and tributyltin can cause immune suppression in rodents; however, at the moment there are no evidences for teratogenic or carcinogenic effects of organotins towards animals[88].
On the other hand, the dialkyltin compounds show a toxic behaviour quite different from the tetra- and trialkyltin ones: in fact they combine with coenzymes or enzymes possesing dithiol groups, thus inhibiting methabolic reactions. As we have seen for the R_3SnX derivatives, the mammalian toxicity of the di-*n*-alkyltins decreases when the length of the chain increases; however this property seems to be dependent on the toxic nature

of the X groups. At the present time, anyway, the only commercial application of the dialkyltins involving their biological and toxic effects is as anthelmintics: they are able to selectively kill parasitic worms in chickens and turkeys, without harming the infected birds. In this case dibutyltin dilaurate has been reported as the most effective products.

So far, little is known about the effects of organotin compounds on humans, except for those related to accidental or other few cases of occupational exposure. The monoorganotins $RSnX_3$ have generally low toxicity and do not appear to have any important biological action in mammals.

Commonly reported symptoms of dialkyl- and trialkyltin poisoning are vomiting, headache, visual defects and electroencephalographic abnormalities[88]. Irritation of skin and respiration tract is caused even by a short contact with these chemicals. It has been reported[89], moreover, that *in vitro* mono-, di- and tributyltin derivatives affected natural killers lymphocytes, the primary immune defense in humans, and reduce the number of thymocytes in human blood. However, there are no reports of any organotins showing carcinogenic properties and the results of bioassays test conduced on a number of compounds, such as Ph_3SnOH, $Ph_3SnOCOCH_3$, Bu_3SnF and $Bu_2Sn(OCOMe)_2$, for possible carcinogenicity were negative[88].

4 - General Applications of Organotin Compounds

As previously underlined, organotins show a wide variety of physical, chemical and biological properties; moreover, tin has a larger amount of its organometallic derivatives than any other element. This is reflected in their different industrial applications (**Table 8**), which can be related in particular to the R_3SnX, R_2SnX_2 and $RSnX_3$ compounds. Tetraorganotin compounds actually are only important as intermediates in the production of less alkylated derivatives.

Table 8. **Industrial uses of organotin compounds**

Application	*Function*	*Organotin Compound*
PVC stabilizers	Stabilization against decomposition by heat and light	$\mathbf{R_2SnX_2}$ and $\mathbf{RSnX_3}$
Antifouling paints	Biocide	$\mathbf{R_3SnX}$
Agrochemical	Fungicide, insecticide, antifeedant	$\mathbf{R_3SnX}$
Wood preservation	Fungicide, insecticide	$\mathbf{Bu_3SnX}$
Glass treatment	Precursor for tin (IV) oxide films on glass	$\mathbf{Me_2SnX_2}$ and $\mathbf{RSnX_3}$
Materials protection (stone, leather, paper)	Fungicide, bactericide	$\mathbf{Ph_3SnX}$
Impregnation of textiles	Insecticide, antifeedant	$\mathbf{Bu_2SnX_2}$

4.1 - Stabilization of PVC

Approximately the 75% of the overall annual organitin production is applied as additives for thermal and light stabilization of plastics[90]. Polyvinyl chloride (PVC), in particular, has the tendency to decompose upon heating (at about 200 °C) or on prolungated exposure to light, leading to loss of HCl from the polymer. In order to prevent this degradation, certain organotins, generally mono and diorganotin derivatives, are added to the polymer[91]

These additives are supposed to:

- Inhibit the dehydrochlorination;
- Scavenge the produced HCl;
- Prevent atmospheric oxidation of the polymer acting as antioxidants.

Organotin-stabilized PVC has a lot of applications, in particular household products, including packaging materials, piping of drinkable water, window frames and coating materials. The substitutes for tin stabilizers are manufactured from lead or mixed metals such as calcium and zinc. However, lead stabilizers, in spite of their low cost, have a limited use, due to environmental concerns and, hence, tin and metal mixed stabilizers are quickly replacing them.

These additives are firmly bound to the plastic matrix, thus leaching of tin form rigid PCV is negligible. However, it has to be said that leaching rates depend on various conditions, such the alkyl chain lenght of the stabilizer or on the type of PVC material.

PVC stabilizers have been classified in three main group, among which the organotin derivatives are considered to be the most efficient and versatile ones, being successfully employable in a wide variety of applications.

In particular, tin-mercaptide stabilizers, that contain both tin and sulfur, are reported to be the most effective stabilizers currently avaible.

Tin stabilizers can be further divided in three major types, distinguished by their alkyl groups: octyl, butyl and methyl, respectively. They are reported in **Table 9** with the most common diorganotin derivatives.

Table 9. The most important organotin PVC stabilizers

Stabilizer	***Alkylic substituent R***
$R_2Sn(SCH_2CO_2Oct^i)_2$	Me, Bu, Oct, $BuOCOCH_2CH_2$-
$RSn(SCH_2CO_2Oct^i)_3$	Me, Bu, Oct, $BuOCOCH_2CH_2$-
$R_2Sn(SC_{11}H_{23})_2$	Me, Bu
$R_2Sn(OCOC_{11}H_{23})_2$	Bu
$[R_2Sn(OCOCH=CHCO_2)]_n$	Me, Bu, Oct
$R_2Sn(OCOCH=CHCO_2R')_n$	Bu[a]

[a] R'= Me, Bu, **i**-Oct.

However in several cases, up to 60% of the corresponding monolakyltin compound $RSnX_3$ is added to the dialkyltin stabilizer, in order to produce a relevant synergistic improvement in the stabilizing effect[92].

Moreover, specific requirement, such as transparency and outdoor wheatherability, are achievable by simply changing the nature of the ligand.

Octyl- and dodecyltin stabilizers, instead, having a lower tin content, are supposed to be less effective. However, they have been approved for food contact applications by most regulatory authorities worldwide.

It has to be said, moreover, that butyltins have been the most important stabilizers until methyltins were introduced: the latter have in fact an higher tin content and lower raw material cost compared too the other two series of derivatives. In addition methyl-, octyl- and dodecyltin stabilizers have had widespread national approvals for food-contact applications for many years.

As regard to other kind of stabilizers, the metal mixed ones are more expensive than tin and, often, less effective in their action. It is estimated that the amount of tin used annually in tin stabilizers grows about 4% every year.

Although PVC is not biodegradable, the greatest part of plastic stabilizer can undergo to degradation, leading to a marked decrease of polymers properties. For this reason it is often required the addition of biostabilizer in the PVC formulation, in order to provide protection against biological degradation. To this end, one of the most suitable compounds avaible is bis-tributyltin oxide, resulting active against a wide variety of bacteria even in low concetration; moreover it does not interact with other additives, not affecting the final material properties[93].

Finally, little is known about chemical leaching of organotin compounds mobilized by degration of PVC materials in dumping sites. The increased production and use of PVC and its consequent disposal will likely lead to an accumulation of mono- and dialkyltin derivatives in the environment, with possible long-term effects on men and biota.

4.2 - Biocides in Marine Antifouling Paints

Primary marine antifouling paints were based on Cu_2O, but these coatings became quickly ineffective, so have been replaced by the more effective tributyltin-based ones in the early 1970s. The use of tributyl and, to a lesser extent, triphenyltin compounds as additives in antifouling paints and coatings for protection of ships and yachts hulls[94,95, 96] and sea water cooling pipes from the attachment of barnacles, sea grass and other marine organisms, represents one of their most important biological applications[97].

An antifouling consists of a film forming material with a biocidal ingredient and a pigment. It works by releasing small amounts of the biocide from the painted hull into the water, thus forming a thin envelope of highly concentrated tributyltin derivative around the boat. The toxic concentration repells the settling stages of fouling organisms on the boat's bottomed. Different types of antifoulant paints are reported:

- Fre-association antifouling paints (FAP), in which the biocides are physically mixed in the paint matrix and are released into the aquatic environment by diffusion (**Figure 14**)[98]. Their effective period is about 2 years. Following legislative regulation, this kind of products was banned in many countries.

- Self-polishing antifouling paints (SPC)[99], in which the toxic component is chemically bonded with a polymer, causing a delay of the biocide into the water, its release caused by a chemical reaction with seawater, exposing it by the gradual erosion of paint coating. Because the biocidic components are released only at the paint surface the releasing rate is low, thus resulting in a lifetimes of 5-7 years.

Figure 14. Free association antifouling paint

Figure 15. Self polishing copolymers

Surfaces treated with modern tributyltin-based copolymer paints are designed to reach a constant biocide leach rate of 1.6 µg of tin for cm^{-2} per day.

The organotin –based marine paints usually contain up to 20% by weight of a suitable tributyl- or triphenyl-tin toxicant incorporated in a standard paint vehicle. Typically, those compounds have polymeric intermolecularly associated structures, such as Ph_3SnOH, Bu_3SnF or Ph_3SnF. The most used compounds are reported in **Table 10**.

In a marine environment, the biologically active triorganotin species are slowly leached from the paint film into the sea water, forming probably hydrated cations $[R_3Sn(H_2O)_2]^+$. The lifetimes of these paints are usually 1-2 years, after which the vessel must be re-painted with the antifoulig formulation. Throughout the 1980s many countries worldwide began restricting the use of tributyltin paints, because of their environmental impact . In order to extend the lifetime of FAPs, tributyltin mathacrylate copolymer systems were developed with self-polishing behaviour[99], becoming then the standard for the industry production.

In the last years extensive researches and developments for replacing tributiltin paints have been made, resulting in antifouling paints based on binder systems made from copper-, silyl- and zinc acrilates. However this systems require the addition of a co-biocide and are less effective that the tin-based ones. Currently, the researches concern the development of new systems having a higher lifetime, alghout they are only in the early stages. In particular silicones and fluoropolymers based products have been proposed: they are called non-stick or foul release coatings and do not contains any biocide. They simply produce surfaces to which fouling organisms will not stick or can be easily cleaned off by brushing, water spray, or the vessel's own movement through the water.

Table 10. Common organotin derivatives used in antifouling paints

Organotin compounds
Bu_3SnF
$(Bu_3Sn)_2O$
$Bu_3SnOCOMe$
$Bu_3SnOCO(CH_2)_4CO_2SnBu_3$
$(—CHMeCHCO_2SnBu_3—)$
Ph_3SnX (X= F, OH, OCOMe)

4.3 - Agrochemicals.

The first organotin compounds to reach commercialization in agriculture in the early 1960s, were triphenyltin acetate[100] and triphenyltin hydroxide[101]. They are are widely used to combact a number of fungal diseases in various crops, particularly potato blight, leaf spot on sugar beet and celery, rice blast and coffee leaf rust. A further interesting property of these fungicides is that they can work as antifeedants: deterring insects from feeding, and as insects chemosterilants[102]. The third organotin agrochemical was the tricyclohexyltin hydroxide, introduced in 1968, as an acaricide for the control of mites on apples, pears and citrus fruits. The two most recent tin compounds to enter the agrochemical market, bis(trineophenyltin) oxide and 1-tricyclohexylstannyl-1,2,4-triazole are also acaricides. As previously observed, the trimethyltin derivatives, such as $Me_3SnSnMe_3$[103], possess a high insecticidal activity, but their mammalian toxicity has precluded their applications in this field. The currently used organotin fungicides and acaricides mainly possess prophylactic action and do not have any systemic activity[101]. Their advantages include their low phytoxicity, their environmental degradation, mainly by microorganisms and UV light, to non-toxic monoorganotin and inorganic tin residues and their generally low toxicity to non-target organisms. Additionally, the organotin products typically have a cost advantage for growers, considering the product rate applied, the cost itself and the number of days between sprayings. However, a single treatment method is not normally used: growers usually turn two or three types in order to avoid the build-up of resistence to any fungicide.

Table 11. The most common organotin-based products in agrochemical applications

Organotin compound	***Trade name***
Triphenyltin acetate	Brestan®
Triphenyltin hydroxide	Duter®
Tricyclohexyltin hydroxide	Plictran®
Bis(trineophyltin) oxide	Vendex®, Torque®
Tricyclohexyltin triazole	Peropal®

4.4 - Precursors for Forming SnO_2 Films on Glass

The tin oxide is widely used in ceramic and glass industry to polish or glaze the surface of finished products, as well as to harden just put out glass containers in the so-called Hot End Coatings. The metallic oxide is used as monoorganotin precursors for forming thin surface films of SnO_2 on glass at temperaturs of 500-600°C, thereby preventing microfissures.

$$Me_2SnCl_2 + O_2 \longrightarrow SnO_2 + 2MeCl$$

The resulting films, which are formed in air (oxidising atmosphere) can vary in thickness from about 100 Å to > 10000 Å, depending on the final application[104].

The chemical vapour deposition was formely achieved with some inorganic stannic chloride, such as $SnCl_4$, thus leading to problems of corrosion. In order to overcome this serious drawback, the $SnCl_4$ has been progressively replaced by monobutyltin trichloride and dimethyltin chloride, which are, at the moment, the dominant products[105].

Stannic chloride in actually applied, but only in less sophisticated processes.

4.5 - Preservation of Wood, Cellulose and Stonework

Bis(tributiltin)oxide has been used since 1958[106] for preventing fungal attack of cellulosic material, such as wood, cotton textiles and cellulose-based household fillers. In the field of wood preservation, tributyltin phosphate and naphtalenate are also used as fungicides, and these compounds, along with bis(tributiltin)oxide, are usually applied to the wood as 1-2% w/v solution in an organic solvent, by dipping, spraying, brushing or double-vacuum impregnation methods[107,108]. A conventional chlorinated hydrocarbon contact insecticide is usually added to the formulation containing the tributyltin fungicide, in order to combat wood boring pests.

Many wood preservative chemicals are applied as aqueous solutions, in order to reduce the fire hazard and toxicity problems associated with organic solvents and also to minimize their cost. Until recently, tributyl derivatives were not used as aqueous wood preservatives, since they have a very low solubility in water (for instance $Bu_3SnOSnBu_3$ = 0.001% w/v at 25°C). However, bis(tributiltin)oxide may be made water-dispersible by the addition of certain quaternary ammonium chlorides: this kind of formulation are useful for eradication of moss, algae and lichens on stoneworks and also for treating cotton textiles to prevent fungal attack. Subsequent work demonstred their effectiveness as aqueous wood preservatives[109] and by now they are used for timber treatments[110].

4.6 - Disinfectants

Although tributyltin compounds are reported to be only active against Gram-positive bacteria[111, 112], their combination with a second chemical Gram-negative specific, produces a highly effective disinfectant which may be used on open areas posing a risk of infection, such as hospital floors and sport pavilions. One such commercial formulation contains a mixture of tributyltin benzoate and formaldehyde (Incidin®).

Another very common association is bis(tributiltin)oxide with a quaternary ammonium halide, which is also used for preventing biodegradation of various materials, as previously described.

4.7 - Homogeneous Catalysts[113]

The most common application for mono- and diiorganotin catalysts are in the chemical synthesis and curing of coatings. In chemical synthesis organotins are used expecially in the esterification and transesterification reactions of mono- and polyesters. These products are then used for plasticizers, synthetic lubricants manufacturing, as well as for some coating applications. Most of the organotin derivatives are able to catalyze esterification and transesterification reactions: among these compounds, distannoxanes are reported to be the most efficient (see **7.3**).

As curing catalysts, one of the largest uses of organotins is in electrocoat (Ecoat) coatings. These electrocoating products are sold into a wide range of applications, particularly in automotive industry, where they provide excellent rust resistence. This kind of catalysts are also used in urethane coatings as well as polyurethane foam production. In addition, they can be applied as cross-linking agents in room-temperature vulcanisation of silicones.

4.8 - Antitumoural Agents

Recent studies has raised the possibilty that certain dialkyltin compounds may have a role to play in cancer chemoterapy[114]. The diorganotin complexes with bidentate N-donor ligands, containing *trans* organic groups and *cis* halogens, which bear a close structural resemblance to the platinum antitumour drug *cis*-$Pt(NH_3)_2Cl_2$ are active in vivo towards the lymphocytic leukemia tumour in mice, particularly when R = Et.

Dibutyltin dichloride and dioctyltin dichloride exert a selective cytotoxic action on T-lynphocytes and may therefore be potential anti-t-cell tumour agents.

AIM OF THE WORK

5 - Aim of the work

Organotin compounds have found in the last few decades a wide variety of applications. In fact, they can be used successfully in antifouling paints, as PVC stabilizers and anti-tumour drugs as well as anion carriers in electrochemical membranes.

Organotin derivatives are also well known as catalysts in transesterification reactions: indeed these compounds are able to promote the reaction between alcohol and ester, due to the Lewis acidity of tin atom. For this reason they have been used for a long time as homogeneous catalysts in this kind of reactions, but presently their use is fairly restricted by their toxic nature. Coupled to their difficult recovery from the reaction mixture it represents, certainly, a serious drawback. A useful approach to conveniently overcome these problems, however, consists on grafting, by a covalent bond, the organotin derivative onto an insoluble macromolecular support. Accordingly, an heterogeneous catalyst constituted by a tin derivative grafted onto a polymeric cross-linked resin, operating at the solid-liquid interface, has been synthesized and investigated. The catalyst obtained can be easily recovered from the reaction mixture by simple filtration of the solid support, thus eliminating the presence of any toxic organotin residue in solution or tin release in the environment and leading to the so-called "clean organotin reagents".

In previous investigations several insoluble cross-linked polystyrene resins bearing the triorganotin carboxylate moiety have been synthesized and their catalytic activity assessed. The basic structure of the above resins consists of a cross-linked polystyrene backbone obtained by free radical copolymerization of three co-monomers (**Figure 16**): a styrene derivative containing the triorganotin carboxylate moiety, 1,4-divinylbenzene, as cross-linking co-monomer, and styrene, added in variable amount in order to modulate the content of stannylated co-units in the final resin.

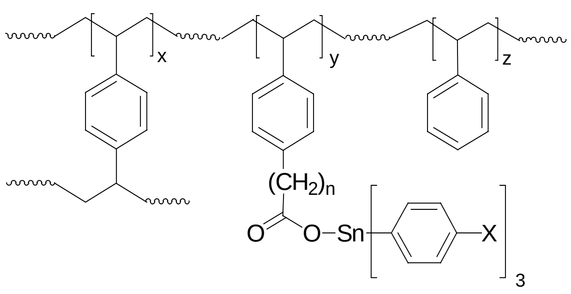


Figure 16. Basic structure of the resins synthesized.

Aim of the present work, hence, is to opportunely modify the chemical structure of the stannylated resins in order to improve their catalytic activity and optimize their properties as catalysts in transesterification reactions. Actually, different parameters have been taken into account and conveniently changed, such as Lewis acidity of the tin atom, its accessibility by the reactants and type of substituents at the metal atom. To address this purpose, we have tested various organotin carboxylate resins in a model reaction between ethyl acetate and 1-octanol (**Figure 17**), a primary alcohol that appears to be more sensitive to the reaction conditions, in order to clearly understand how the catalytic activity is affected. The alcohol conversion was assessed by gas-chromatography, determining the relative amounts of transesterified product and starting alcohol after an established interval time, usually 24 and 48 hours. The reaction was also performed in the absence of catalyst, to check the presence of additional contributions other than those given by the organotin carboxylate moiety. As expected, no conversion at all of ethyl acetate was detected.

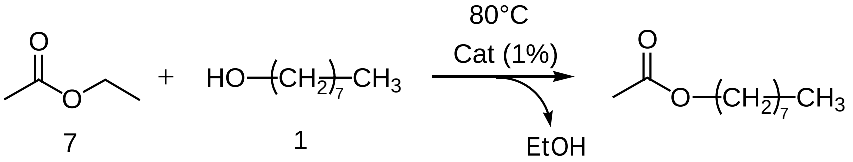


Figure 17. Model transesterification reaction between ethyl acetate and 1-octanol

In previous investigations several important features of the catalyst structure, such as, in particular, high cross-linking degree, low amount of stannylated monomer and phenyl group as tin substituent, seemed to be essential to achieve the best catalytic performances.

In the present work, starting from the information previously obtained, we have focused our attention onto two other aspects of the organotin monomer structure. Firstly, the carboxylic moiety was spaced furtherly from the aromatic ring by an aliphatic chain with the aim of increasing the mobility and accessibility to the catalytic centre. Thus, some monomers bearing a dimethylenic or a tetramethylenic chain acting as a flexible spacer between the catalytic centre and the polymeric backbone have been synthesized.

Secondly, as the Lewis acidity of the tin atom is recognized as having a key role in the catalytic activity of these products, a promising modification seemed to be link to the tin atom different organic substituents, having different electronic effects. Therefore some monomers bearing substituents with electron-donor or electron-withdrawing properties have been prepared, with the purpose of tuning the Lewis acidity at the metal centre (**Figure 18**). In particular we have assessed the influence of different substituents on the behaviour of these organotin resins in the transesterification reaction.

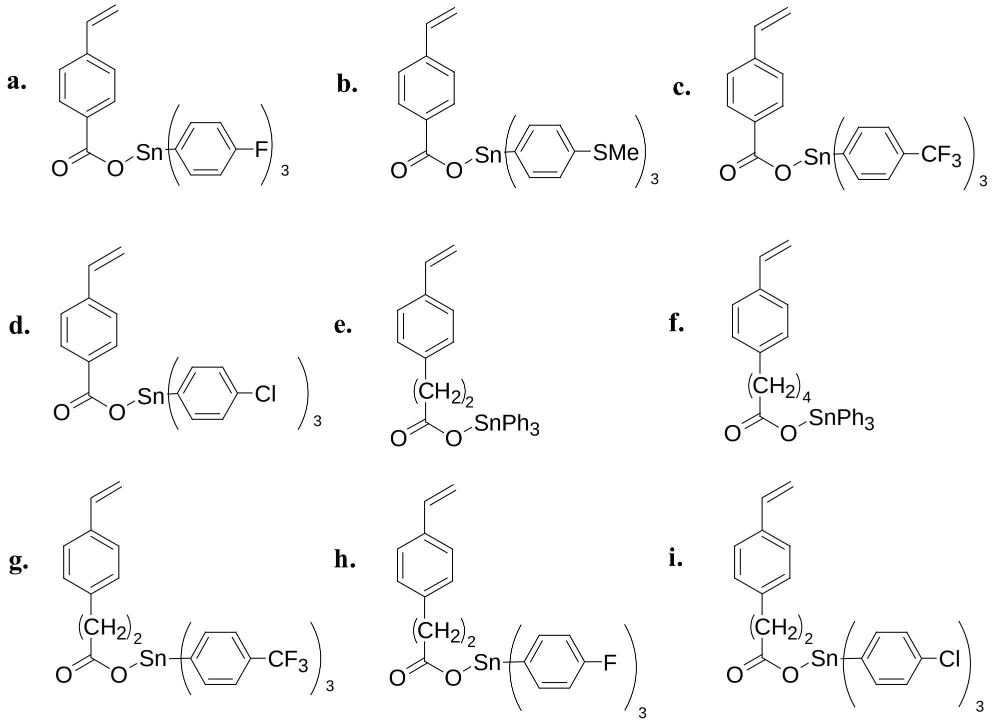


Figure 18. Structures of the monomers synthesized.

Recently, another important modification, very concerning the structure itself of the resins gas been tested. Indeed, the polymeric matrix was replaced by an inorganic one, in order to dispose of a quite cheaper and easily available support. To address this purpose mesoporose MCM-41 silica has been selected.

In particular, three MCM-41 silica containing the triorganotin carboxylate moiety have been synthesized starting from commercial Cab-O-Sil M5 silica. The prepared products, having a different degree of functionalisation, bear a trimethylene spacer between the core and the tin-carboxylate moiety (**Figura 19**). They have been investigated by IR, solid state and hr-MAS NMR techniques in order to elucidate the coordination at tin.

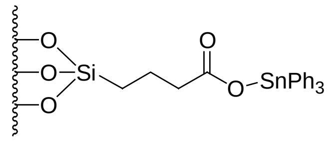


Figure 19. Structure of the tin-functionalized silica

It has also to be mentioned that in all the tests carried out no contamination by tin was present after filtration of the catalyst from the reaction mixture, suggesting that no hydrolysis of the organometallic carboxylate occurred. It can be therefore concluded that the organometallic ester is stable under the transesterification conditions and the reaction takes place only at the solid-liquid interface.

RESULTS AND DISCUSSION

6 - Introduction

6.1 - Organotin compounds as transesterification catalysts

Organotin derivatives in years have found a wide variety of applications in industry, agriculture and medicine. In industry they are used for the stabilization of PVC, as catalysts for polyurethanes synthesis and for the cold vulcanisation of silicone polymers. Their biological properties are exploited for in antifouling paints on ships, in wood preservatives and as agricultural fungicides and insecticides. In addition they are showing promises in cancer therapy and in the treatment of fungal infections.

Organotin compounds are also known as homogeneous catalysts in transesterification reactions: their activity is due to the Lewis acidity of the tin atom, which promotes the interaction between ester and alcohol. Therefore the Lewis acidity of the metal centre is an important feature to pay attention to, because it plays a key role: indeed, if this is too strong, the linkage between metal and ester carbonyl could become irreversible, leading to no catalysis at all.

Notwithstanding all these applications, the organotin compounds are limited in their use because of their proved toxicity. In order to overcome the release of such compounds in the environment it has been already proposed in the last years to link them to a macromolecular support, in particular onto a resin[113]. In this way an easy recovery of the catalyst from the reaction mixture by simple filtration is possible, avoiding the release of organotin compounds in the environment, thus leading to the so-called “clean organotin reagents”. Although an heterogeneous catalyst is less active with respect to an homogeneous one, this kind of organotin derivatives show a good catalytic activity in the transesterification reaction.

The former compounds synthesized are resins obtained by functionalization of ionic exchange resins, such as Amberlites, with triorganotin carboxylate:

they show activity in transesterification reaction, but the disadvantage of such a post-functionalized resin is, apart from the detection of tin amount actually linked to this support, the difficulty of predicting the functionalisation degree[115, 116].

Another reliable approach to obtain this kind of cross-linked supports is the polymerization of monomers already bearing the tin atom on their own. Hence we have synthesized heterogeneous catalysts by radical co-polymerization of styrene (Sty), 1,4-divinylbenzene (DVB) and a tin functionalized monomer, a styrene derivative bearing the triorganotin carboxylate moiety just linked in *para* position. In the above resins 1,4-divinylbenzene acts as crosslinking agent, while styrene is added to tune the cross-linking degree. These catalysts have been compared with structural models of the organotin repeating co-units of the polymer to better understand the properties of the polymeric derivatives.

After the assessment of their catalytic activity in transesterification reaction, an investigation on the chemical structure of these resins has been performed, in order to improve their performances as catalysts.

In previous works, some important features of these products were shown and considered as the basis for future studies, in particular:

- polystyrene as main macromolecular support;
- triphenyl moiety as substituent at tin, instead of the methyl or butyl;
- 5% of tin monomer in the polymerizatin mixture;
- high degree of crosslinking.

Starting from the above data, the present Ph. D. thesis has been devoted to the evaluation of the effects of two new modifications of these compounds, in order to obtain improved activity: on one hand the carboxylic moiety has been spaced from the polymeric backbone by an aliphatic chain, in order to increase the accessibility to the tin atom; on the other one organic substituents with different inductive effect on tin have been introduced in conjugated position on the aromatic ring, with the purpose of tuning the

Lewis acidity of the metal centre, that, as well known, plays a key role on the catalytic activity of this kind of catalysts.

The general structure of these new resins has been reported in the figure below (**Figure 20**). As it can easily be seen, it respects the features already mentioned. As far as the comonomer feed in the polymerization mixture, all the resins synthesized in this work contain a 5% of stannylated monomer and a variable amount of DVB, from 20% to 70%.

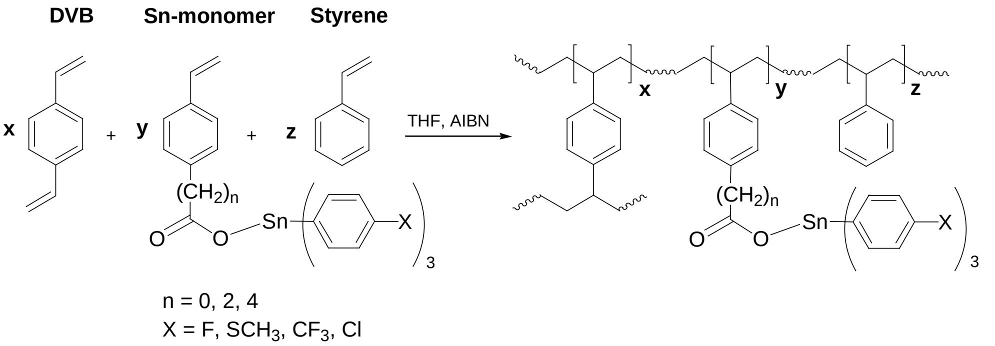


Figure 20. General structure of the tin functionalized resins investigated in this work.

With the aim of providing a clear overview of the overall obtained products, for an easier understanding of the structure-activity relationship, the tin-fuctionalised resins have been divided into three main groups, although this distribution doesn't respect the chronological order of their synthesis:

- Resins bearing a substituent on the phenyl ring;
- Resins bearing an aliphatic spacer between the resin core and the metal centre;
- Resins bearing both these two structural modifications.

Hence, in the following paragraphs synthesis and chacterisation of the obtained catalyst will be described and explained. Moreover, their catalytic behaviour will be shown, trying to find a relationship between the obtained data and the structural modification made.

Besides the studies above described, another important and radical structural modification of these products have been tested. Indeed, in order to have a quite cheap and easily avaiable support, the macromolecular backbone has been replaced with an inorganic one, a mesoporose silica. To this pourpose it has been chosen MCM-41 silica, leading to tin-fuctionalised MCM-41 silica. All the obtained products, that show different degrees of functionalisation, contain a triphenyltin carboxylate moiety and bear a trimethylene spacer between the core and the metal centre. For this reason they have also been tested, similarly to the other products prepared, as transesterification catalysts.

Their synthesis, characterization, and catalytic performances will be described in the final part of this chapter.

Before starting the discussion it seemed to be important providing a brief overview about the transesterification reaction and its characteristic, in order to better understand the features required by such a kind of catalysts.

7 - Transesterification Catalysis

7.1 - Esterification and Transesterification Reaction[117]

A transesterification reaction takes place when the alkoxy group of an ester compound exchanges with another alcohol, giving a new ester and a new alcohol[113].

$$\mathrm{RCOOR'} + \mathrm{R''OH} \rightleftharpoons \mathrm{RCOOR''} + \mathrm{R'OH}$$

This is a common organic reaction, widely used both in lab practises and in industrial applications[118]. It occupies a central position in organic synthesis, being as important as direct esterification.
In this process, also called "Fischer esterification", a carboxylic acid reacts directly with an alcohol to give the corresponding ester and water as a side product.

$$\mathrm{RCOOH} + \mathrm{R'OH} \rightleftharpoons \mathrm{RCOOR'} + \mathrm{H_2O}$$

Both reactions are equilibrium processes, so they share the need to shift the reaction system to the product side at the highest degree. It's also possible to reach higher yields playing on the amounts of acid and alcohol: the latter, for example, if it is not much expensive, can be added in wide excess. Another effective and easy possibility, in order to displace the equilibrium towards the products, is to remove the water formed, for instance by adsorption on drying agents or by azeotropic distillation. To this respect it may generally be said that esterification is more advantageous, because the water co-product is readily separable from the reaction medium, owing to its common incompatibility with organic solvents. On the other hand, this can represent an advantage for transesterification, since water-sensible materials are employable in this case. Accordingly, once effective methods for removal of the produced alcohol are established, transesterification is a better choice of reaction for ester preparation.

It has to be said, moreover, that the reactivity of alcohols and carboxylic acids towards the esterification reaction depends largely on their steric hindrance. For this reason esterifications of tertiary acids or alcohols proceed slowlier than secondary or primary ones, according to the following speed rank:

Methanol > primary alcohols > secondary alcohols > tertiary alcohols

$HCOOH > CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3CCOOH$

Transesterification is considered as an alternative synthetic pathway with respect to the direct esterification, in particular when the acid has high viscosity or low solubility. For instance, some carboxylic acids are little soluble in and consequently it can be diffucult to submit them to direct esterification under homogeneous conditions, while esters are commonly soluble in the majority of organic solvents. In addition, some esters, in particular the methyl and ethyl ones, are commercially avaible or readily prepared, serving conveniently as strarting materials in transesterification.

However, it is important to remind that the transesterification reaction, as esterification, is a reversible process and usually needs the presence of a catalyst in order to improve its rate.

A lot of studies about suitable catalysts, acid or basic, have been developed in the 50th, but the first appreciable results came in the second half of the 60th.

Besides the laboratory applications, the transesterification reaction is well known also in industry, where it plays a key role. In fact it is commonly used, for instance, for the synthesis of acrilic monomers, by reaction of methyl acrilate with different alcohols, under acid catalysis. It has also been used for the production of PET (polyethylene terephthalate), by the transesterification between dimethylterephthalate and ethylene glycol, catalyzed by zinc acetate[119].

Another important feature to be taken into account is that by a transesterifcation reaction it is possible to obtain the *biodiesel*, an alternative diesel engines fuel, currently famous for its environmental implications.

Biodiesel actually consists of methyl esters deriving from vegetable oils, such as the soybeen, the sunflower and the rapeseed one, that consist of fatty acid esters of glycerin[120]. Nowadays *biodiesel* is produced by transesterification of large, branched triglycerides into smaller, straight-chain methyl esters, in presence of an acid or alkali catalyst, usually NaOH, KOH or sodium metoxide[121]. The latter, however, usually requires an high quality oil and can causes production of some by-products, in particular sodiul salts, which need to be eliminated. On the other hand, KOH has the advatage to be neutralized at the end of the process by phosphoric acid, giving potassium phosphate, whic actually is a fertilizer. In addition KOH is said to be a better catalyst than NaOH with respect to the transesterification reaction of safflower seed oil.

7.2 - Transesterification Reaction Catalysts

As we have seen in the previous paragraph, the transesterification is a reversible reaction and it requires catalysis in order to achieve high reaction rates. At the moment a lot of suitable catalysts for this rection are avaiable. They will be described in the following paragraphs, dividing them into the main chemical categories they belong to.

7.2.1 - Acid transesterification catalysts

Transesterification is commonly carried out with the aid of acids. Brønsted acids are classical, but they are still employed quite often; amongst the most popular applied are usually mineral acids, such as sulphuric, *p*-

toluenesulphonic[122], hydrochloric or phosphoric ones. Other high utilized acid are HBr, HF, HI, AcOH and $HClO_4$. However, their use is rather limited in presence of acid-sensitive substrates and due to the possible damage to the structures, operated by the acids themselves.

7.2.2 - Base transesterification catalysts

The most frequently used basic catalysts are metal alkoxides, even though also metal acetate, oxides and carbonates could be used, in particular when the involved alcohol is a primary one.

In the biodiesel formation reaction between methanol and triglycerides this catalytic systems can be successfully used, as we have seen before. Base catalyst can be applied also in the transesterification of fatty acid with sucrose[123], usually catalyzed by K_2CO_3.

7.2.3 - Lewis acid transesterification catalysts

The most synthetically versatile methodology for transesterification reactions is provided by Lewis acids, due to their mildness, simplicity in oparating and catalytic capabilities. They are useful expecially whenever a Brønsted acid catalyst fails to transesterificate, for instance, olefinic alcohols, such as allylic ones, owing to a possible polymerization, isomerization or decomposition of the starting reactant. In this case aluminium isopropoxide is reported to be the most active catalyst[124]. Other important catalysts belonging to this group are definitely titanium, aluminium and tin compounds, which have long been used in both laboratories and industry.

In addition some alkoxide of transition metal complexes were found to be active in transesterification, for example products as $(RO)Cu(PPh_3)_n$, where R = Me, Et, *i*Pr, Ph and n = 1 or 2.

Also titanium alkoxides are well known as transesterification catalysts and they have been applied in industry for many years, since they seems to be compatible with a wide variety of functional groups. The above products, moreover, have a mild mechanism reaction, that doesn't affect the stereochemistry of chiral centers[125]. Titanum tetraalkoxides are specifically useful in terms of their availability and handling: heating an ester in alcoholic solvent, in the presence of $Ti(OR)_4$, smoothly affects transesterification, even though the titanate catalyst usually has to be employed in rather large amount (0.2-0.6 mol per ester). A number of functionl groups are tolerated and the use of dry solvent is not necessary.

Organotin compounds belong to this group of catalysts and will be carefully described in the next paragraph.

7.2.4 - Enzymes as transesterification catalysts

Finally, it could be reminded that the transesterification reaction can be catalysed also by enzymes, although industriallyit isn't a common way. Recently this possibility has raised more interest, expecially because of the high degree of specifity this process could achieves.

To this pourpose in particular lipases have been widely used.

7.3 - Organotin Compounds as Catalysts

A lot of low molecular weight organotin derivatives have been used for years as transesterification catalysts[126].

For example tri-*n*-butyltin methoxide and ethoxide were applied for the first time in the late 1969, giving quite good conversions, from 31 up to 72%. Subsequently a lot of investigations have been performed in order to increase their activity; in particular different substituents have been tested, with the aim of improve the Lewis acididy of these compounds.

At this regard, it can be said that compounds having the general structure R_nSnX_{4-n}, where X is an alogen, usually a chlorine atom, show a good degree of Lewis acidity and, therefore, could act as efficient catalysts.

However, their use is affected by the low final yields and the elimination of chlorine in solution.

For this reason the introduction of the distannoxanes (**Figure 21**) as transesterification reaction catalysts was very important for this kind of reaction. In the same way these compounds can be used as esterification catalysts.

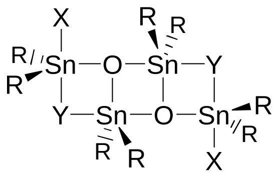


Figure 21. General structure of distannoxanes

They show a lot of advantages with respect to the organotin molecules previously used: they are air-stable crystalline compounds having high melting point and low toxicity. In addition, because the catalytic activity is not related to the kind of the substituent (X and Y), they don't contain acid species or halogens, thus overcoming the problem of corrosive substances release in solution.

Besides, in spite of the inorganic nature of their internal structure, they are soluble in most of the common organic solvents; this property derives from the alkyl chains that sorround the metalloxane core, protecting it from interaction with the solvent.

In addition distannoxanes presents an high catalytic activity, even with a catalyst concentration of 0,05% mol referred to the ester[127]. This property is related to their particular ladder structure, derived from the molecular association they adopt and is not related to the nature of the X and Y substituents. As depicted in **Figure 22**, in fact, distannoxanes present two different kind of tin atoms able to approach and coordinate the ester and the alcohol, thus promoting the direct interaction of the reactants.

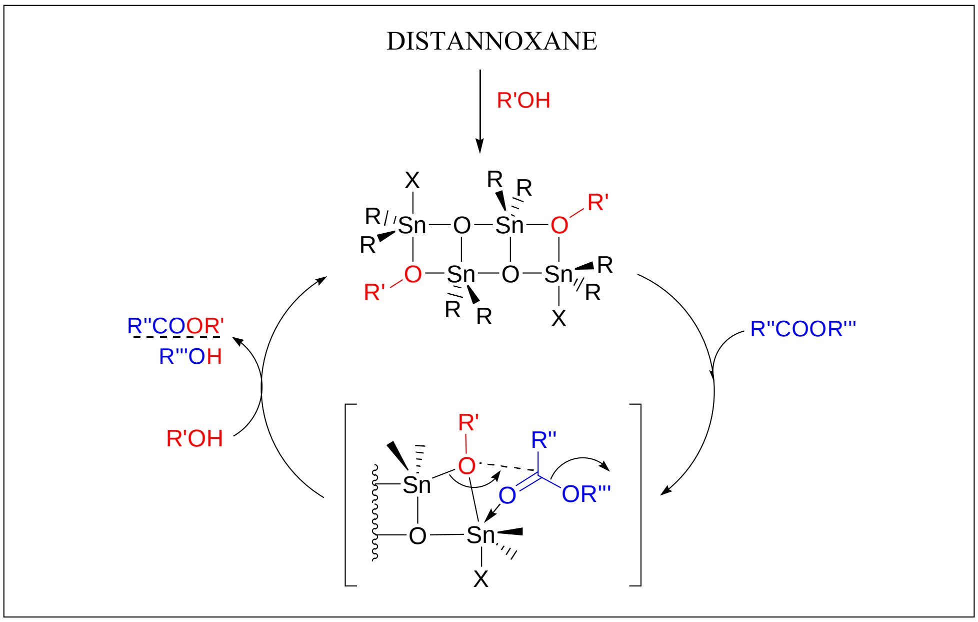


Figure 22. Mechanism of transesterification reaction in presence of distannoxanes.

However it might be added that with this catalyst bulky esters fail to react, owing to their sterical hindrance, while this behaviour has not been observed with alcohols.

8 - Cross-linked Polystyrenic Resins Bearing the Tri(4-fluorophenyl)tin Carboxylate Moiety

In this section the synthesis of resins bearing the tin atom bound to three phenylic rings substituted in the 4 position is described. In particular in these tin derivatives the functionalized monomer has been modified with a fluorine atom in the *para* position onto the phenylic moieties. We have chosen this substituent with the aim of investigating how the catalytic activities of these compounds is affected by variation or tuning of the metal Lewis acidity. We expected, indeed, that in presence of a electron withdrawing substituent the Lewis acidity would increase and, consequently, the catalytic activity as these two properties are tightly connected.

To clearly understand the role this property has in the transesterification reaction, it is important to consider the mechanism of reaction. It is well know, in fact, that an high degree of Lewis acidity is necessary in order to allow the tin to coordinate the ester; on the other hand, a too high Lewis acidity will make the tin-carbonyl interaction too strong and, therefore, irreversible, that means that no catalysis takes place in these conditions. It has to be underlined, finally, that the chosen substituent, the fluorine atom, and the halogens in general, being more electronegative than the carbon, display an inductive electron withdrawing effect. On the other hand, they are also electron-donor, owing to their mesomeric effect. These properties can be very useful in order to tune the tin Lewis acidity and have to be taken carefully into account.

To summarize, it can be said the goal of this synthetic modification is not simply to try to improve the Levis acidity of the metal centre, but, rather, to modulate it opportunely.

8.1 - Synthesis of the Tin-functionalized Monomer Tri(4-fluorophenyl)tin-4-vinylbenzoate

The synthesis of the monomer tri(4-fluorophenyl)tin-4-vinylbenzoate is a multi-step reaction and starts from 1-bromo-4-fluorobenzene to give the tetrakis-(4-fluorophenyl)tin. This preparation needs two different steps to be carried out.

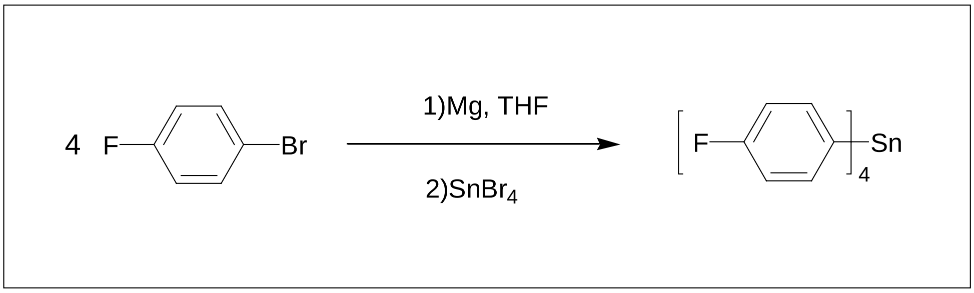


Figure 23. Synthesis of tetrakis(4-fluorophenyl)tin.

The first one concerns the preparation of the Grignard derivative. It acts as nucleofilic in the second step of this reaction, where $SnBr_4$ is added to give the relative tetra-substitued tin derivative.

The obtained product has been characterised by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy analysis, which confirmed the strucuture of the compound synthesized. In particular the ^{1}H-NMR spectrum shows the resonances of the aromatic protons at 7.1 and 7.5 ppm, confirmed by the ^{13}C-NMR signals from 116 ppm to 166 (**Figure 24**). Moreover, apart from the splitting of the quaternary carbon atom due to its connection with fluorine, in this spectrum it can be noticed that also the aromatic signals are splitted, due to C-F coupling. In addition, satellites bands due to the coupling with the tin atom are also evident. The ^{19}F-NMR and ^{119}Sn-NMR have been also recorded and exihibit two resonances, at -111 and -120 ppm respectively, indicating that it is present only one product.

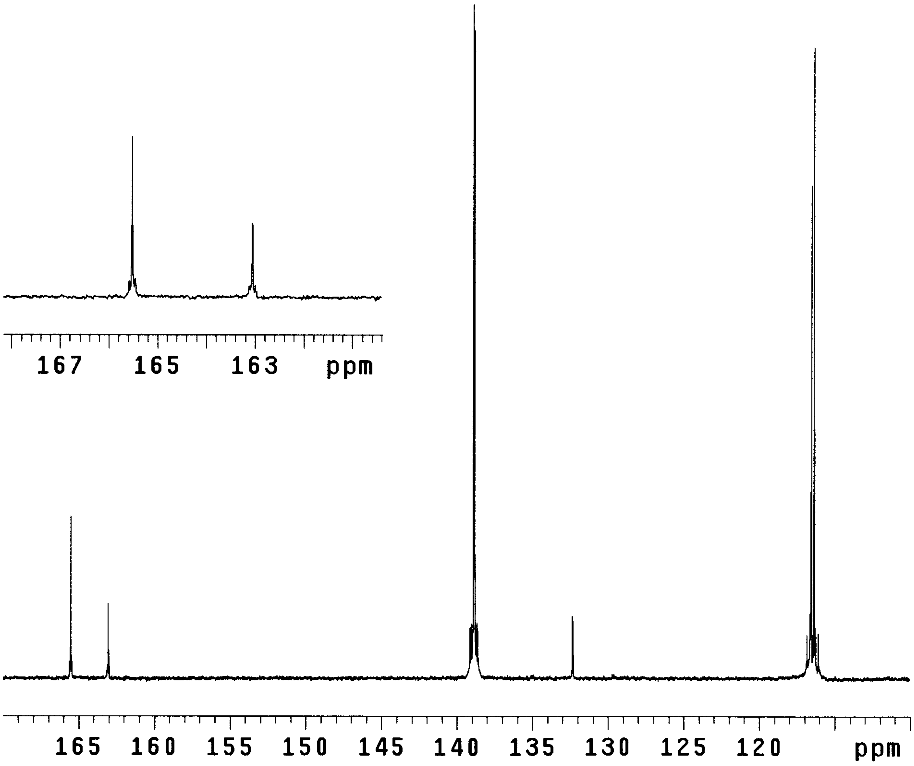


Figure 24. ^{13}C-NMR spectrum of the tetrakis(4-fluorophenyl)tin.

To synthesize the tri(4-fluorophenyl)tin chloride it has been used $SnCl_4$ (**Figure 25**). This is a redistribution reaction in absence of solvent, the socalled Kocheskov reaction[128], in which the alkyl and the halogen groups exchange each other. This reaction is strongly related to the stoichiometry: in fact with a 1:3 ratio of reagents the *tris* derivative is formed in good yield. However it is possible to obtain the mono and the di-substitued derivatives also, simply making little changes of reactants' amounts.

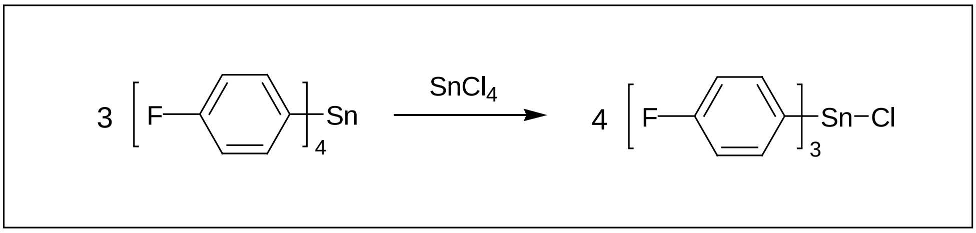


Figure 25. Synthesis of tri(4-fluorophenyl)tin chloride.

Unfortunately the FT-IT and NMR spectroscopic analysis can not confirm the compound structure because the recorded spectra look very similar to the tetrakis ones. Therefore, ^{19}F-NMR and ^{119}Sn-NMR spectra have been recorded, showing two peaks at -110 and -76, respectively.

In order to obtain the triorganotin oxide derivative, the corresponding chloride has been hydrolysed using KOH. The obtained hydroxide, subsequently, reacts with another molecule to give the oxide derivative (**Figure 26**). The hydroxide and oxide differ a little in their elemental analyses and, in solution, they can exist in equilibrium.

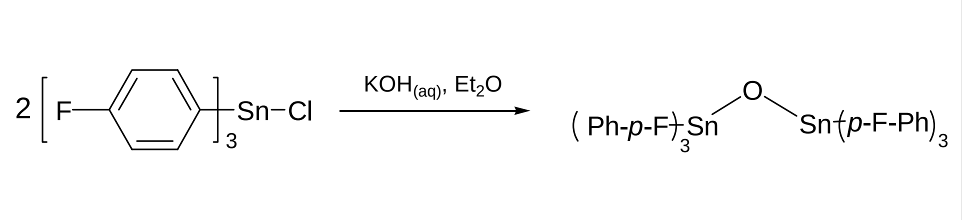


Figure 26. Synthesis of bis[tri(4-fluorophenyl)tin] oxide.

To distinguish them an useful technique could be FT-IR spectroscopy, because the bond Sn-O-Sn shows stretching frequencies between 740 and 770 cm^{-1}, while the hydroxide is characterised by OH stretching and bending frequencies at about 3400 and 900 cm^{-1}, respectively. In this case in the FT-IR spectrum is visible an absorption at 748 cm^{-1}, due to the Sn-O-Sn bond stretching, confirming the oxide structure (**Figure 27**).

Anyway, the reactivity of the oxide derivative is completely the same as the reactivity of the hydroxide one, therefore it doesn't matter which derivative really reacts.

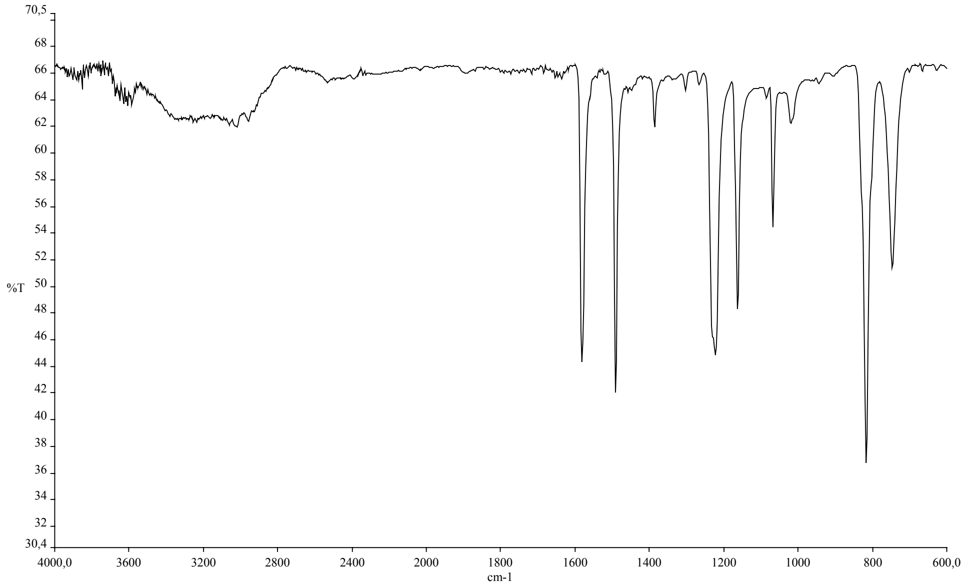


Figure 27. FT-IR spectrum of bis[tri(4-fluorophenyl)tin] oxide.

The monomer tri(4-fluorophenyl)tin-4-vinylbenzoate was finally obtained by esterification of the oxide with 4-vinylbenzoic acid in refluxing toluene, eliminating the formed water by azeotropic distillation, using a Dean-Stark apparatus, in presence of a small amount of hydroquinone as a polymerization inhibitor (**Figure 28**).

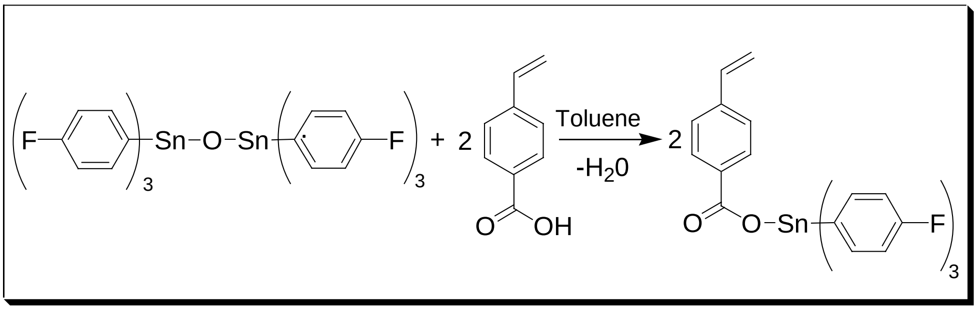


Figure 28. Synthesis of monomer tri(4-fluorophenyl)tin *p*-vinylbenzoate.

The monomer has been largely characterised by FT-IR and ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H-NMR spectrum shows the typical signals related to styrene: at 5.3, 5.8 and 6.7 ppm vinyl protons and the aromatic ones at 7.4 and 7.8 ppm. The ^{13}C-NMR spectrum, instead, displays a signal at 173 ppm, corresponding to the ester C=O bond. The ^{19}F and ^{119}Sn spectra have been also recorded, that show signals at -110 ppm, unmodified with respect to the oxide, and at -113 ppm, respectively, as expected in case of tetracoordinated tin carboxylate.

The progress of the stannilation reaction has been monitored by FT-IR spectroscopy: in fact it is expected a progressive decrease of the band centered at 1715 cm^{-1} related to the carbonyl stretching of the 4-vinylbenzoic acid and the appearance of a new absorption, attributed to the organotin ester. In this case the FT-IR spectrum shows a band at 1610 cm^{-1} that can be related to the new formed organotin carboxylate.

8.2 - Synthesis of the tin-functionalized resins

The polymerization of the monomer tri(4-fluorophenyl)tin-4-vinylbenzoate with different amounts of styrene and divinylbenzene was performed in dry THF, in presence of AIBN as a thermal radical initiator(1% on the total weight), keeping the reaction under vacuum for 3 days at 60°C (**Figure 29**).

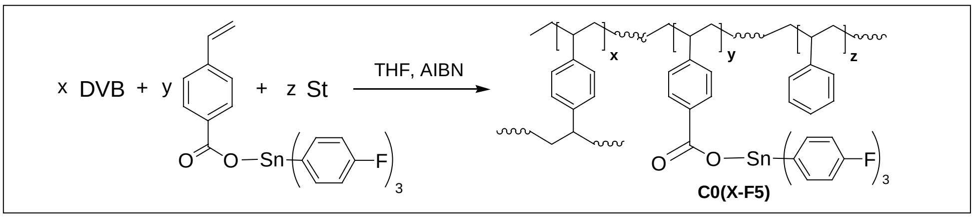


Figure 29. Synthesis of the resins bearing the monomer tri(4-fluorophenyl)tin-4-vinylbenzoate.

This kind of synthetic pathway is usually defined as "*in solution*", because at the beginning the co-monomers are dissolved in the THF, but, as the cross-linking starts, the resin becomes insoluble and precipitates.

The tin-fuctionalised polymers, after the polymerization reaction in an heterogeneous phase, were recovered by simple filtration and submitted to swelling in different solvents in order to be purified from the unreacted starting products and oligomers. The monomer feedings and the polymer yield are shown in the table below (**Table 12**).

Table 12. Polymerization data and yields for the C0(X-F5) resins.

Catalyst	*St (mmol)*	*DVB (mmol)*	*Yield (%)*	*Organotin Monomer (mmol)*
C0(20-F5)	13.5	3.61	52	0.902
C0(35-F5)	11.8	6.90	79	0.985

The obtained resins have been labelled as **C0(X-F 5)**, where **C0** indicates absence of spacer and **X** represents the DVB content in the catalysts, 20% and 35% respectively, while **F 5** concerns the presence of fluorine as substituent in the tin containing monomer having 5% concentration referred to the polymerization mixture.

The prepared resins have been characterised by FT-IR spectroscopy only, because of their insolubility that makes impossible to use other common analytical techniques.

To confirm that the polymerization was carried out successfully, in the FT-IR spectrum the bands at 990 and 915 cm^{-1}, related to the bending of the vinyl moiety, have disappeared, while the signal of the organotin ester carboyl at 1620 cm^{-1}, typical value of tetracoordinated tin, still remains (**Figure 30**). This latter band frequency refers to a carbonyl moiety free from any interactions, therefore implying a tetracoordinated tin.

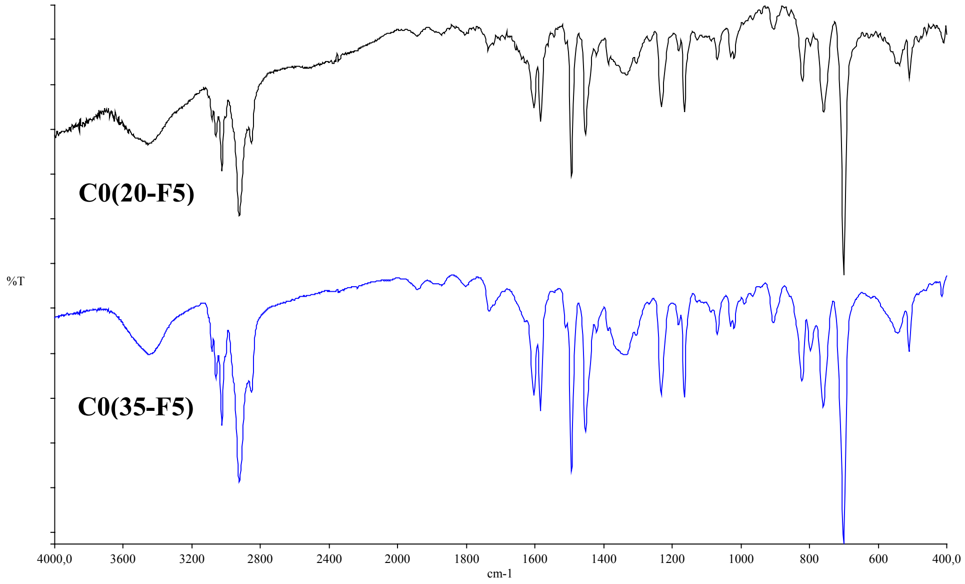


Figure 30. FT-IR spectra of the resins of the C0(X-F5) series.

In order to evaluate the final polymer composition tin and oxygen elemental analysis were carried out, as reported in **Table 13**.

Table 13. Tin and oxygen content for the resins of the C0(X-F5) series.

	Oxygen content (mmol/100g)		*Tin content (mmol/100g)*	
	Theorical	**Elem. Anal. results**	**Theorical**	**Calculated**[a]
C0(20-F5)	76	102	38	51
C0(35-F5)	74	100	37	50

[a]Calculated on the basis of the oxygen elemental analysis

8.3 - Assessment of catalytic activity of the C0(X-F5) resins

The catalytic activity of the synthesized stannilated resins has been assessed in a transesterification model reaction between ethyl acetate and 1-octanol, a primary alcohol chosen for its features. In fact, as observed in previous work[129.], it is more sensitive than secondary o tertiary ones to little changes of the catalytic system or the catalyst structure.

The results obtained are reported in the table below (**Table 14**) and represented by histograms in **Figure 31**. These data were compared with those collected for the resin **C0(35-5)**, prepared in a previous work, in order to investigate the role of a electron withdrawing substituent, as fluorine, on the overall catalytic performances. It has to be said, however, that we don't have at disposal the **C0(35-5)** conversion data before the 24 hours, because it belongs to past studies, in which the synthesized resins were tested only after 24 and 48 hours.

Table 14. Conversions of 1-octanol in trasesterification reaction with ethyl acetate, catalyzed by resins of the C0(X-F5) series.

Catalyst	***Conversion*** [a] ***(%)***				
	2 h	**4 h**	**8 h**	**24 h**	**48 h**
C0(20-F5)	5	9	22	87	88
C0(35-F5)	6	19	38	90	94
C0(35-5)	n.a.	n.a.	n.a.	67	84

[a] Determined on the basis of the starting alcohol 1-octanol

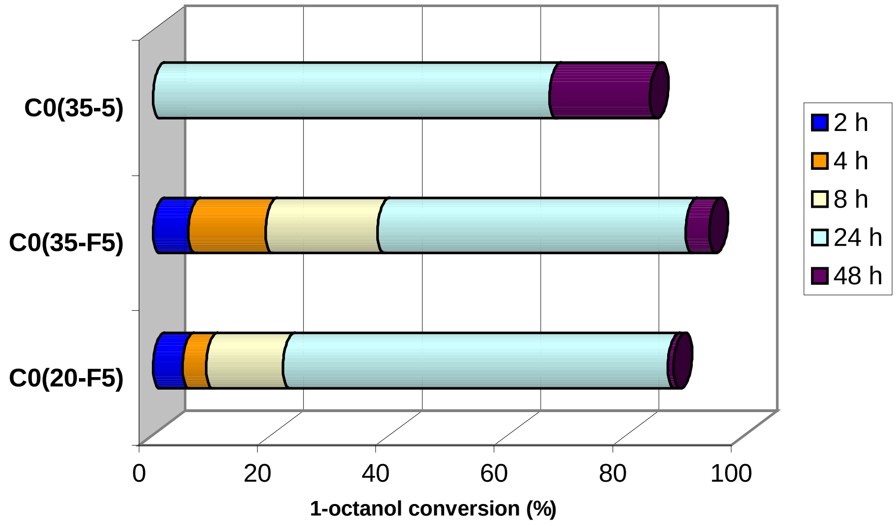


Figure 31. -Histograms of 1-octanol conversions in the transesterification reaction with ethyl acetate, catalyzed by the C0(X-F5) and C0(35-5) series resins.

As it can be seen looking at the table above, both the **C0(X-F5)** resins show better catalytic activity than **C0(35-5)**. In addition the alcohol conversions improve from **C0(20-F5)** to **C0(35-F5),** as the amount of DVB increases, confirming the trend observed.

Finally, it has to be observed that no significant differences were found between the data reported after 24 and 48 hours, thus indicating that probably the resins **C0(X-F5)** reach their best performances in 24 hours.

9 - Cross-linked Polystyrenic Resins Bearing the Tri[(4-thiomethyl)phenyl]tin Carboxylate Moiety

9.1 - Synthesis of the tin-functionalized monomer tri(4-thiomethylphenyl)tin-4-vinylbenzoate

This synthetic pathway is very similar to the one reported for the tri(4-fluorophenyl)tin-4-vinylbenzoate. It starts from 1-bromo-4-thiomethylbenzene to give the tetrakis(4-thiomethylphenyl)tin, in a two steps reaction (**Figure 32**).

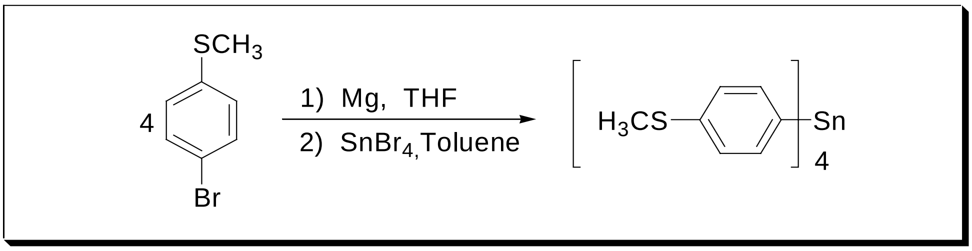


Figure 32. Synthesis of the tetrakis (4-thiomethylphenyl)tin.

The first step is the preparation of the Grignard derivative and the second one the addition of $SnBr_4$ to give the corresponding tetra-substitued tin derivative. The *tetrakis* has been characterised by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy analysis, to confirm its structure. In particular the ^{1}H-NMR spectrum shows the resonaces of the aromatic protons at 7.2 and 7.5 ppm, confirmed by the ^{13}C-NMR signals from 127 ppm to 141 (**Figure 33**). In this spectrum the “satellite” bands due to the coupling with the tin atom are also visible.

The signals related to the S-CH_3 bond are found at 2.5 ppm in the ^{1}H-NMR spectrum and at 15.7 in the ^{13}C-NMR one.

Regarding the ^{119}Sn- NMR spectrum, it displays one signal at -121.6 ppm, indicating that only one product was obtained.

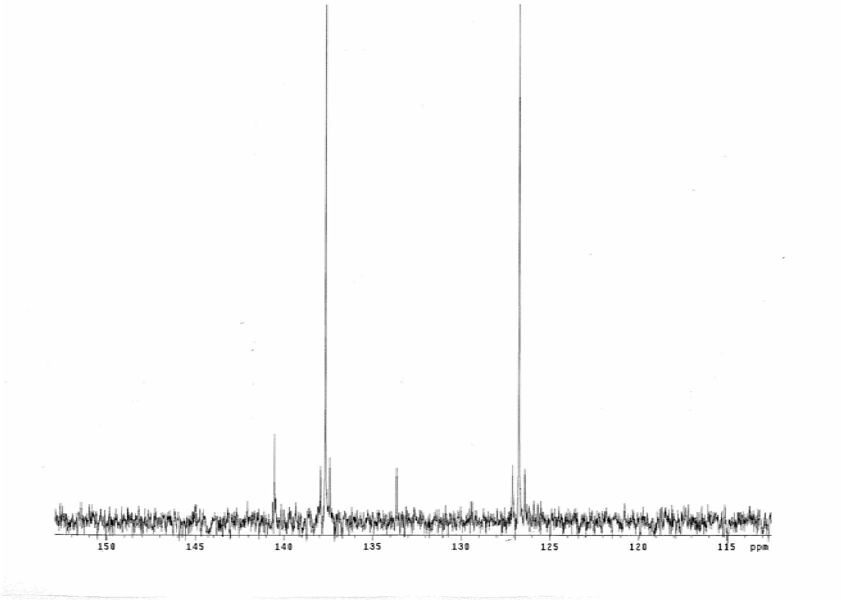


Figure 33. ^{13}C-NMR spectrum of the tetrakis(4-thiomethylphenyl)tin.

The synthesis of the tri(4-thiomethylphenyl)tin chloride consists of a redistribution reaction, the Kocheskov reaction, where the 4-thiomethylphenyl moiety exchanges with the chlorine, given by SnCl$_4$ (**Figure 34**).

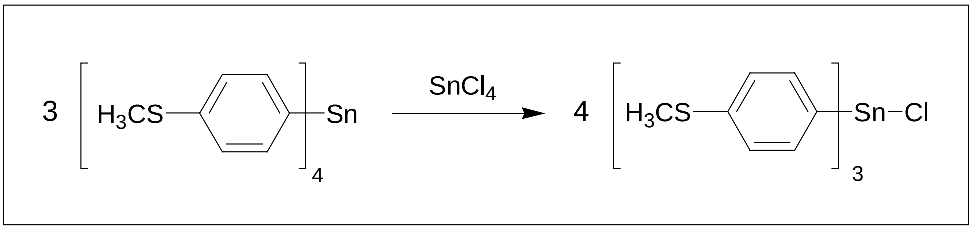


Figure 34. Synthesis of the tri(4-thiomethylphenyl)tin chloride.

Then the *tris* derivative has been hydrolized with KOH 10 % to obtain tri(4-tiomethylphenyl)tin hydroxide. In this kind of reaction theoretically is possible to have either the oxide or the hydroxide, depending on varius parameters. In this case we have synthesized the hydroxide, as confirmed by the FT-IR spectrum (**Figure 35**). It shows in fact the bands related to the stretching and bending of the OH at 3428 and 929 cm^{-1} respectively, and no signal could be found in the region from 800 to 700 cm^{-1}, where usually is present the absorption of the Sn-O-Sn bond, typical of the oxide derivative. The signal at 794 cm^{-1}, in fact, that can be observed also in the starting product spectrum, concerns the bending of the 1,4-disubstituted aromatic ring. It has to be added, however, that it is not important for the synthetic pathway which one reacts, because the next reaction takes place with the hydroxide and the oxide as well.

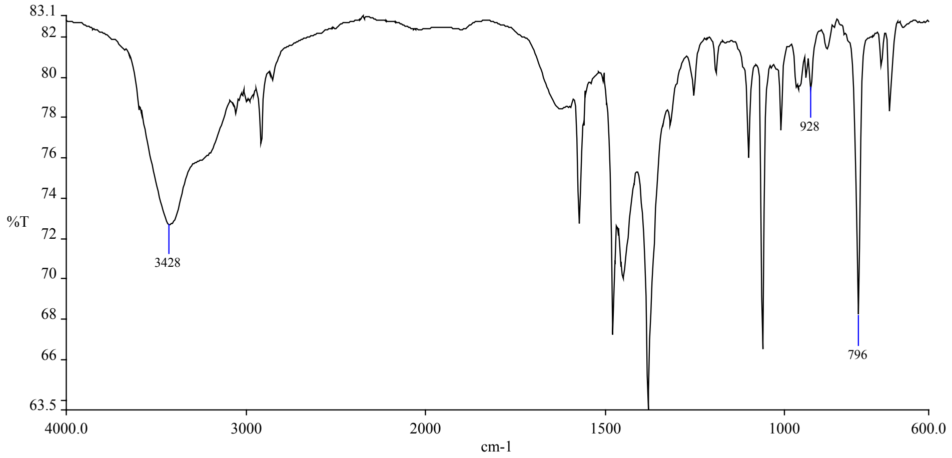


Figure 35. FT-IR spectrum of tri(4-thiomethylphenyl)tin hydoxide.

Due to the very low solubility of this product, it was not possible to record its ^{119}Sn-NMR spectrum.

The monomer tri(4-thiomethylphenyl)tin-4-vinylbenzoate was finally obtained by the esterification of the above hydroxide with 4-vinylbenzoic acid in refluxing toluene, in the presence of a small amount of hydroquinone as polymerization inhibitor. The water formed was distilled off using a Dean-Stark apparatus (**Figure 36**), in order to shift the equilibrium towards the products.

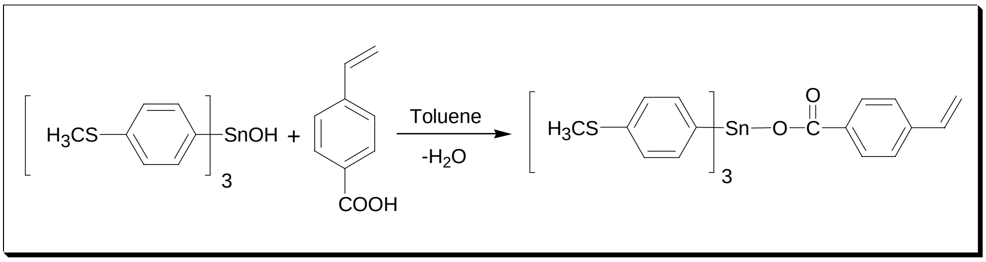


Figure 36. Synthesis of the monomer tri(4-thiomethylphenyl)tin 4-vinylbenzoate.

The characterization of the obtained product has been performed by FT-IR and NMR spectroscopy. The ^{1}H-NMR spectrum shows the typical signals of the styrene: the vinyl protons resonances are visible at 5.35, 5.85 and 6.7 ppm, while the aromatic ones, concerning 1,4-disubstitued aromatic ring, are at 7.45 and 7.7 ppm. The ^{13}C-NMR spectrum, moreover, confirm the structure of the monomer, although the signal related to the carbonyl, due to the low solubility of the product, was not observed. However, in the FT-IR spectrum are clearly visible two absorption bands at 1620 cm^{-1} and 1334 cm^{-1} (**Figure 37**). They are ascribible respectively to the asymmetric and symmetric stretching of the carbonyl, confirming the presence of the tin carboxylate in tetracoordinated form.

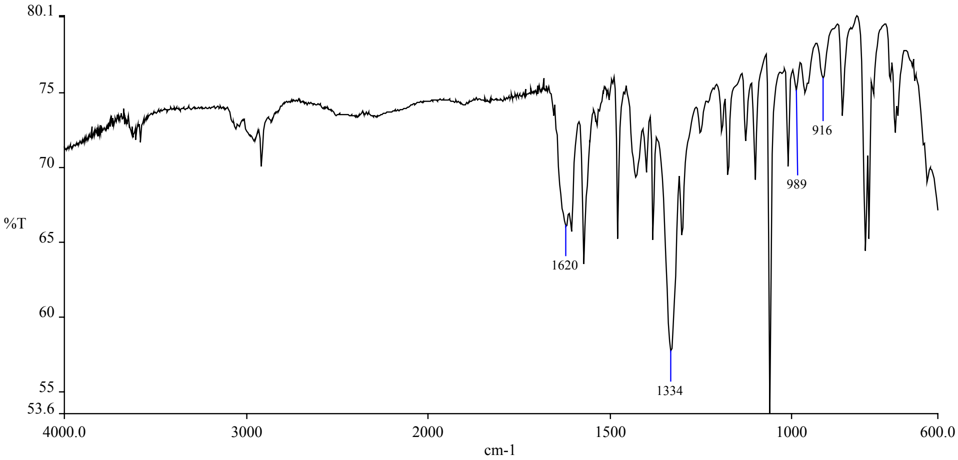


Figure 37. FT-IR spectrum of the monomer tri(4-thiomethylphenyl)tin-4-vinylbenzoate.

The band at 1630 cm^{-1}, related to the stretching of the vinyl bond, is not visible since it is overlapped by the carbonyl signal at 1620 cm^{-1}, as previously reported.

9.2 - Synthesis of the tin-functionalized resins of the C0(X-SCH_3 5) series

The radical co-polymerization of tri(4-thiomethylphenyl)tin-4-vinylbenzoate with different amounts of styrene and divinylbenzene was carried out in dry THF, using AIBN (1% in weight) as a thermal radical initiator. The reaction was kept under vacuum for 3 days at 60°C (**Figure 38**).

The stannilated monomer was added always in the same amount, corresponding to the 5%, while the amount of DVB and, consequently, of the styrene was changed, as it is reported in the table below, as well as theoretical tin content and yields (**Table 15**).

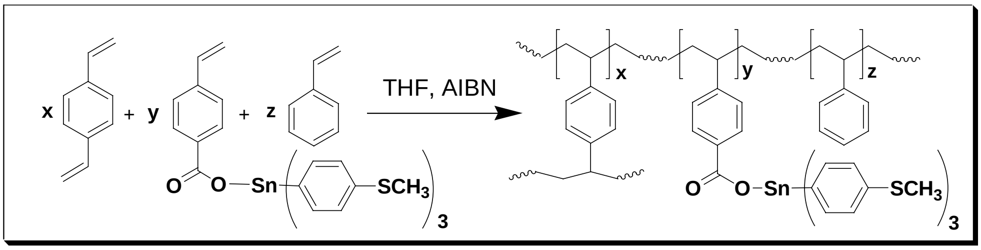


Figure 38. Synthesis of the resins bearing the monomer tri(4-tiomethylphenyl)tin-4-vinylbenzoate.

Table 15. Polymerization data and yields for the C0(X-SCH_3 5) resins.

	St (mmol)	*DVB (mmol)*	*Functionalized monomer (mmol)*	*Yield(%)*	*mmol Sn/g cat*
C0(35-SCH_3 5)	8.30	4.85	0.708	78	0.49
C0(20-SCH_3 5)	9.15	2.44	0.630	40	0.50

As mentioned before, this kind of resins can be characterised only by FT-IR spectroscopy, due to their insolubility.

In **Figure 39** and **40** FT-IR spectra of the resins **C0(35-SCH$_3$ 5)** and **C0(20-SCH$_3$ 5)** are reported. In both spectra it is possible to appreciate the peak at 1620 cm^{-1}, meaning that the tin carboxylate was maintained.

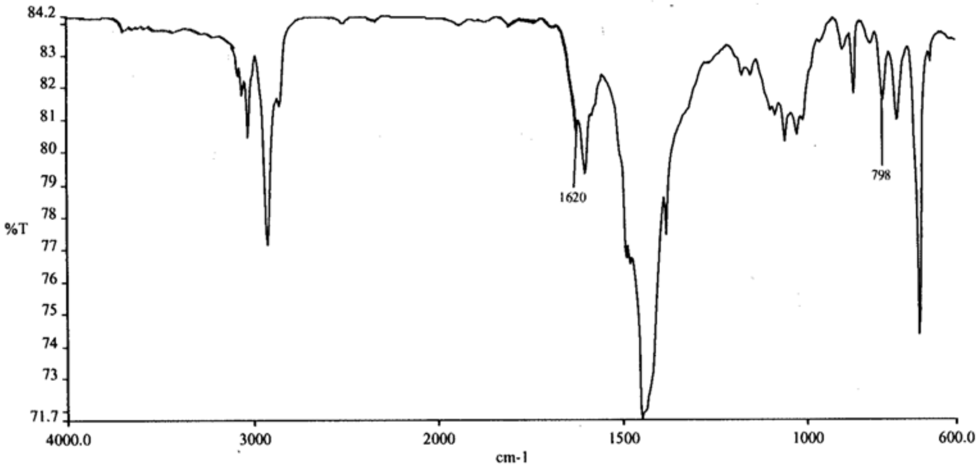


Figure 39. FT-IR spectrum of the resin C0(35-SCH$_3$ 5).

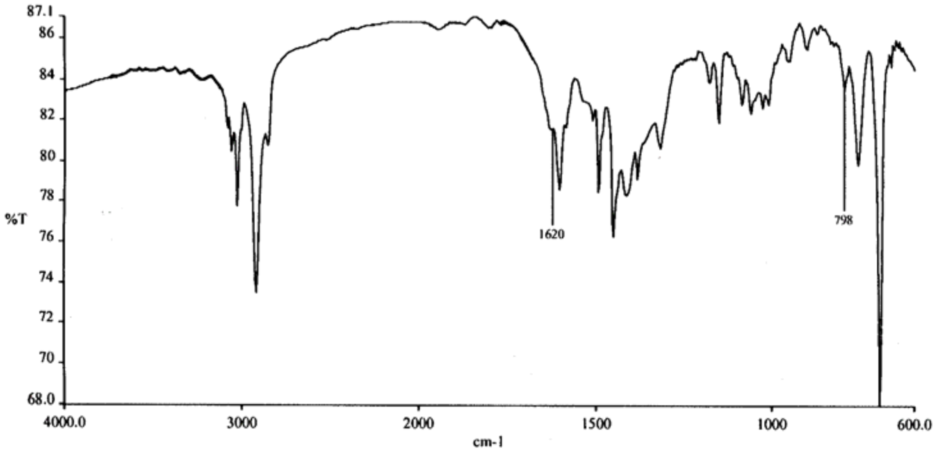


Figure 40. FT-IR spectrum of the resin C0(20-SCH$_3$ 5).

9.3 - Assessment of catalytic activity of the C0(X-SCH_3 5) series resins

The obtained resins have been labelled as **C0(X-$SCH_3$5)**, where **C0** indicates no presence of spacer and **X** represents the DVB amount that is 35 and 20 % respectively, while **$SCH_3$5** concerns the presence of SCH_3 as substituent and the concentration of the stannylated monomer equal to 5%.
The catalytic activity of these resins has been subsequently investigated in a model transesterfication reaction between ethyl acetate and 1-octanol. The alcohol conversion in each catalysed reaction (**Table 16**) was determined by GC after evaluation of the response factor of each species present.

Table 16. 1-octanol conversions for the C0(X-SCH_3 5) resins.

	Conversion (%)				
	2 h	**4 h**	**8 h**	**24 h**	**48 h**
C0(35-$SCH_3$5)	4.4	17.7	37.3	69	92
C0(20-$SCH_3$5)	0.2	2.7	26.7	63	89

Looking at the reported data, it can be easily noticed that the resin having the largest amount of DVB reaches, as expected, the best performances. However important informations can be achieved comparing the conversions obtained by **C0(35-SCH_3 5)** and its omologues **C0(35-5)** and **C0(35-F5)** ones (**Figure 42**).
Although after 48 hours of reaction the three catalysts provide very close values of alcohol conversion, the most effective seems to be **C0(35-F5)**, giving the highest conversion after 24 hours, as expected on the basis of its stronger Lewis acidity. This is in agreement with the statement that a resin bearing an electron withdrawing substituent, since it increases the Lewis acidity of tin, allows the alcohol to reach better conversions. It can be also concluded that the presence of an electron-donor substituent in this kind of catalysts does not improves, as expected, their catalytic performances.

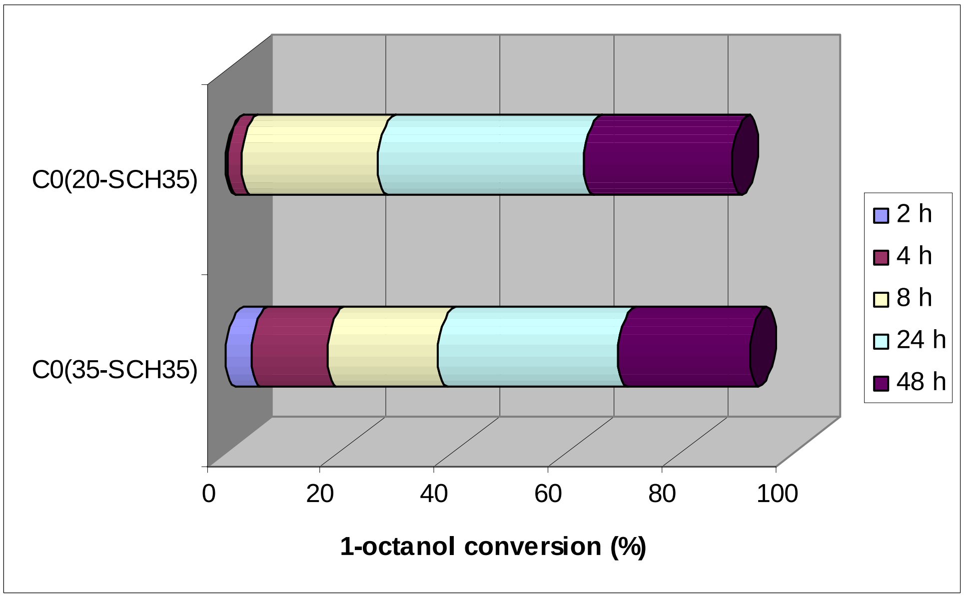


Figure 41. **Histogram of 1-octanol conversions the resins in the transesterification reaction with ethyl acetate, catalized by the C0(X-$SCH_3$5) series resins.**

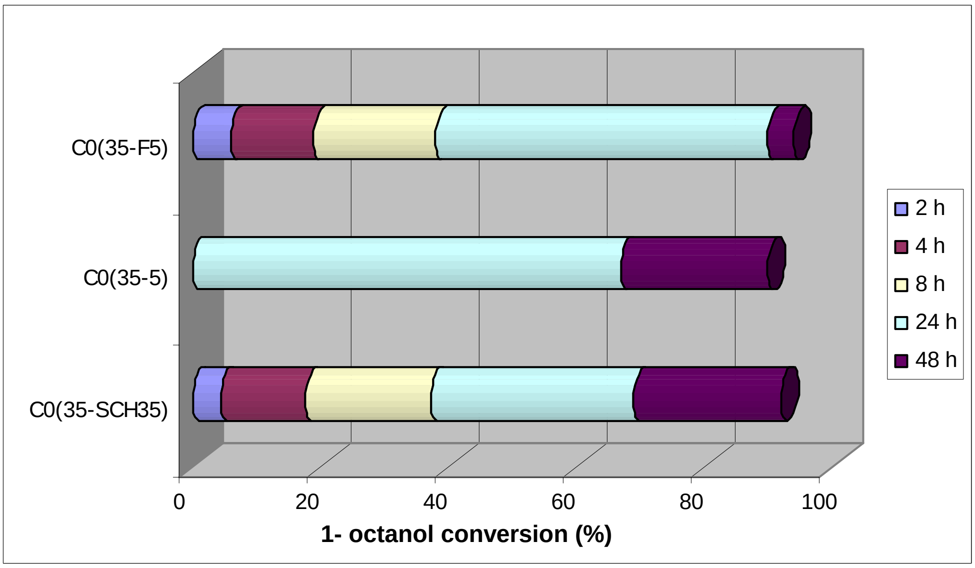


Figure 42. Histogram of 1-octanol conversions in the transesterification reaction with ethyl acetate, catalized by the C0(X-Y5) series resins.

10 - Cross-linked polystyrenic resins bearing the (4-trifluoromethylphenyl)tin carboxylate moiety

After having synthesized a monomer and the corresponding resins bearing an electron-withdrawing substituent, the fluorine atom, and an electron-donor group, as $–SCH_3$, the investigation of the effects of substituents having different electronic properties on the catalytic activity of these stannylated compounds has been continued by inserting in the *para* position the CF_3 group, selected to test a strong electron-withdrawing substituent.

10.1 - Synthesis of the tin-functionalized monomer tri[(4-trifluoromethyl)phenyl]tin-4-vinylbenzoate

This synthesis, that starts with the preparation of the suitable Grignard derivative followed by reaction with $SnBr_4$ to give *tetrakis* [(4-trifluoromethyl)phenyl]tin (**Figure 43**). The procedure is very close to the ones we performed for the other monomers (see **8.1**), except for the starting product, in this case 1-bromo-4-trifluoromethyl benzene.

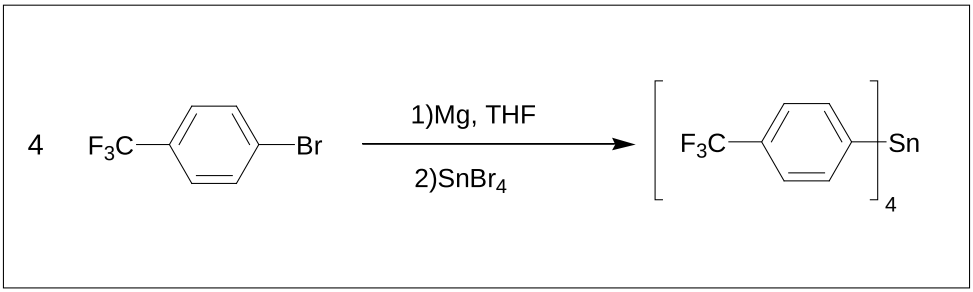


Figure 43. Synthesis of *tetrakis* (4-trifluoromethylphenyl)tin.

The *tetrakis* derivative obtained was characterised by FT-IR and NMR spectroscopy: in particular the ^{1}H-NMR spectrum shows signals at 7.5 and 7.75 ppm related to the aromatic ring, data confirmed by the ^{13}C-NMR spectrum. The latter is very interesting, because it displays the signal related to the CF_3, a quadruplet centered at 124.3 ppm (**Figure 44, red arrows**), having a very high coupling constant ($^1J = 273$ Hz). Moreover the resonance of the carbon bound to the CF_3 group, a quadruplet at 132.5 (**Figure 44, yellow arrow**), having $^2J = 34$ Hz, can also be observed.

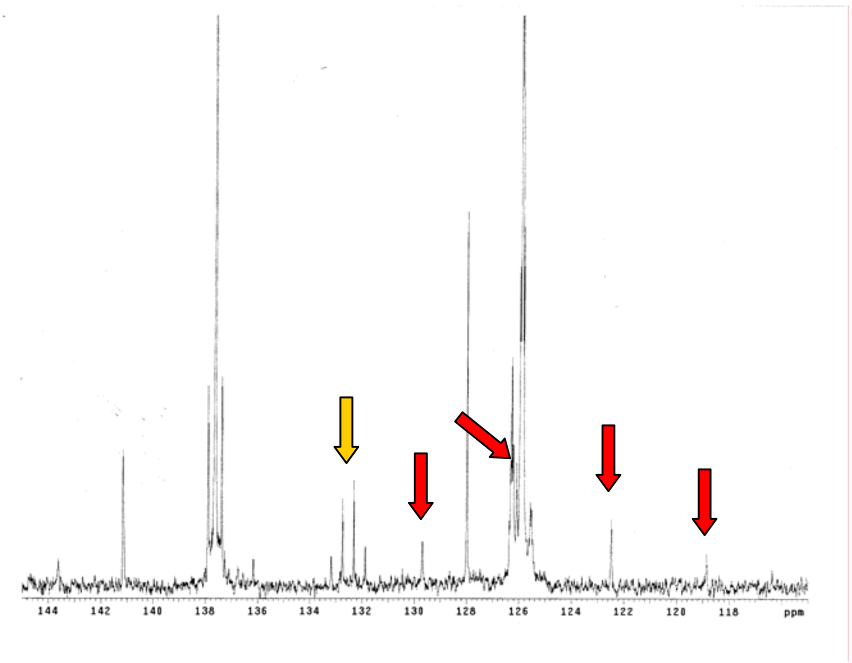


Figure 44. ^{13}C-NMR spectrum of the tetrakis[(4-trifluoromethyl)phenyl]tin.

This product was also submitted to mass spectrometry analysis, using electrospray ionization (ESI-MS), which shows the molecular ion at 701 m/z (positive ions) and at 735 m/z (negative ions). A signal at 555 m/z deriving from the loss of the 4-(trifluoromethyl)phenyl group ($C_7H_4F_3$) is also present.

To synthesize the tri[4-(trifluoromethyl)phenyl]tin chloride a redistribution reaction in the presence of $SnCl_4$ was perfomed, involving the exchange of one 4-(trifluoromethyl)phenyl group with Cl, as explained in previous paragraphs (**Figure 45**).

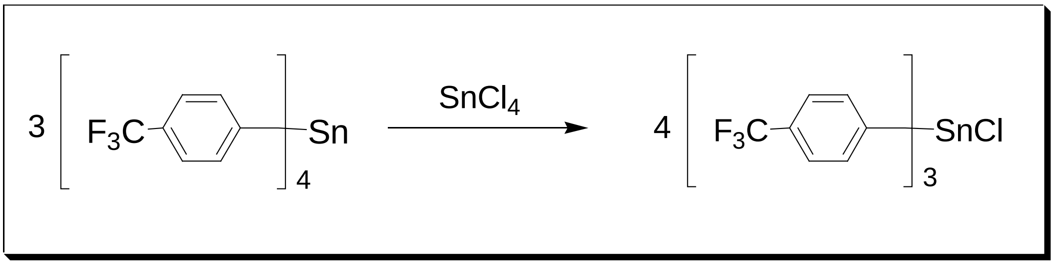


Figure 45. Synthesis of tri[4-(trifluoromethyl)phenyl]tin chloride

Due to their very similar structures, a clear distinction between the *tris* and the *tetrakis* derivative using FT-IR and NMR spectroscopy only was not possible, although the ^{19}F-NMR shows a unique signal at -64 ppm. Therefore the product was characterised by electronic impact mass spectrometry (EI-MS). In this case the spectrum recorded shows the molecular ion at 590 m/z, as expected, confirming that the reaction was occurred.

To synthesize the tri[4-(trifluoromethyl)phenyl]tin hydroxide, the *tris* derivative was hydrolysed in the presence of KOH 10% (**Figure 46**). As previously noticed, this reaction can give either the oxide or the hydroxide. In this case we obtained the hydroxide, as confirmed by the FT-IR spectra, showing the bands related to the OH group at 3450 (stretching) and 930 cm^{-1} (bending), with no absorption between 800 and 700 cm^{-1}, where the Sn-O-Sn bond stretching signal is expected to appear.

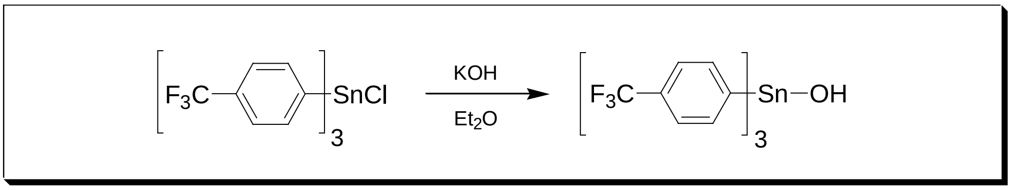


Figure 46. Synthesis of the tri[4-(trifluoromethyl)phenyl]tin hydroxide

Finally, the synthesis of the monomer was completed by the esterification of the tri[4-(trifluoromethyl)phenyl]tin hydroxide with 4-vinylbenzoic acid, in refluxing toluene, using a Dean-Stark apparatus to distill off the water formed as side-product (**Figure 47**).

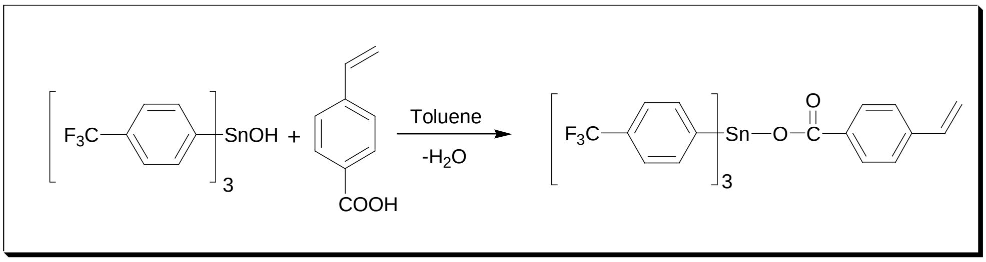


Figure 47. Synthesis of the monomer tri[4-(trifluoromethyl)phenyl]tin 4-vinylbenzoate

The obtained monomer was characterised by NMR spectroscopy. In particular it is possible to appreciate in the ^{1}H-NMR spectrum the signals related to the vinyl group of the styrene moiety at 5.4, 5.9 and 6.75 ppm and at 7.6 and 7.9 ppm the aromatic protons. Due to the very low solubility of the product we were unable to record a ^{13}C-NMR spectrum of good quality, as well as the ^{119}Sn-NMR. However the ^{19}F-NMR spectrum shows a unique resonance at -63.7 ppm. Looking at the FT-IR spectrum, it is possible to recognize an absorption band at 1630 cm^{-1}, related to the stretching of the residual vinyl bond, and the band of the C=O asymmetric stretching at 1542 cm^{-1}(**Figure 48**). The spectra displays also a signal at 1168 cm^{-1}, typical of the C-F$_3$ bond.

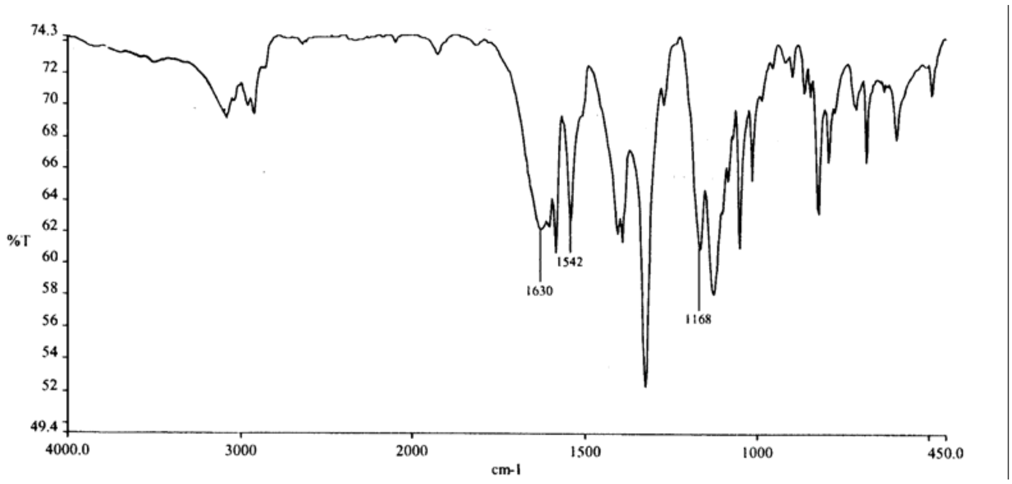


Figure 48. FT-IR spectrum of the monomer tri[4-(trifluoromethyl)phenyl]tin 4-vinylbenzoate

The monomer has been characterised by also EI-MS, showing the molecular ion at 730 m/z and two different pathway of fragmentation. In the first one the loss of $C_{11}H_{12}O_2$ (176 m/z), the vinylbenzoic acid moiety, giving a signal at 555 m/z, was evidenced, while the second one displays a signal at 585 m/z, due to the loss of the $C_7H_4F_3$ group (146 m/z).

10.2 - Cross-linked polystyrenic resins of the C0(X-CF_3 5)series

The reaction was performed in the same way as previously described for the other functionalized resins.

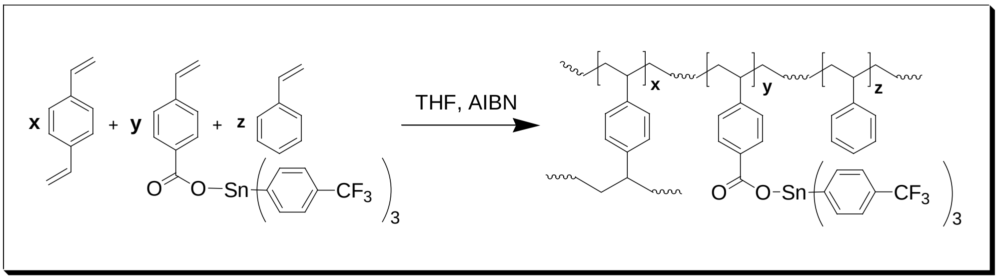


Figure 49. Synthesis of the resins bearing the monomer tri(4-trifluoromethylphenyl)tin 4-vinylbenzoate.

In the table below (**Table 17**) the polymerization data, feeding ratio, calculated tin content and yields are reported.

Table 17. Polymerization data and yields for the C0(X-CF_3 5) resins.

	St (mmol)	*DVB (mmol)*	*Functionalized Monomer (mmol)*	*Yield (%)*	*mmol Sn/g cat*
C0(35-CF_3 5)	4.3	2.5	0.36	5%	0.49
C0(20-CF_3 5)	4.3	1.14	0.28	15%	0.45

The obtained resins have been labelled as **C0(X-CF_3 5)**, where **C0** indicates no presence of spacer, **X** represents the DVB amount, in this case 35 and 20%, while the two terms **CF_3 5** concern, respectively, the presence of CF_3 group as substituent and the tin containing monomer of 5%.

In the figures below (**Figure 50** and **51**) the FT-IR spectra of the resins of the series **C0(X-CF_3 5)** are shown. As frequently reminded, this is the only technique suitable to characterize these products, because of their insolubility. It can be appreciated that the signal at 1630 cm^{-1}, related to the vinyl bond, has disappeared, while the C=O stretching band of the tin carboxylate still remains at 1542 cm^{-1}, indicating that the structure of the carboxylate has been mantained.

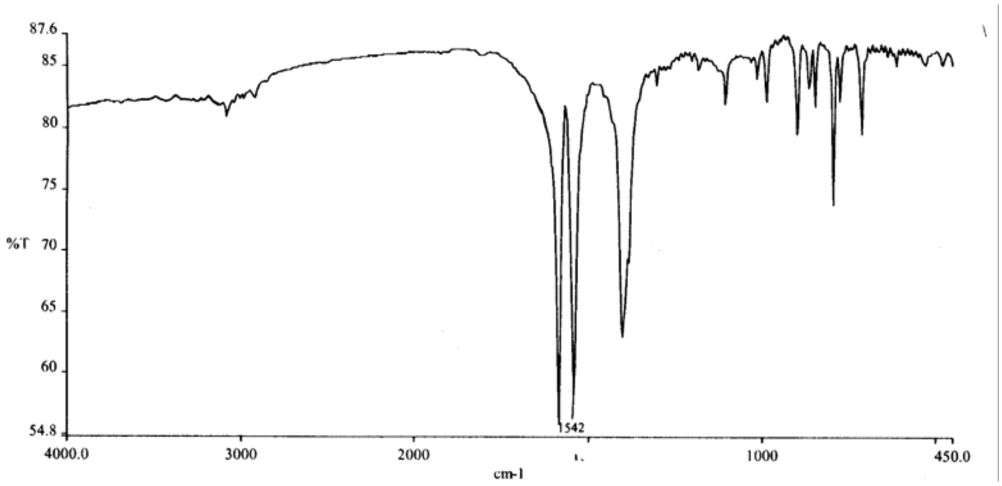


Figure 50. FT-IR spectrum of the resin C0(35-CF$_3$ 5).

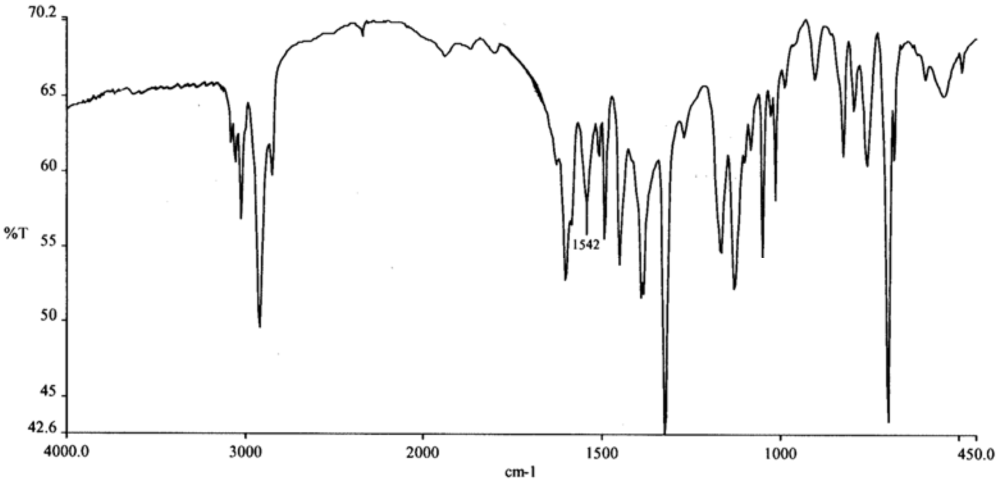


Figure 51. FT-IR spectrum of the resin C0(20-CF$_3$ 5).

10.3 - Assessment of catalytic activity of the C0(X-CF$_3$ 5) series resins

In this case, due to the low yield obtained in the polymerization reaction (**Table 18**), the catalytic activity tests has been performed only onto the **C0(20-CF$_3$ 5)** resin.

In **Table 18** and **Figure 52** the conversions obtained by this catalyst have been compared with its omologues of the **C0(20-X 5)** series, in order to investigate the effects of the substituent nature on the catalytic activity of the corresponding resins.

Table 18. Conversions of 1-octanol in trasesterification reaction with ethyl acetate, catalyzed by resins of the C0(20-X 5) series.

Catalyst	***Conversion (%)***				
	2 h	**4 h**	**8 h**	**24 h**	**48 h**
C0(20-5)	n.a.	n.a.	n.a.	36	58
C0(20-F5)	5	9	22	87	88
C0(20-SCH$_3$ 5)	0.2	3	27	63	89
C0(20-CF$_3$ 5)	0.2	3	16	24	50

Resins **C0(20-SCH$_3$5)** and **C0(20-F5)** achieve the best conversions rate at 48 hours, but the latter gives the best performance already after 24 hours. This results are very close to what expected. Regarding the new **C0(20-CF$_3$5)** resin, instead, that from previously obtained data was supposed to reach excellent conversions, it has to be said that it actually appears as the worst catalyst of the series. The reason of this unexpected behaviour could be found in the strong electron-withdrawing nature of the substituent CF$_3$ that might cause an excessive increase of the Lewis acidity of the catalytic centre. As frequently underlined, in these conditions the interaction between tin and carbonyl oxygen becomes too strong and, consequently, almost irreversible, leading to a weak catalytic activity or to no catalysis at all.

These results actually are not in contaddiction with our previous investigations, but they rather confirm the importance of the nature of the substituent at tin useful to oppurtunely modulate its Lewis acidity.

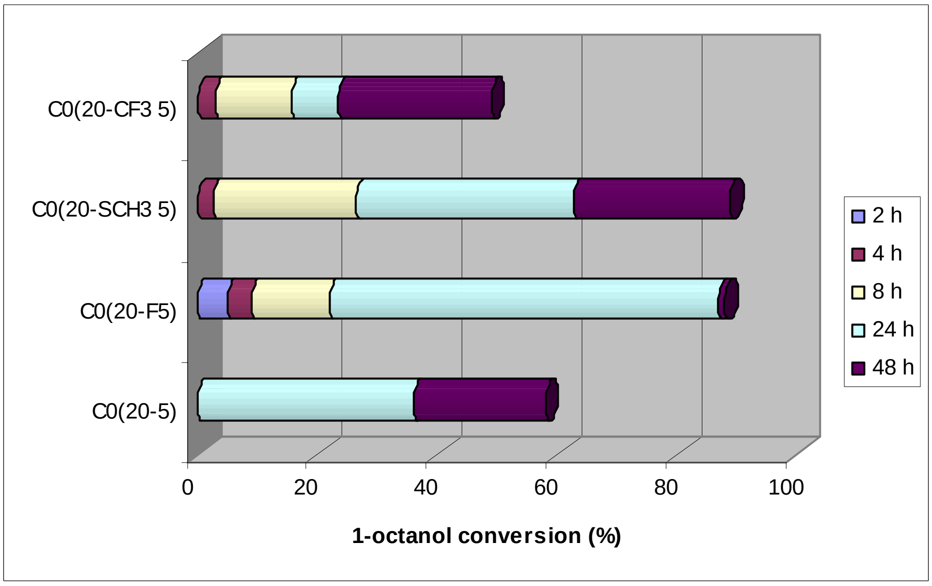


Figure 52. Histograms of 1-octanol conversions in the transesterification reaction with ethyl acetate, catalized by the C0(20-X 5) resins.

11 - Cross-linked polystyrenic resins bearing the tri(4-chlorophenyl) tin carboxylate moiety.

In previous studies the synthesized resins show their best catalytic performances when the aromatic ring bears an electron-withdrawing substituent, in particular the fluorine atom. However, the catalyst bearing CF_3, a strong electron withdrawing group, gives the worst alcohol conversions. Therefore an halogen seemed to be the best substituent for these kind of compounds and consequently we continued our investigation with another halogen substituent, the chlorine. A first attempt to synthesize a product bearing the tri(4-chlophenyl)tin carboxylate moiety had been already made, but it failed, mainly due to the difficult purification procedures and the very low yields obtained. Hence these features have been taken into account during the successful synthesis described in the following paragraphs.

11.1 - Synthesis of the tin-functionalized monomer tri(4-chlorophenyl)tin 4-vinylbenzoate

The synthesis of the monomer starts with the preparation of the Grignard derivative of 1-bromo-4-chlorobenzene. It then reacts with $SnBr_4$ to give the tetrakis(4-chlorophenyl)tin (**Figure 53**), as already mentioned for the other monomers reported in this work.

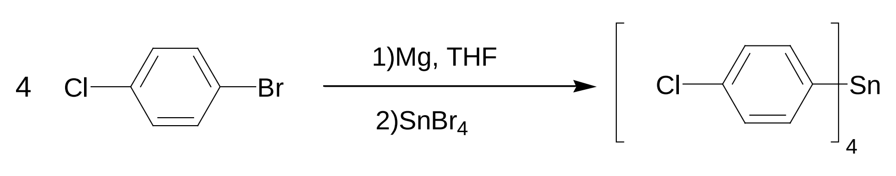


Figure 53. Synthesis of tetrakis (4-chlorophenyl)tin.

Then the tetrakis has been submitted to the Kocheskov reaction, where it reacts strictly in stoichiometric amounts with $SnCl_4$, without solvent, giving the tri(4-chlorophenyl)tin chloride (**Figure 54**).

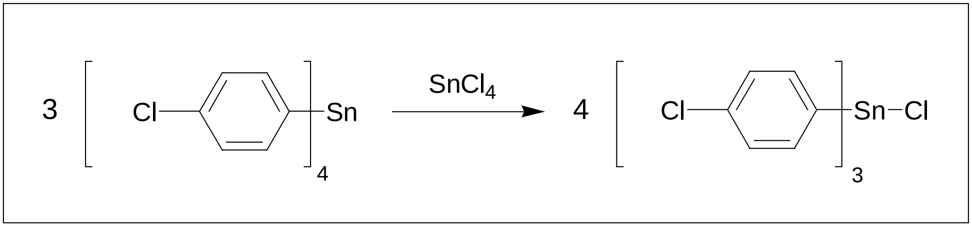


Figure 54. Synthesis of the tri(4-chlorophenyl)tin chloride

In the subsequent step the *tris* derivative was hydrolised by 10% solution of KOH, in order to obtain the tri(4-chlorophenyl)tin oxide (**Figure 55**). The product was characterised by NMR and FT-IR spectroscopy. In particular, the FT-IR spectrum displays the absorption at 802 cm^{-1}, related to Sn-O-Sn stretching, and no signal in the area of O-H stretching at about 3600 cm^{-1} can be found, thus confirming the oxide nature of the obtained product.

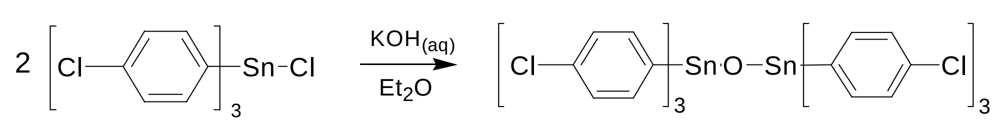


Figure 55. Synthesis of bis[tri (4-chlorophenyl)tin] oxide

The last reaction of this synthetic pathway is between the above oxide and the 4-vinylbenzoic acid in refluxing toluene, to give the monomer tri(4-chlorophenyl)tin 4-vinylbenzoate (**Figure 56**).

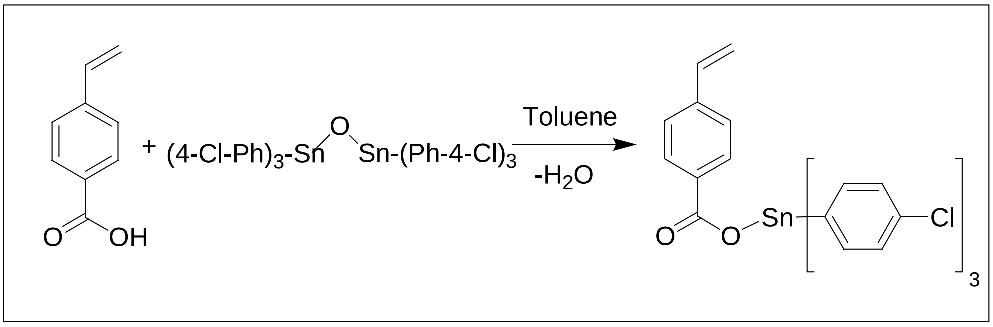


Figure 56. Synthesis of tri (4-chlorophenyl)tin 4-vinylbenzoate

The reaction progress was monitored by FT-IR spectroscopy. The absorption typical of the acid carbonyl at about 1700 cm^{-1} progressively disappears, while a new absorption, related to the organotin ester carbonyl stretching, appears at about 1630 cm^{-1}. Unfortunately, this band has overlapped the vinyl double bond one.

In order to assess its structure this product was investigated also by ^{1}H, ^{13}C- and ^{119}Sn-NMR spectroscopy. The ^{1}H-NMR spectrum shows the vinyl double bond resonances at 5.4, 5.8 e 6.7 ppm and those related to the aromatic hydrogens at 7.6 and 8.1 ppm. In addition, the ^{13}C-NMR one displays a signal at 171.2 ppm, related to the new formed organotin carbonyl. Finally, in the ^{119}Sn- NMR spectrum only one signal at -116 ppm, typical of tetracoordinated tin carboxylate, can be observed, thus confirming the occurrence of the reaction.

11.2 - Synthesis of the tin-functionalized resins of the C0(X-Cl 5) series

To synhesize the **C0(X-Cl 5)** resins a radical co-polymerization between 5% of stanilated monomer, tri(4-chlorophenyl)tin 4-vinylbenzoate, and different amounts of styrene and divinylbenzene was carried out in dry THF, using AIBN (1% with respect to the total fed) as a thermal radical initiator. The reaction mixture, kept under vacuum, was allowed to react three days at 60°C under stirring.

The obtained resins have been labelled as **C0(X-Cl 5)**, where **C0** indicates no presence of spacer, **X** represents the DVB amount that it is specific of each of the four different product, starting from 20% to a maximun of 70%, while **Cl 5** represents chlorine as substituent and the tin containing monomer present at 5%.

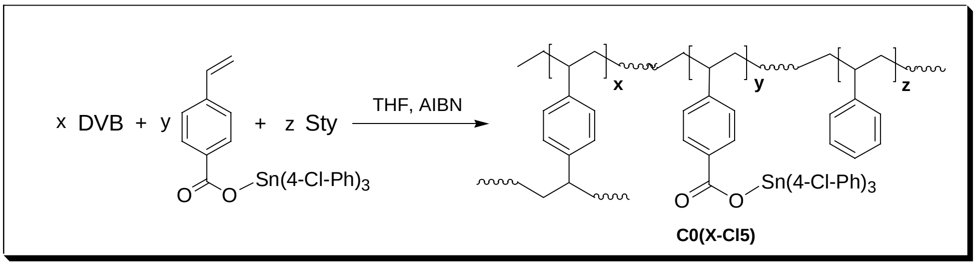


Figure 57. Synthesis of the resins bearing the monomer tri (4-chlorolphenyl)tin 4-vinylbenzoate

The polymeric derivatives have been recovered by simple filtration and purified from the unreacted comonomers and oligomers by swelling in different solvents, as diethyl ether and *n*-pentane, and further filtration.

The comonomers feeds and the obtained resins yields, as well as the calculated content of tin, are reported in the **Table 19**.

Table 19. Polymerization data and yields for the C0(X-Cl 5) resins.

	Sty (mmol)	*DVB (mmol)*	*Organotin Monomer (mmol)*	*Yield (%)*	*mmol Sn/g cat*
C0(20-Cl 5)	4.5	1.33	0.33	26	0.50
C0(35-Cl 5)	4.0	2.33	0.33	43	0.49
C0(50-Cl 5)	3.0	3.33	0.33	17	0.48
C0(70-Cl 5)	1.66	4.66	0.33	42	0.47

As in previous cases, due to the complete insolubility of these compounds, the only analytical technique suitable for their characterisation is the FT-IR spectroscopy (**Figure 58**). In this spectrum however, the band of the vinyl double bond stretching at about 1630 cm^{-1} is overlapped by the absorption of the carbonyl . The occurence of the polymerization is proved by the band related to vinyl double bond bending at about 900 cm^{-1}, that has disappeared. It is also clearly visible a band at 1491 cm^{-1}, related to the carbonyl symmetric stretching.

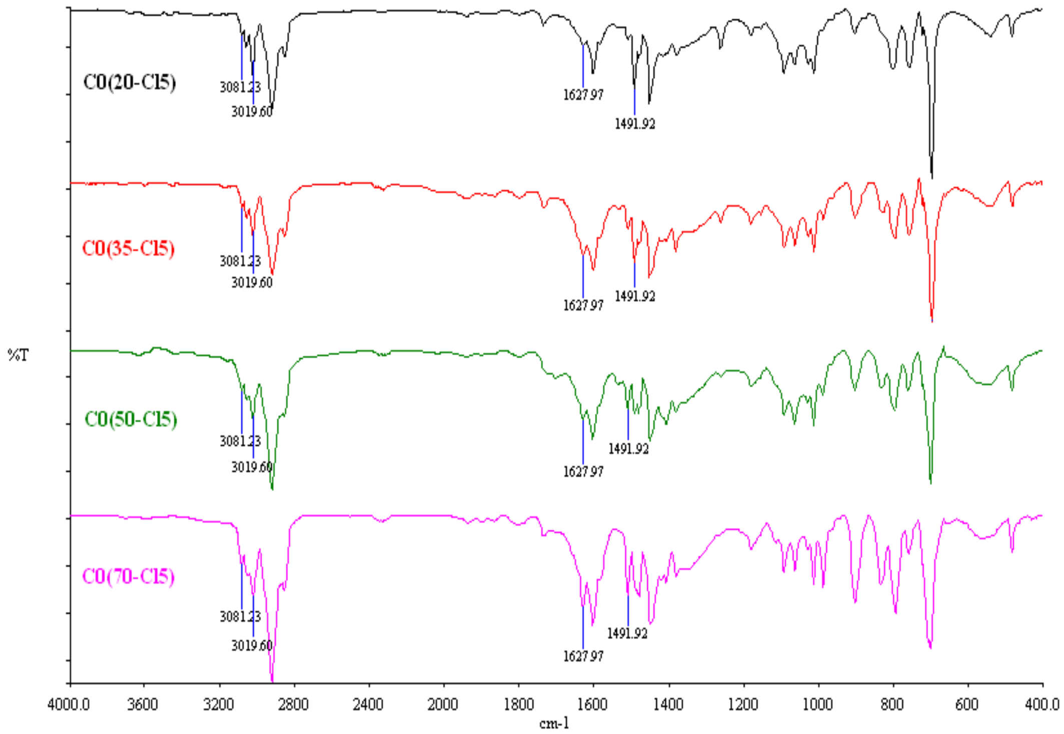


Figure 58. FT-IR spectrum of the C0(X-Cl 5) series resins.

11.3 - Assessment of catalytic activity of the C0(X-Cl 5) resins

As already observed, the catalytic activity of the synthesized stannylated resins has been assessed in a transesterification model reaction between ethyl acetate and 1-octanol.

The results obtained are shown in the **Table 20** and represented by histograms in **Figure 59**.

Table 20. Conversions of 1-octanol in trasesterification reaction with ethyl acetate, catalyzed by resins of the C2(X-Cl 5) series.

Catalyst	*Conversion[a] (%)*				
	2 h	**4 h**	**8 h**	**24 h**	**48 h**
C0(20-Cl5)	3	10	22	50	88
C0(35-Cl5)	9	24	41	92	100
C0(50-Cl5)	1	2	8	32	44
C0(70-Cl5)	12	37	49	100	100

[a] Determined on the basis of the starting alcohol 1-octanol

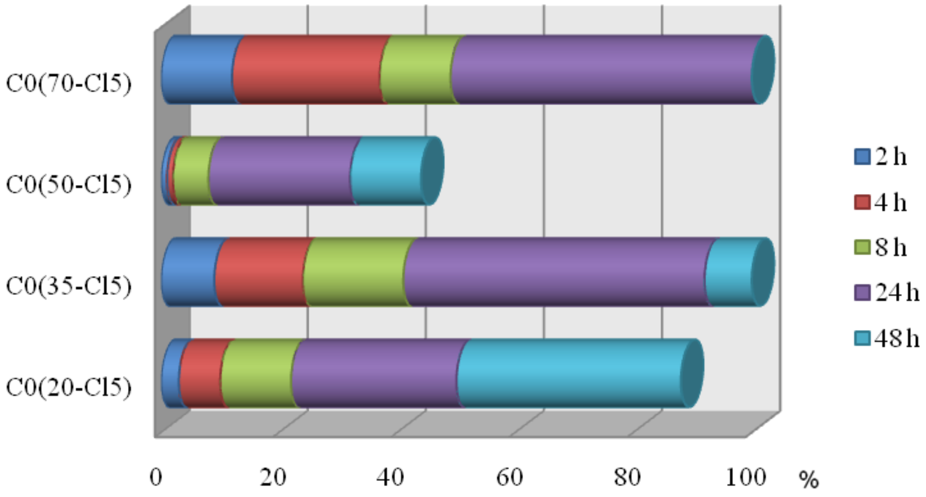


Figure 59. Catalytic activity test histogram for the C0(X-Cl 5) series resins.

All the **C0(X-Cl5)** resins have shown a certain catalytic activity, that improves as the amount of DVB increases, confirming the trend observed in previous works.

The most surprising data concerns the **C0(50-Cl5)** catalyst, that gives not only the worst performances of the series, but also conversions too low to seem believable, if compared to the other catalysts. However, a possible explaination can be found into synthetic problems of the sample, idea also supported by the low yield achieved in the polymerization reaction of this product (**Table 19**). It has, therefore, to be re-synthesized before making conclusions about its effective catalytic performances.

As far as the three other resins, all they give high alcohol conversions. In particular the best of the group, the **C0(70-Cl5)** one, completes the reaction after 24 hours. However, the **C0(35-Cl5)** resin achieves excellent result after 24 hours and the 100% of conversion after 48 hours. Regarding to the **C0(20-Cl5)** resin, although it reaches only a maximum of 88% conversion, it shows good catalytic activity, confirming the effectiveness of this series of catalysts.

In **Figure 60** a comparision of the catalytic test results for the resins containing 35 % of DVB is shown. It can be noticed that **C0(35-Cl5)** has the best catalytic activity, followed by **C0(35-F5)** and, finally, **C0(35-5)**, as expected.

It can be therefore concluded that, under these reaction conditions, the chlorine is the tin substituent in the organotin monomer allowing the corresponding resin to achieve the best conversion as catalyst in transesterification reactions.

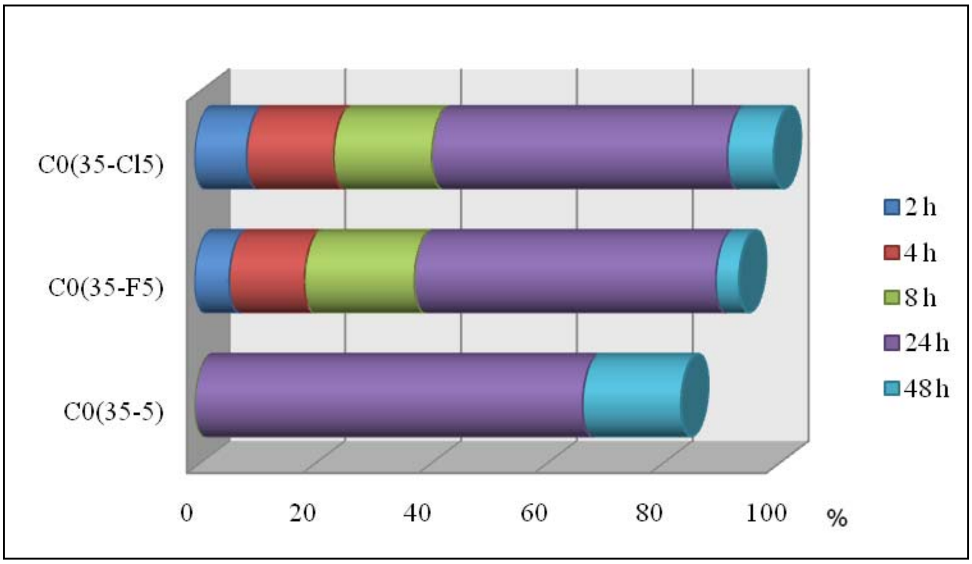


Figure 60. Catalytic activity test histogram for the C0(35-X 5) resins

12 - Cross-linked polystyrenic resins bearing a C4 spacer and the triphenyltin carboxylate moiety

In a previous work it has been synthesized a monomer and the corresponding resins bearing a dimethyl spacer between the aromatic ring and the triphenyltin carboxylate moiety, in order to increase the mobility of the catalytic centre, with the aim to improve the alcohol conversions with respect to the resins prepared before. Since these resins haves shown excellent catalytic activity in transesterification reaction, it was investigated how the spacer length affectes the catalytic activity. For this reason the synthesis of a monomer and the relative resins bearing a tetramethyl spacer has been performed. Unfortunately, it was not possible to use the same synthetic pathway applied for the monomer containig the dimethylenic spacer; therefore the following multistep synthesis was proposed.

12.1 - Synthesis of the tin-functionalized monomer triphenyltin 5-(4-styryl)pentanoate

The first step concerns the preaparation of the Grignard derivative of the 4-bromovinylbenzene which acts as nucleofilic in the second step, during the addition of 1-4 dibromobutane, using Li_2CuCl_4 as catalyst (**Figure 61**).

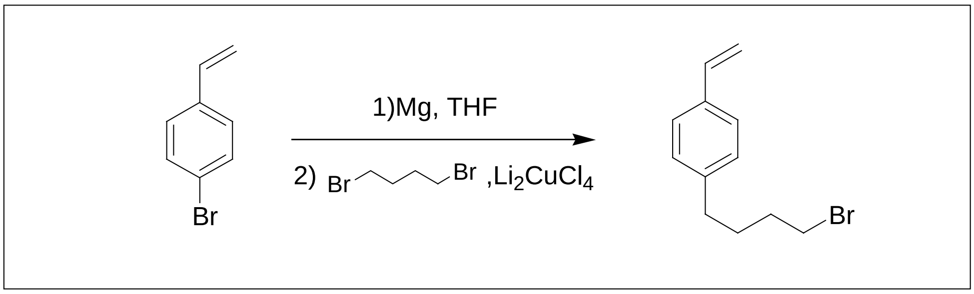


Figure 61. Synthesis of 1-(4-bromobutyl)-4-vinylbenzene.

The ^{1}H-NMR spectrum of the product displays the signals at 5.2, 5.7 and 6.7 ppm, referred to the vinyl protons, and the aromatic ones at 7.1 and 7.3 ppm while the resonances of the four aliphatic protons are at 1.70, 1.90, 2.60 and 3.40 ppm, respectively. These data show that the substitution of only one bromine atom occurs, while the styrenic moiety does not take part in the reaction. Moreover, in the ^{13}C-NMR spectrum four segnals between 30 and 35 ppm, related to the alipyhatic chain, can be observed. Carefully observing the ^{1}H-NMR spectrum, it can be noticed that the product obtained wasn't totally pure: actually resonaces related to the starting product are still visible. Anyway, they disappear after the subsequent reaction, giving a pure product (**Figure 62** and **64**).

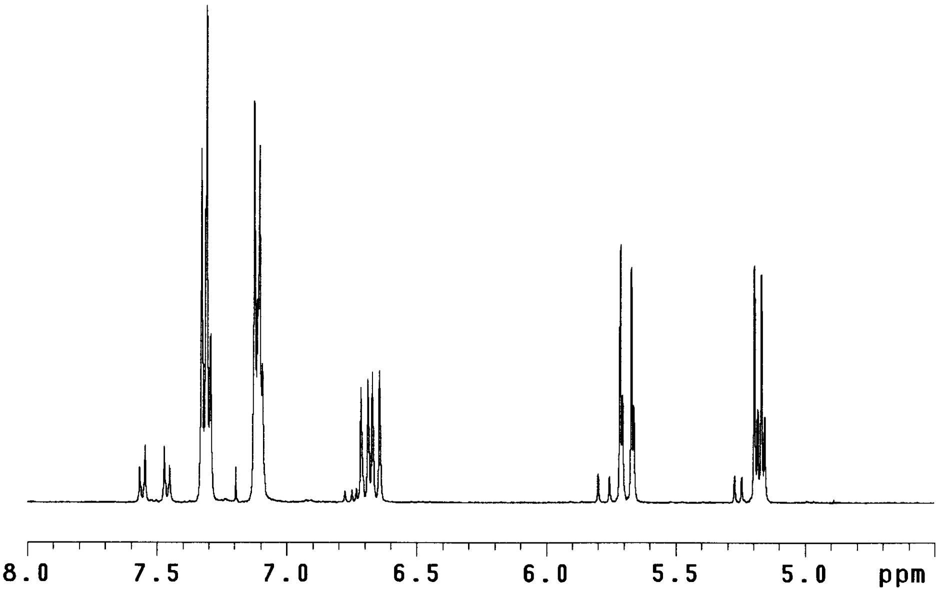


Figure 62. ^{1}H-NMR spectrum of 1-(4-bromobutyl)-4-vinylbenzene.

The synthesis of the 5-(4-styryl)pentanoic acid is a two steps reaction that needs firstly the formation of a Grignard derivative of 1-(4-bromobutyl)-4-vinylbenzene and then its reaction with CO_2 to give a carboxylate, finally neutralized by HCl (**Figure 63**).

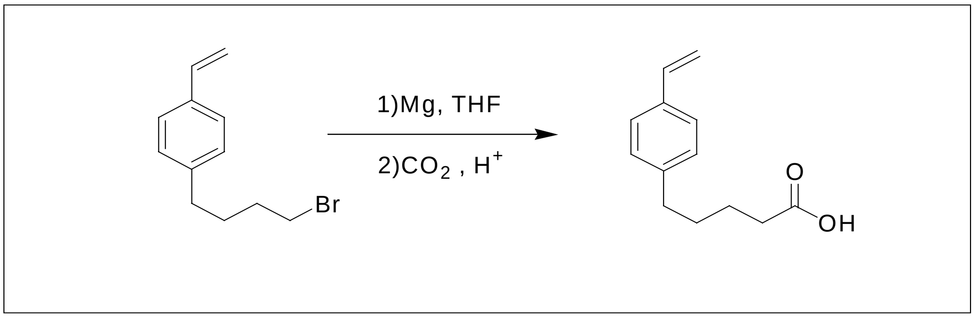


Figure 63. Synthesis of the 5-(4-styryl)pentanoic acid.

To confirm the occurrence of the reaction the ^{1}H-NMR spectrum recorded displays the typical signals of the styrenic group, the resonances at 5.20, 5.70 and 6.70 ppm, indicating that only the bromine reacts (**Figure 64**).

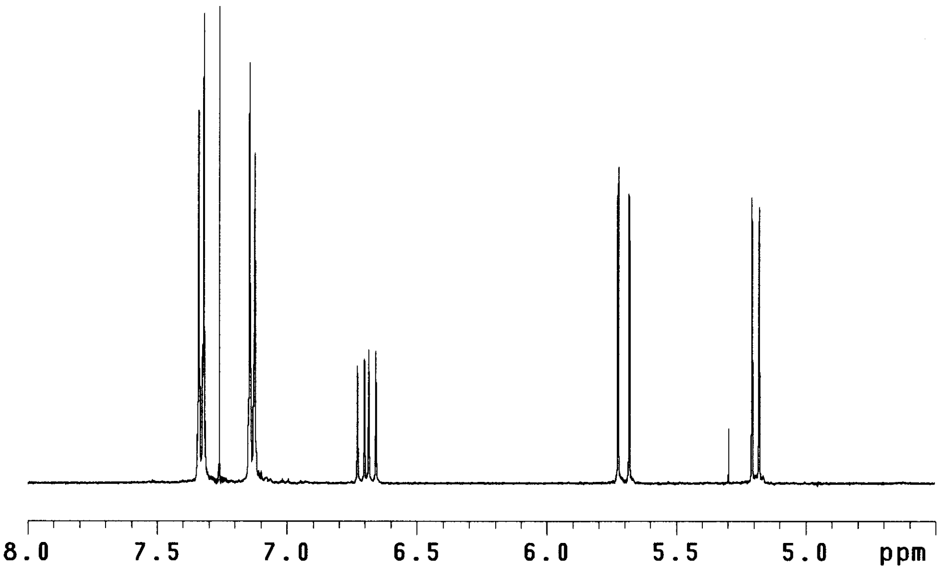


Figure 64. ^{1}H-NMR spectrum of the 5-(4-styryl)pentanoic acid.

The synthesis of the triphenyltin ester of 5-(4-styryl)pentanoic acid was achieved by direct esterification of the acid with triphenyltin hydroxide, using toluene as reaction solvent. The water formed as side product has been removed by azeotropic distillation using a Dean Stark apparatus, in order to shift the equilibrium towards the desired products (**Figure 65**).

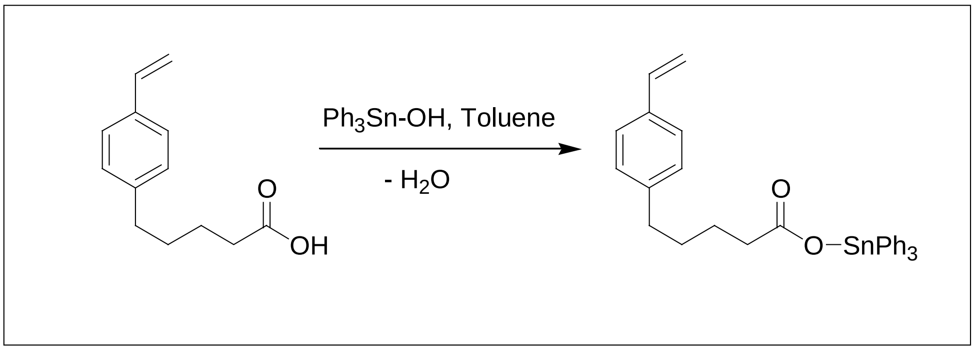


Figure 65. Synthesis of triphenyltin 5-(4-styryl) pentanoate.

The progress of the reaction was monitored by FT-IR spectroscopy (**Figure 66**).

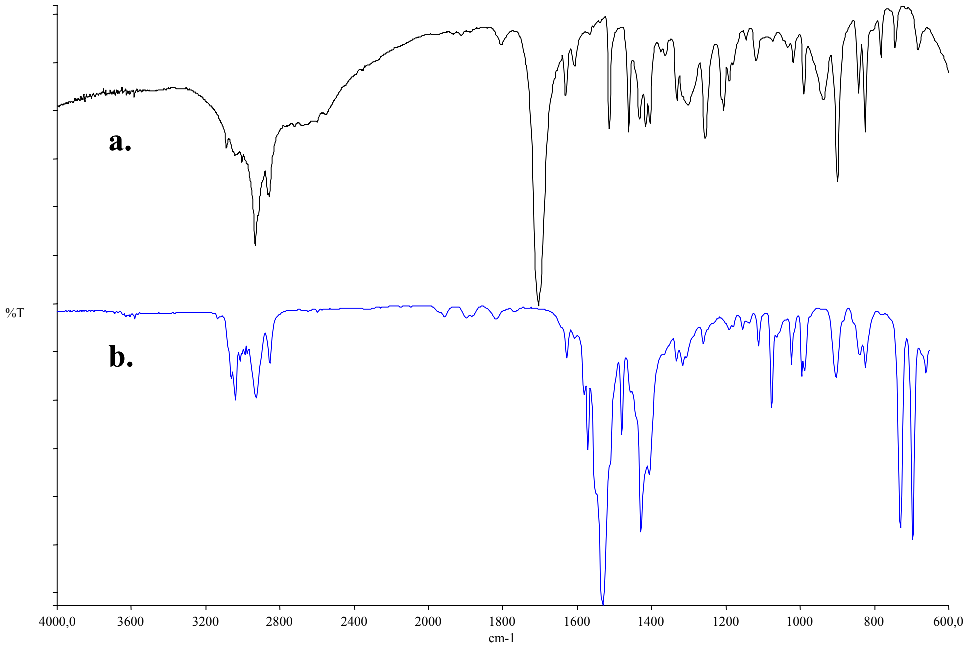


Figure 66. FT-IR spectrum of 5-(4.styryl)pentanoic acid (a) and the corresponding triphenyltin ester (b).

Comparing the spectra of the acid and its correspondig ester the disappearance of the absorption at 1703 cm^{-1} related to the carbonylic acid stretching can be observed, while the band at 1629 cm^{-1} of the vinyl double bond stretching still remains. It is important also to underline the appearance of absorptions related to the asymmetric and symmetric stretching of the organotin carboxylate at 1532 and 1429 cm^{-1}. These vibration values are typical of a pentacoordinated tin (**Figure 67**). As mentioned, in the monomers without the aliphatic spacer, instead, the tin was in always in its tetracoordinated form, probably due to the lower mobility of the organotin group and to the reduced steric hindrance.

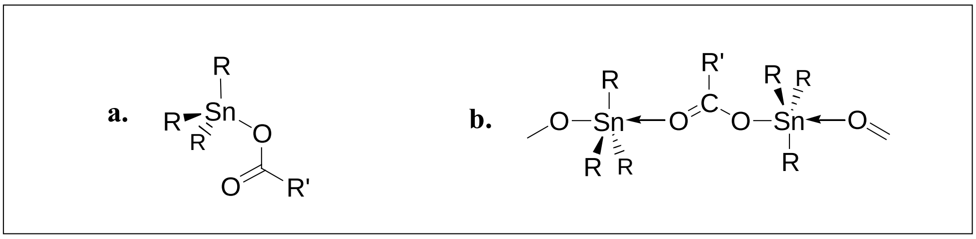


Figure 67. Structure of tetra (a) and penta-coordinated (b) tin in organotin esters

The synthesized monomer was characterised also by ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectroscopy using two-dimensional techniques, in order to assign correctly all the signals found. In particular the ^{119}Sn-NMR spectrum recorded in $CDCl_3$ solution displays only a resonace of the tin atom at -115 ppm, typical of tetracoordinated tin, demonstrating that the monomer is free from any unreacted organometallic compound used in the functionalization reaction.

12.2 - Synthesis of the tin-functionalized resins of the C4(X- 5) series

This series of resins have been synthesized by radical colipolymerization of 1,4-divinylbenzene, styrene and stannilated monomer (**Figure 68**), using the same amount of the latter in all reactions (5%). It has been changed the content of 1,4 DVB, the cross-linking agent, added as 35, 50 and 70% on the total moles in the reaction mixture respectively.

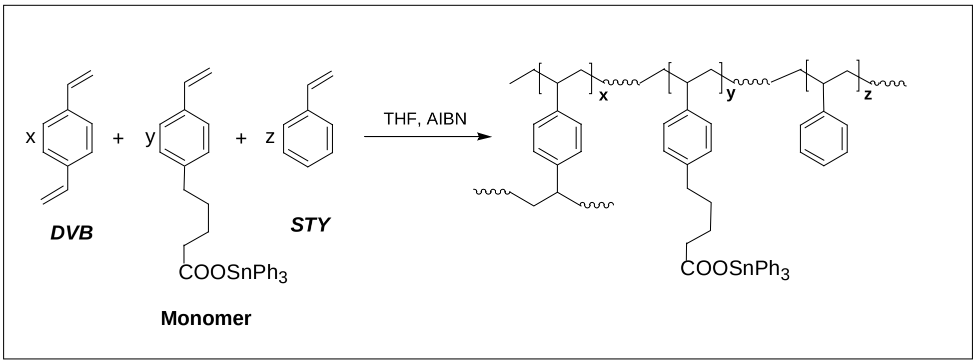


Figure 68. **Synthesis of the resins bearing the monomer triphenyltin 5-(4-styryl) pentanoate.**

As previously underlined, the polymerization was carried out in dry THF, using AIBN as thermal iniziator, and kept under vacuum for three days at 60° C, under stirring.

In **Table 21** the complete polymerization data, concerning the co-monomer feeds, the final yields and the calculated tin content have been reported. The obtained resins have been labelled as **C4(X- 5)**, where **C4** indicates the presence of a tetramethylenic spacer, **X** represents the DVB amount that it is specific of each of the three different product, starting from 20% to a maximun of 70%, while **5** concerns 5% content of stannylated monomer.

Table 21. **Polymerization data and yields for the C4(X-5) resins.**

	Sty (mmol)	*DVB (mmol)*	*Organotin monomer (mmol)*	*Yield (%)*	*mmol Sn/g cat*
C4(20-5)	6.52	3.79	0.54	69	0.50
C4(35-5)	4.87	5.40	0.54	81	0.46
C4(70-5)	2.72	7.85	0.54	90	0.41

Due to the complete insolubility of the obtained resins, the analytical technique suitable for assessing their structure was the FT-IR spectroscopy only.

The recorded spectra are shown in **Figure 69**. The occurence of the polymerization was confirmed by the disappearance of the bands around 1630, 990 and 900 cm^{-1}, features of vinyl double bond stretching and bending respectively. Althought it is crowded by a lot of absorbances, the region typical of the out of plane bendings of the aromatic C-H bonds could be a useful tool to characterize the products: in fact the intensification of the bands at 830 and 795 cm^{-1}, related to the aromatic rings of DVB, along the series **C4(X-5)**, can be observed. This behaviour is close related to the increase of the amount of cross-linker agent in the resins composition.

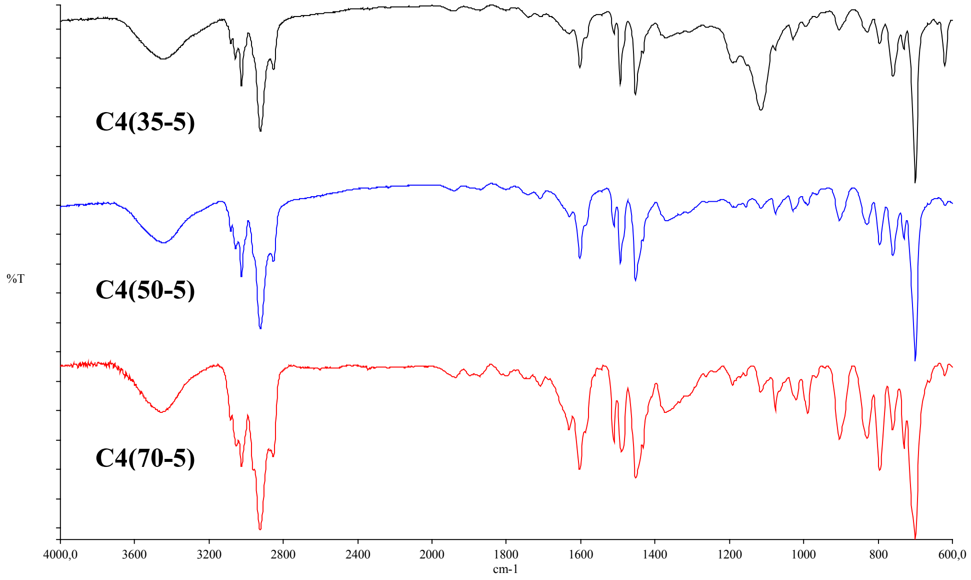


Figure 69. FT-IR spectrum of the C4(X-5) resins.

Moreover it can be underlined that no spectra show the absorption band around 1700 cm^{-1}, a value typical of carboxylic acid carbonyl vibration, thus suggesting that no hydrolysis of the organometallic ester during the polymerization reaction occur. This is also supported by the absorption at

1532 cm^{-1}, related to the monomer carbonyl stretching, visible in all the products, indicating a pentacoordinated tin also in these resins.

Table 22. Tin and oxygen content for the resins of the C4(X-5) series.

	Oxygen content (mmol/100g)		***Tin content (mmol/100g)***	
	Theoretical	**Elem. Anal**	**Theoretical**	**Calculated**[a]
C4(35-5)	74	101	37	50
C4(50-5)	71	92	36	46
C4(70-5)	69	82	35	41

[a] Calculated on the basis of oxygen elemental analysis

In order to have a reliable quantitative analysis of these resins elemental analyses oxygen have been performed. They are reported in **Table 23**, as well as the corresponding calculated tin content. However in this way is not possible to determine the relative amounts of styrene and DVB, because the ratio C/H is the same in the two co-monomers.

Table 23. Tin and oxygen content for the resins of the C4(X-5) series.

	Oxygen content (mmol/100g)		***Tin content (mmol/100g)***	
	Theoretical	**Elem. Anal**	**Theoretical**	**Calculated**[a]
C4(35-5)	74	101	37	50
C4(50-5)	71	92	36	46
C4(70-5)	69	82	35	41

[a] Calculated on the basis of oxygen elemental analysis

In addition a SEM analysis has been performed, using an EDS probe, in order to assess the distribution of the stannilated monomer into the resin. Indeed this technique allows to know the distribution of the tin atom not only onto the surface, but also inside the resin, as far as a depth of 1 μm.

In **Figure 70** the photographs obtained by this analysis performed on a fragment of polymer are shown. It could be easily observed that the tin image (**c**)can be perfectly overlapped either to the carbon (**b**) or to the polymer one (**a**), thus suggesting that the stannylated monomer is homogeneously distributed on the surface of the resin.

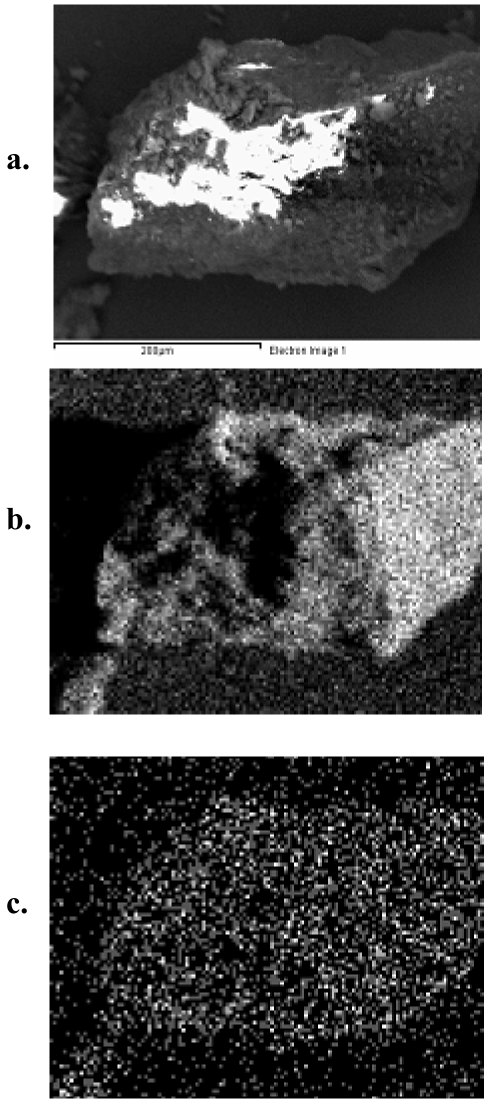


Figure 70. SEM photographs of the resin C4(35-5) (a), carbon (b) and tin (c) respectively contained in it (enlarging 400x).

12.3 - Assessment of catalytic activity of the C4(X- 5) series resins

The catalytic activity of the synthetized stannylated resins has been assessed in a transesterification model reaction between ethyl acetate and 1-octanol. The obtained results are reported in the **Table 24** and represented by histograms in **Figure 71**. These data were compared with those have been recorded for the resins **C2(35-5)** and **C0(35-5)**, prepared in previous works[130], in order to investigate and understand the role of the aliphatic spacer C4 on the overall catalytic performances.

Table 24. **Conversions of 1-octanol in trasesterification reaction with ethyl acetate, catalyzed by resins of the Cn(X-5) series.**

Catalyst	***Conversion[a] (%)***				
	2 h	**4 h**	**8 h**	**24 h**	**48 h**
C4(35-5)	2	3	8	31	86
C4(50-5)	2	6	18	62	92
C4(70-5)	3	6	22	77	97
C2(35-5)	4	13	29	93	100
C0(35-5)	-	-	-	67	84

[a] Determined on the basis of the starting alcohol 1-octanol

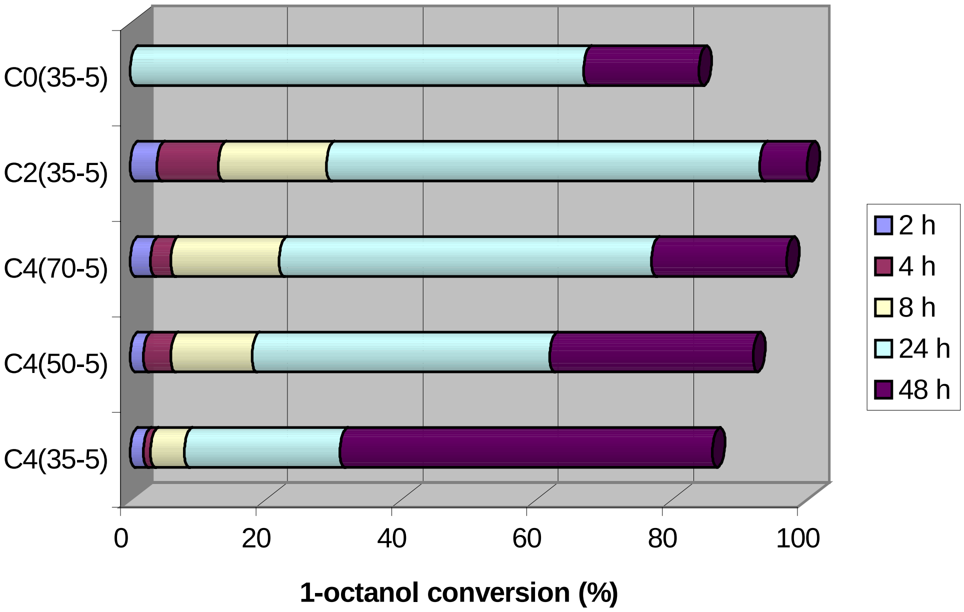


Figure 71. Catalytic activity test histograms of the Cn(X-5) series resins.

As it can be see from the table above, all the **C4(X-5)** resins have shown a certain catalytic activity, that improves as the amount of DVB increases, confirming the trend observed. However an important result emerging from the data is that the alcohol conversions are always considerably lower than those given by the **C2(35-5)** catalyst, expecially after 24 h, although the latter has only the 35% of DVB. In addition no significant differences were found between the data reported for the product **C0(35-5)** and the **C4(X-5)** series catalysts, thus indicating that this synthetic modification does not lead to a better transesterification catalyst. Finally, regarding to the aliphatic spacer lenght it may be suggested that the catalytic activity pass through a maximun in correspondence of the use of a dimethylenic spacer. It can therefore be assumed that the introduction of a dimethylenic spacer between the polymeric backbone and the catalytic centre is the best modification, because it considerably improves the overall catalytic performances.

13 - Cross-linked polystyrenic resins bearing a dimethylenic spacer and the tri[4-(trifluoromethyl)phenyl]tin carboxylate moiety

After having synthesized two groups of resins differently substituted, one bearing a substituent on the triphenyltin moiety and the other a dimethylenic or a tetramethylenic spacer, it was prepared a new kind of catalyst, having both the two modifications. In particular, new resins with the spacer lenght and the tin substituent giving the best catalytic performances, as suggested by the previous results, the dimethylenic spacer and an electron withdrawing group respectively, were synthesized. Actually for the latter, a group of electron withdrawing substituents was chosen, joined by the presence of a halogen. Thus three monomers and the corresponding resins bearing the dimethylenic spacer coupled to the triphenyl carboxylate moiety, having in the 4 position the substituent CF_3, F and Cl, respectively, were synthesized.

The following paragraph concerns the preparation of 3-(4-styryl)-propionic acid. This part is shared by the three monomers and for this reason it is reported only once, at the beginning of this section. Then, the synthesis of every single monomer through the esterification reaction between the opportune oxide and the 3-(4-styryl)propionic acid is described, as well as the polymerization reaction and the catalytic properties of the resins.

All the oxides and hydroxides used in this reactions have been synthesized in our laboratory in previously sections of this works, therefore their syntheses were omitted.

13.1 - Synthesis of 3-(4-styryl)propionic acid

The 3-(4-styryl)propionic acid was synthesized starting from the 3-phenylpropionic acid through a five steps synthetic pathway, reported in the **Figure 72**. In the first step the 3-phenyl-propionic acid (**I**) reacts with methanol leading to the corresponding methyl ester (**II**), purified by fractioned distillation. This esterification reaction, conducted using acetyl chloride, $AlCl_3$ as Lewis acid catalyst and CS_2 as solvent, has been made with the purpose to preserve the carboxylic moiety before the Friedel-Crafts acylation to the 4-acetyl derivative (**III**).

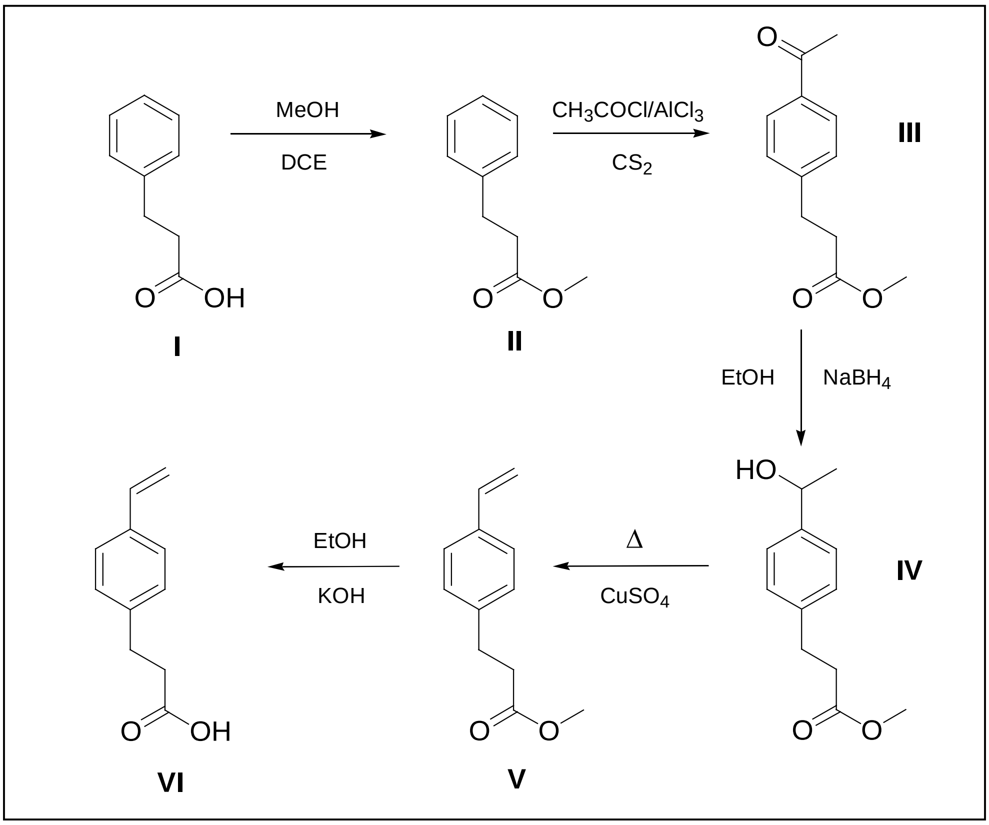


Figure 72. Synthetic pathway for 3-(4-styryl)-propionic acid

It has to be said that it may be possible to have the substitution also in 2 position, not only in the 4 one. In this case, however, it has been obtained only the 1,4-disubstituted derivative, owing to chemical hindrance of the substrate. The obtained ester has been purified by fractioned distillation.

The next step concerns the selective reduction of the ketonic carbonyl, using $NaBH_4$, giving the desired alcohol **IV**. This product was then submitted to thermal dehydration by distillation in the presence of $CuSO_4$, thus giving a vinyl double bond (**V**). The product **V** was finally hydrolyzed by NaOH, in order to obtain again the desired free carboxylic acid (**VI**).

13.2 - Synthesis of the tin-functionalized monomer tri(4-trifluoromethylphenyl)tin 3-(4-styryl)propionate

In previous works the synthesis of tin functionalized monomers was carried out by direct esterification of the suitable acid with the stannylated hydroxide or oxide. Consequently, the monomer tri(4-trifluoromethylphenyl)tin 3-(4-styryl)propionate (**VII**) was prepared through the reaction between 3-(4-styryl)propionic acid (**VI**) and tri(4-trifluoromethylphenyl)tin hydroxide, as depicted in **Figure 73**.

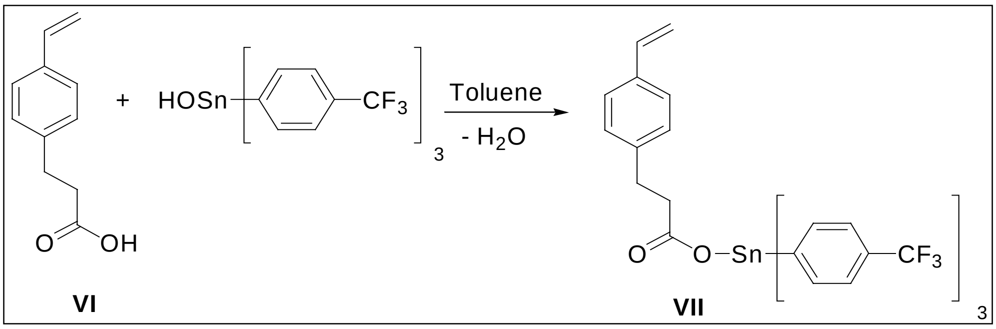


Figure 73. First attempt to synthesize the monomer tri(4-trifluoromethylphenyl)tin 3-(4-styryl)propionate through direct esterification.

In this case, however, this reaction was very difficult to achieve, leading to low yields, probably due to the high electron-withdrawing properties of the CF_3 group. For this reason, after various unsuccessful attempts, the direct esterification was discarted and the stannylated ester was synthesized by another way. To synthesize an ester the direct esterification, that occurs between acid and alcohol, is not the only reaction allowed: it is also possible to use the chloride, as well as the anhydride, of the acid, and the opportune hydroxide. In addition it has to be considered that the esterification is an equilibrium reaction and generally needs catalysis to improve its rate. For these reasons the 3-(4-styryl)propanoic chloride (**VIb**) was prepared by reaction of the 3-(4-styryl)propionic acid and oxalyl chloride, and then let to react with tri[(4-trifluoromethyl)phenyl]tin hydroxide, in presence of triethyl ammine, to neutralize the HCl acid formed as coproduct (**Figure 74**). The synthesis of the tin hydroxide is explained in the paragraph **10.1** of this work.

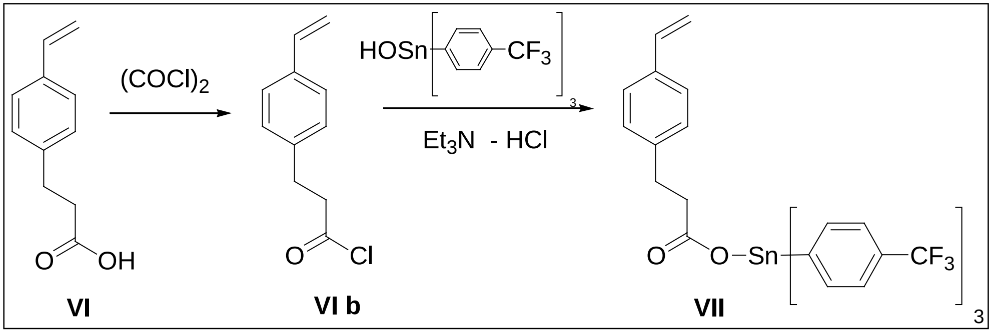


Figure 74. Synthesis of the monomer tri(4-trifluoromethylphenyl)tin 3-(4-styryl) propionate through chloride intermediate.

By this way the reaction is achieved with a sligh improving of the yields, although they still remain very low.

13.3 - Synthesis of the tin-functionalized resins of the C2(X-CF$_3$ 5) series

A resin was synthesized by radical co-polymerization of three comonomers: the stannylated monomer, added as 5%, 1,4-divinylbenzene, the cross-linking agent, as 35% and styrene, the remaining 60%. The amount of DVB

(35%) has been chosen in order to compare the catalytic conversions of the resulting resin with the ones previously prepared.

It has to be underlined actually that the catalytic activity tests performed in previous works shown a strong relationship beetween the amount of cross-linker and the the alcohol conversions, so the amount of DVB added plays a key role for the catalysis and it is a parameter to take care of very carefully.

The resin's general structure has been reported in **Figure 75**, while the polymerization data, including yields, are shown in the **Table 25**.

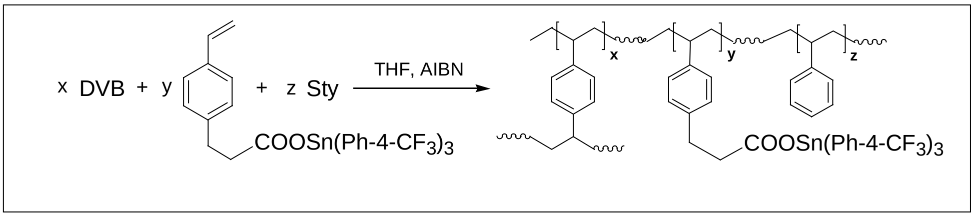


Figure 75. Synthesis of the resin bearing the monomer tri[4-(trifluoromethyl)phenyl] tin 3-(4-styryl)propionate.

The obtained resin has been labelled as **$C2(35-CF_35)$**, where **C2** indicates the presence of a dimethyl spacer, **35** represents the amount of DVB and **CF_35** represent the 5% of the tin containing monomer bearing the CF_3 group as substituent.

Table 25. Polymerization data and yields for the $C2(35-CF_35)$ resin.

	Sty (mmol)	*DVB (mmol)*	*Organotin monomer (mmol)*	*Yield (%)*	*mmol Sn/g cat*
$C2(35-CF_35)$	4.9	2.8	0.39	58	0.49

Owing to the complete insolubility of the obtained resin, its structure has been assessed by FT-IR spectroscopy, the only suitable technique.

In the figures below (**Figure. 76** and **77**) have been reported the FT-IR spectra of the stannylated monomer and the functionalized resin, respectively.

The occurrence of the polymerization involving the vinyl functionality has been confirmed by a strong decrease of the bands at 1627 and 1406 cm^{-1}, typical of vinyl double bond stretching and bending, respectively.

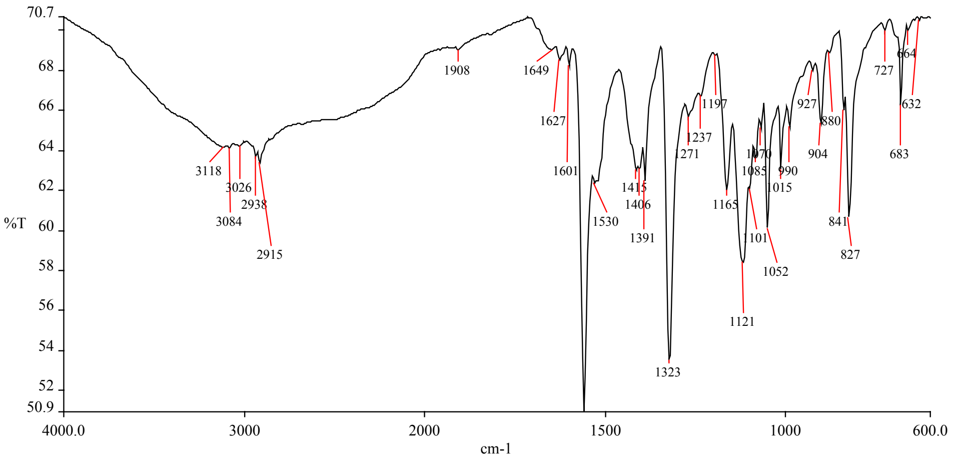


Figure 76. FT-IR spectrum of the monomer tri[4-(trifluoromethyl)phenyl]tin 3-(4-styryl)propionate.

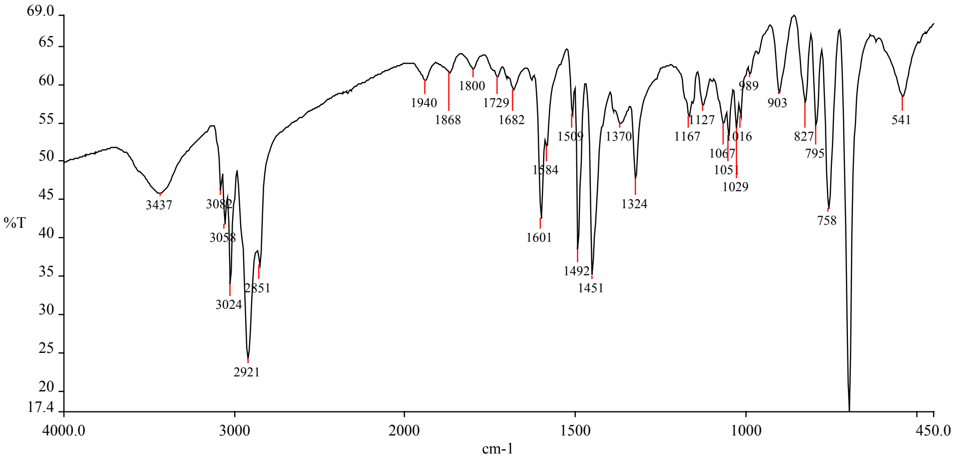


Figure 77. FT-IR spectrum of the resin bearing the monomer tri[4-(trifluoromethyl)phenyl] tin 3-(4-styryl)propionate.

13.4 - Assessment of catalytic activity of the C2(X-CF_3 5) resins

The synthesized resin underwent to catalytic activity test in order to evaluate its effectiveness as catalyst. To this purpouse a transesterification model reaction between ethyl acetate and 1-octanol has been used, as previously explained.

The conversion results are reported in **Table 26** and represented by histogram in **Figure 78**, where they are compared to its analogues resins, **C2(35-5)** and **C0(35-F5)**, performances.

Table 26. Conversions of 1-octanol in trasesterification reaction with ethyl acetate, catalyzed by resins of the C2(35-X 5) series.

Catalyst	***Conversion (%)***				
	2 h	**4 h**	**8 h**	**24 h**	**48 h**
C2(35-$CF_3$5)	8	18	30	45	71
C0(35-F5)	6	19	38	90	94
C2(35-5)	4	13	29	93	100

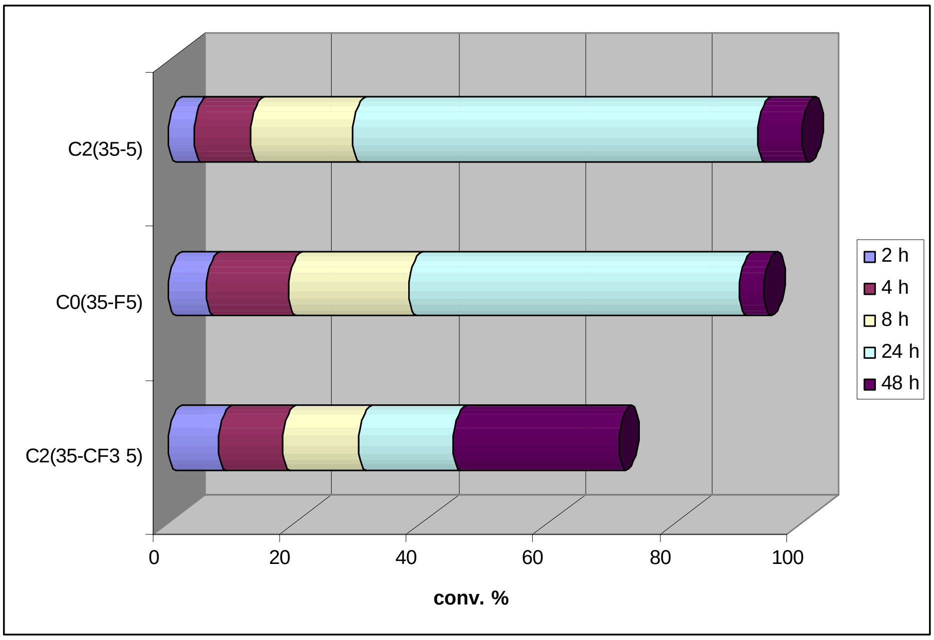


Figure 78. Catalytic activity test histogram of the C2(35-X5) resins.

The three catalysts achieve good conversion results after 8 hours. However, **C0(35-5)** and **C0(35-F5)** improve drammatically their performances after 24 hours, reaching the nearly complete conversion, while the resin **C2(35-CF$_3$5)** does not show this effect. In particular, it gives conversion values very lower than its analogue, not reaching the complete conversion even after 48 hours.

The reasons of this unexpected behaviour could be ascribed to the "too" high electron withdrawing nature of the CF$_3$ substituent, as described for the analogue **C0(20-CF$_3$5)**. In fact this feature increases the tin Lewis acidity, making the interaction Sn-O too strong, maybe quite irreversible. In additon important information could be obtained by a direct comparison of the two series of resins bearing CF$_3$ substituent, but, unfortunately, it wasn't possible, owing to the different amount of DVB they contain.

14 - Cross-linked polystyrenic resins bearing a dimethylenic spacer and the tri (4-fluorophenyl)tin carboxylate moiety.

14.1 - Synthesis of the tin-functionalized monomer tri(4-fluorophenyl)tin 3-(4-styryl)propionate

The synthesis of the stannylated monomer tri(4-fluorophenyl)tin 3-(4-styryl)propionate has been performed by direct esterification between 3-(4-styryl)propionic acid and bis[tri(4-fluorophenyl)tin] oxide, removing the water from the reaction mixture by azeotropic distillation with toluene, in order to shift the equilibrim towards the products (**Figure 60**). The synthetic pathway followed is reported on paragraphs **8.1** and **13.1**, respectively, where the synthetic procedures are carefully described.

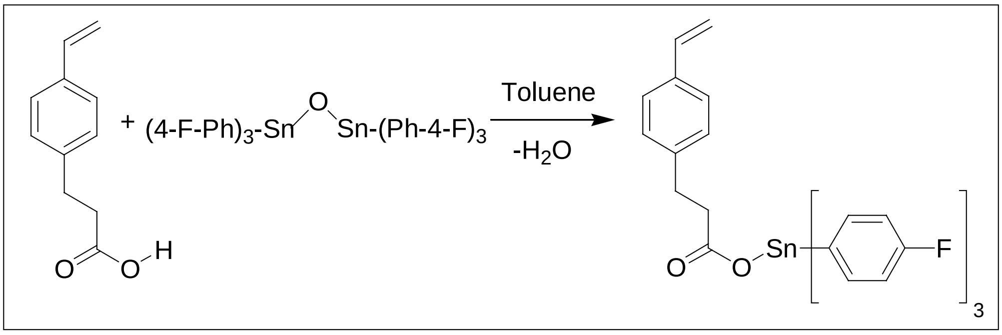


Figure 79. Synthesis of the monomer tri(4-fluorophenyl)tin 3-(4-styryl)propionate.

The obtained ester has been characterized by FT-IR as well as ^{1}H- and ^{13}C-NMR spectroscopy, both techniques confirming the structure of the desired product. In particular the ^{1}H-NMR spectrum displays the resonances of the vinyl protons at 5.2, 5.7 and 6.6 ppm and those related to aliphatic hydrogens at 2.7 and 2.9 ppm, proving that the reaction has not involved these functionalities (**Figure 80**).

Figure 80. ^{1}**H-NMR spectrum of the tri(4-fluorophenyl)tin 3-(4-styryl)propionate.**

Unfortunately the ^{13}C-NMR spectrum does not show the carbonyl resonance, due to the low solubility of the product as well as the long relaxation time required by a quaternary carbon. However, the ^{19}F- and ^{119}Sn-NMR spectra have been recorded, showing both only one signal, at -109 and -110 ppm, respectively.

It has to be considered also the FT-IR spectrum (**Figure 81**), where the absorption referred to the 3-(4-styryl)propionic acid at about 1700 cm^{-1} has disappeared, while is clearly visible a new band at 1629 cm^{-1} related to the carbonyl of the tin ester. Unfortunately, the latter has overlapped the band of double vinyl bond stretching, an useful tool for characterising this kind of products. However, in order to confirm the presence of a double bond, the absorption of the $CH=CH_2$ bending at about 990 cm^{-1} is visible.

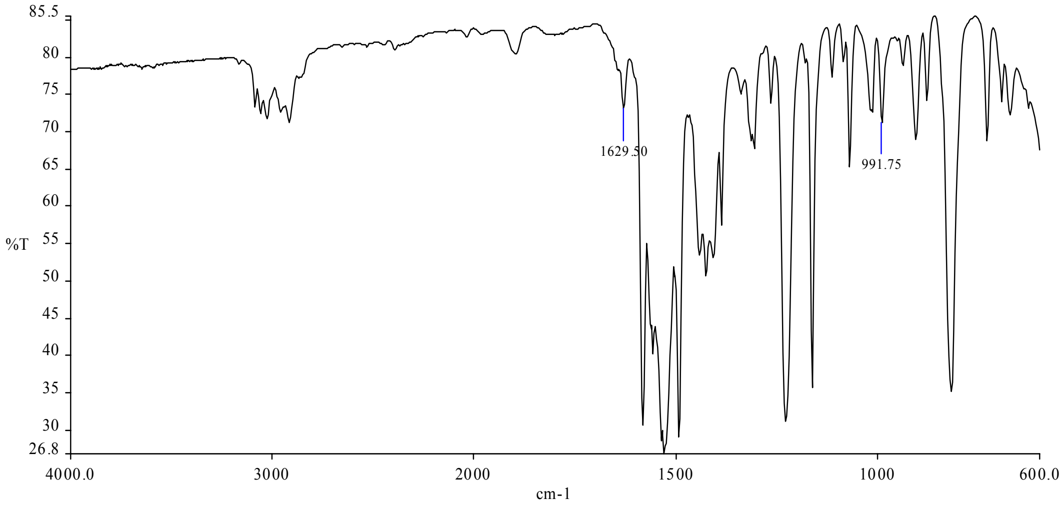


Figure 81. FT-IR spectrum of the monomer tri(4-fluorophenyl)tin 3-(4-styryl)propionate.

14.2 - Synthesis of the tin-functionalized resins of the C2(X-F5) series

This synthesis consist of a radical copolymerization of three comonomers, styrene, 1,4-divinylbenzene, acting as cross-linking agent, and stannylated monomer (**Figure 82**). The latter is always added in the same amount, 5%, while DVB content rises from 20% up to 70% and, consequentely, the styrene comes down. The reaction has been carried out in dry THF, using AIBN as thermal radical iniziator, keeping the mixture under vacuum and stirring for 3 days at 60° C.

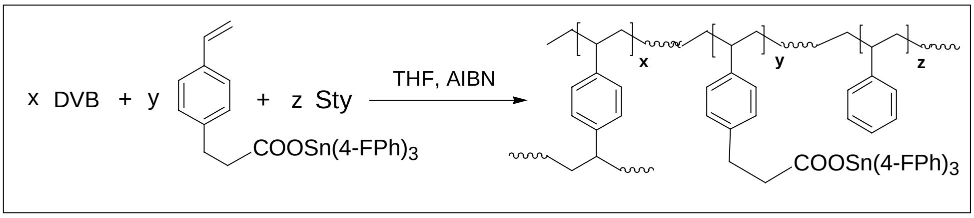


Figure 82. Synthesis of the resin bearing the monomer tri(4-fluorophenyl)tin 3-(4-styryl)propionate.

The polymeric derivatives have been recovered by filtration and then submitted to swelling in different solvents, in order to purify them from unreacted comonomers or oligomers.

The comonomers feeds and resins yields are reported in **Table 27**.

The obtained resins have been labelled as **C2(X-F5)**, where **C2** indicates the presence of a dimethylenic spacer, **X** represents the DVB amount that it is specific of each of the four different products, starting from 20% to a maximun of 70%, while **F5** concerns the amount of the tin containing monomer fixed at 5% and fluorine as tin substituent in the aromatic ring.

Table 27. Feed, yields and tin content for C2(X-F 5) series resins.

	Sty (mmol)	***DVB (mmol)***	***Organotin monomer (mmol)***	***Yield (%)***	***mmol Sn/g cat***
C2(20-F5)	10.4	2.8	0.69	20	0.51
C2(35-F5)	8.2	4.8	0.69	48	0.50
C2(50-F5)	6.2	6.9	0.69	77	0.50
C2(70-F5)	3.5	10.3	0.69	76	0.47

As in previous cases, these products have been characterized only by FT-IR spectroscopy, because their insolubility makes the other common analytical techniques unusable. The FT-IR spectrum recorded (**Figure 83**) confirms that the reaction succeded. It shows the absorption of the organotin carbonyl ester at about 1629 cm^{-1}, suggesting that it has not been involved in the polymerization reaction, and, moreover, the high decrease of the vinyl double bond bending.

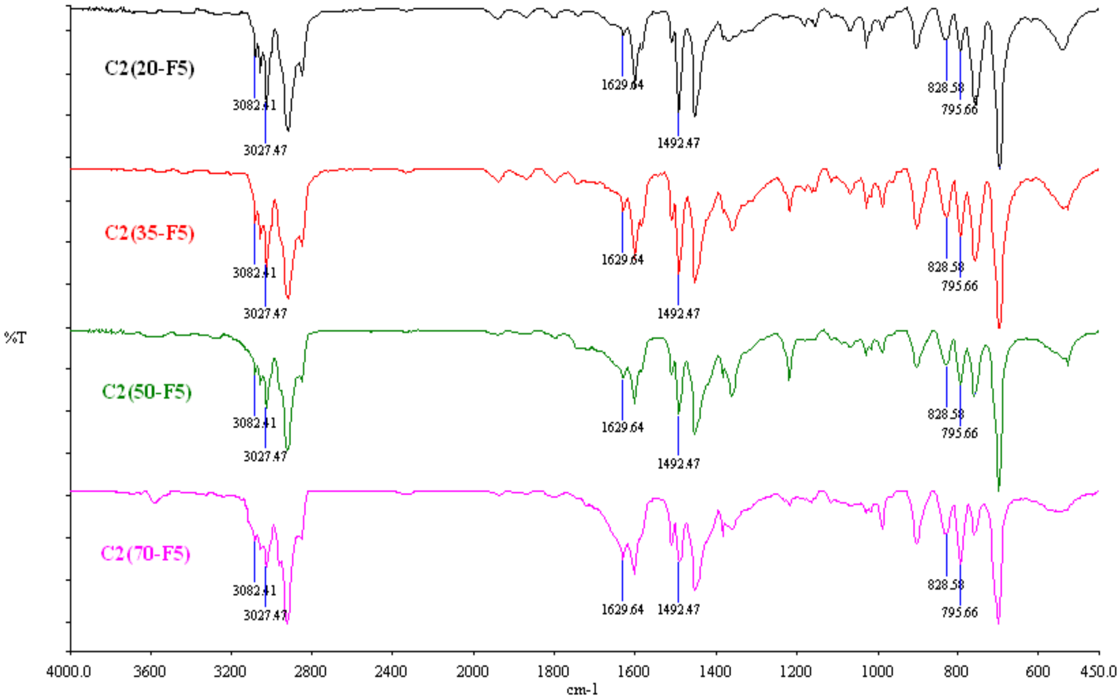


Figure 83. FT-IR spectra of the C2(X-F5) series resins.

14.3 - Assessment of catalytic activity of the C2(X- F5) series resins

The 1-octanol conversions obtained by the **C2(X-F5)** series catalysts in the transesterification reaction have been shown in **Table 28** and represented by histogram in **Figure 84**.

Table 28. Conversions of 1-octanol in trasesterification reaction with ethyl acetate, catalyzed by resins of the C2(X-F5) series.

Catalyst	***Conversione (%)***				
	2 h	**4 h**	**8 h**	**24 h**	**48 h**
C2(20-F5)	1	2	6	16	37
C2(35-F5)	3	8	18	62	92
C2(50-F5)	3	6	22	77	97
C2(70-F5)	4	13	29	93	100

All the resins of this series have shown catalytic activity that, as it can be inferred, is closely related to their cross linking degree. In particular the **C2(70-F5)** reach the complete conversion after 48, giving excellent results even after 24, although also the **C2(50-F5)** achieves high conversions. As expected the worst result has been given by **C2(20-F5)**, the resins having the lowest content of DVB.

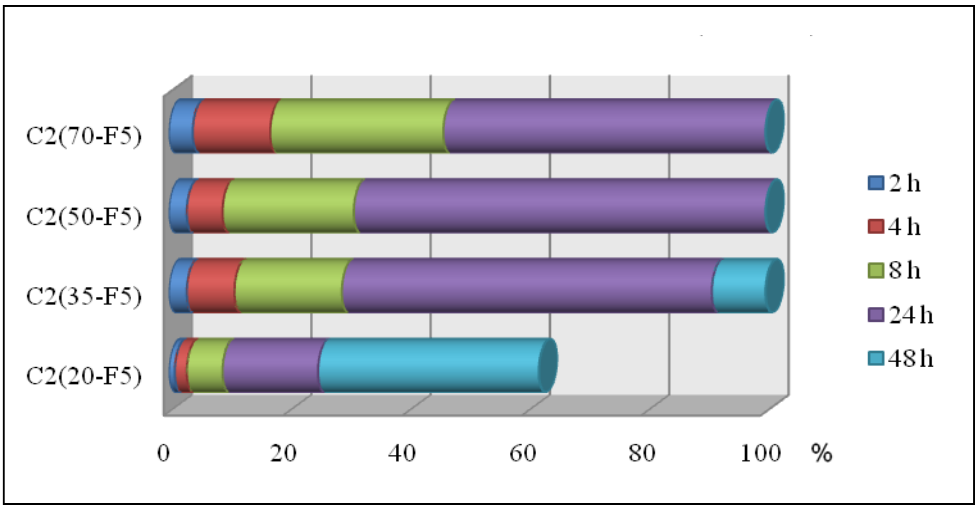


Figure 84. Catalytic activity test histogram for the C2(X-F5) series resins

15 - Cross-linked Polystyrenic Resins Bearing a Dimethylenic Spacer and the Tri(4-chlorophenyl)tin Carboxylate Moiety

15.1 - Synthesis of the tin-functionalized monomer tri(4-clorophenyl)tin 3-(4-styryl)-propionate

This product has been prepared by direct esterification of 3-(4-styryl)propionic acid with bis[tri(4-chlorophenyl)tin] oxide in toluene, removing the water formed by azeotropic distillation, using a Dean-Stark apparatus, in order to shift the equilibrium towards the desired product (**Figure 85**).

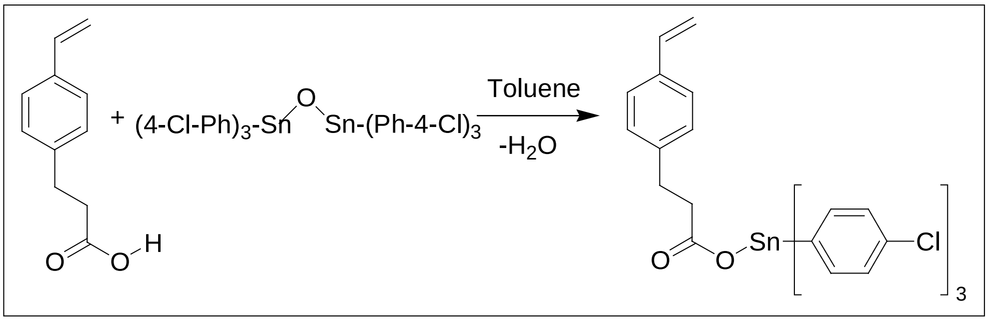


Figure 85. Synthesis of the monomer tri(4-chlorophenyl)tin 3-(4-styryl)-propionate.

The proceeding of the functionalization reaction has been monitored by FT-IR spectroscopy, through observation of progressive disappearing of the band centered at about 1700 cm^{-1}, related to the carbonyl stretching of 3-(4-styryl)propanoic acid and, on the other hand, the appearance of a new absorption, attributed to the organotin ester, at 1630 cm^{-1}, that, unfortunately, has overlapped the double vinyl bond stretching. However the presence of the double bond is confirmed by the bending absorption at 909 cm^{-1}.

The obtained monomer has been characterised also by NMR spectroscopy, confirming the structure of the desired product. In particular, the ^{1}H-NMR spectrum displays the resonance of the vinyl protons at 5.2, 5.7 and 6.7 ppm. In addition, in the ^{13}C-NMR spectrum a signal at 173 ppm, related to the new formed carboxylate group, can be observed.

15.2 - Synthesis of the tin-functionalized resins of the C2(X-Cl5) series

This reaction has been carried out through radical copolymerization of 1,4-divinylbenzene, styrene and the stannylated monomer tri(4-fluorophenyl)tin 3-(4-styryl)propionate (**Figure 86**). The latter has been always added in the same amount, corresponding to the 5%, while the content of the other two comonomers has been changed. In fact in previous studies it has been found that the optimal amount of tin functionalized monomer, in order to have the best catalytic performances, was 5%. On the contrary, regarding to the DVB content, its amount seemed to be related to the increase of the alcohol conversion. For these reasons we have tested 4 different systems, where the DVB feed rise from 20% up to 70%. Obviously, at the same time the styrene feed proportionally decreases.

The synthesis has been carried out dissolving the comonomers in dry THF, in the presence of AIBN as thermal radical iniziator. The reaction mixture was kept under vacuum and allowed to react for 3 days at 60 °C.

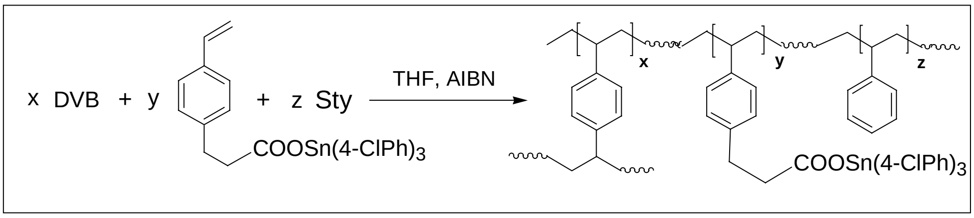


Figure 86. Synthesis of the resin bearing the monomer tri(4-chlorophenyl)tin 3-(4-styryl)propionate.

The obtained resins have been recovered by simple filtration and subsequently purified by swelling in diethyl ether and n-pentane, followed by further filtration. The comonomers feeds and polymerization yields are reported on **Table 29**.

The resins have been labelled as **C2(X-Cl5)**, where **C2** indicates the presence of a dimethylenic spacer, **X** represents the DVB amount that it is specific of each of the four different product, starting from 20% to a maximun of 70%, while the term **Cl5** represents the presence of chlorine as substituent and tin containing monomer amount equal to 5%.

Table 29. Feeding, yields and tin content of the C2(X-Cl5) series resins.

	Sty (mmol)	*DVB (mmol)*	*Organotin monomer (mmol)*	*Yield (%)*	*mmol Sn/g cat*
C2(20-Cl 5)	4.8	1.3	0.32	23	0.50
C2(35-Cl 5)	3.8	2.2	0.32	75	0.49
C2(50-Cl 5)	5.7	6.4	0.64	59	0.48
C2(70-Cl 5)	3.2	8.9	0.64	60	0.47

As in previous cases, owing to the complete insolubity of the prepared resins, the only analytical technique suitable to characterize these derivatives is the FT-IR spectroscopy.

Indeed, the spectra recorded for this series of resins are quite similar to those of the **C2(X-F5)** series, as it could be expected. It can be noticed the strong decrease of the band related to the double vinyl bond bending at 909 cm^{-1} and an adsorption at 1630 cm^{-1}, related to the organotin carboxylic ester, that persists, as desired.

15.3 - Assessment of catalytic activity of the C2(X-Cl5) series resins

The catalytic test results obtained by using the **C2(X-Cl5)** resins in the transesterification reaction of 1-octanol and ethyl acetate have been reported in **Table 30** and represented by histograms in **Figure 87**.

Table 30. Conversions of 1-octanol in trasesterification reaction with ethyl acetate, catalyzed by resins of the C2(X-Cl 5) series.

Catalyst	*Conversion (%)*				
	2 h	**4 h**	**8 h**	**24 h**	**48 h**
C2(20-Cl5)	2	9	21	82	100
C2(35-Cl5)	4	12	35	93	100
C2(50-Cl5)	6	19	53	100	100
C2(70-Cl5)	6	12	38	100	100

All the catalysts tested achieve the 100% of 1-octanol conversion after 48 hours. In particular **C2(50-Cl5)** and **C2(70-Cl5)** reach the complete conversion already after 24 hours, confirming that a higher crosslinking degree leads to better conversion values, as observed for all the catalysts investigated in this work. However, it can not be ignored the fact that the **C2(50-Cl5)** catalyst gives the best catalytic performances after 8 hours.

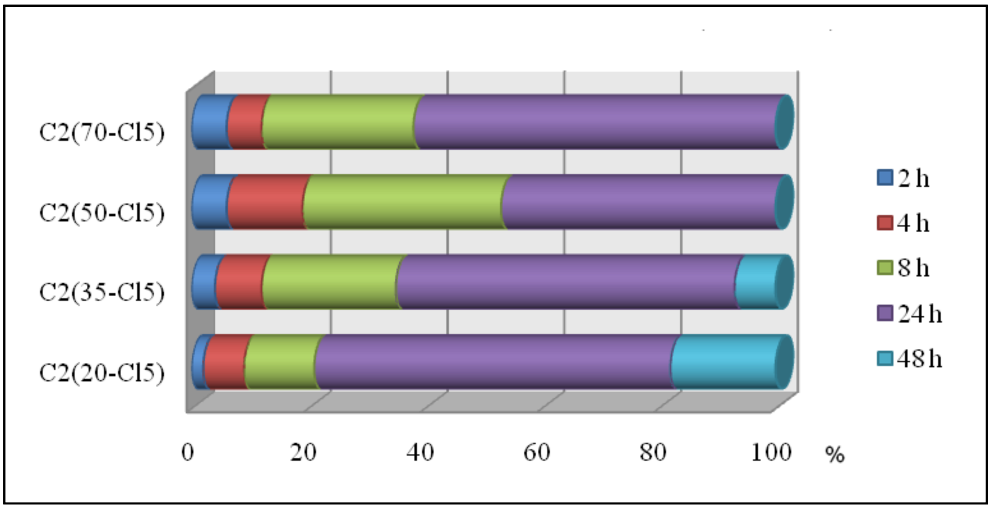


Figure 87. Catalytic activity test histogram for the C2(X-Cl5) series resins

16 - MCM-41 silica functionalized with the triphenìltin carboxylate moiety

Porous materials with regular geometry have recently received much attention owing to their scientific importance and great potentials in particular applications, such as catalysis, adsorption, separation, sensing and nanotechnology[131]. Depending on the predominant pore size, the porous materials are classified by IUPAC into three classes: microporous, having a pore diameter in the size range of 0.2-2.0 nm, mesoporous, diameter of 2.0-50.0 nm, and macroporous, having sizes exceeding 50 nm (**Figure 88**). Pores size of the mesoporous materials allows not only easy accessibility for molecules with size up to a certain range, but also possible control for functions depending on pore geometries.

Figure 88. Different classes of porous materials: macroporous, mesoporous and microporous size, respectively.

Recently, the demand for well ordered mesoporous materials has triggered major synthetic efforts due to commercial interest in their use as adsorbents, catalysts and catalyst supports owing to their high specific surface area, large specific volume and pore diameter. In 1990 was firsty reported[132] the preparation of mesoporous silica with uniform size distribution through intercalation of cetyltrimethylammonium cations into the layered polysilicate kanemite, followed by calcination in order to remove the organic moiety: this new material was named FSM-16. Then other studies has been performed, leading to the M41S family of silicate/aluminosilicate mesoporous molecular sieves[133], where long chain cationic surfactant were used as template or pore-forming agents. These materials have large uniform pore structures, high specific surface area and specific pore volume. Depending on the shape of the supramolecular templates and the respective resulting pore structure, four different phases can be distinguished: hexagonal-MCM-41, cubic MCM-48, lamellar MCM-50 and cubic octomer-$[(CTMA)SiO_{2.5}]_8$, a molecular species.

Hexagonal Mesoporous Silica (HMS) have been prepared using neutral amine as template[134]. Relative to MCM-41, HMS structures generally possess slightly disordered hexagonal structure and thicker walls, higher thermal stability upon calcination in air and a smaller crystalline size.

Anyway, the regular pore structure of these mesoporous materials can be used to introduce molecules or particles that are stabilized by the solid framework and spatially organized by the regular pores system. Practical applications or technology based on these materials utilize these unique characteristics and use them as substrate for many chemical and biological processes. As the mesoporous silica frame work provides optical transparency in visible and near UV range, the materials with optically active functional groups are promising candidates for optical applications, such as ligh filters, sensors, solar cells, etc. Another important application of functionalized mesoporous silica is in the field of catalysis and environmental remediation. In order to achieve desired applications, modifications of these mesoporous silica are required. As regard to the preparation, it can be said that silica source is usually condensed in the presence of structure directing templates and several additional processes such as teplate removal result in mesoporous materials. Therefore, the addition of functional elements is possible at three stages: functionalization of silica source, use of functional template and post modification of mesoporous silica. In addition, it has to be said that for modifying the mesoporous materials through covalent linkage between functional groups and silica frame-work, two major methods, grafting (post synthesis) and co-condensation (direct incorporation) have been investigated. Grafting is one of the modification methods for pre-synthesized mesoporous silica and introduction of various groups including amino, thiol and alkyl groups. It can be carried out by different procedures. For example, organic functional groups can by introduced by direct reaction of organosilanes to silica surface. Other functionalities can be fixed to the previously introduced functional groups through covalent bonding.

The grafting of specific organosilane into the preformed mesoporous silica is widely used for introduction of organic functions. The distribution and concetration of the groups are influenced by reactivity of the organosilane and their accessibility to surface silanols, which are limited by diffusion and steric factors. Another important method shoud be the co-condensation, where organosilane is hydrolytically condensed togheter with conventional silica sources, such as tetramethyl and tetraethyl orthosilicate. The one-pot pathway of this mathod provides some advantages, such as homogeneous distribution of the functional groups and short preparation time.

Thus, by grafting homogeneous catalysts on the inner surface of a porous silica, important features such as separability, reuse and selectivity might be addressed at the same time. In this Ph. D thesis the triphenyltin moiety has been grafted onto an inorganic support, with the aim of disposing of new heterogeneous transesterification catalysts. In particular MCM-41 silica seems to be useful because it is relative cheap and easily avaiable.

16.1 - Preparation of MCM-41 silica

As previously reported, MCM-41 silica is an high surface area silica and it is synthesized using a template agent (**Figure 89**). In this case, following a literature reported procedure[135], a solution of Cab-O-Sil M5, a silica precursor, and tetramethylammoniumhydroxide was added under stirring to a water solution of sodium silicate.Then to this solution further Cab-O-Sil M5 silica was added under stirring. To this resulting solution then a template solution of cetyl trimethylammonium bromide in water was added; heating was require in order to dissolve the template in water. After stirring for 1 hour the obtained white suspension was sealed and placed in an oven at 100°C for 2.5 days. The resulting suspension then was filtered and the residue was washed extensively with water until neutrality. After drying at 70°C in vacuum for 2 days, the solid was calcinated in air at 550°C, thus eliminating the template and forming an exagonal structure with monodimesional and parallel channels of 3 nm diameter.

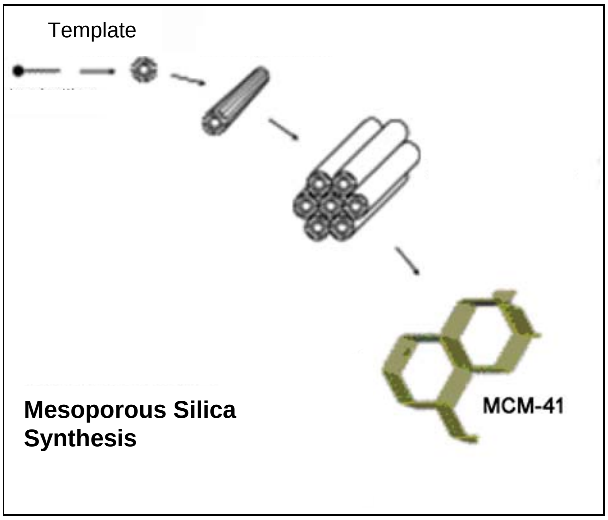


Figure 89. General synthesis of MCM-41 silica

16.2 - Functionalization of MCM-41 silica

16.2.1 - Synthesis of MCM-41-$(CH_2)_3$-CN

In the first step the silica has been activated at 70°C in vacuum for 2 hours. This process has the aim of eliminating trapped water inside the structure. Subsequently, the outer surface silanolic groups (10% of total amount) were protected by reaction with dimethoxydimethylsilane in refluxing toluene, in order to avoid the functionalization of these more reactive groups.

After 3 hours the protected silica has been functionalized adding an amount of 4-(trichlorosilyl)butyronitrile equals to 10% of surface silanolic groups and refluxing was continued overnight (**Figure 90**). The remaining surface silanolic groups were then protected with a large amount of dimethoxydimethylsilane and the mixture was refluxed for a further 3 hours. The obtained product, **MCM-41-$(CH_2)_3$-CN FE1** precursor, was filtered off, washed extensively with water and ethanol and finally dried overnight at 70° in vacuum.

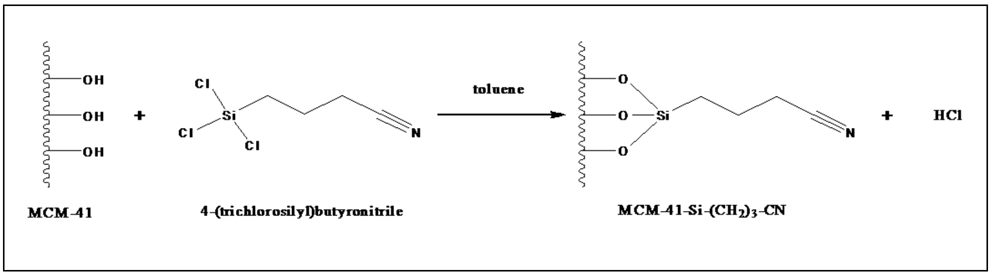


Figure 90. Synthesis of MCM-41-$(CH_2)_3$-CN

In order to synthesize silica having an higher functionalisation degree, two more products have been prepared, starting from a direct functionalized silica, obtained skipping the first protection reaction with dimethoxydimethylsilane: in the first case the MCM-41 silica reacts with the same amount of 4-(trichlorosilyl)butyronitrile previously used, leading to **MCM-41-$(CH_2)_3$-CN FE2** precursor, while in the second one it has been added a double amount of nitrile, in order to have a high functionalized silica, obtaining the **MCM-41-(CH_2)$_3$-CN FE3** precursor.

The functionalized silica have been characterised by FT-IR spectroscopy: in the recorded spectra an absorption at about 2255 cm^{-1}, related to the CN stretching, is visible, confirming the functionalization succeeded.

The BET analysis data, moreover, displays a decrease of the surface area, as expected in presence of a functionalized MCM-41 silica[135].

16.2.2 - Synthesis of MCM-41-$(CH_2)_3$-COOH

This reaction concerns the hydrolyses of the CN group previously anchored to the mesoporous silica.

In order to obtain the free carboxylic acid the three functionalized MCM-41 silica have been hydrolised by heating them for three hours in 50% aqueous sulphuric acid.

The mixture was then stirred overnight at room temperature, filtered, washed with water until neutrality and finally dried overnight in vacuum at 80°C (**Figure 91**).

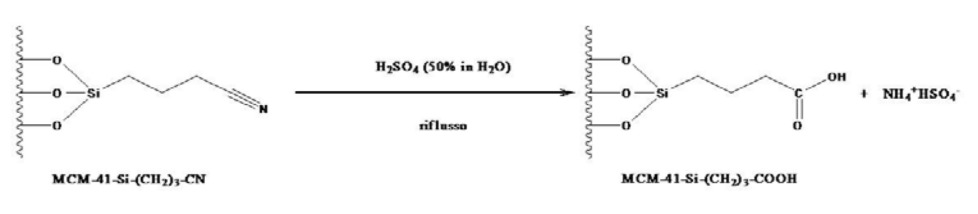


Figure 91. Synthesis of MCM-41-$(CH_2)_3$-COOH

The FT-IR spectra recorded show the disappearing of the band related to the CN group, while a new absorption at about 1700 cm^{-1}, related to the stretching of the carboxylic double bond is clearly visible for all three products. However, it has to be added that the bands of C-O and O-H bonds aren’t appreciable, because they have been overlapped by the high intensity absorptions of silica .

As regard to BET analyses, they show a further surface area decrease, as expected.

16.2.3 - Synthesis of MCM-41-$(CH_2)_3$-COOSn-Ph_3

Before proceeding with stannylation reaction, it has been necessary to estimate the amount of OH group, deriving from the carboxylic acid, free to be esterificated by triphenyltin hydroxide. For all the silica it has been assumed that, as desired, the 10% of the silanolic groups have been functionalized.

As reported for the resins monomers, the acid functionality of the **MCM-41-$(CH_2)_3$-COOH** react with triphenyltin hydroxide in refluxing toluene, removing the water formed by azeotropic distillation, using a Dean-Stark apparatus, in order to shift the equilibrium towards the desired product (**Figure 92**). In this case an excess of triphenyltin hydroxide has been added.

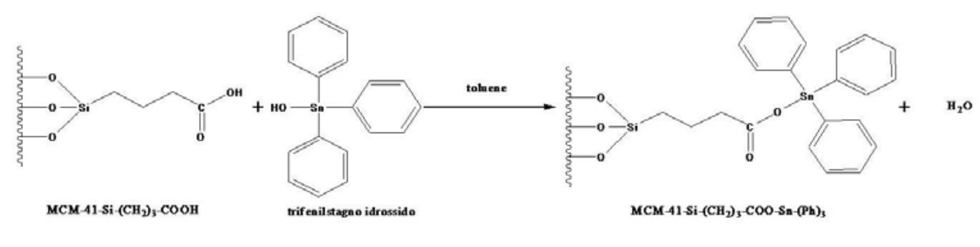


Figure 92. Synthesis of MCM-41-$(CH_2)_3$-COOSn-Ph_3

The stannylation reaction progress has been monitored by FT-IR (**Figure 93**), observing the shift of the band related to the carboxylic stretching from 1700 to about 1640 cm^{-1}, as desired. Finally, the stannylated obtained product has been filtered and then dried overnight in vacuum at 60°C.

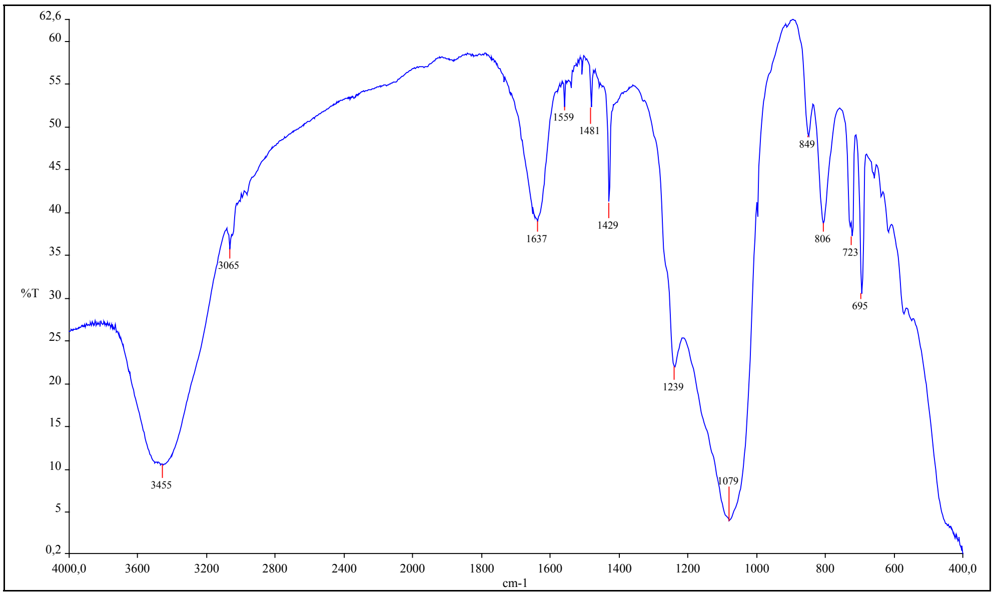


Figure 93. FT-IR spectrum of MCM-41-$(CH_2)_3$-COOSn-Ph_3

Observing the above spectrum, it is possible to noticed some important bands closely related to the silica nature. In particular the broad absorptions at about 3450 and 1079 cm^{-1} concern the stretching of the O-H bond and Si-O-Si, respectively; moreover at 3065 cm^{-1} is visible the band related to the aromatic C-H bond (whose bending is at about 695 cm^{-1}), while at 2966 and 1481cm^{-1} we can find the stretching and the bending of the aliphatic C-H. In order to evaluate the tin content in the functionalized silica an atomic absorption analyses has been performed after hydrolysis of the samples and subsequently dissolution in hydrofluoric acid. The data obtained are depicted in **Table 31**. They confirm the highest degree of functionalisation for the **FE3** silica, while unexpectedly the **FE2** sample has a low amount of tin, containing less metal than **FE1**, probably due to the absence of the first protection with dimethoxydimethylsilane.

Table 31. Tin content in the functionalized MCM-41 silica synthesized

Catalyst	*Tin amount in mg/g*[a]	*Tin amount in mmol/g*
FE1	130	$1.1 \cdot 10^{-3}$
FE2	85	$7.2 \cdot 10^{-4}$
FE3	210	$1.8 \cdot 10^{-3}$

[a] with respect to 1 gram of catalyst

16.3 - Assessment of catalytic activity of the MCM-41-$(CH_2)_3$-COOSn-Ph_3 silica

As reported for the organotin resins, these tin functionalized MCM-41 silica have been tested as catalysts in the transesterification model reaction between ethyl acetate and 1-octanol.

The 1-octanol conversions have been reported in **Table 32** and represented by histograms in **Figure 94**, where they have been also compared to **C2(35-5)** and **C4(35-5)** resins.

Table 32. Conversions of 1-octanol in trasesterification reaction with ethyl acetate, catalyzed by MCM-41-$(CH_2)_3$-COOSn-$(Ph)_3$ silica

Catalyst	***Conversione (%)***				
	2 h	**4 h**	**8 h**	**24 h**	**48 h**
FE1	40	50	81	98	100
FE2	7	23	24	62	91
FE3	29	48	96	99	100
C4(35-5)	2	3	8	31	86
C2(35-5)	4	13	29	93	100

In order to assess that the catalytic activity of these compounds is due to the triphenyltin moiety only, catalytic activity tests also to a not stannylated precursor, as **MCM-41-$(CH_2)_3$-COOH**, have been performed, giving no conversion at all, as expected.

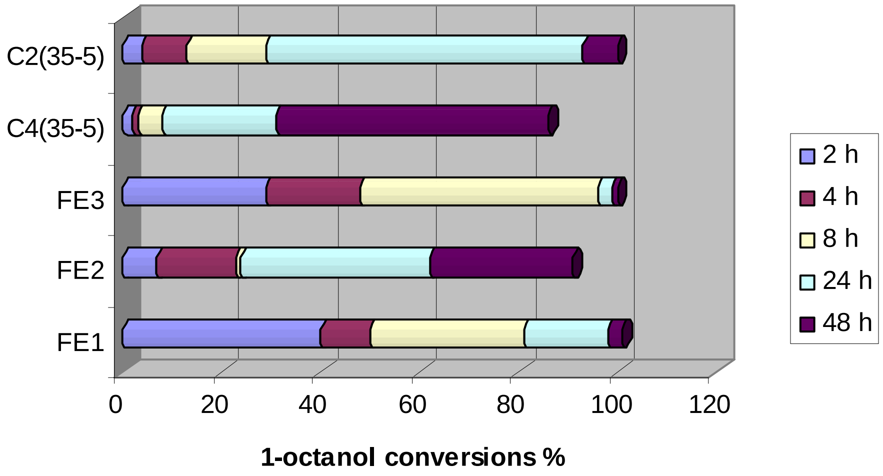


Figure 94. Conversions of 1-octanol histograms in transesterification reaction with ethyl acetate, catalyzed by MCM-41-$(CH_2)_3$-COOSn-Ph_3 silica

As it can be seen from the above data, all the prepared silica have provided high catalytic conversions, that appear to be strictly related to their functionalization degree. Indeed the best results are achieved by the **FE3** catalyst, the one having the highest tin content. However it has to be noticed that this statement is true only after 8 hour; in fact, after 4 hours, the conversions obtained by **FE1**, that actually posses half tin content, are vey close to the **FE3** ones. It can be suggested, therefore, that an important topic which needs to be more clearly investigated is the tuning of the tin amount, in order to optimize the catalytic activity of this kind of catalyst.

regarding to the data reported for **C2(35-5)** and **C4(35-5)** resins, chosen for the comparision because they bear an alyphatic spacer as well as the functionalzed silica, interesting information can be obtained. They show, in fact, considerably lower alcohol conversions than the silica until 8 hours, although after 48 the results are comparable for all the considered products. It could be hypothesised therefore that this different behaviour is likely due to high surface area of the silica and to their controlled pores size, that currently is not possible with the resins synthesized in this work. This way it could be favoured the interaction between tin and carboxylic group, through an easy diffusion of the reagents inside the resin structure. In addition the consequently possibility of having the desired pores size, simply using a different template agent, could be an attractive perspective for these products.

GENERAL CONCLUSIONS

AND

PERSPECTIVES

17 - General Conclusions and Perspectives

This Ph. D thesis has been devoted to the investigation of the most suitable structural modifications on polystyrenic resins bearing the triphenyltin carboxylate moiety in order to dispose of an effective heterogeneous catalyst for the transesterfication reaction. This has been carried out taking into account two different parameters, such as the Lewis acidity of tin atom and the accessibility to the catalytic centre that, as known, affect the overall catalytic performances of these products. To address this purpose two different synthetic pathways were followed.

The first one concerns the introduction on the aromatic ring of organic substituents, having different electronic properties, in conjugated position with respect to the tin atom. The aim of this modification was to tune opportunely the Lewis acidity of the metal centre. The tested substituents were, in chronological order of synthesis: F, SCH_3, CF_3 and Cl. As expected, the resins deriving from the monomer bearing the fluorine atom gave a higher alcohol conversion in a transesterification model reaction than those having the SCH_3 group as substituent. In fact, as known, the presence of an electron-withdrawing substituent such as F increases the Lewis acidity of tin, while SCH_3, that is electron-donor, reduces it. This result has led to the idea of introducing as tin substituent a strong electron-withdrawing group. To this purpose the CF_3 group was chosen, but its catalytic performances were the lowest of the series. It has been supposed, indeed, that a too high Lewis acidity degree actually affects the catalytic performances of the resins, probably due to the very strong interaction between the tin and the oxygen of the carboxylic moiety, leading to low catalysis, as reported in the previous paragraphs. Thus, it has been decided to test a substituent having close properties to the fluorine atom, which displays, as previously reported, both electron-withdrawing and donor properties, owing to inductive and mesomeric effect, respectively. Thus, a monomer bearing a chlorine atom as tin substituent has been synthesized, as well as the corresponding resins that, tested as transesterification catalyst, finally gave the best catalytic results of the overall series **C0(X-Y5). A**t the same time, a second modification was apported with the aim of increasing the catalytic centre mobility so as to obtain an easier contact between substrate and catalyst, and therefore better catalytic performances. To address it, the metal centre was spaced from the polymeric backbone by introducing an aliphatic spacer of a certain lenght. In particular, a dimethylenic and a tetramethylenic spacer have been introduced and the corresponding resins tested as catalyst: as a result the **C2(35-5)** sample gave the highest alcohol conversions of the series and, moreover, better results than those achieved by the **C0(X-F5)**, while **C4(35-5)** provides worse conversions**,** lower than those obtained by the **C0(35-5)** catalyst. Finally, the two above modifications have been combined in a unique product, thus preparing monomers and the corresponding resins having both the aromatic substituent $CF_{3,}$ F, or Cl and the C2 spacer. Unexpectedly, the obtained conversions, although they respected the conversion rank order observed for corresponding catalysts without the spacer, are lower than the ones obtained with the Cl substituent only. From this data it can be stated that tuning opportunely the Lewis acidity may play a fundamental role in improving the catalytic activity of these systems and this could be addressed with the use of a chlorine substituent, that although has electron-withdrawing properties lower than fluorine is able to increase the Lewis acidity of the tin atom, but not excessively. The latter feature, in fact, as we has previously observed, can have a negative effect on the catalysis process, leading to high affinity of the tin atom for the carbonyl oxygen that results in a more stable complex and a reduced alcohol conversion, as seen for the **C0(X-CF$_3$5)** series catalysts.

As regards the dimethylenic spacer, however, the consideration that could be made involves the overall structure of the resins. In fact, a clear decrease of the catalytic activity was observed for the catalyst bearing both the spacer and an electron withdrawing aromatic substituent, in the **C2(X-Y5)** series, while the **C2(35-5)** gave very high conversions. This seems to be related to the increased mobility of the metal centre, thus leading to higher catalytic activity, as for the **C2(35-5)** catalyst**,** but also, on the other hand, it can make easier the coordination between two catalyst molecules, which in this way are not anymore able to interact with the substrate, thus resulting in an overall less effective catalysis. In addition, this phenomenon, as observed in the catalytic activity test, seems to be more evident in presence of high Lewis acidity, induced by electron-withdrawing substituent, probabably due to a synergic effect, in this case, negative, of the two parameters.

By comparing the results obtained for the different classes of catalysts, the products giving the better catalytic performances at least after 24 hours of reaction, excepted for the **C2(35-5)** one, are those having a carboxylate stretching frequency at about 1620 cm^{-1}, typical of a tin atom in its tetracoordinated form.

Summarizing the reported data, it can be concluded that at the moment the resins of the **C0(X-Cl5)** series are those giving the best catalytic performances and for this reason they require to be further investigated. As known, the possibility of recovering and then reusing more times a catalyst is fundamental, considering their future industrial exploitation. Therefore this products will be submitted to recycling tests as soon as possible.

Anyway, in order to give a quite complete overwiev on the products properties, some more considerations about the catalytic activity test, referring to the overall product prepared, have to be made.

All the catalysts investigated in the present work provide a certain degree of catalytic activity, depending on their own structure and properties. The model reaction was also performed in the absence of catalyst, with the aim of detecting the presence of additional contributions other than those given by the organotin carboxylate moiety, resulting in the lack of conversion of ethyl acetate at all, as expected.

Even if NMR and IR techniques are not able to assess perfectly the absence of tin amounts trace or tin oligomers, no organometallic derivatives could be observed using one of these techniques when the final transesterification reaction mixture was analyzed. This is a point of relevant interest, because this observation implies that the organometallic ester would reamain unmodified under the transesterification conditions and no leaching from the solid support was reported in any case. However, a smart approach to the problem of detecting possible traces of tin is suggested in the literature, where the release in solution of catalytically active species from a heterogeneous support is hypothesized and defined using the locution ”Greek warriors from the Trojan Horse”[136]. So, in order to exclude the possibility of this presence, a simple experiment has been carried out, where the catalyst is throughly filtered off and separated from the transesterification mixture after an interrval of time, usually 24 hours; then the clear solution is allowed to react for further 24 h. At the end of the reaction the mixture is submitted to GC analysis. If no further reaction proceeding is observed, it can be concluded that there is no release of tin traces during the reaction. As regard to the catalyst prepared in this work, several of them underwent to this test: in all cases no conversion at all was detected, thus proving that in the absence of solid catalyst no transesterification reaction takes place, as expected and desired.

The recovered solid catalyst, after washing with diethyl ether and chloroform, were analyzed in order to assess their stability when submitted to the reaction conditions. In particular it has been observed that the FT-IR of the recovered catalysts look similar to those recorded before their use and, moreover, the carboxylic ester bond appears to be unchanged. As anexample, in **Figure 95** the FT-IR spectra of the **C0(35-CF$_3$5)** catalyst are reported, before and after its use in the model transesterification reaction.

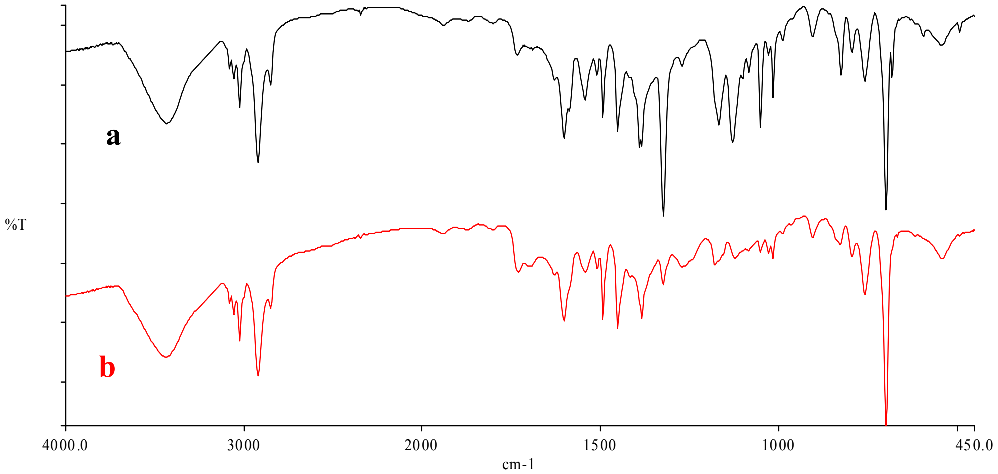


Figure 95. FT-IR of native C0(35-CF35) catalyst (a) and after transesterification reaction (b).

Considering all the above reported arguments, it can be safely said that any significant tin leaching from grafted materials into the reaction medium do not occurr, the organometallic ester is stable under the transesterification conditions and the reaction takes place only at the solid- liquid interface.

Another important feature of these compounds is that to an increase of the amount of cross-linking agent, in this case DVB, corresponds an improvement of the alcohol conversions operated by these catalysts, until to a maximun of 70% of DVB, although in the **C2(X-Cl5)** series, the catalyst **C2(50-Cl5)** gives better results, more evident after 4 and 8 hours, than its analogue **C2(70-Cl5).**

An explanation of this behaviour might be the enhancement of the specific surface area of the catalyst. This is reported in the literature[137] for systems containing styrene and DVB and attributed to the creation of smaller pores, but it refers particularly to only those having a maximum of 10% of cross-linking agent and until to a limit value of surface area about some hundreds of m^2/g[138,139]. However, it has to be considered that an excessive increase of cross-linking degree results in a reduced accessibility to the catalytic centre by the substrate, thus producing a decrease of catalytic activity. So, further investigation to do on these materials could be to find the opportune DVB amount leading to a higher quantity of surface area which is effectively accessible by the substrate.

In addition, it could be useful to prepare these catalysts by emulsion polymerization in water as reaction medium, in order to obtain a material with a controlled particle size. In fact, a catalyst having a homogeneous microsphere shape could allow to know how tin is distributed inside the resin, which actually represents a key point of this work, not yet completely elucidated, and therefore needing further investigations. In a past work[140] an unsuccessful attempt of this kind of synthesis was made.

Finally, another interesting possibility in this contet could be the change of the feed amount of tin into the resin, that represents actually a key factor in the catalytic performances, in order to make less important the interaction between tin atoms and to find the optimal fuctionalization degree, that at the moment is assumed to be 5%. To evaluate the importance of this contribution, catalysts having a lower tin-functionalized monomer amount should be synthesized and tested.

EXPERIMENTAL

PART

18 - Characterization of products

- ^{1}H-NMR, ^{19}F-NMR e ^{13}C-NMR spectra were recorded on Varian Gemini 300, Mercury 400 ed Inova 600 spectrometers, working respectively at 300, 400 e 600 MHz and using $CDCl_3$ or DMSO solutions and TMS or $CFCl_3$ as internal standard.

- The ^{119}Sn-NMR solution spectra were recorded on a Bruker AMX 500 or on a Varian Mercury 400 NMR spectrometer, using $CDCl_3$ solutions and tetramethylsilane as external standard.

- Solid state ^{117}Sn-NMR spectra were recorded at 89.15 MHz on a Bruker Avance 250 spectrometer, using tetra(cyclohexyl)tin as external standard.

- Oxygen elemental analyses were performed by REDOX s.n.c., Milano; carbon, hydrogen and tin elemental analyses were performed by Centre National de la Recherche Scientifique (CNRS), Service Central d'Analyse, Vernaisson (France).

- Infrared spectra in $CHCl_3$ solution or on KBr pellets were recorded on Perkin Elmer 1750 FT-IR and Spectrum One spectrometers interfaced with a computer, using for the solid state analysis the ATR technique.

- Tin amounts in the fuctionalized silica were determined after atomization in graphite fornace using a Varian SpectrAA-100 Spectrometer interfaced with Varian GTA-110 autosampler.

- Surface areas of the silica samples were measured by a Carlo Erba SORPTY 1750 BET surface area analyser.

- Mass spectrometric determinations were performed on a Thermo Finnigan Mat 95 xp instrument, using electron impact ionization.

- The catalytic activity test conversion was assessed by gas-chromatography, using an Agilent 6890 instrument equipped with a capillary methylsilicone column and having an Agilent 5973M mass spectrometer detector.

- Scanning electron microscopy (SEM) analyses were performed on a EVO® 50 Series instrument (LEO ZEISS) operating at 20 keV with either 4Q-BSD (4 Quadrant Back Scattered Detector) or VPSE (Variable Pressure Secondary Electron) detectors, and equipped with INCA Energy EDS microanalysis system for SEM. INCASmartMap has been used imaging the spatial variation of elements in a sample.

19 - Chemicals and Materials

Chemicals were supplied by Sigma Aldrich and generally used as received. Solvents were purified using standard techniques and stored under nitrogen[141].

19.1 - Tetrahydrofuran (THF)

Commercial THF was left in contact for some hours with KOH, distilled on Na under nitrogen atmosphere and then ridistilled on Na and benzophenone.

19.2 - Styrene and 1,4- Divinylbenzene

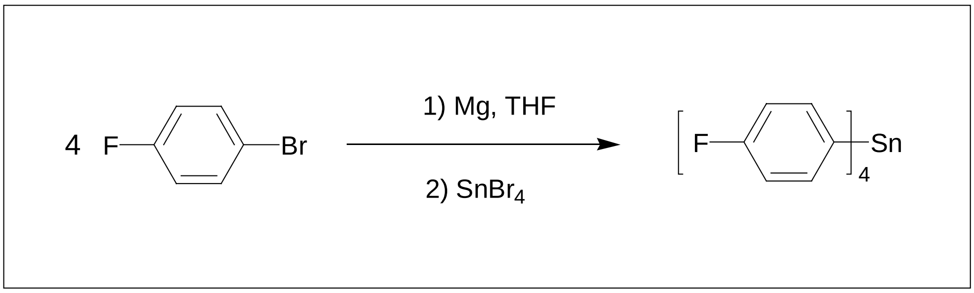
Commercial products have been treated with NaOH 5% solution in order to remove polymerisation inhibitors and subsequently dried for 4-5 hours over anhydrous $MgSO_4$. Moreover styrene was distilled at 16 mmHg (b.p. = 35°C), 1,4-divinylbenzene was distilled at 4 mmHg (b.p. = 40°C). The distilled products were stored at 0°C under nitrogen atmosphere.

19.3 - α, α'-azo-bis-isobutyrronitrile (AIBN)

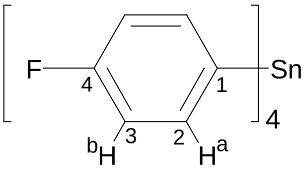
Commercial AIBN was crystallized from absolute ethanol before use and stored at 4 °C.

20 - Synthesis of polystyrenic resins bearing the tri(4-fluorophenyl)tin carboxylate moiety

20.1 - Tetrakis(4-fluorophenyl)tin (M.W. = 499.08 g/mol)



The first step of this reaction was the synthesis of a Grignard derivative.
Thus 4.2 g (28.1 mmol) of 1-bromo-4-fluorobenzene in 20 ml of anhydrous THF was slowly added to 0.75 g (30.9 mmol) of metallic magnesium suspended in anhydrous THF in a three neck flask equipped with stirrer, reflux condenser and dropping funnel, kept under nitrogen atmosphere. After addition, the mixture was stirred at room temperature for one hour. Then 2.96 g (6.75 mmol) of stannic bromide in 20 ml of toluene was added dropwise in 1.5 hours. The obtained light brown mixture was refluxed for 1 hour and stirred overnight at room temperature, then slowly hydrolized with water and NH_4Cl. The solution was extracted with diethyl ether and the organic phase was dried with anhydrous Na_2SO_4.
The organic solvent was distilled off and the solid obtained purified by crystallization from cyclohexane, to give white crystals.
Yield: 2.55 g (75%).



^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS):
7.1 (m, 8H, **H^b**), 7.5 (m, 8H, **H^a**).

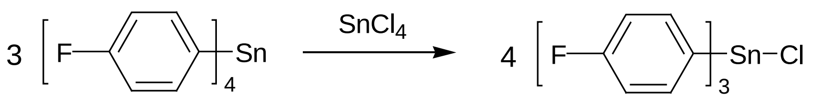
^{13}C-NMR in CDCl$_3$ (δ in ppm referred to TMS):
116.5 (d, $^2J(^{13}C-^{19}F) = 19.8$, **C$_3$**), 132.3 (d, $^4J(^{13}C-^{19}F) = 4.1$, **C$_1$**), 138.9 (d, $^3J(^{13}C-^{19}F) = 7.3$, **C$_2$**), 164.3 (d, $^1J(^{13}C-^{19}F) = 249$, **C$_4$**).

^{119}Sn-NMR in CDCl$_3$ (δ in ppm referred to SnMe$_4$): -120.

^{19}F-NMR in CDCl$_3$ (δ in ppm referred to CFCl$_3$): -111.

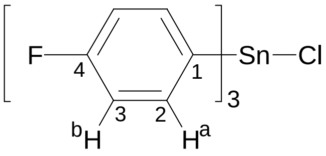
FT-IR in NaCl (cm^{-1}):
3085-3033 (stretch. CH arom.), 1581-1493 (stretch. C=C arom. ring.), 1225 (stretch. C-F), 818 (bend. CH 1,4-disubst. arom.).

20.2 - Tri(4-fluorophenyl)tin chloride (M.W.= 439.43 g/mol)



4.44 g (8.90 mmol) of tetrakis(4-flurophenyl)tin were added to 0.35 ml of $SnCl_4$ (2.96 mmol) in a 50 ml round-bottomeded flask equipped with a magnetic stirrer and a reflux condenser bearing a drying tube. This reaction mixture was heated between 200-210 °C for 2.5 h, to give a dark red solid which was crystallized from hexane.

Yield: 3.45 g (66%).



^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS):
7.2 (m, 6H, **H^b**), 7.6 (m, 6H, **H^a**).

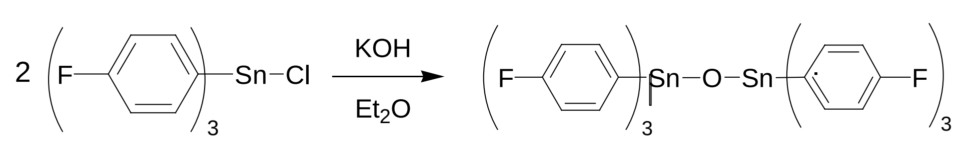
^{13}C-NMR in CDCl$_3$ (δ in ppm referred to TMS):
116.9 (d, $^2J(^{13}C\text{-}^{19}F) = 20.1$, **C$_3$**), 132.1 (d, $^4J(^{13}C\text{-}^{19}F) = 4.1$, **C$_1$**), 138.1 (d, $^3J(^{13}C\text{-}^{19}F) = 7.8$, **C$_2$**), 164.8 (d, $^1J(^{13}C\text{-}^{19}F) = 251.1$, **C$_4$**).

^{119}Sn-NMR in CDCl$_3$ (δ in ppm referred SnMe$_4$): -39.

^{19}F-NMR in CDCl$_3$ (δ in ppm referred to CFCl$_3$): -109.

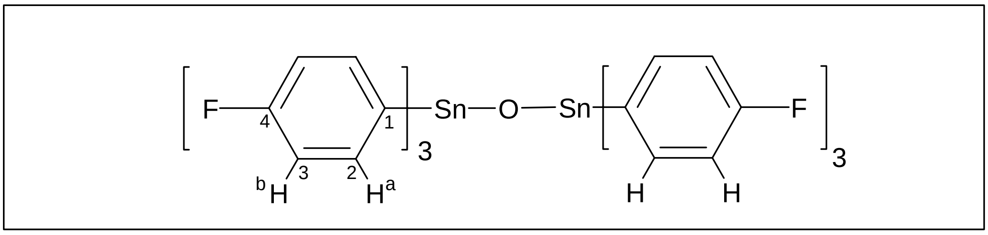
FT-IR in NaCl (cm^{-1}):
3080-3033 (stretch. CH arom.), 1583-1493 (stretch. C=C arom.), 1231 (stretch. C-F), 818 (bend. CH 1,4 disubst. arom.).

20.3 - Bis[tri(4-fluorophenyl)tin] oxide (M.W. = 823.96 g/mol)



In a 250 ml round bottomed flask equipped with a magnetic stirrer and reflux condenser 16.0 ml of a 10% aqueous solution of KOH were added under stirring to 3.50 g of tri(4-fluorophenyl)tin chloride (8.0 mmol) dissolved in 80 ml of diethyl ether. The reaction mixture was refluxed for 1 h to give a white solid product. After cooling at 25 °C the product was purified by crystallization from hexane.

Yield: 2,65 g (80%).



^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS):
7.0 (m, 12H, **H^b**), 7.4 (m, 12H, **H^a**).

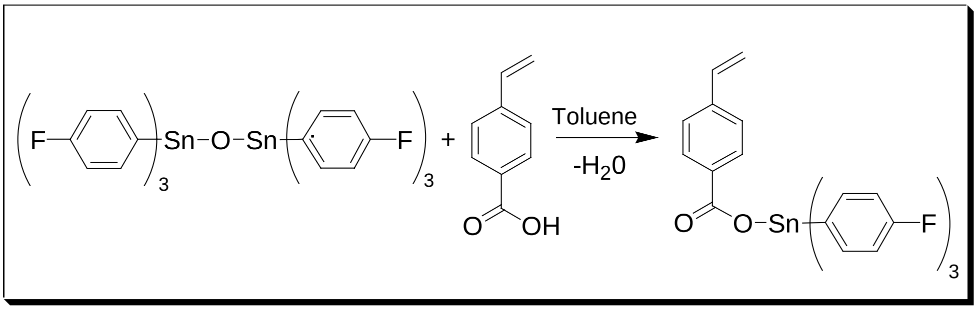
^{13}C-NMR in CDCl$_3$ (δ in ppm referred to TMS):
116.4 (d, $^2J(^{13}C-^{19}F) = 20.1$, **C$_3$**), 135.1 (d, $^4J(^{13}C-^{19}F) = 4.2$, **C$_1$**), 138.2 (d, $^3J(^{13}C-^{19}F) = 7.2$, **C$_2$**), 164.5 (d, $^1J(^{13}C-^{19}F) = 249$, **C$_4$**).

^{119}Sn-NMR in CDCl$_3$ (δ in ppm referred al SnMe$_4$): -76.

^{19}F-NMR in CDCl$_3$ (δ in ppm referred to CFCl$_3$): -110.

FT-IR on NaCl (cm^{-1}):
3085-3033 (stretch. CH arom.), 1583-1492 (stretch. C=C arom. ring), 1223 (stretch. C-F), 818 (bend. CH 1,4-disubst. arom.), 748 (stretch. Sn-O-Sn).

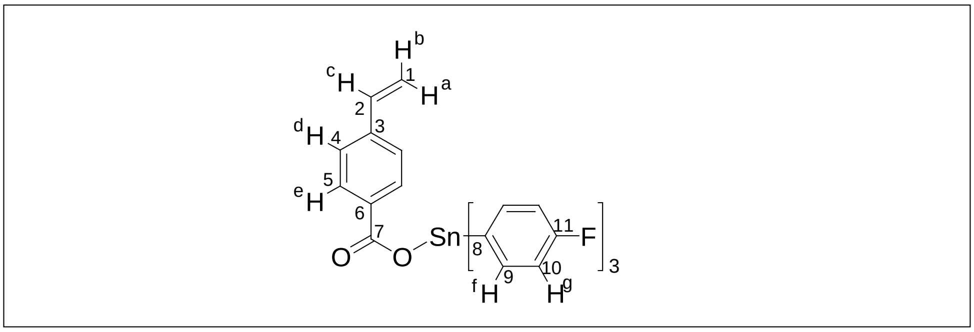
20.4 - Tri(4-fluorophenyl)tin 4-vinylbenzoate (MW = 551.13 g/mol).



In a 250 ml round bottomed flask equipped with a magnetic stirrer, reflux condenser and a Dean-Stark apparatus 2.50 g of bis[tri(4-fluorophenyl)tin] oxide (3.00 mmol) were added to 1.05 g of 4-vinylbenzoic acid (6.0 mmol) dissolved in 80 ml of toluene. Then hydroquinone was added and the reaction mixture heated to reflux until no more water formation was seen in the Dean-Stark apparatus. The reaction progress has been monitored by FT-IR spectroscopy.

The mixture was allowed to cool and the solvent was evaporated under reduced pressure leaving a crude product that was purified by crystallization from ethanol and water.

Yield: 3.05 g (89 %).



^{1}H-NMR in $CDCl_3$ (δ in ppm referred to TMS):
5.3 (d, $^{3}J(H_{cis},H)$=11 Hz, 1H; =$CH_{trans}\mathbf{H_{cis}}$), 5.8 (dd, $^{3}J(H_{trans},H)$=17.4 Hz, 1H; =$\mathbf{CH_{trans}}H_{cis}$), 6.7 (dd, $^{3}J(H,H_{cis})$=11 Hz, $^{3}J(H,H_{trans})$=17.4 Hz, 1H; **=CH**), 7.2 (m, 6H, **H^{g}**), 7.4 (d, $^{3}J(H,H)$=9.7 Hz, 2H; **H^{d}**), 7.8 (m, 6H, **H^{f}**), 8.1 (d, $^{3}J(H,H)$=9.7 Hz, 2H; **H^{e}**).

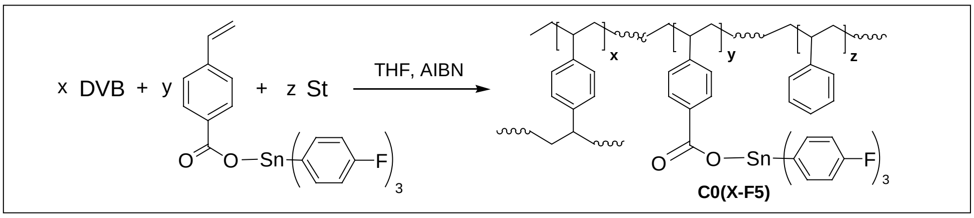
^{13}C-NMR in $CDCl_3$ (δ in ppm referred to TMS):
116.8 (d, $^{2}J(^{13}C-^{19}F)$ = 19.7, **C$_{10}$**), 116.9 (**C$_{1}$**), 126.3 (**C$_{4}$**), 129.4 (**C$_{6}$**), 131.3 (**C$_{5}$**), 133.4 (d, $^{4}J(^{13}C-^{19}F)$ = 4.0, **C$_{8}$**), 136.3 (**C$_{2}$**), 139.0 (d, $^{3}J(^{13}C-^{19}F)$ = 7.2, **C$_{9}$**), 142.3 (**C$_{3}$**), 164.8 (d, $^{1}J(^{13}C-^{19}F)$ = 250, **C$_{11}$**), 173.2 (**C$_{7}$**).

^{119}Sn-NMR in $CDCl_3$ (δ in ppm referred to $SnMe_4$): -113.

^{19}F-NMR in $CDCl_3$ (δ in ppm referred to $CFCl_3$): -110.

FT-IR on NaCl (cm^{-1}):
3088-3039 (stretch. CH arom.), 1565 (stretch. C=O), 1493 (stretch. C=C arom. ring), 1230 (stretch. C-F), 990-918 (bend. $CH=CH_2$ vinyl), 819 (bend. C-H 1,4-disubst. arom. ring).

20.5 - C0(X-F5) cross-linked polystyrenic resins



A free radical polymerization method was employed to copolymerize the synthesized stannilated monomer with 1,4 divinylbenzene and styrene. The reaction was carried out in dry THF using AIBN as a thermal radical iniziator (1% by weight with respect to the co-monomers' mixture).

All the solutions, prepared under nitrogen atmosphere into a polymerization vial, were submitted to three freeze-thaw cycles, in order to remove all the oxygen.

The vials were kept at 60°C under stirring for three days. The insoluble polymers obtained were filtered and washed with ethanol, then purified by repeated swelling in diethyl ether and n-pentane, followed by filtration. Finally the solvent was evaporated under vacuum to give a white coloured material.

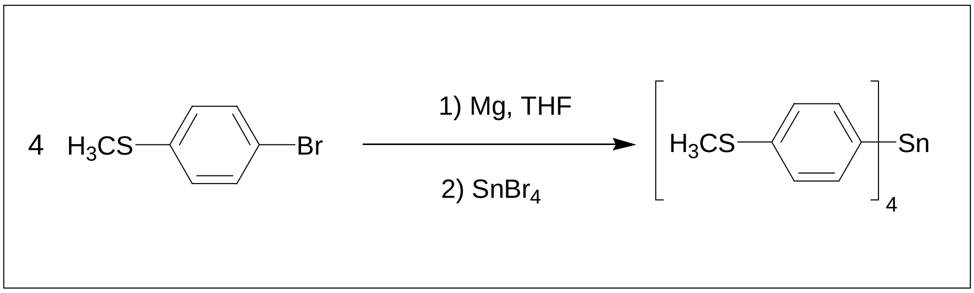
Polymerization yields and composition of the copolymers are reported in **Table 33**.

Table 33. Polymerization data: feeding, yields and tin content for the C0(X-F5) resins.

	Sty (mmol)	*DVB (mmol)*	*Organotin monomer (mmol)*	*Yield (%)*	*mmol Sn/g cat*
C0(20-F5)	13.5	3.61	0.902	52	0.509
C0(35-F5)	11.8	6.90	0.985	79	0.498

21 - Synthesis of polystyrenic resins bearing the (4-thiomethylphenyl)tin carboxylate moiety

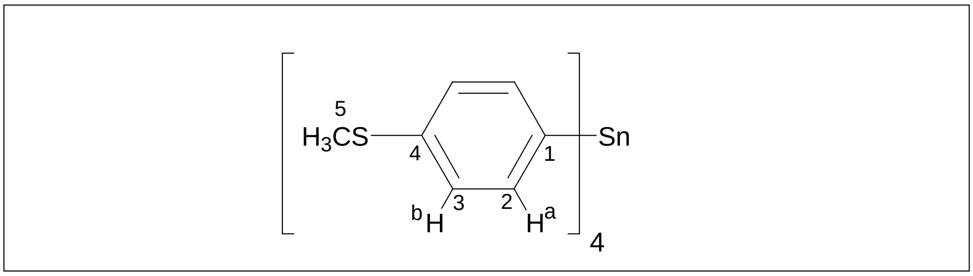
21.1 - Tetrakis(4-thiomethylphenyl)tin (M.W. = 610.7 g/mol)



The first step of this reaction was the synthesis of the Grignard derivative. A solution of 10 g (49.0 mmol) of 4-thiomethylbromobenzene in 40 ml of anhydrous THF was added slowly to 1.21 g of metallic magnesium (54.0 mmol) suspended in dry THF in a 250 ml three necked flask equipped with stirrer, reflux condenser, dropping funnel and under nitrogen atmosphere, giving a dark green solution. After the addition was completed, the mixture was stirred at room temperature for one hour. Then a solution of 5.15 g of stannic bromide (11.8 mmol) in 20 ml of anhydrous toluene was added dropwise in 1.5 hours. The formation of a solid was observed, changing its colour from yellow to brown. Then the light brown suspension obtained was refluxed for 2 hours and stirred overnight at room temperature, then slowly hydrolized with water and NH_4Cl. The solution was extracted with diethyl ether and the organic phase was with anhydrous Na_2SO_4.

The organic solvent was distilled off under reduced pressure leaving a yellowish solid that was purified by crystallization from cyclohexane, to give white crystals.

Yield: 4.00 g (56%).



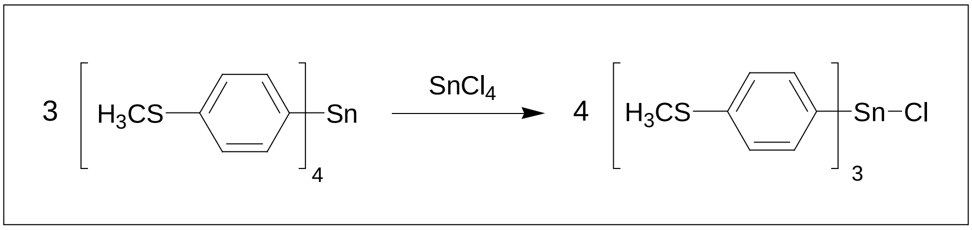
^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS):
2.5 (s, 12H, **SCH$_3$**), 7.2 (m, 8H, **H^b**), 7.5 (m, 8H, **H^a**).

^{13}C-NMR in CDCl$_3$ (δ in ppm referred to TMS):
15.7 (**C$_5$**), 126.3 (**C$_3$**), 133.7 (**C$_1$**), 137.7 (**C$_2$**), 140.6 (**C$_4$**).

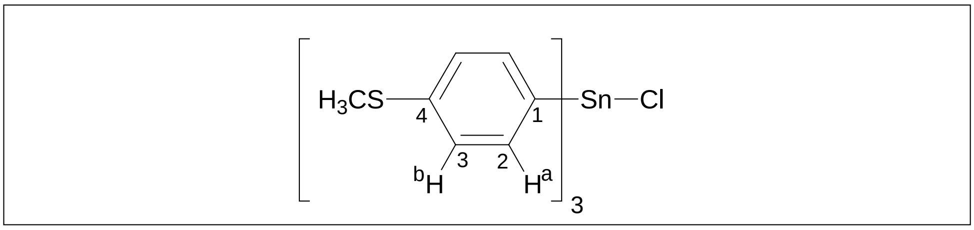
^{119}Sn-NMR in CDCl$_3$ (δ in ppm referred to SnMe$_4$): -121.6

FT-IR in NaCl (cm^{-1}):
3069 (stretch. CH arom.), 2916 (stretch. asim. CH aliph.), 1572-1478 (stretch. C=C arom. ring), 1429 (bend. asym. CH aliph.), 1380 (bend. sym. CH aliph.), 804 (bend. CH 1,4-disubst. arom.), 732 (stretch. CH$_3$-S)

21.2 - Tri(4-thiomethylphenyl)tin chloride (M.W.= 523.4 g/mol)



In a 50 ml round bottomed flask equipped with a magnetic stirrer, reflux condenser with a drying tube, 2.30 g (3.80 mmol) of tetrakis(4-thiomethylphenyl)tin were added to 0.16 ml of $SnCl_4$ (1.30 mmol). This reaction mixture was heated at 200-210 °C for 2.5 h, to give a brown solid that was dissolved in hot petrolium ether, leaving a small dark brown residue that was set apart, after decantation. Then the solvent was removed under reduced pressure leaving a solid which was crystallized as white crystals from cyclohexane, after being stored at 4° for 24 h.
Yield: 1.10 g (42%).

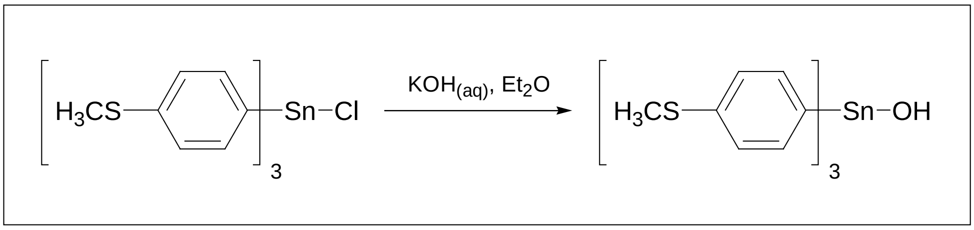


^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS):
2.5 (s, 9H, **SCH$_3$**), 7.2 (m, 6H, **H^b**), 7.6 (m, 6H, **H^a**).

^{13}C-NMR in CDCl$_3$ (δ in ppm referred to TMS):
15.4 (**C$_5$**), 126.8 (**C$_3$**), 133.0 (**C$_1$**), 136.5 (**C$_2$**), 142.5 (**C$_4$**).

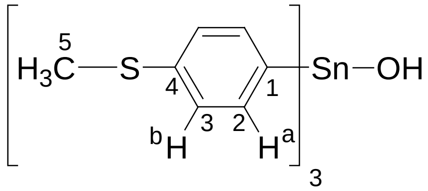
FT-IR in NaCl (cm^{-1}):
3060 (stretch. CH arom.), 2917 (stretch. asym. CH aliph.), 1571-1479 (stretch. C=C arom. ring), 1429 (bend. asym. CH aliph.), 1384 (bend. sym. CH aliph.), 800 (bend. CH 1,4-disubst. arom. ring), 731 (stretch. CH$_3$-S).

21.3 - Tri(4-thiomethylphenyl)tin hydroxide (M.W. = 506.6 g/mol)



In a 100 ml round bottomed flask equipped with a magnetic stirrer and reflux condenser 12.3 ml of a 10% aqueous solution of KOH were added to a stirred solution of 3.00 g of tri(4-thiomethylphenyl)tin chloride (6.3 mmol) in 60.5 ml of diethyl ether. The reaction mixture was refluxed under stirring for 1 h to give a white solid residue. After cooling it was dissolved in dichloroethane, then precipiteted with petroleum ether and filtered.

Yield: 2.08 g (65%).

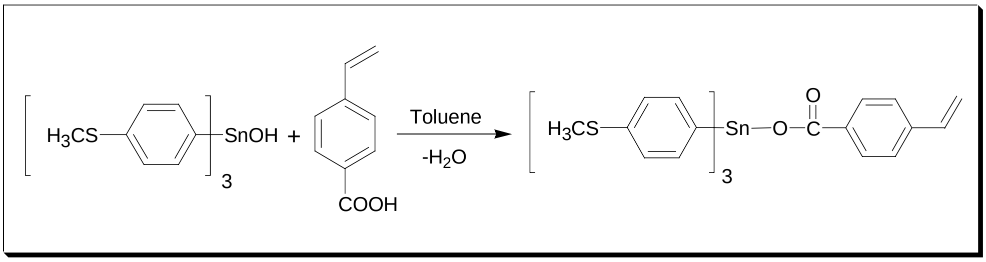


^{1}H-NMR in $CDCl_3$ (δ in ppm referred to TMS):
2.5 (s, 9H, **SCH_3**), 7.15 (m, 6H, **H^b**), 7.35 (m, 6H, **H^a**).

^{13}C-NMR in $CDCl_3$ (δ in ppm referred to TMS):
15.6 (**C_5**), 126.4 (**C_3**), 134.1 (**C_1**), 136.8 (**C_2**), 140.9 (**C_4**).

FT-IR on NaCl (cm^{-1}):
3432 (stretch. OH), 3058 (stretch. CH arom.); 2917 (stretch. CH aliph), 1601-1573 (stretch. C=C arom.), 1479 (stretch. C=C arom.), 929 (bend. OH), 796 (bend. CH 1,4-disubst. arom. ring), 733 (stretch. CH_3-S).

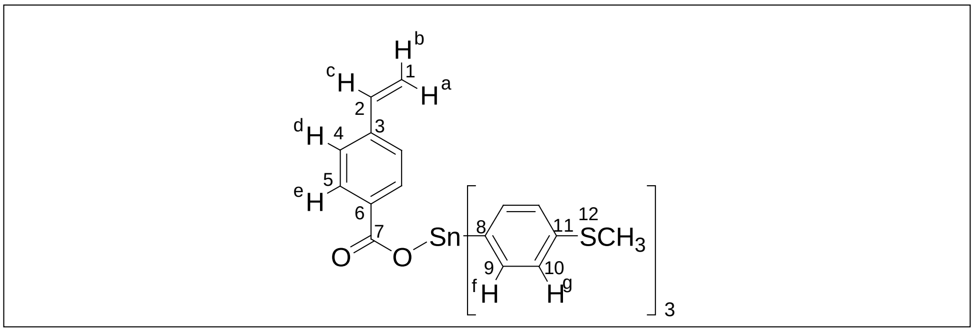
21.4 - Tri(4-thiomethylphenyl)tin 4-vinylbenzoate (MW = 551.13 g/mol).



In a 100 ml round bottom flask equipped with a magnetic stirrer, reflux condenser and a Dean-Stark apparatus 1.72 g of tri(4-thiomethylphenyl)tin hydroxide (3.40 mmol) were added to 0.50 g of 4-vinylbenzoic acid (3.40 mmol), dissolved in 40 ml of toluene. Then hydroquinone (0.15 g) was added. The reaction mixture was heated to reflux until no more water formation was collected in the Dean -Stark. The reaction progress was monitored by FT-IR spectroscopy.

At the end of the reaction the solvent was evaporated under reduced pressure and the crude product obtained purified by crystallization from ethanol/ water.

Yield: 1.30 g (60 %).



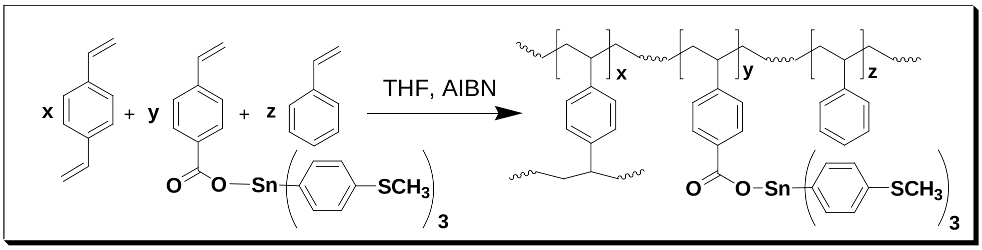
^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS):
2.5 (s, 9H, SCH$_3$), 5.35 (d, $^3J(H_{cis},H)$= 10.8 Hz, 1H; =CH$_{trans}$**H$_{cis}$**), 5.85 (d, $^3J(H_{trans},H)$=17.8 Hz, 1H; =C**H$_{trans}$**H$_{cis}$), 6.7 (dd, $^3J(H,H_{cis})$= 10.8 Hz, $^3J(H,H_{trans})$= 17.8 Hz, 1H; **=CH**), 7.30 (m, 6H, **H^g**), 7.45 (d, $^3J(H,H)$= 9.3 Hz, 2H; **H^d**), 7.70 (m, 6H, **H^f**), 8.10 (d, $^3J(H,H)$= 9.3 Hz, 2H; **H^e**).

^{13}C-NMR in CDCl$_3$ (δ in ppm referred to TMS):
15.5 (**C$_{12}$**), 116.6 (**C$_1$**), 126.3 (**C$_4$**), 126.7 (**C$_{10}$**), 127.1 (**C$_6$**), 131.3 (**C$_5$**), 134.1 (**C$_8$**), 136.5 (**C$_2$**), 137.35 (**C$_9$**), 141.9 (**C$_3$**), 142.1 (**C$_{11}$**).

^{119}Sn-NMR in CDCl$_3$ (δ in ppm referred to SnMe$_4$): -103.9

FT-IR on NaCl (cm^{-1}):
3060 (stretch. CH arom.), 2919 (asym. stretch. CH aliph.), 1630 (stretch. vinyl), 1620 (stretch C=O), 1607-1573 (stretch. C=C arom.), 1480 (stretch. C=C arom.), 989-916 (bend. CH=CH$_2$ vinyl), 799 (out of plane bend. CH 1,4-disubst. arom. ring), 732 (stretch. CH$_3$-S).

21.5 - C0(X-SCH$_3$5) cross-linked polystyrenic resins



Both the **C0(X-SCH$_3$5)** resins were prepared following the same, above reported, synthetic routes and procedures used for the **C0(X-F5)** ones, previously reported.

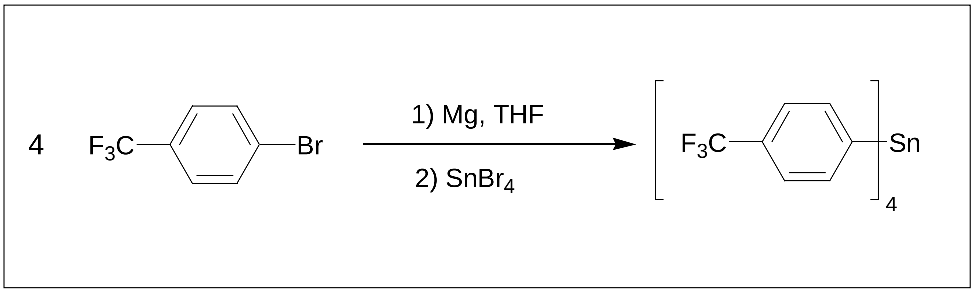
Composition of the copolymers and polymerization yields are shown in **Table 34**.

Table 34. Feeding, yields and tin content in C0(X-SCH$_3$5) resins.

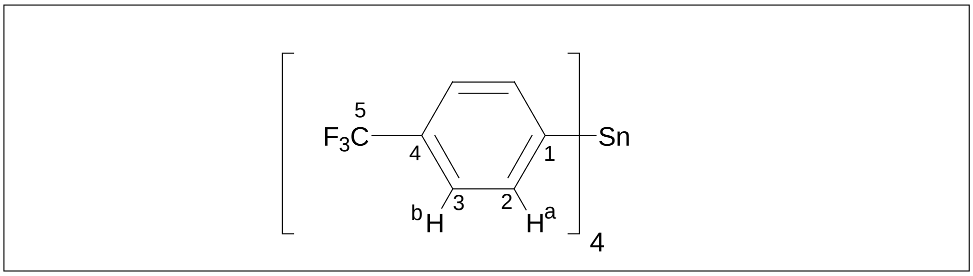
	Sty (mmol)	*DVB (mmol)*	*Organotin monomer (mmol)*	*Yield (%)*	*mmol Sn/g cat*
C0(20- SCH$_3$5)	9.15	2.44	0.63	39	0.50
C0(35-SCH$_3$5)	8.30	4.85	0.71	78	0.49

22 - Synthesis of polystyrenic resins bearing the (4-trifluoromethylphenyl)tin carboxylate moiety

22.1 - Tetrakis(4-trifluoromethylphenyl)tin (M.W. = 698.97 g/mol)



In a 250 ml three necked flask equipped with stirrer, reflux condenser, dropping funnel a solution of 16 g of 4-trifluoromethylbromobenzene (71 mmol) in 40 ml of anhydrous THF was slowly added under nitrogen stream to 1.90 g of metallic magnesium (77.5 mmol) suspended in THF anhydrous, giving a dark green solution. After the completion of addition, the mixture was stirred at room temperature for one hour. Then a solution of 7.50 g of stannic bromide (17.1 mmol) in 20 ml of anhydrous toluene was added dropwise, in 1.5 hour. The red coloured obtained solution was refluxed for 2 hours and stirred overnight at room temperature. At the end of the reaction the Grignard derivative already active was slowly hydrolized with satured NH_4Cl solution. The dark red solution obtained was extracted with 1,2-dichloroethane and the organic phase dried with anhydrous Na_2SO_4. The organic solvent was distilled off under reduced pressure leaving a solid product which was purified by crystallization from cyclohexane.
Yield: 7.30g (60%).



^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS):
7.5 (m, 8H, **H^{b}**), 7.75 (m, 8H, **H^{a}**).

^{13}C-NMR in CDCl$_3$ (δ in ppm referred to TMS):
124.3 (q, $^{1}J(^{13}C-^{19}F)$= 273 Hz; **C$_5$**), 125.8 (**C$_3$**), 132.5 (q, $^{2}J(^{13}C-^{19}F)$= 34 Hz**;** **C$_4$**), 137.6 (**C$_2$**), 141.1 (**C$_1$**).

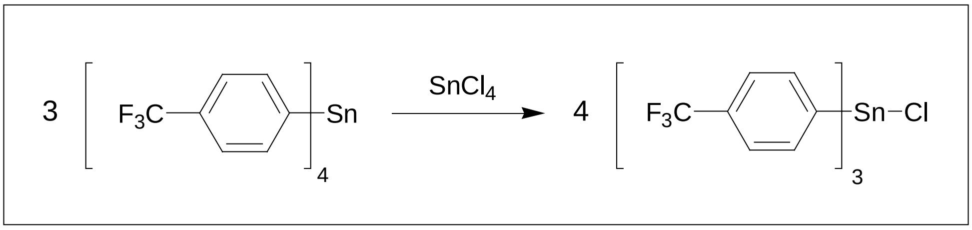
^{119}Sn-NMR in CDCl$_3$ (δ in ppm referred to SnMe$_4$): -132.4

^{19}F-NMR in CDCl$_3$ (δ in ppm referred to CFCl$_3$): -63.7

FT-IR in NaCl (cm^{-1}):
3034 (stretch. CH arom.), 1601 (stretch. C=C arom. ring), 1429 (bend. asym. CH aliph.), 1166 (stretch CF$_3$), 823 (bend. CH 1,4-disubst. arom.)

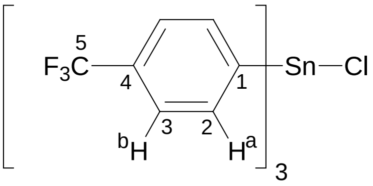
ESI-MS (m/z)
701 m/z (molecular ion, positive ion mode); 535 m/z (molecular ion, negative ion mode), 555 m/z (lost of $C_7H_4F_3$).

22.2 - Tri(4-trifluoromethylphenyl)tin chloride (M.W.= 589.06 g/mol)



In a 50 ml round bottomed flask equipped with magnetic stirrer and reflux condenser with a drying tube, 0.40 ml of $SnCl_4$ (3.43 mmol) were added to 7.20 g (10.3 mmol) of tetrakis(4-trifluoromethylphenyl)tin. This reaction mixture was heated between 200-210 °C for 2.5 h, to give a brown solid. It was dissolved in hot petrolium ether, formimg a very small dark brown residue. After decantation, the solvent was removed under reduced pressure. The yellow oily residue obtained was purified by crystallization from cyclohexane.

Yield: 4.64 g (57%).



^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS):
7.70- 8.00 (m, 12H, **H^a, H^b**,).

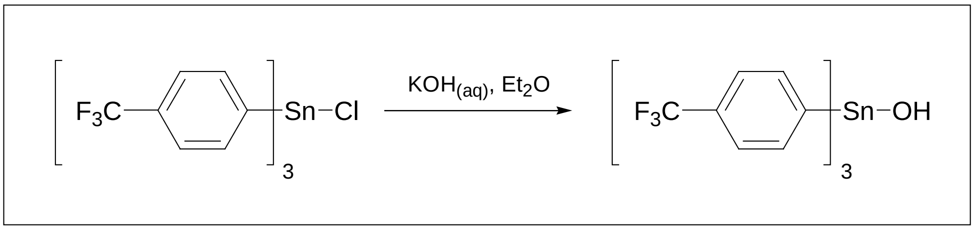
^{13}C-NMR in CDCl$_3$ (δ in ppm referred to TMS):
126.2 (q, $^1J(^{13}C-^{19}F)$= 271 Hz; **C$_5$**), 127.9 (**C$_3$**), 135.7 (q, $^2J(^{13}C-^{19}F)$= 33.6 Hz; **C$_4$**), 136.6 (**C$_2$**), 141.0 (**C$_1$**).

^{19}F-NMR in CDCl$_3$ (δ in ppm referred to CFCl$_3$): -63.95

FT-IR in NaCl (cm^{-1}):
3034 (stretch. CH arom.), 1610-1571 (stretch. C=C arom. ring), 1167 (stretch. CF$_3$), 824 (bend. CH 1,4-disubst. arom.).

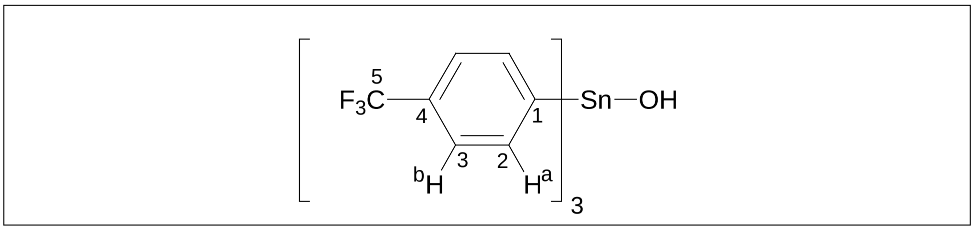
EI-MS (m/z)
590 m/z (molecular ion); 571 m/z (lost of F), 445 m/z (lost of $C_7H_4F_3$).

22.3 - Tri(4-trifluoromethylphenyl)tin] hydroxide (M.W. = 570.7 g/mol)˙



In a 100 ml round bottomed flask equipped with a magnetic stirrer and reflux condenser 19 ml of a 10% aqueous solution of KOH were added to a stirred solution of 4.64 g of tri(4-trifluoromethylphenyl)tin chloride (7.90 mmol) in 95 ml of diethyl ether. The reaction mixture was refluxed under stirring for 1 h to give a light yellow solid product. After cooling it was crystallized from methanol/ water.

Yield: 3.26 g (72%).



^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS):
7.55 (m, 6H, **H^b**), 7.70 (m, 6H, **H^a**).

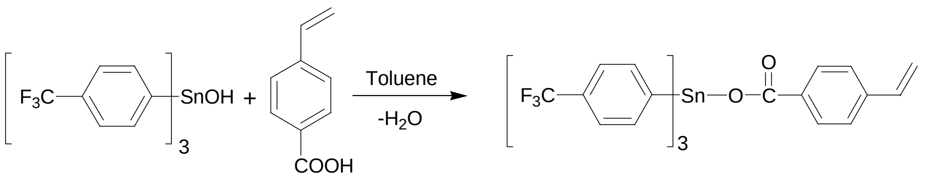
^{13}C-NMR in CDCl$_3$ (δ in ppm referred to TMS):
125.5 (q, $^1J(^{13}C-^{19}F)$= 272 Hz; **C$_5$**) 125.8 (**C$_3$**), 132.6 (q, $^2J(^{13}C-^{19}F)$= 35 Hz; **C$_4$**), 137.6 (**C$_2$**), 141.1 (**C$_1$**).

^{119}Sn-NMR in CDCl$_3$ (δ in ppm referred to SnMe$_4$): -90.6

^{19}F-NMR in CDCl$_3$ (δ in ppm referred to CFCl$_3$): -63.67

FT-IR on NaCl (cm^{-1}):
3436 (stretch. OH), 3032 (stretch. CH arom.), 1603 (stretch. C=C arom. ring), 1166 (stretch. CF$_3$), 930 (bend. OH), 822 (bend. CH 1,4-disubst. arom.).

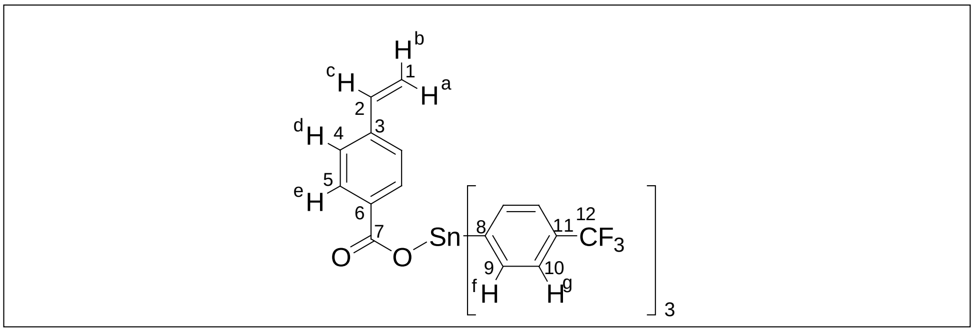
22.4 - Tri(4-trifluoromethylphenyl)tin 4-vinylbenzoate (MW = 729.2 g/mol).



In a 100 ml round bottom flask equipped with a magnetic stirrer, reflux condenser and a Dean-Stark apparatus, 0.9 g of tri(4-trifluoromethylphenyl)tin hydroxide (1.60 mmol) were added to 0.23 g of 4-vinylbenzoic acid (3.40 mmol) dissolved in 30 ml of toluene. Then an hydroquinone, 2,6-diter-butyl-4-methylphenol, was added. This reaction mixture was heated to reflux until no more water formation was observed in the Dean-Stark. The reaction progress has been monitored by FT-IR spectroscopy.

At the end of the reaction the toluene was evaporated under reduced pressure and the crude product obtained was purified by crystallization from ethanol and water.

Yield: 0.48 g (53 %).



^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS):
5.4 (dd, ^3J(H$_{cis}$,H)= 10.4 Hz, ^2J(H$_{gem}$)= 0.9 Hz, 1H; =CH$_{trans}$**H$_{cis}$**), 5.9 (dd, ^3J(H$_{trans}$,H)= 18.1 Hz, ^2J(H$_{gem}$)= 0.9 Hz, 1H; =C**H$_{trans}$**H$_{cis}$), 6.75 (dd, ^3J(H,H$_{cis}$)= 10.4 Hz, ^3J(H,H$_{trans}$)= 18.1 Hz, 1H; **=CH**), 7.45 (m, 6H, **H^g**), 7.6 (dd, ^3J(H,H)= 9 Hz, 2H, **H^d**), 7.70 (m, 6H, **H^f**), 8.10 (dd, ^3J(H,H)= 8.9 Hz, 2H, **H^e**).

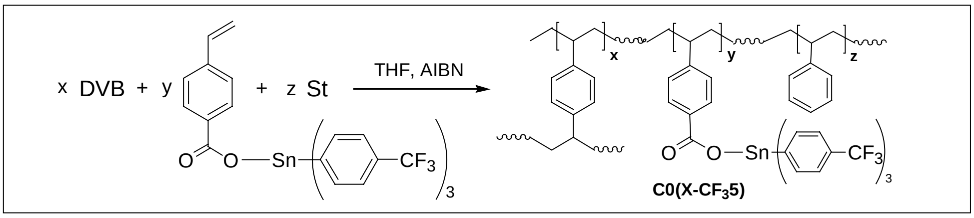
^{13}C-NMR in CDCl$_3$ (δ in ppm referred to TMS):
117.2 (**C$_1$**), 125.2 (q ^1J(^{13}C-^{19}F)= 273 Hz; **C$_{12}$**) 125.9 (**C$_{10}$**), 126.0 (**C$_{11}$**), 126.5 (**C$_4$**), 128.0 (**C$_6$**), 131.4 (**C$_5$**), 136.5 (**C$_2$**), 137.4 (**C$_9$**), 142.7 (**C$_8$**), 142.9 (**C$_3$**).

^{19}F-NMR in CDCl$_3$ (δ in ppm referred to CFCl$_3$): -63.73

FT-IR on NaCl (ν in cm^{-1}):
3035 (stretch. CH arom.), 1630 (stretch. CH=CH$_2$), 1602-1585 (stretch. C=C arom. ring), 1542 (stretch. COOSn ester), 1167 (stretch. CF$_3$), 987-916 (bend. CH=CH$_2$ vinyl), 823 (bend. CH 1,4-disubst. arom. ring).

EI-MS (m/z)
730 m/z (molecol ion); 585 m/z (fragment $C_7H_4F_3$), 555 m/z (fragment $C_{11}H_{12}O_2$).

22.5 - C0(X-CF$_3$5) cross-linked polystyrenic resins



Both the **C0(X-CF$_3$ 5)** resins were prepared following the same synthesis and procedures used for the **C0(X-F 5)** ones, previously reported.

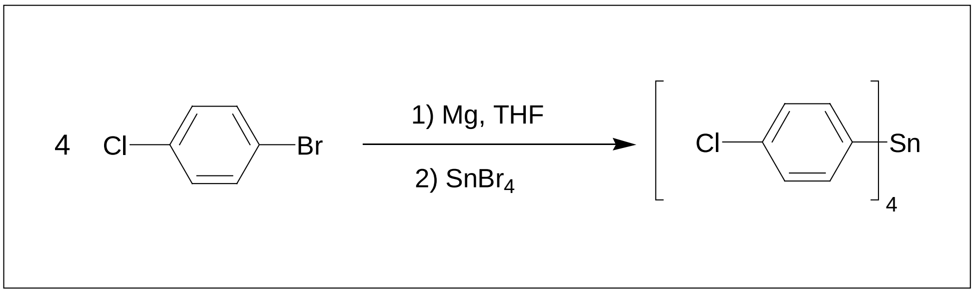
Composition of the copolymers and polymerization yields are shown in **Table 35**.

Table 35. Feeding, yields and tin content in C0(X-CF$_3$ 5) resins.

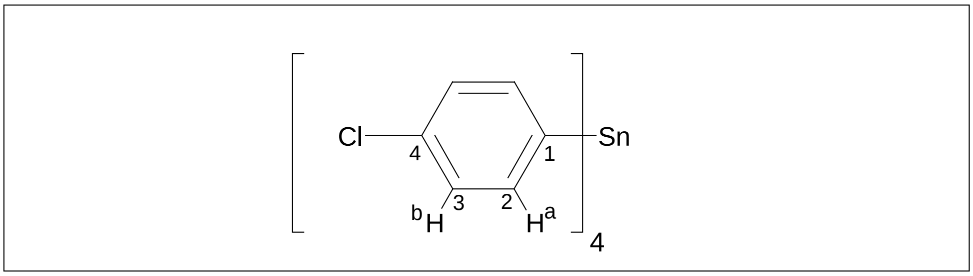
	Sty (mmol)	***DVB (mmol)***	***Organotin monomer (mmol)***	***Yield (%)***	***mmol Sn/g cat***
C0(20- CF$_3$5)	4.3	1.2	0.28	15	0.49
C0(35-CF$_3$5)	4.3	2.5	0.36	5	0.48

23 - Synthesis of polystyrenic resins bearing the (4-chlorophenyl)tin carboxylate moiety

23.1 - Tetrakis(4-chlorophenyl)tin (M.W. = 564.75 g/mol)



A solution of 10 g of 4-chlorobromobenzene (52 mmol) in 40 ml of dry THF was slowly added to 1.39 g of metallic magnesium (57 mmol) suspended in anhydrous THF in a 250 ml three necked flask equipped with stirrer, reflux condenser, dropping funnel and a nitrogen source, to give a dark green solution. After the addition, the mixture was stirred at room temperature for one hour. Then a solution of 5.47 g of stannic bromide (12.5 mmol) in 15-20 ml of anhydrous toluene was added dropwise in 1.5 h. After the addition was completed, the red solution formed was refluxed for 2 hours and stirred overnight at room temperature. At the end of the reaction the Grignard reagent already active was slowly hydrolized with saturated NH_4Cl solution. This dark red solution was extracted with 1,2-dichloroethane and the organic phase dried with anhydrous Na_2SO_4. The organic solvent was distilled off under reduced pressure and the solid obtained purified by crystallization from cyclohexane.
Yield: 4.90 g (70%).



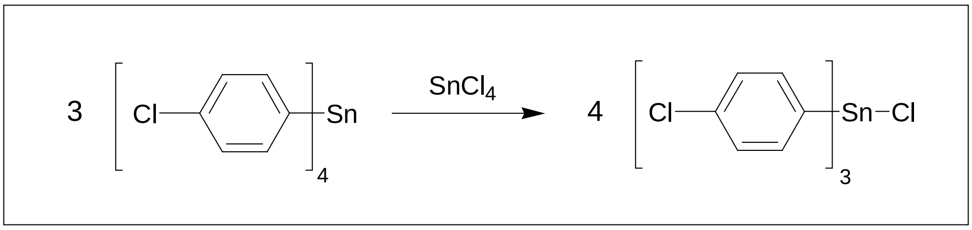
^{1}H-NMR in $CDCl_3$ (δ in ppm referred to TMS):
7.4 (m, 8H, **H^b**), 7.5 (m, 8H, **H^a**).

^{13}C-NMR in $CDCl_3$ (δ in ppm referred to TMS):
129.5 (**C_3**), 135.0 (**C_4**), 136.6 (**C_1**), 138.4 (**C_2**).

^{119}Sn-NMR in $CDCl_3$ (δ in ppm referred to $SnMe_4$): - 121

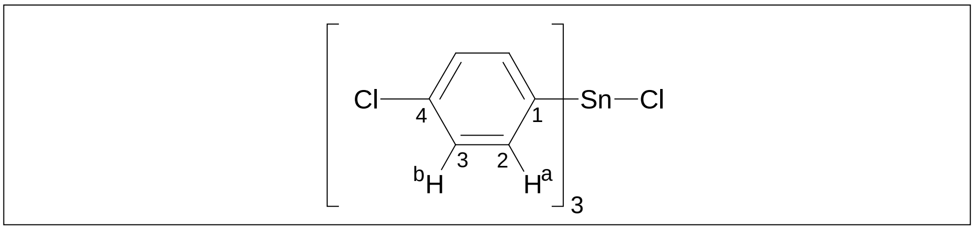
FT-IR in KBr (cm^{-1}):
3079-3010 (stretch. CH arom.), 1493 (stretch. CH arom.), 818 (bend. 1,4-disubst. arom.), 706 (stretch. C-Cl).

23.2 - Tri(4-chlorophenyl)tin chloride (M.W.= 488.69 g/mol)



In a 50 ml round bottomed flask equipped with a magnetic stirrer, reflux condenser with a drying tube, 4.66 g (8.25 mmol) of tetrakis(4-chlorophenyl)tin were added to 0.32 ml of $SnCl_4$ (2.7 mmol). This mixture was heated at 200-210 °C for 2.5 h, to give a dark red oil., then was dissolved in hot petrolium ether, leaving a very small dark brown residue, and filtered. The solid part, constituted by unreacted product, was eliminated and the solvent removed under reduced pressure. The yellow oil obtained was purified by dissolution in hot ethyl acetate followed by cooling and addition of n-hexane.

Yield: 4.64 g (88%).



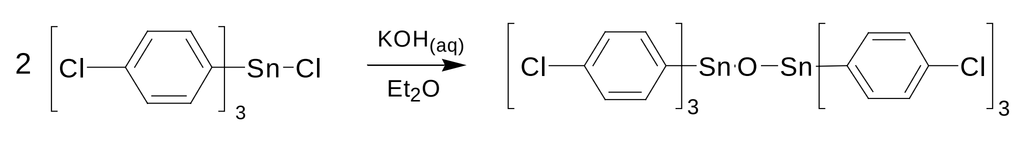
^{1}H-NMR in $CDCl_3$ (δ in ppm referred to TMS):
7.4 (m, 6H, **H^b**), 7.5 (m, 6H, **H^a**).

^{13}C-NMR in $CDCl_3$ (δ in ppm referred to TMS):
129.9 (**C_3**), 134.8-135.7 (**C_1 + C_4**), 137.4 (**C_2**).

^{119}Sn-NMR in $CDCl_3$ (δ in ppm referred to $SnMe_4$): -41

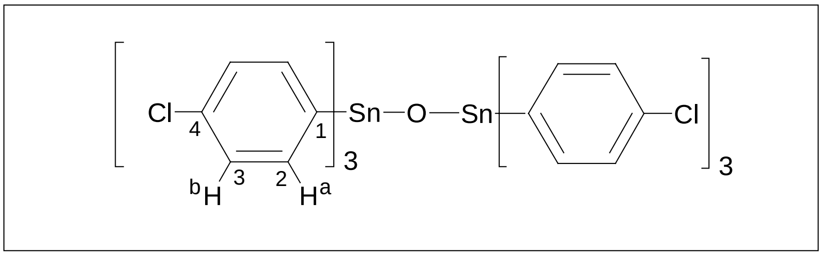
FT-IR in NaCl (cm^{-1}):
3079-3010 (stretch. CH arom.), 1580-1493 (stretch. C=C arom.), 818 (bend. CH 1,4-disubst. arom. ring), 724 (stretch. C-Cl).

23.3 - Tri[(4-chlorophenyl)tin] hydroxide (M.W. = 470.36 g/mol)˙



In a 100 ml round bottomed flask equipped with a magnetic stirrer and reflux condenser 19 ml of a 10% aqueous solution of KOH were added to a stirred solution of 4.64 g of tri(4-chlorophenyl)tin chloride (9.50 mmol) in 95 ml of diethyl ether. The reaction mixture was refluxed under stirring for 1 h to give a light yellow solid product. After cooling it was crystallized from methanol and water.

Yield: 3.26 g (73%).



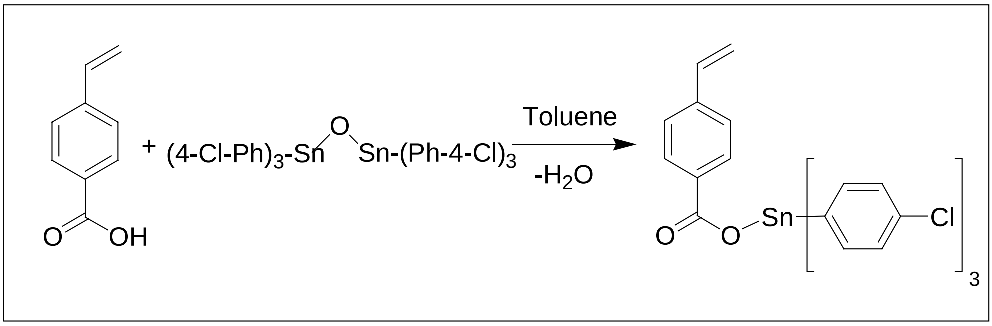
^{1}H-NMR in $CDCl_3$ (δ in ppm referred to TMS):
7.4 (m, 6H, **H^b**), 7.5 (m, 6H, **H^a**).

^{13}C-NMR in $CDCl_3$ (δ in ppm referred to TMS):
129.5 (**C_3**), 134.9(**C_4**), 137.5 (**C_1**), 140.0 (**C_2**).

^{119}Sn-NMR in $CDCl_3$ (δ in ppm referred to $SnMe_4$): -78

FT-IR on KBr (cm^{-1}):
3078-3011 (stretch. CH arom.), 1581-1492 (stretch. C=C arom.), 1012 (bend. CH 1,4- disubst. arom.), 805 (stretch. Sn-O-Sn), 724 (stretch. C-Cl).

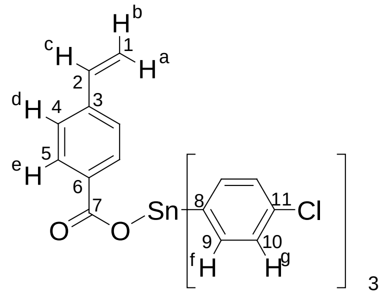
23.4 - Tri(4-chlorophenyl)tin 4-vinylbenzoate (MW = 600.33 g/mol).



In a 100 ml round bottomed flask equipped with a magnetic stirrer, reflux condenser and a Dean-Stark apparatus 1.23 g of tri(4-chlorophenyl)tin hydroxide (2.62 mmol) were added to 0.39 g of 4-vinylbenzoic acid (2.62 mmol) and dissolved in 30 ml of toluene. Then hydroquinone 2,6-di*ter*-butyl-4-methylphenol was added. The reaction mixture was heated to reflux until no more water formation was observed in the Dean-Stark. The reaction progress was monitored by FT-IR spectroscopy.

At the end of the reaction the toluene was evaporated under reduced pressure to leave a crude product which was purified by crystallization from ethanol and water.

Yield: 0.95 g (60 %).



^{1}H-NMR (CDCl$_3$) (δ in ppm riferiti al TMS):

5.4 (dd, ^3J(H$_{cis}$,H) = 10.4 Hz, ^2J(H$_{gem}$)= 1.2 Hz, 1H; =CH$_{trans}$**H**$_{\mathbf{cis}}$), 5.8 (dd, ^3J(H$_{trans}$,H) = 18 Hz, ^2J(H$_{gem}$) = 1.2 Hz, 1H; =C**H**$_{\mathbf{trans}}$H$_{cis}$), 6.7 (dd, ^3J(H,H$_{cis}$) = 10.4 Hz, ^3J(H,H$_{trans}$) = 18 Hz, 1H; **=CH**), 7.4 (m, 6H, **H**$^{\mathbf{f}}$), 7.5 (m, 6H, **H**$^{\mathbf{g}}$), 7.6 (d, ^3J(H,H) = 8.7 Hz, 2H; **H**$^{\mathbf{d}}$), 8.1 (d, ^3J(H,H) = 8.7 Hz, 2H, **H**$^{\mathbf{e}}$).

^{13}C-NMR (CDCl$_3$) (δ in ppm riferiti al TMS):

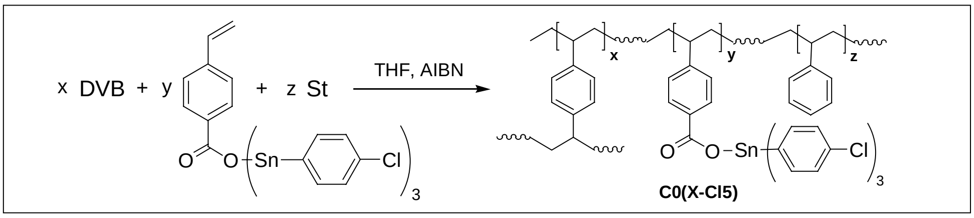
116.9 (**C**$_{\mathbf{1}}$), 126.4 (**C**$_{\mathbf{4}}$), 129.5 (**C**$_{\mathbf{10}}$), 130.3 (**C**$_{\mathbf{2}}$), 131.4 (**C**$_{\mathbf{5}}$), 134.5 (**C**$_{\mathbf{3}}$), 136.4 + 136.6 (**C**$_{\mathbf{8}}$ + **C**$_{\mathbf{11}}$), 138.4 (**C**$_{\mathbf{9}}$), 138.7 (**C**$_{\mathbf{6}}$), 171.2 (**C**$_{\mathbf{7}}$).

^{119}Sn-NMR (CDCl$_3$) (δ in ppm riferiti al SnMe$_4$): -116.

FT-IR (cm^{-1} in KBr):

3087-3026 (stretch. CH arom.), 1628 (stretch. COOSn ester), 1582-1477 (stretch. C=C arom.), 1406 (bend. =CH$_2$), 1013 (bend. CH 1,4-disubst. arom. ring), 906 (bend. vinyl double bond, C=CH$_2$).

23.5 - C0(X-Cl 5) cross-linked polystyrenic resins



All the **C0(X-Cl5)** resins were prepared following the same synthetic procedures used for the **C0(X-F5)** ones, previously reported.

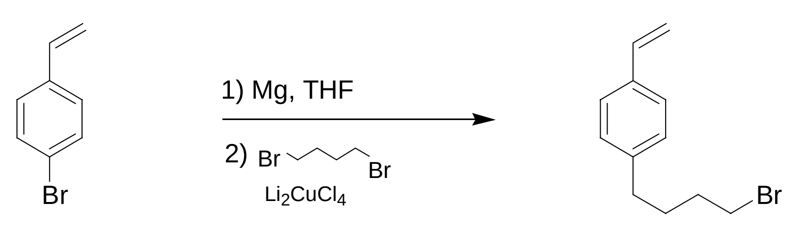
Composition of the copolymers and polymerization yields, as well as tin content, are shown in the **Table 36**.

Table 36. Feeding, yields and tin content for the C0(X-Cl 5) resins.

	Sty (mmol)	*DVB (mmol)*	*Organotin monomer (mmol)*	*Yield (%)*	*mmol Sn/g cat*
C0(20-Cl5)	4.5	1.33	0.33	26	0.50
C0(35-Cl5)	4.0	2.33	0.33	43	0.49
C0(50-Cl5)	3.0	3.33	0.33	17	0.48
C0(70-Cl5)	1.66	4.66	0.33	42	0.47

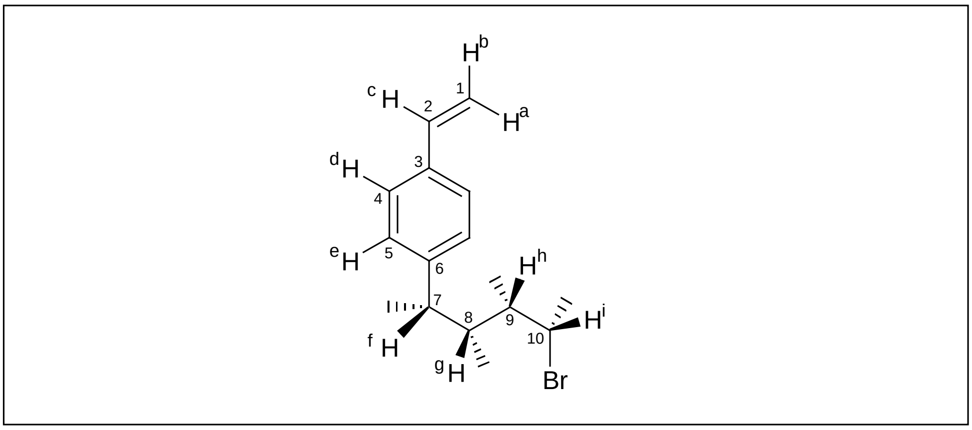
24 - Synthesis of cross-linked polystyrenic resins bearing a C4 spacer and the triphenyltin carboxylate moiety

24.1 - 1-(4-bromobutyl)-4-vinylbenzene (M.W.=239.16 g/mol)



The first step of this reaction was the synthesis of the Grignard reagent. In a 250 ml three necked flask equipped with stirrer, reflux condenser, dropping funnel and a nitrogen source a solution of 10 g of *p*-bromostryrene (54.6 mmol) in 50 ml of anhydrous THF was added slowly to 1.46 g of metallic magnesium (60.1 mmol) suspended in THF anhydrous to give a dark green solution. After the completion of addition, the mixture was stirred at room temperature for one hour. Then in another 250 ml three necked flask, equipped with a stirrer, dropping funnel and a nitrogen source, 2.73 ml of a 0.2 M solution of Li_2CuCl_4 (prepared adding 2 mol LiCl to 1 mol $CuCl_2$ in anhydrous THF at room temperature) in THF (0.546 mmol) were added to 6.45 ml of 1,4-dibromobutane in 10 ml of THF. Then the Grignard reagent previously prepared was put into the dropping funnel and added very slowly to the solution , at a temperature of 2-5 °C. After the addition, the solution was left for 5 hours at room temperature. At the end of the reaction the Grignard reagent already active has been slowly hydrolized with water and NH_4Cl. This solution was extracted with 1,2-dichloroethane and the organic phase was dried with Na_2SO_4 anhydrous. The organic solvent was distilled

off under reduced pressure to give a brown oily residue, which was purified by column cromatography eluted with petrolium ether/CH_2Cl_2 7/1.
Yield: 6.20g (48%).

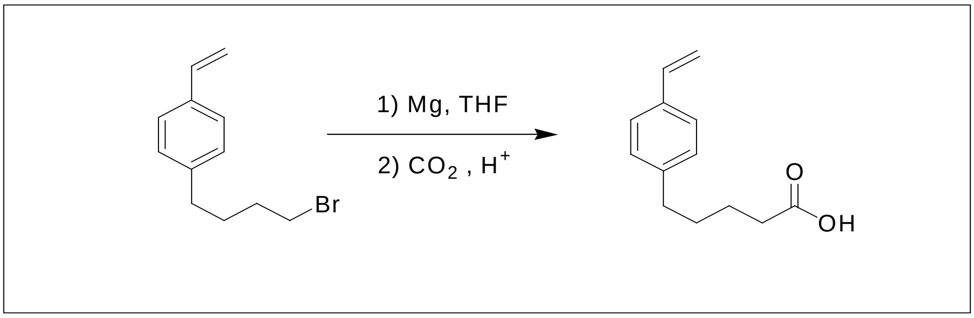


^{1}H-NMR in $CDCl_3$ (δ in ppm referred to TMS):
1.70-1.90 (m, 4H, **H^g** + **H^h**), 2.60 (t, ^3J(H,H)= 7.5 Hz, 2H; **H^f**), 3.40 (t, ^3J(H,H)= 5.9 Hz, 2H, **H^i**), 5.20 (dd, $^3J(H_{cis}$,H) = 10.9 Hz, $^2J(H_{gem})$ = 0.9 Hz, 1H; =CH_{trans}**H_{cis}**, **H^b**), 5.71 (dd, 1H, $^3J(H_{trans}$,H)= 17.8 Hz, $^2J(H_{gem})$= 0.9 Hz, 1H; =C**H_{trans}**H_{cis}, **H^a**), 6.69 (dd, $^3J(H,H_{cis})$= 10.9 Hz, $^3J(H,H_{trans})$= 17.8 Hz, 1H; **=CH, H^c**), 7.14 (d, ^3J(H,H)= 8.3 Hz, 2H, **H^e**), 7.32 (d, ^3J(H,H)= 8.3 Hz, 2H, **H^d**).

^{13}C-NMR in $CDCl_3$ (δ in ppm referred to TMS):
30.0 (**C_8**), 32.5 (**C_9**), 33.9 (**C_{10}**), 34.9 (**C_7**), 113.3 (**C_1**), 126.5 (**C_4**), 128.8 (**C_5**), 135.7 (**C_3**), 136.9 (**C_2**), 141.8 (**C_6**).

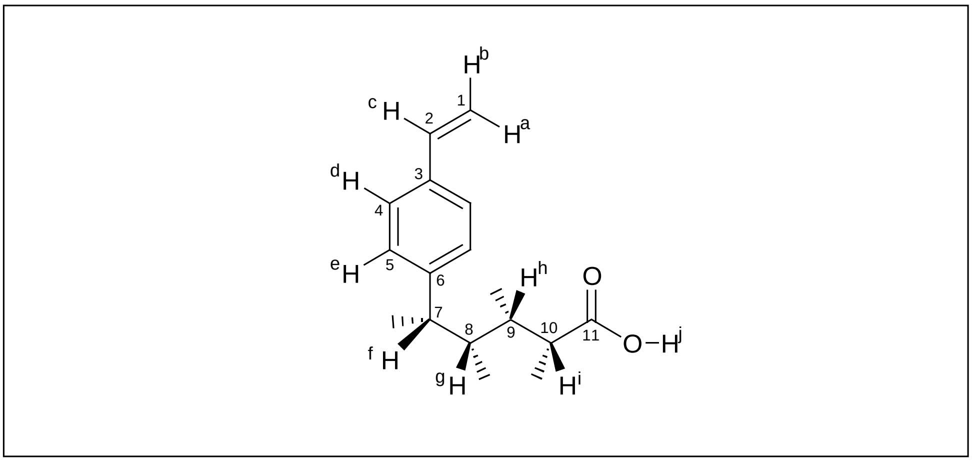
FT-IR in NaCl (cm^{-1}):
3084-3005 (stretch. CH arom.), 2935-2857 (stretch. CH aliph.), 1629 (stretch. C=C vinyl), 1609 (stretch. C=C arom.), 1406 (bend. CH_2 vinyl), 1250 (bend. α CH_2), 990- 906 (bend. CH=CH_2 vinyl), 826 (bend. CH 1,4-disubst. arom. ring).

24.2 - 5-(4-styryl)pentanoic acid (M.W.= 204.27 g/mol)



The first step was the synthesis of the Grignard reagent. The reaction was the same used for preparing the 1-(4-bromobutyl)-4-vinylbenzene. The amount of reagents used were: 6.20 g of 1-(4-bromobutyl)-4-vinylbenzene (54.6 mmol) in 30 ml of anhydrous THF, added slowly to 0.63 g of metallic magnesium (25.9 mmol) suspended in THF anhydrous. Then in another 250 mL were put 50 g of dry ice. This flask was connected to the first one by a hose, in order to put the CO_2 sublimate directly into the Grignard reagent solution. This procedure lasted 3 hours. After the addition, were added 20 ml of sulphuric acid and then the solution was extracted twice with CH_2Cl_2 (30 ml) and dried with Na_2SO_4 anhydrous. The organic solvent was distilled off under reduced pressure to give a white solid.

Yield: 0.66 g (13 %).

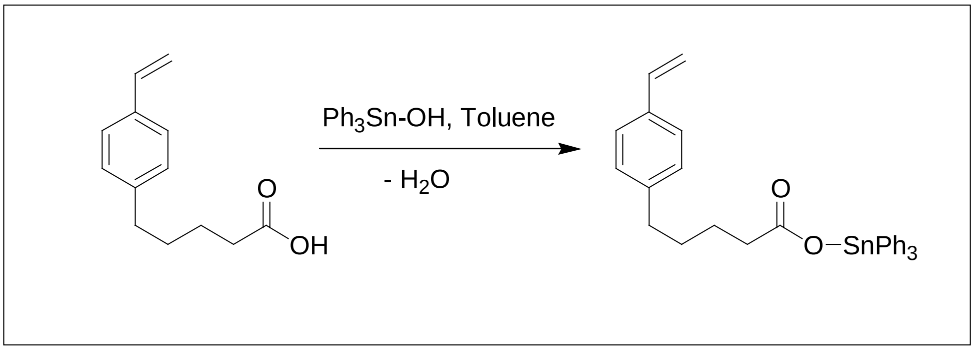


^{1}H-NMR in $CDCl_3$ (δ in ppm referred to TMS):
1.60-1.75 (m, 4H, **H^g** + **H^h**), 2.35 (t, ^3J(H,H)=7.0 Hz, 2H; **H^i**), 2.65 (t, ^3J(H,H)= 6.0 Hz, 2H, **H^f**), 5.20 (dd, $^3J(H_{cis},H)$ =11 Hz, $^2J(H_{gem})$ = 0.9 Hz, 1H; =$CH_{trans}\mathbf{H}_{\boldsymbol{cis}}$, **H^b**), 5.70 (dd, $^3J(H_{trans},H)$ = 17.9 Hz, $^2J(H_{gem})$ = 0.9 Hz, 1H; =$C\mathbf{H}_{\boldsymbol{trans}}H_{cis}$, **H^a**), 6.70 (dd, $^3J(H,H_{cis})$ = 11 Hz, $^3J(H,H_{trans})$ = 17.9 Hz, 1H; **=CH**, **H^c**), 7.15 (d, ^3J(H,H) = 8.2 Hz, **H^e**), 7.35 (d, ^3J(H,H) = 8.2 Hz, 2H, **H^d**), 11.1 (bs, 1H, **H^j**).

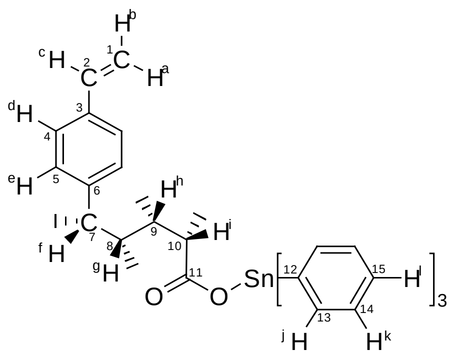
^{13}C-NMR in $CDCl_3$ (δ in ppm referred to TMS):
24.5 (**C_9**), 30.9 (**C_8**), 34.0 (**C_{10}**), 35.4 (**C_7**), 113.2 (**C_1**), 126.4 (**C_4**), 128.8 (**C_5**), 135.5 (**C_3**), 136.9 (**C_2**), 142.0 (**C_6**), 179.6 (**C_{11}**).

FT-IR in NaCl (cm^{-1}):
3087-3005 (stretch. CH arom.), 2932-2857 (stretch. CH aliph), 1703 (stretch. C=O carbox.), 1631 (stretch. C=C vinyl), 1607 (stretch. C=C arom.), 1461 (bend. CH_2 aliph.), 1404 (bend. CH_2 vinyl), 989- 899 (bend. $CH=CH_2$ vinyl), 825 (bend. CH 1,4-disubst. arom. ring).

24.3 - Triphenyl tin derivative of the 5-(4-styryl)pentanoic acid (M.W. = 553.28 g/mol)˙



In a 100 ml round bottomed flask equipped with a magnetic stirrer, reflux condenser and a Dean-Stark apparatus 0.66 g of 5-(4-styryl)-pentanoic acid (3.23 mmol) were added to 1.18 g of triphenyltin hydroxide (3.23 mmol), dissolved in 40 ml of toluene. Then an hydroquinone, 2,6-diterz-butyl-4-methylphenol, was added (0.15 g). The reaction mixture was heated to reflux until no more water formation was seen in the Dean -Stark. The reaction developement has been monitored by FT-IR spectroscopy.
Finally the toluene was evaporated under reduced pressure and the crude product obtained purified by crystallization from ethanol (40°C max) and water.
Yield: 1.45 g (81 %).



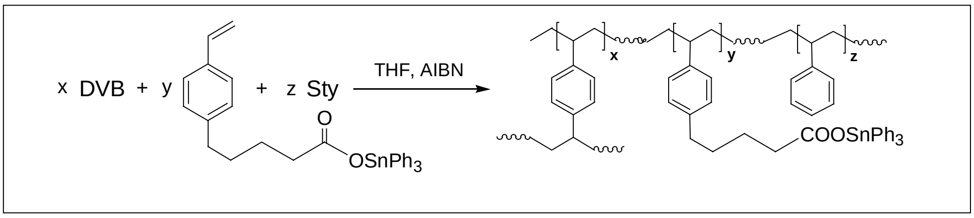
^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS):
1.60 (m, 2H, $\mathbf{H^g}$), 1.70 (m, 2H, $\mathbf{H^h}$), 2.45 (t, ^3J(H,H)= 7.4 Hz, 2H, $\mathbf{H^i}$), 2.55 (t, ^3J(H,H)= 7.8 Hz, 2H, $\mathbf{H^f}$), 5.20 (dd, ^3J(H$_{cis}$,H) = 10.7 Hz, ^2J(H$_{gem}$) = 1.1 Hz, 1H; =CH$_{trans}\mathbf{H}_{\mathbf{cis}}$, $\mathbf{H^b}$), 5.70 (dd, ^3J(H$_{trans}$,H) = 18 Hz, ^2J(H$_{gem}$) = 1.1 Hz, 1H; =C$\mathbf{H}_{\mathbf{trans}}H_{cis}$, $\mathbf{H^a}$), 6.70 (dd, ^3J(H,H$_{cis}$)= 10.7 Hz, ^3J(H,H$_{trans}$)= 18 Hz, 1H; **=CH**, $\mathbf{H^c}$), 7.15 (dd, ^3J(H,H)= 8.3 Hz 2H, $\mathbf{H^e}$), 7.35 (dd, ^3J(H,H)= 8.3 Hz, $\mathbf{H^d}$), 7.45 (m, 9H, $\mathbf{H^k}$+ $\mathbf{H^l}$), 7.75 (m, 6H, $\mathbf{H^j}$).

^{13}C-NMR in CDCl$_3$ (δ in ppm referred to TMS):
25.6 ($\mathbf{C_9}$), 31.1 ($\mathbf{C_8}$), 34.2 ($\mathbf{C_{10}}$), 35.5 ($\mathbf{C_7}$), 113.1 ($\mathbf{C_1}$), 126.4 ($\mathbf{C_4}$), 128.8 ($\mathbf{C_5}$), 129.1 ($\mathbf{C_{14}}$), 130.3 ($\mathbf{C_{15}}$), 135.4 ($\mathbf{C_3}$), 137.0 ($\mathbf{C_2}$), 137.1 ($\mathbf{C_{13}}$), 138.6 ($\mathbf{C_{12}}$), 142.3 ($\mathbf{C_6}$), 180.8 ($\mathbf{C_{11}}$).

^{119}Sn-NMR in CDCl$_3$ (δ in ppm referred to SnMe$_4$): -115

FT-IR on NaCl (cm^{-1}):
3064-3018 (stretch. CH arom), 2992-2857 (stretch. CH aliph.), 1629 (stretch. C=C vinyl), 1608 (stretch. C=C arom.), 1532 (stretch. asymm. C=O carbox.), 1429 (stretch. symm. C=O carbox.), 989-904 (bend. CH=CH$_2$ vinyl), 825 (bend. CH 1,4-disubst. arom.), 731 (bend. CH monosubst. arom.), 698 (bend. C-C bond monosubst. arom. ring).

24.4 - C4(X-5) cross-linked polystyrenic resins



All the **C4(X-5)** series resins were prepared following the same synthesis and procedures used for the **C0(X-F 5)** ones, previously reported.

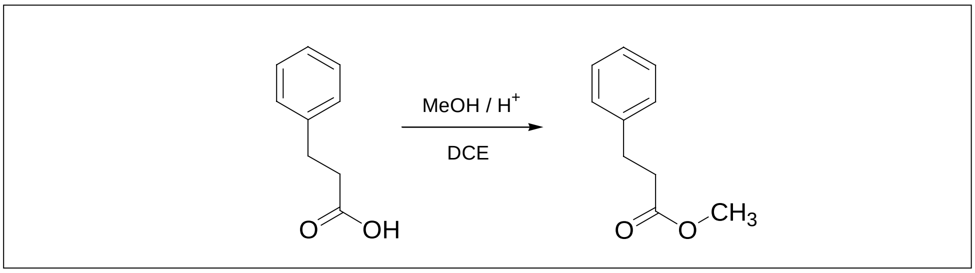
Composition of the copolymers and polymerization yields are shown in **Table 37**.

Table 37. **Feeding, yields and tin content in C4(X-5) resins.**

	Sty (mmol)	*DVB (mmol)*	*Organotin monomer (mmol)*	*Yield (%)*	*mmol Sn/g cat*
C4(20-5)	6.52	3.79	0.54	69	0.50
C4(35-5)	4.87	5.40	0.54	81	0.46
C4(70-5)	2.72	7.85	0.54	90	0.41

25 - Synthesis of cross-linked polystyrenic resins bearing a dimethylenic spacer and the (4-fluorophenyl)tin carboxylate moiety

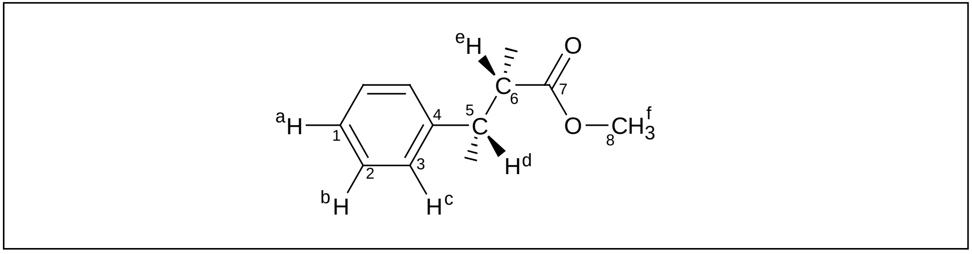
25.1 - 3-phenyl-propionic acid methyl ester (PM=164,20)



In 250 ml round bottomed flask equipped with magnetic stirrer 30 g (200 mmol) of 3-phenyl-propionic acid were dissolved in 60 ml of dichloroethane (DCE); then a solution of 24 ml of methanol and 0.6 ml of sulphuric acid 96 % was added. The mixture was heated to reflux for 8 hours.

After completion of reaction, the mixture was transferred in a separatory funnel and, then, the organic phase washed with water, $NaHCO_3$ solution and water again, and finally dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product purified by fractional distillation (b.p. = 116 °C at 16 mmHg).

Yield: 29.9 g (91 %).



^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS) :

2.65 (t, ^3J(H,H)= 7.4 Hz, 2H, **H^d**), 2.95 (t, ^3J(H,H)= 7.4 Hz, 2H, **H^e**), 3.65 (s, 3H, **H^f**), 7.15-7.30 (m, 5H, **H^a** + **H^b** + **H^c**).

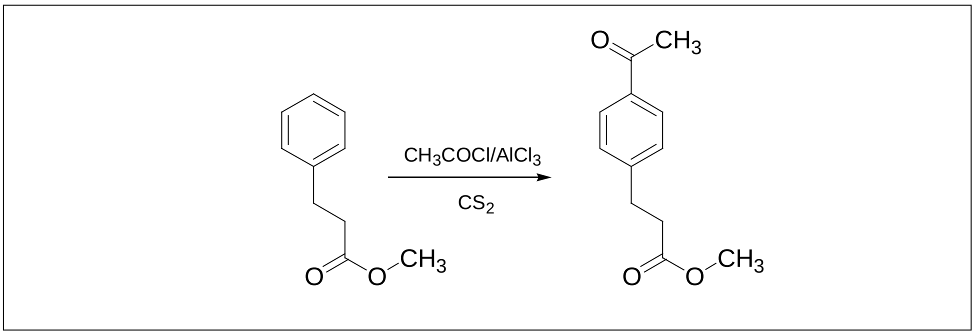
^{13}C-NMR in CDCl$_3$ (δ in ppm referred toTMS) :

31.6 (**C$_5$**), 36.4 (**C$_6$**), 52.3 (**C$_8$**), 126.9 (**C$_1$**), 128.9+129.2 (**C$_2$** + **C$_3$**), 141.2 (**C$_4$**), 174.0 (**C$_7$**).

FT-IR (cm^{-1} in KBr pellets):

3087-3029 (stretch. CH arom.), 2952-2845 (stretch. CH aliph.), 1740 (stretch. C=O ester), 1605 (stretch. C=C arom.), 1497-1437 (bend. CH_3 and CH_2), 752 (bend. CH monosubst. arom.).

25.2 - 3-(4-acetyl-phenyl)-propionic acid methyl ester (PM=206)



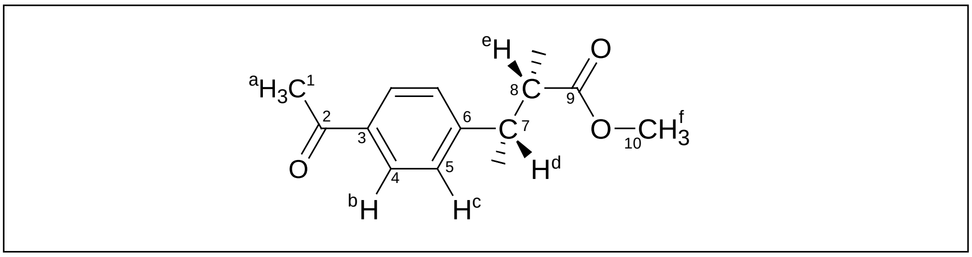
In a three necked round bottom flask, equipped with a magnetic stirrer and termometer, 58.6 g (0.44 mol) of solid $AlCl_3$ and 50 ml of CS_2 were added. Then 29 g (178 mmol) of 3-phenylpropionic acid methyl ester were dissolved in 70 ml di CS_2. The obtained solution so obtained was dropped into the the first at 0°C, very slowly and under stirring. Then were added much more slowly 18.8 g (0.24 mol) of CH_3COCl during 40 min time and, after the flask has been equipped with a reflux condenser, the solution was heated to reflux for 4 hours.

After completion of the reaction, ice (400 g) and HCl 36% (200 ml) were added to give a biphasic solution which was separeted by a separatory funnel.

The organic phase was washed with a HCl solution 10%, water, Na_2CO_3 10%, then water again and finally anhydrified with Na_2SO_4.

The CS_2 was evaporated under vacuum and the residue purified by fractional distillation (b.p.= 218-220 °C at 0.03 mmHg).

Yield: 26.9 g (72%).



^{1}H-NMR in $CDCl_3$ (δ in ppm referred to TMS) :

2.60 (s, 3H, **H^a**), 2.65 (t, ^3J(H,H)= 7.6 Hz, 2H, **H^d**), 3.05 (t, ^3J(H,H)= 7.6 Hz; 2H, **H^e**), 3.65 (s, 3H, **H^f**), 7.30-7.90 (m, 4H, **H^b**+**H^c**).

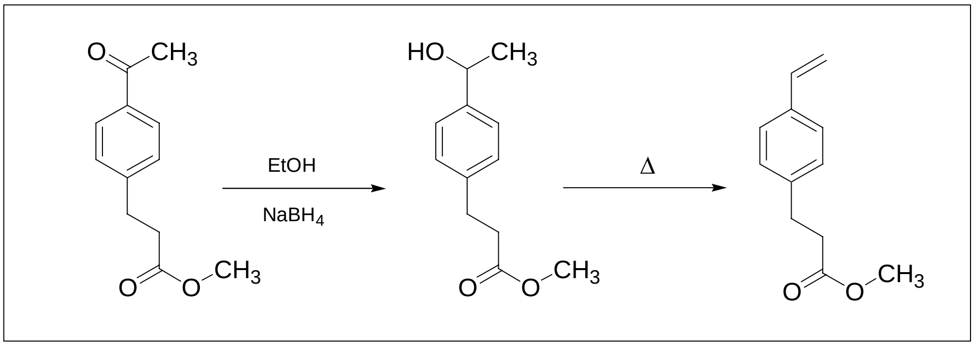
^{13}C-NMR $CDCl_3$ (δ in ppm referred to TMS) :

27.1 (**C_1**), 31.4 (**C_7**), 35.7 (**C_8**), 52.2 (**C_{10}**), 129.1+129.2 (**C_4**+**C_5**), 136.0 (**C_3**), 146.8 (**C_6**), 173.5 (**C_9**), 198.2 (**C_2**).

FT-IR (cm^{-1} in KBr pellets):

3030-3002 (stretch. CH arom.), 2953-2847 (stretch. CH aliph. and vinyl), 1738 (stretch. C=O ester), 1682 (stretch. C=O ket.), 1608 (stretch. C=C arom.), 1437-1359 (bend. CH_3 and CH_2), 840+671 (bend. CH 1,4-disubst. arom.ring.).

25.3 - 3-(4-styryl)-propionic acid methyl ester (PM=190.24)

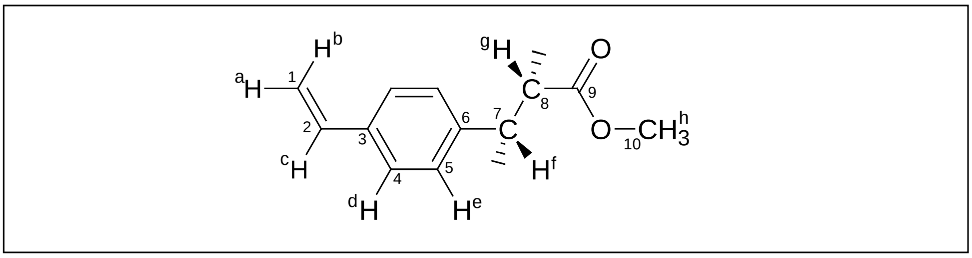


In a 250 ml round bottom flask equipped with a magnetic stirrer and dropping funnel, 26 g (126 mmol) of 3-(4-acetyl-phenyl)-propionic acid methyl ester were dissolved in 80 ml of diethyl ether.

Then a solution of 2.2 g (0.06 mol) of $NaBH_4$ dissolved in 10 ml of methanol were slowly added under stirring. After completion of the addition, the mixture was allowed to react, the reaction progress being monitored by TLC and FT-IR spectroscopy (the ketonic signal at 1682 cm^{-1} disappeared).

Finally, the reaction mixture was acidified with HCl 10% and the aqueous phase was subsequently extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 and the ether evaporeted under reduced pressure to give a high viscous residue, which was subjected to a heat-treatment in distiller under high vacuum to give a product having b.p. 115-118 °C at 1mmHg

Yield: 13.89 g (58%).



^{1}H-NMR (CDCl$_3$) (δ in ppm referred to TMS) :

2.60 (t, ^3J(H,H)= 7.2 Hz, 2H, **H^f**), 2.95 (t, ^3J(H,H)= 7.2 Hz, 2H, **H^g**), 3.65 (s, 3H, **H^h**), 5.20 (dd, ^3J(H$_{cis}$,H) = 10.7 Hz, ^2J(H$_{gem}$) = 0.9 Hz, 1H; $=\mathrm{CH}_{trans}\mathbf{H}_{\boldsymbol{cis}}$, **H^a**), 5.70 (dd, ^3J(H$_{trans}$,H) = 17.6 Hz, ^2J(H$_{gem}$) = 0.9 Hz, 1H; $=\mathrm{C}\mathbf{H}_{\boldsymbol{trans}}\mathrm{H}_{cis}$, **H^b**), 6.70 (dd, ^3J(H,H$_{cis}$) = 10.7 Hz, ^3J(H,H$_{trans}$) = 17.6 Hz**,** **H^c**), 7.15-7.35 (m, 4H, **H^e**+**H^d**).

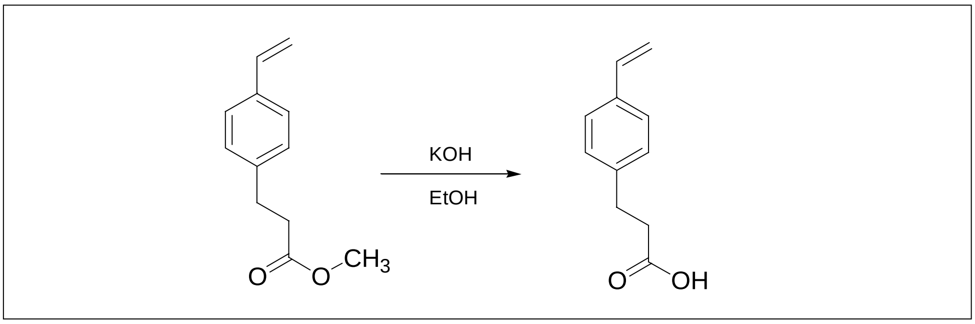
^{13}C-NMR (CDCl$_3$) (δ in ppm referred to TMS) :

31.3 (**C$_7$**), 36.3 (**C$_7$**), 52.2 (**C$_{10}$**), 113.9 (**C$_1$**), 127.0+129.0 (**C$_4$**+**C$_5$**), 136.4 (**C$_3$**), 137.2 (**C$_2$**), 140.8 (**C$_6$**), 173.9 (**C$_9$**).

FT-IR (cm^{-1} in KBr pellets):

3085-3005 (stretch. CH arom), 2955-2863 (stretch. CH aliph), 1733 (stretch. C=O ester), 1630 (stretch. C=C vinyl.), 1606 (stretch. C=C arom.), 1436-1407 (bend. CH$_3$ and CH$_2$), 904 (bend. CH=CH$_2$ vinyl), 842 (bend. CH 1,4-disubst. arom. ring).

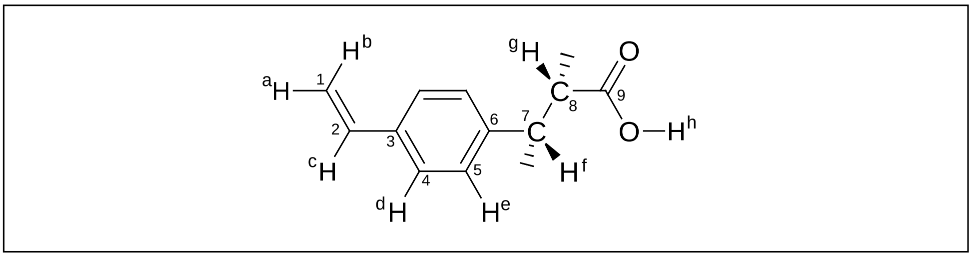
25.4 - 3-(4-styryl)-propionic acid (PM=176,18)



In a 250 ml round bottomedflask equipped with a magnetic stirrer 13 g (68 mmol) of 3-(4-styryl)-propionic acid methyl ester were dissolved in 60 ml of absolute ethanol. A solution of 5.3 g of KOH in 10 ml of absolute ethanol containing 0.1 of copper (as polymerization inhibitor) was added under stirring and the mixture allowed to react for two days at 25 °C.

After remotion of ethanol under vacuum, the solution was made acid with sulphuric acid 5 %. The crude product precipitated was purified by crystallization from EtOH/ water.

Yield: 9.3 g (78%).



^{1}H-NMR in $CDCl_3$ (δ in ppm referred TMS) :

2.60 (t, ^3J(H,H)= 7.0 Hz, 2H, **H^f**), 2.95 (t, ^3J(H,H) = 7.0 Hz, 2H, **H^g**), 5.20 (dd, ^3J(H_{cis},H) = 10.8 Hz, ^2J(H_{gem}) = 0.9 Hz, 1H; =CH_{trans}**H_{cis}**, **H^a**), 5.70 (dd, ^3J(H_{trans},H) =17.4 Hz, ^2J(H_{gem}) =0.9 Hz, 1H; **=CH_{trans}**H_{cis}, **H^b**), 6.70 (dd, ^3J(H,H_{cis}) =10.8 Hz, ^3J(H,H_{trans}) =17.4 Hz, 1H, **=CH**, **H^c**), 7.15-7.35 (m, 4H, **H^e**+**H^d**), 11.50 (bs, 1H, **H^h**).

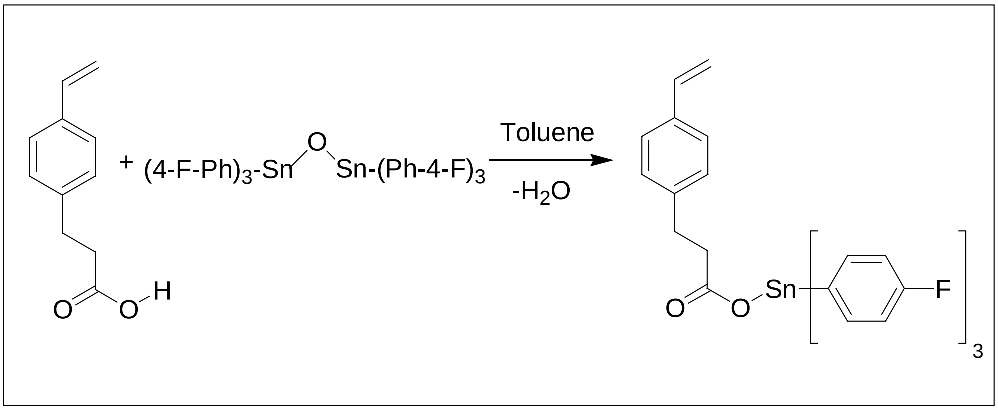
^{13}C-NMR in **$CDCl_3$ (δ in ppm referred to TMS) :**

30.9 (**C_7**), 36.2 (**C_8**), 114.0 (**C_1**), 127.1+129.1 (**C_4+C_5**), 136.5 (**C_3**), 137.2 (**C_2**), 140.5 (**C_6**), 180.0 (**C_9**).

FT-IR (cm^{-1} in KBr pellets):

3437 (stretch. OH carb.), 3085-3005 (stretch. CH arom.), 2906-2853 (stretch. CH aliph. and vinyl), 1703 (stretch. C=O carb), 1630 (stretch. C=C vinyl), 1606 (stretch. C=C arom.), 1439-1328 (bend. CH_3 and CH_2), 902 (bend. CH=CH_2), 839 (bend. CH 1,4-disubst. arom. ring).

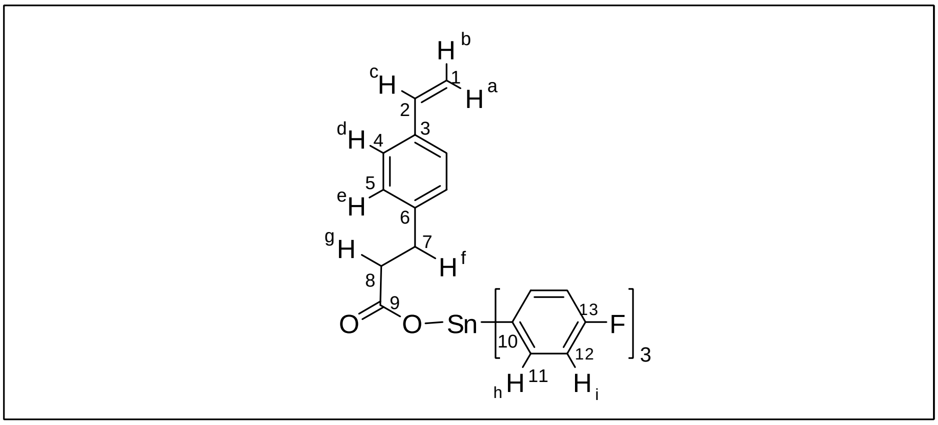
25.5 - Tri(4-fluorophenyl)tin 3-(4-styryl)propionate (PM = 525.21)



In a 150 ml round bottomed flask equipped with a magnetic stirrer, reflux condenser and a Dean-Stark apparatus 1.05 g of 3-(4-styryl)-propionic acid (5.9 mmol) were added to 2.17 g of bis[tri(4-fluorophenyl)tin] oxide (5.9 mmol), dissolved in 90 ml of toluene. Then hydroquinone 2,6-diter-butyl-4-methylphenol was added. The reaction mixture was heated to reflux until no more water formation was observed in the Dean-Stark. The reaction progress was monitored by FT-IR spectroscopy.

At the end of reaction the toluene was evaporated under reduced pressure and the crude product obtained was purified by crystallization from ethanol/ water at 40°C max.

Yield: 3.00 g (87%).



^{1}H-NMR in CDCl$_3$ (δ in ppm referred to TMS) :

2.6 (t, ^3J(H,H) = 8.0 Hz, 2H, **H^f**), 2.9 (t, ^3J(H,H) = 8.0 Hz, 2H; **H^g**), 5.2 (dd, ^3J(H$_{cis}$,H) = 10.8 Hz, ^2J(H$_{gem}$) = 1.0 Hz, 1H; =CH$_{trans}$**H$_{cis}$**, **H^b**), 5.7 (dd, ^3J(H$_{trans}$,H) = 17.6 Hz, ^2J(H$_{gem}$) = 1.2 Hz, 1H; =**CH$_{trans}$**H$_{cis}$, **H^a**), 6.7 (dd, ^3J(H,H$_{cis}$) = 10.8 Hz, ^3J(H,H$_{trans}$) = 17.6 Hz, 1H; **=CH**, **H^c**), 7.2 (m, 6H, **H^h**), 7.4 (d, ^3J(H,H) = 8.9 Hz, 2H; **H^d**), 7.8 (m, 6H, **H^i**), 8.1 (d, ^3J(H,H) = 8.9 Hz, 2H; **H^e**).

^{13}C-NMR in **CDCl$_3$ (δ in ppm referred to TMS) :**

31.6 (**C$_7$**), 35.7 (**C$_8$**), 113.5 (**C$_1$**), 116.5 (d, ^2J = 20.3, **C$_{12}$**), 126.4 (**C$_4$**), 128.7 (**C$_5$**), 135.8 (**C$_3$**), 136.4 (**C$_{10}$**), 136.7 (**C$_2$**), 138.7 (d, ^3J = 7.7, **C$_{11}$**), 140.4 (**C$_6$**), 164.6 (d, ^1J = 251.6, **C$_{13}$**), 180.2 (**C$_9$**).

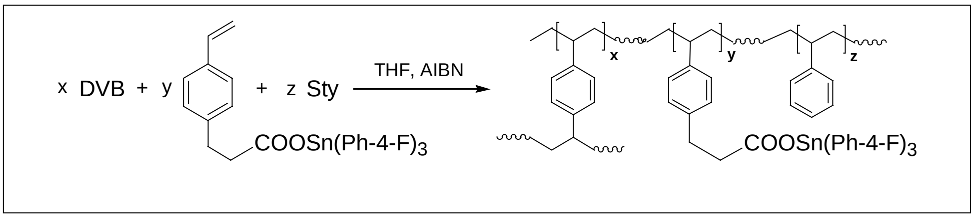
^{119}Sn-NMR in CDCl$_3$ (δ in ppm referred to SnCy$_4$): -110

^{19}F-NMR in CDCl$_3$ (δ in ppm referred to CFCl$_3$): -109.5

FT-IR (cm^{-1} in KBr pellets):

3087-3026 (stretch. CH arom.), 2906-2853 (stretch. CH aliph. and vinyl.), 1629 (stretch. C=O ester), 1601 (stretch. C=C arom.), 1492 (bend. C-H arom.), 1408 (bend. =CH$_2$), 1229 (stretch. C-F), 991-918 (bend. C=C vinyl), 819 (bend. CH 1,4-disubst. arom. ring).

25.6 - C2(X-F5) cross-linked polystyrenic resins



All the **C2(X-F 5)** series resins were prepared following the same synthesis and procedures used for the **C0(X-F 5)** ones, previously reported.

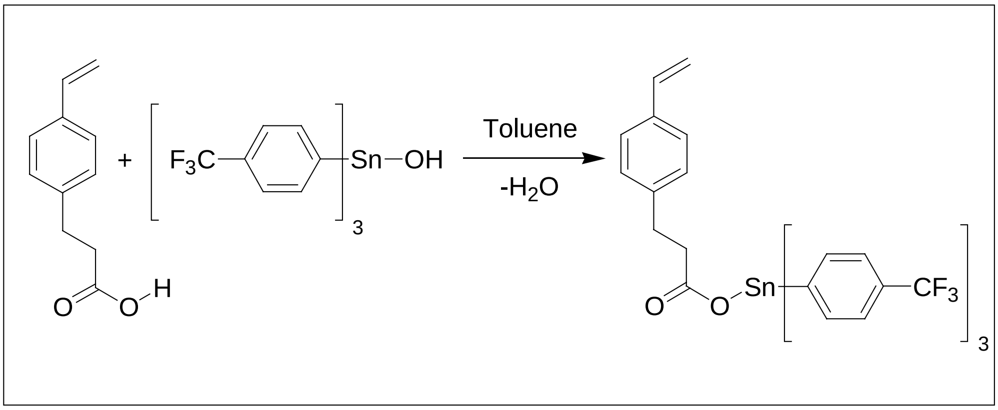
Composition of the copolymers, polymerization yields and tin content are shown in **Table 38**.

Table 38. Feeding, yields and tin content in C2(X-F 5) resins.

	Sty (mmol)	*DVB (mmol)*	*Organotin monomer (mmol)*	*Yield (%)*	*mmol Sn/g cat*
C2(20-F 5)	10.4	2.8	0.69	20	0.51
C2(35-F 5)	8.2	4.8	0.69	48	0.50
C2(50-F 5)	6.2	6.9	0.69	77	0.50
C2(70-F 5)	3.5	10.3	0.69	76	0.47

26 - Synthesis of cross-linked polystyrenic resins bearing a dimethylenic spacer and the [(4-trifluoromethyl)phenyl]tin carboxylate moiety

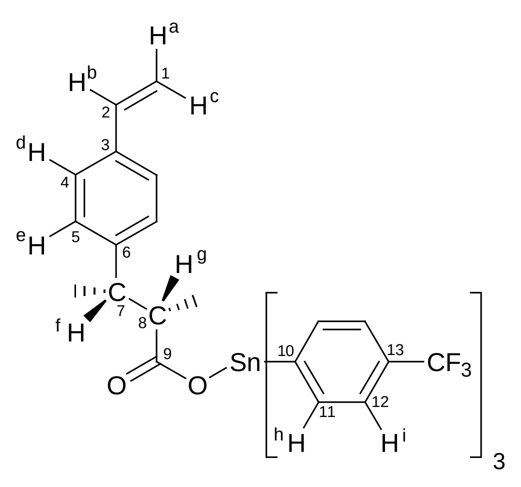
26.1 - Tri[(4-trifluoromethyl)phenyl]tin 3-(4-styryl)propionate (PM = 525.21)



In a 150 ml round bottomed flask equipped with a magnetic stirrer, reflux condenser and a Dean-Stark apparatus 0.23 g of 3-(4-styryl)-propionic acid (1.3 mmol) were added to 1.5 g of tri[(4-trifluoromethyl)phenyl]tin hydroxide (5.9 mmol), dissolved in 100 ml of toluene. Then an hydroquinone, 2,6-diterz-butyl-4-methylphenol, was added (0.15 g). The reaction mixture was heated to reflux until no more water formation was seen in the Dean -Stark. The reaction developement has been monitored by FT-IR spectroscopy.

Finally the toluene was evaporated under reduced pressure and the crude product obtained was purified by crystallization from ethanol/ water at 40°C max.

Yield: 0.65 g (68%).



^{1}H-NMR in $CDCl_3$ (δ in ppm referred toTMS) :

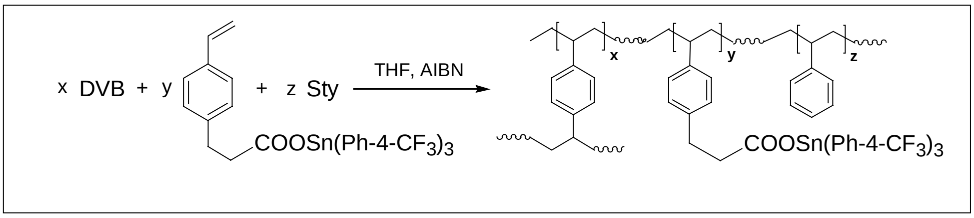
2.75 (t, ^3J(H,H) = 7.8 Hz, 2H; **H^f**), 2.95 (t, ^3J(H,H) = 7.8 Hz, 2H; **H^g**), 5.25 (dd, $^3J(H_{cis},H)$ = 10.7 Hz, $^2J(H_{gem})$ = 1.0 Hz, 1H; =$CH_{trans}\mathbf{H_{cis}}$, **$H^a$**), 5.7 (dd, $^3J(H_{trans},H)$ = 17.4 Hz, $^2J(H_{gem})$ = 1.0 Hz, 1H; =$C\mathbf{H_{trans}}H_{cis}$, **$H^c$**), 6.7 (dd, $^3J(H,H_{cis})$ = 10.7 Hz, $^3J(H,H_{trans})$ = 17.4 Hz, 1H, **=CH_2, H^b**), 7.1 (d, ^3J(H,H) = 8.5 Hz, 2H; **H^e**), 7.25 (d, ^3J(H,H)=8.5 Hz 2H; **H^d**), 7.65-7.85 (m, 12 H, **H^h+H^i**).

^{19}F-NMR in $CDCl_3$ (δ in ppm referred to $CFCl_3$): -63.7

FT-IR (cm^{-1} in KBr pellets):

3084-3005 (stretch. CH arom.), 2906-2853 (stretch. CH aliph. and vinyl.), 1627 (stretch. C=C vinyl), 1601 (stretch. C=C arom.), 1559 (stretch. symm. C=O), 1406 (bend. =CH_2), 904 (bend. C=CH_2 vinyl).

26.2 - C2(X-CF_3 5) cross-linked polystyrenic resins



The **C2(35-$CF_3$5)** resin was prepared following the same synthesis and procedures used for the **C0(X-F5)** ones, previously reported.

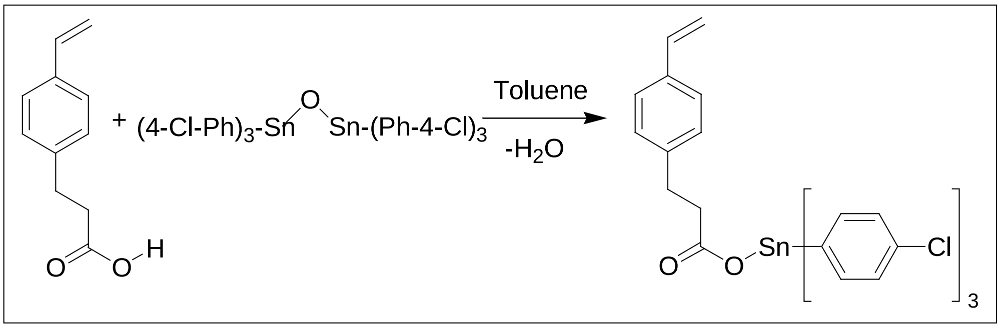
Composition of the polymer and polymerization yields are shown in **Table 39**.

Table 39. Feeding, yields and tin content in C2(35-CF_3 5) resin.

	Sty (mmol)	*DVB (mmol)*	*Organotin monomer (mmol)*	*mmol Sn/g cat*	*Yield (%)*
C2(35-CF_3 5)	4.9	2.8	0.39	0.35	58

27 - Synthesis of cross-linked polystyrenic resins bearing a dimethylenic spacer and the (4-chlorophenyl)tin carboxylate moiety

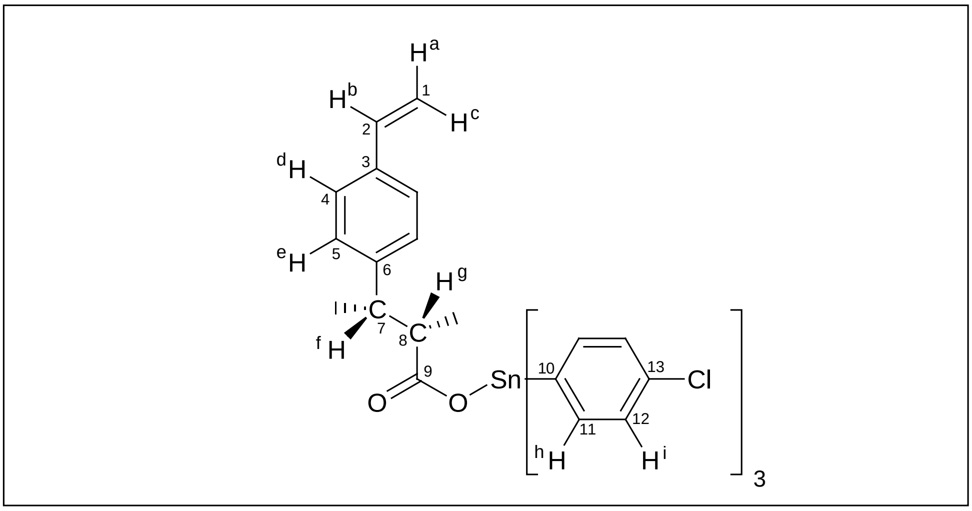
27.1 - Tri(4-clorophenyl)tin 3-(4-styryl)-propionate (PM = 628.33)



In a 250 ml round bottomed flask equipped with a magnetic stirrer, reflux condenser and a Dean-Stark apparatus 0.37 g of 3-(4-styryl)-propionic acid (2.13 mmol) were added to 1.0 g of tri [4-(chlorophenyl)]tin hydroxide (2.13 mmol), dissolved in 100 ml of toluene. Then hydroquinone 2,6-diterz-butyl-4-methylphenol was added. The reaction mixture was heated to reflux until no more water formation was seen in the Dean-Stark. The reaction progress has been monitored by FT-IR spectroscopy.

Finally the toluene was evaporated under reduced pressure and the crude product obtained was purified by crystallization from ethanol/ water at 40°C max.

Yield: 0.68 g (51%).



^{1}H-NMR (CDCl$_3$) (δ in ppm riferiti al TMS):

2.6 (t, ^3J(H,H) = 8.4 Hz, 2H; **H^f**), 2.9 (t, ^3J(H,H) = 8.4 Hz, 2H; **H^g**), 5.2 (dd, ^3J(H$_{cis}$,H) = 11.1 Hz, ^2J(H$_{gem}$) = 1.0 Hz, 1H; =CH$_{trans}$**H$_{cis}$**, **H^a**), 5.7 (dd, ^3J(H$_{trans}$,H) = 17.9 Hz, ^2J(H$_{gem}$) = 1.0 Hz, 1H; =C**H$_{trans}$**H$_{cis}$, **H^c**), 6.7 (dd, ^3J(H,H$_{cis}$) = 11.1 Hz, ^3J(H,H$_{trans}$) = 17.9 Hz, 1H; **=CH**, **H^b**), 7.4 (m, 6H, **H^h**), 7.5 (m, 6H, **H^i**), 7.6 (dd, ^3J(H,H) = 8.7 Hz, 2H; **H^d**).

^{13}C-NMR (CDCl$_3$) (δ in ppm riferiti al TMS):

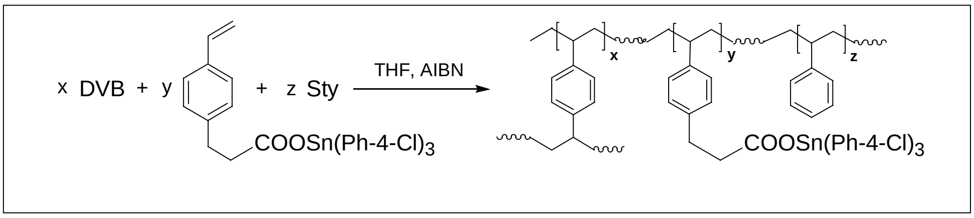
31.6 (**C$_7$**), 35.6 (**C$_8$**), 113.5 (**C$_1$**), 126.5 (**C$_4$**), 128.7 (**C$_5$**), 129.5 (**C$_{12}$**), 136.0 (**C$_3$**), 137.2 + 136.7 (**C$_{10}$ + C$_{13}$**), 137.7 (**C$_2$**), 138.0 (**C$_{11}$**), 140.4 (**C$_6$**), 142.3 (**C$_3$**), 173.0 (**C$_9$**).

^{119}Sn-NMR (CDCl$_3$) (δ in ppm riferiti al SnMe$_4$): -115.

FT-IR (cm^{-1} in pasticca di KBr):

3087-3026 (stretch. CH arom.), 2922 (stretch. asim. CH aliph.), 1630 (stretch. C=O ester), 1585-1478 (stretch. C=C arom.), 1452 (bend. CH aliph.), 1408 (bend. =CH$_2$), 1012 (bend. CH 1,4-disubst. arom.ring), 907 (bend. C=CH$_2$ vinyl).

27.2 - C2(X-Cl 5) cross-linked polystyrenic resins



All the **C2(X-Cl5)** resins were prepared following the same synthesis and procedures used for the **C0(X-F5)** ones, previously reported.

Composition of the copolymers and polymerization yields are shown in **Table 40**.

Table 40. Feeding, yields and tin content in C2(X-Cl 5) resins.

	Sty (mmol)	*DVB (mmol)*	*Organotin monomer (mmol)*	*Yield (%)*	*mmol Sn/g cat*
C2(20-Cl 5)	4.8	1.3	0.32	23	0.50
C2(35-Cl 5)	3.8	2.2	0.32	75	0.49
C2(50-Cl 5)	5.7	6.4	0.64	59	0.48
C2(70-Cl 5)	3.2	8.9	0.64	60	0.47

28 - Synthesis of MCM-41 silica functionalized with the triphenyltin carboxylate moiety

28.1 - Synthesis of MCM-41 silica

A mixture of Cab-O-Sil M5 silica (4.18 g) and 25% aqueous solution of tetrabutylammonium hydroxide (12.70 g) in 26.15 g of water was added under stirring to a solution of 20.2 g sodium silicate in water. To this mixture further 14.81 g of Cab-O-Sil M5 silica were added under stirring. Then a previously prepared template solution (47.69 g of cetyl trimethylammonium bromide in 319 g of water, heated until dissolution of the salt) was added. After stirring for 1 h, the solution was transferred in polypropylene 1000 ml plastic container, usually made of PP, sealed and placed in oven at 100°C for 2.5 days. The resulting milky suspension was filtered and the residue washed extensively with water. Then the silica was dried at 70°C in vacuo for 2 days and finally calcinated in the air. The thermal process started from room temperature to 550°C at a 1°C/min heating rate. The silica was kept at this temperature for 10 h, then cooled at 1°C/min to room temperature.

Yield: 20.55 g of MCM-41 (97 %).

Because of the long time required the filtration step was successively replaced by centrifugation (6000 rpm/ 20 min).

Yield: 19.76 g of MCM-41 silica (94%).

FT-IR Spectroscopy (ν in cm^{-1} in KBr pellets)

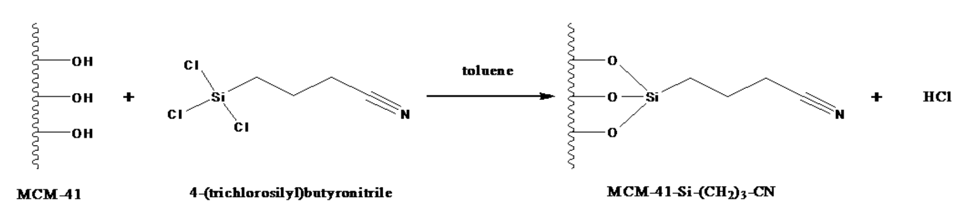
3455 (stretch. O-H), 1079 (stretch. Si-O-Si).

BET Analysis

MCM-41 (filtration) 990 m^2/g at 200 °C

MCM-41 (centrifugation) 994 m^2/g at 200 °C

28.2 - Functionalization of MCM-41 silica to MCM-41-$(CH_2)_3$-CN



MCM-41 (4.08 g, 0.032 mol of OH) was activated at 200°C in vacuum for 2 h, in order to eliminate water present on the silica surface. Then 0.197 g of dimethoxydimethylsilane were added ($1.63 \cdot 10^{-3}$ moli, 10.2% of the total amount of surface silanolic groups). Then 0.210 g of 4-(trichlorosilyl)butyrronitrile ($1.04 \cdot 10^{-3}$ mol, 9.7% of the total amount of surface silanolic groups) were added under stirring and refluxed overnight. At the end 2.30 g of dimethoxydimethyl silane (0.0192 mol, 119% the total amount of surface silanolic groups) were added again and the reaction mixture was refluxed for a further 3 hours. The product was filtered off, washed extensively with water and ethanol and dried overnight at 70°C under vacuum. The product finally obtained following this procedure is the **FE1** catalyst precursor.

With the aim to synthesize a silica having a higher functionalisation degree the protection of the more active silanolic surface groups with dimethoxydimethylsilane was eliminated. Following this new procedure, two further precursors were prepared by addition of 0.210 g ($1.04 \cdot 10^{-3}$ mol) and 0.420 g ($2.08 \cdot 10^{-3}$ mol) of 4-(trichlorosilyl)butyrronitrile to the previously activated MCM-41 silica, thus obtaining the **FE2** and **FE3** precursors, respectively.

Yields:

MCM-41-$(CH_2)_3$-CN (**FE1** precursor) → 4.49 g

MCM-41-$(CH_2)_3$-CN (**FE2** precursor) → 5.09 g

MCM-41-$(CH_2)_3$-CN (**FE3** precursor) → 4.79 g

BET Analysis

MCM-41-$(CH_2)_3$-CN (**FE1** precursor) → 830 m^2g^{-1} at 100°C

MCM-41-$(CH_2)_3$-CN (**FE2** precursor) → 710 m^2g^{-1} at 200°C

MCM-41-$(CH_2)_3$-CN (**FE3** precursor) → 730 m^2g^{-1} at 200°C

FT-IR Spectroscopy (ν in cm^{-1} in KBr pellets)

MCM-41-$(CH_2)_3$-CN (**FE1** precursor)

2966 (stretch. aliph. C-H), 2256 (stretch.CN), 1481 (bend. aliph. C-H)

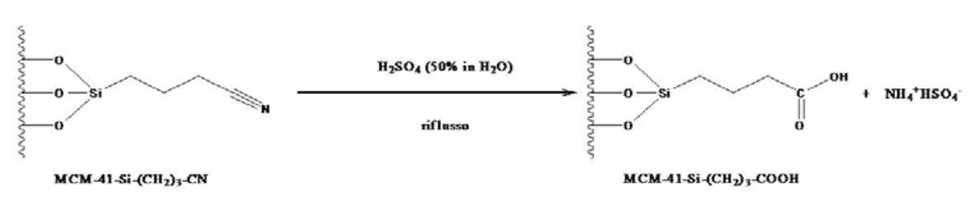
MCM-41-$(CH_2)_3$-CN (**FE2** precursor)

2963 (stretch. aliph. C-H), 2258 (stretch.CN), 1480 (bend. aliph. C-H)

MCM-41-$(CH_2)_3$-CN (**FE3** precursor)

2965 (stretch. aliph. C-H), 2255 (stretch.CN), 1483 (bend. aliph. C-H)

28.3 - Hydrolysis of MCM-41-$(CH_2)_3$-CN to MCM-41-$(CH_2)_3$-COOH



2.18 g of MCM-41-$(CH_2)_3$-CN silica (0.303 mmol of CN) were hydrolysed by 70 ml of 50% sulphuric acid at 60 °C for 3 h. This mixture was subsequently stirred overnight at room temperature, filtered on filtering funnel and washed with a great amount of water until it was neutral.
The obtained product was dried overnight at 80 °C under vacuum.
The same procedure was also applied to the other MCM-41-$(CH_2)_3$-CN silica, prepared as it has been previously reported, leading to MCM-41-$(CH_2)_3$-COOH **FE2** and **FE3** precursors, respectively.

Yields:
MCM-41-$(CH_2)_3$-COOH (**FE1** precursor) → 2.02 g
MCM-41-$(CH_2)_3$-COOH (**FE2** precursor) → 1.86 g
MCM-41-$(CH_2)_3$-COOH (**FE3** precursor) → 2.05 g

BET Analysis
MCM-41-$(CH_2)_3$-COOH (**FE1** precursor) → 995 m^2g^{-1} at 100°C
MCM-41-$(CH_2)_3$-COOH (**FE2** precursor) → 640 m^2g^{-1} at 200°C
MCM-41-$(CH_2)_3$-COOH (**FE3** precursor) → 630 m^2g^{-1} at 200°C

FT-IR Spectroscopy (ν in cm^{-1} in KBr pellets)

MCM-41-$(CH_2)_3$-COOH (**FE1** precursor)

2966 (stretch. aliph. C-H), 1697 (stretch. C=O acid), 1471 (bend. aliph. C-H)

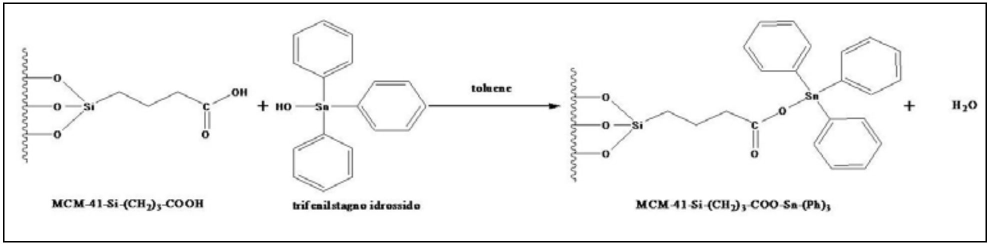
MCM-41-$(CH_2)_3$-COOH (**FE2** precursor)

2968 (stretch. aliph. C-H), 1710 (stretch. C=O acid)

MCM-41-$(CH_2)_3$-COOH (**FE3** precursor)

2969 (stretch. aliph.C-H), 1711 (stretch. C=O acid)

28.4 - Triorganotin functionalised MCM-41 silica



In a 100 ml round bottomed flask equipped with a magnetic stirrer, reflux condenser and a Dean-Stark apparatus 1,00 g di MCM-41-$(CH_2)_3$-COOH silica were added to 1.6 g of triphenyltin hydroxide (5.9 mmol), dissolved in 40 ml of toluene. The reaction mixture was heated to reflux until no more water formation was observed in the Dean -Stark. The reaction progress was monitored by FT-IR spectroscopy.

Finally the functionalised silica was filtered off, washed carefully with CH_3Cl and dried overnight at 60°C. The obtained product has been dried further at 60°C under vacuum for 12 hours, at least.

The same synthetic pathway was followed to functionalize **FE2** and **FE3** MCM-41-$(CH_2)_3$-COOH precursors.

Yields:

FE1 (MCM-41-$(CH_2)_3$-COOSn-$(Ph)_3$) → 1.35 g

FE2 (MCM-41-$(CH_2)_3$-COOSn-$(Ph)_3$) → 1.16 g

FE3 (MCM-41-$(CH_2)_3$-COOSn-$(Ph)_3$) → 1.26 g

BET Analysis

FE1 (MCM-41-$(CH_2)_3$-COOSn-$(Ph)_3$) → 195 m^2g^{-1} at 200°C

FE2 (MCM-41-$(CH_2)_3$-COOSn-$(Ph)_3$) → 625 m^2g^{-1} at 200°C

FE3 (MCM-41-$(CH_2)_3$-COOSn-$(Ph)_3$) → 280 m^2g^{-1} at 200°C

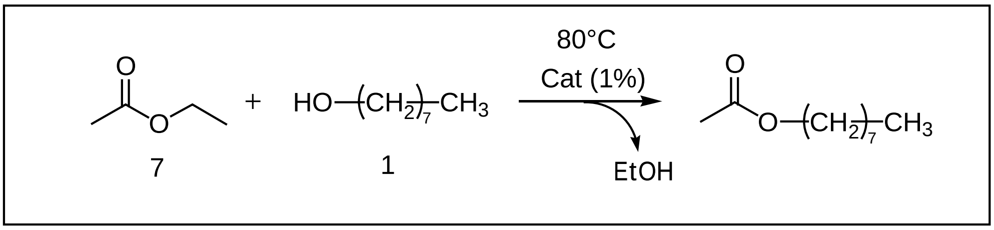
FT-IR Spectroscopy (cm^{-1} in KBr pellets)

FE1 (MCM-41-$(CH_2)_3$-COOSn-$(Ph)_3$)
2966 (stretch. aliph. CH), 1620 (stretch. C=O ester), 1482 (bend. aliph. C-H), 729 (bend. monosubst. aromatic ring).

FE2 (MCM-41-$(CH_2)_3$-COOSn-$(Ph)_3$)
2966 (stretch. aliph. C-H), 1635 (stretch C=O ester), 1482 (bend. aliph. C-H), 729 (bend. monosubst. aromatic ring).

FE3 (MCM-41-$(CH_2)_3$-COOSn-$(Ph)_3$)
2966 (stretch. aliph. C-H), 1637 (stretch. C=O ester), 1482 (bend. aliph. C-H), 730 (bend. monosubst. aromatic ring).

29 - Assessment of catalytic activity in the transesterification reaction: catalytic activity tests.



The synthesized resins were tested as catalysts in a model reaction between ethyl acetate and 1-octanol, with the aim to investigate their catalytic performance. A primary alcohol was chosen because in previous studies it appeared to be more sensitive to the reaction conditions than a secondary or a tertiary one. The amount of catalyst in each trial was calculate so as to achieve a 1% mole ratio of tin containing units with respect to the alcohol.

In a 50 ml round bottomed flask ethyl acetate (7 eq), 1-octanol (1 eq) and the catalyst resin (0,01 eq. respect to the alcohol) were added. The reaction mixture was heated to reflux and the reaction proceeded for 48 h. The alcohol conversion was assessed by gas-chromatography, determining the relative amounts of transesterified product and unreacted 1-octanol, after an established interval of time, usually 2, 4, 8, 24 and 48 hours. The G.C. analysis started from 60°C to 250°C, with a temperature gradient of 5 °C/min G.C. column. The reaction was also performed in the absence of catalyst, to investigate the presence of additional contributions other than those given by the organotin carboxylate moiety.

Under these conditions, no ester conversion was detected, thus confirming that no additional contribution to the catalytic activity of these resins was present.

30 - References

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