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SYNTHESIS OF NEW CALIXARENE-BASED LUBRICANT ADDITIVES

Coordinatore:
Prof. Enrico Dalcanale

Tutor principale:
Prof. Alessandro Casnati

Tutors:
Prof. Francesco Sansone
Dr. Marcello Notari
Dr. Alberto Roselli

Dottorando: Alessandro Burlini

ABSTRACT

The lubricants are normally composed by base oils and a number of additives which are added to improve the performances of the final product. In this work, which is due to the collaboration between ENI S.p.A. and Prof. Casnati's group, significant results in the application of calixarene structures to two classes of lubricant additives (viscosity index improvers and detergents) were shown.

In particular, several calix[8]arene derivatives were synthesized to use as core precursors in the "arm-first" synthetic processes of star polymers for viscosity index improver applications. The use of calixarene derivatives enable the production of star polymers with a high and well-defined number of branches and endowed with a very low dispersivity of molecular weight which can originate better performances than the current commercially available viscosity index improvers of the major competitor. Several functional groups were considered to prepare reactive p-tert-butylcalix[8]arene cores to be used in living anionic polymerization. n-butyllithium was used as model of the living anionic polymer to test the outcome of the reaction of polymer insertion on the calixarene core, facilitating the analyses of the products. The calixarene derivative, which easier reacts with n-BuLi, was selected for the preparation of star polymers by using a isoprene/styrene living anionic polymer. Finally, the lubricant formulations, which include the calixarene-based star polymers or commercially available products as viscosity index improvers, were prepared and comparatively tested.

In the last part of Thesis, the use of calixarenes as polycarboxylic acids to synthetize new sulfur-free detergents as lubricant additives was carried out. In this way, these calcium-based detergents can be used for the formulation of new automotive lubricants with low content of ash, phosphorus and sulfur (low SAPS). To increase the low deprotonation degree of OH groups and their capacity to complex calcium ions, a complete functionalization of the calixarene mixtures with acetic acid groups was required. Futhermore, the "one-step" synthesis of new calixarenes with alkyl chains in para positions longer than the ones already known was necessary to improve the oil solubility and stability of reverse micelles formed by the detergents. Moreover, the separation and characterization of the calixarenes were carried out to optimize their synthetic process, also on pilot scale. For our purpose, the use of p-tert-octylcalixarenes for the preparation of detergents was carried out to compare the properties of the final detergents respect to the use of the p-dodecyl calixarenes. Once achieved the functionalization of both calixarene mixtures with carboxylic acid groups, the syntheses of new calixarene-based detergents were carried out to identify the best calixarene derivative for our research goals. The synthetic process for the preparation of calixarene-based detergent having very high basicity (TBN 400) was also investigated for applications in lubricants for marine engines. In addition, with the aim of testing the calixarene-based detergents in automotive lubricants, several additive packages (concentrated mixture of additives) containing our detergents were prepared. Using these packages the corresponding automotive lubricants can be formulated. Besides, a lubricant containing commercial calcium alkylbenzene-sulfonates detergents was prepared to compare its detergency properties with those of the calixarene-based oils.

DECLARATION

I hereby certify that the material, which I now submit for assessment on the programmes of study leading to the award of a Ph.D., is entirely my own work and has not been taken from the work of others save to the extent that such work has been cited and acknowledged within the text of my own work. No portion of work contained in this thesis has been submitted in support of an application for another degree or qualification to this or any other institution.

Date
14/01/2016 (dd/mm/yyyy)

Signature
Alessandro Buzhini

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ABBREVIATIONS

API = *A*merican *P*etroleum *I*nstitute

ASTM = *A*dditive *M*anufacturing *T*echnology *S*tandards

ATRP = *A*tom *T*ransfer *R*adical *P*olymerization

CCS = *C*old *C*ranking *S*imulator

DBN = *D*irect *B*ase *N*umber

DVB = *D*i*V*inyl*B*enzene

FMs = *F*riction *M*odifiers

HBC = *H*igh melting point p-tert-*B*utyl*C*alixarene

OCPs = *O*lefin *C*o*P*olymers

OIs = *O*xidation *I*nhibitors

PAGs = *P*oly*A*lkylene*G*lycols

PAMAs = *P*oly*A*lkyl*M*eth*A*crylates

PAO = *P*oly*A*lpha*O*lefins

PDVB = *P*oly*D*i*V*inyl*B*enzene

PIBs = *P*oly*I*so*B*utylenes

PPDs = *P*our *P*oint *D*epressants

PS = *P*oly*S*tyrene

SAE = *S*ociety of *A*utomotive *E*ngineers

SANS = *S*mall-*A*ngle *N*eutron *S*cattering

SAPs = *S*ulfurized *A*lkyl *P*henols

SPs = *S*tar-shaped *P*olymers

SSI = *S*hear *S*tability *I*ndex

TBN = *T*otal *B*ase *N*umber

TEM = *T*ransmission *E*lectron *M*icroscopy

TEOST = *T*hermo-oxidation *E*ngine *O*il *S*imulation *T*est

TLC = *T*hin *L*ayer *C*hromatography

VI = *V*iscosity *I*ndex

VIIs = *V*iscosity *I*ndex *I*mprovers

VMs = *V*iscosity *M*odifiers

Part I

Introduction

CHAPTER 1

LUBRICANTS

Lubrication is a word often used in relation to the proper operation, reliability and maintenance of mechanical equipments.

In a mechanical equipment, the lubricant interposes between the metal surfaces in relative motion, in order to prevent the direct contact between the mechanical parts and minimize friction and wear. In this way, the performance of the machine is enhanced and its life lengthened.

Many different substances are used to lubricate metal surfaces: oils are among the most common ones. The oil-based lubricants are composed by base oils and a number of additives. These latter components are added in order to improve the performances of the final product.

1.1 Base oils

The American Petroleum Institute (API) (API 1509, Appendix E) has categorized base oils into five categories described in Table 1.1. The base oils belonging to the first three groups (Group I, Group II and Group III) are obtained from the refining cycle of petroleum crude oil.

Group I refers to solvent-refined base oils. As suggested from their lowest price on the market, they are obtained with the simplest refining process.

Group II base oils are manufactured by hydro-cracking, a more complex process than that one used for Group I base oils. Due to the higher content of saturated hydrocarbon molecules, Group II base oils have better oxidation

Table (1.1): *API Base Oil Classification System*

Group	Saturate wt %	Sulphur wt %	Viscosity index
I	< 90	> 0.03	> 80 to < 120
II	≥ 90	≤ 0.03	≥ 80 to ≤ 120
III	≥ 90	≤ 0.03	≥ 120
IV	All poly α-olefins (PAOs)		
V	All base stocks not included in Groups I – IV		

stability. They also are clearer in color and have higher cost of Group I base oils.

Group III base oils are obtained by hydrocracking at high pressure and heat, followed by solvent or hydro-isomerization dewaxing. This more complex process is designed to achieve a base oil with a more homogeneous composition. Although Group III basestocks are made from crude oil, they are sometimes described as synthetic base oils.

Group IV refers to fully synthetic hydrocarbon (hydrogenated polyalphaolefins, PAO) base oils obtained by oligomerization of α-olefins.

Group V contains all the other base oil types which are not included in Groups I to IV. For example, this last group includes, among others, carboxylic esters, phosphate esters, silicones, polyalkylene glycols (PAGs).

Base oils of different type are usually mixed together in order to enhance the lubricant's properties. A typical base blend for synthetic oils is made of PAO and esters, a mixture that provides excellent rheology and oxidation stability together with good solvency of the additives and seals compatibility.

Since the 30's of the last century, lubricants have been formulated by mixing oils with additives which add, enhance or suppress some base oil properties. The amount of additives strictly depends on the type of oil and application. The most common lubricant additives are described in the following section.

1.2 Additives

Oil additives are chemical compounds which are able to highly improve the performance of the base oils.

Nowadays all commercial engine oils contain additives. The choice of additives is determined by its specific application: for example the oil for a diesel engine with direct injection in a truck has different additives than the oil used in a small gasoline-powered engine of a chainsaw (2-cycle engine oil).

Oil additives are fundamental for the proper lubrication and prolonged use of engine oil in modern internal combustion engines. Without additives, the oil could rapidly become contaminated, decompose, leak out or not properly protect the engine parts at all operating temperatures and conditions. According to the specific role, there are different classes of additives. Nevertheless the total amount of additives in a lubricant usually does not exceed 30 % by weight.

Figure 1.1 shows the development of the different classes of additives since 1932, date that marked the appearance of the first additives in lubricant oils.

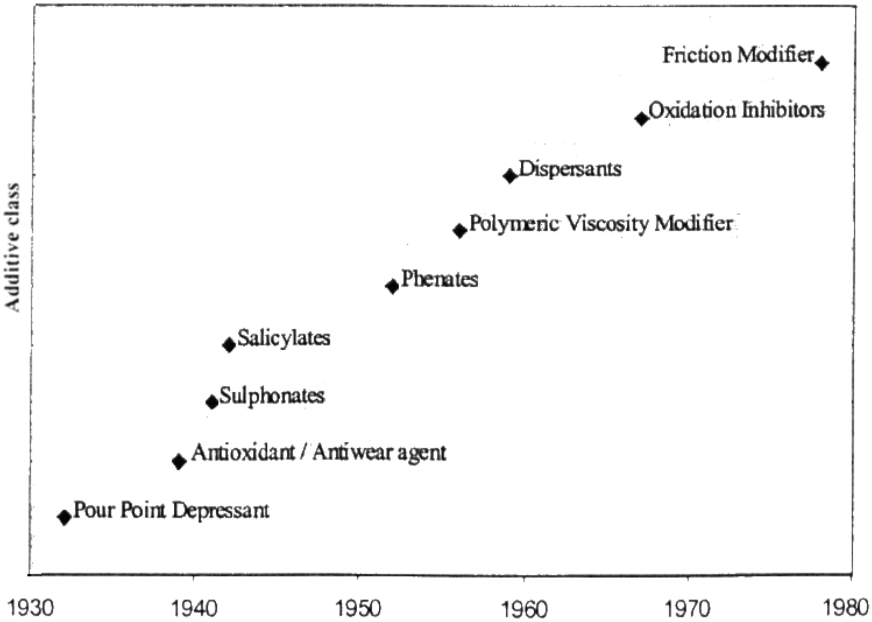

Figure (1.1): *Development of the lubricant additives since 1932*

Some of the most important classes of additives include dispersants, oxidation and rust inhibitors, pour point depressants, friction modifiers, viscosity index improvers and detergents. These types of additives are described below.

1.2.1 Dispersants

One of the most important properties of the engine oils is their ability to suspend products generated by the combustion process and by the thermal and oxidative degradation of the lubricant, preventing their agglomeration and deposition. Degradation products of fuels are transferred to the lubricant through the blow-by gases that flow from the combustion chamber to the crankcase. Deposits, which are due to the thermal and oxidative degradation of the lubricant, form in the hottest part of the engine, in particular near the piston rings and cylinder wall. The degradation products from both fuel and lubricant, are thermally labile and decompose to polar species with a tendency to separate from the lubricant.[1] In this way they can form deposits with filter and channel clogging. If this event happens, there will be a malfunction resulting in a loss of engine performance.

In detail, dispersants are lubricant additives which help to suspend sludges, soot and other deposits, preventing their deposition on critical surfaces.

A dispersant molecule consists of three distinct structural features: a hydrocarbon group, a polar group and a connecting group.

The polar group is usually nitrogen- or oxygen-derived.

The hydrocarbon group has polymeric nature and, depending on its molecular weight, the dispersants can be classified into polymeric dispersants and dispersant polymers. Polymeric dispersants are of lower molecular weight than dispersant polymers. The molecular weight of polymeric dispersants ranges between 3 and 7 KDa as compared to dispersant polymers, which have a molecular weight from 25 KDa to higher.[2] While a variety of olefins, such as polyisobutylene, polypropylene, polyalphaolefins, and mixtures of them, can be used to make polymeric dispersants, the polyisobutylene-derived dispersants are the most common.[3]

The polar group can interact with the oxidized polar species, whereas the hydrocarbon groups allow the suspension in oil of the dispersant-oxidized product adducts. Together with dispersants, oxidation inhibitors and detergents constitute the class of additives called "deposit control agents" because they are designed to inhibit and control the deposit formation.

1.2.2 Oxidation Inhibitors

Oxidation produces harmful species which could compromise the functionalities of the lubricant, shorten its life and even damage the lubricated apparata.

The oxidation process is initiated upon oxygen exposure of lubricant especially at high temperatures. This process can be also activated and catalysed by metals such as iron, copper[4] or nickel. Antioxidants are added to protect the lubricant from oxidative degradation. For this reason, oxidation inhibitors also belong to the class of deposit control agents. As a conseguence of the oxidative chain reactions, several radical species forms together with peroxides and hydroperoxides. Under high-temperature oxidation conditions, the intermediate aldehydes and ketones can undergo further reactions to form acids which can thicken the oil and contribute to the formation of sludge and varnish deposits.

The chemical species used as antioxidants must therefore disrupt the propagation of the oxidation chain of lubricants.

The control of lubricant oxidation can be achieved trapping catalytic impurities and destroying the alkyl radicals, alkyl peroxy radicals and hydroperoxides. These processes can be conducted using a metal deactivator and an appropriate antioxidant with radical scavenging[5] or peroxide decomposing functionality[6].

Several effective antioxidant classes were developed. The main classes include oil-soluble organic and organometallic antioxidants such as sulfur compounds[7], phosphorus derivatives, aromatic amine compounds[8,9], phenol derivatives[10], organo-copper compounds[11] and boron derivatives[12].

1.2.3 Corrosion Inhibitors

Corrosion is a reaction between a material, usually a metal, and its surrounding environment. This process can produce a deterioration of the material and its properties. To limit the degradation of metallic parts in movement, a specific class of lubricant additives called "corrosion inhibitors" can be used. These compounds are usually divided into several categories depending on their duration of use, chemical composition and end-use application. The common corrosion inhibitors are chemical species which include organic compounds containing nitrogen, boron, sulfur and phosphorus atoms. These additives are able to interact with the environmental oxidizing species and the metal surfaces. Similar behaviors are also displayed by carboxylates and sulfonate salts such as with sodium, magnesium, calcium and barium.

The fundamental description of corrosion inhibition mechanism was first proposed by Baker and co-worker and described as the adsorption of a monolayer of the inhibitor on the metal surface to form a protective barrier.[13] The contact with the outside environmental oxidizing species is thus prevented by the protective barrier. The study of this mechanism showed that the corrosion prevention depends on a complex interaction of several variables such as the presence of oxygen and the lifetime of the adsorbed film that is often limited by thermal and mechanical desorption.[14]

Moreover, the monolayer of the adsorbed additives is oriented with the polar head on the surface and the non-polar tails closely packed among them and vertically aligned (Figure 1.2).[15,16]

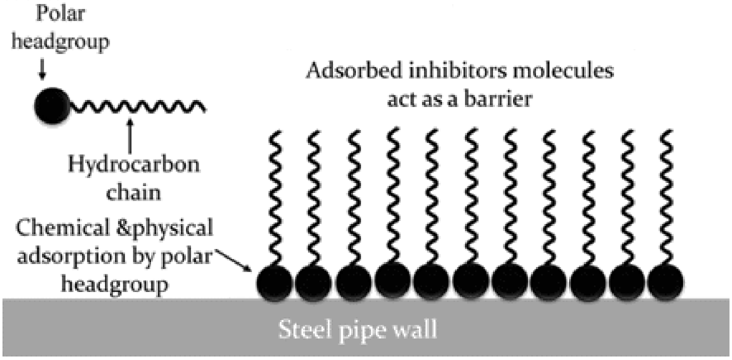

Figure (1.2): *Schematic diagram of adsorbed corrosion inhibitor*

These studies also revealed how the adsorption of the corrosion inhibitor was accomplished by either an electrostatic interaction (physisorption) or an electron transfer to a coordinated bond (chemisorption).[15,16]

Research in this field is still quite active to meet the new environmental and health requirements. For example, the marine toxicity of several amine-based products is pushing different companies to find alternative more eco-friendly materials,[17] whereas for the barium-based compounds the producers have the tendency to replace this metal ion with other metal such as sodium, magnesium and calcium, centainly more present in the environment.[18]

1.2.4 Friction Modifiers

The friction modifiers (FM) are additives which are mainly used to reduce friction.[19,20] The mechanism of their action is similar to the one described for the corrosion inhibitors (Section 1.2.3), in which they form durable and low resistance films of lubricant via adsorption on surfaces and interaction with the oil (Figure 1.3). In this way, the friction is reduced and the wear caused by metal-metal contact, largely decreased. Reducing friction between metallic parts in movement, these additives can also significantly improve fuel efficiency due to the reduced dissipation of the energy into heat and the corresponding higher conversion of the combustion energy into mechanical energy.

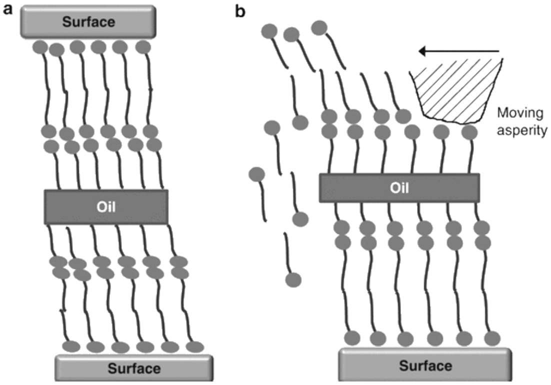

Figure (1.3): *Schematic diagram of friction modifier layers. a) formation of the layers between metal surfaces; b) behaviour of the layers when the metal parts are in movement*

Common materials used for this purpose include long-chain fatty acids, their derivatives and the molybdenum oil-soluble compounds. In detail, the molybdenum is solubilized into the lubricant in the form of organic sulfur-based complexes. By thermal activation these complexes can decompose generating *in-situ* MoS_2 (Figure 1.4), which forms a protective barrier on the metal surfaces. The MoS_2 remains grafted on the metal surface through sulfur atoms which bind to the metal atoms surfaces. In this way, the friction between moving surfaces in metal-to-metal contacts are reduced.

The role of these Molibdenum complexes is therefore that to convey the unsoluble Molibdenum salt into the lubricants. In this way, additives can be directly generated *in situ* when the need of them is high.

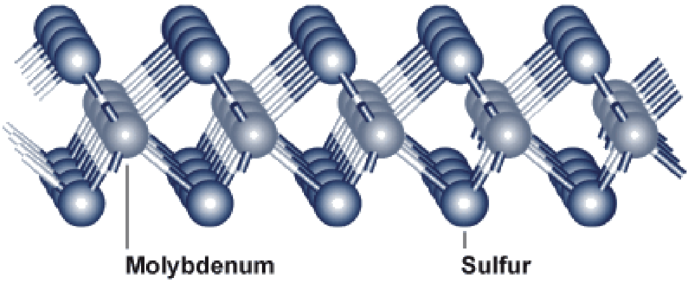

Figure (1.4): *A side view of the layer structure of MoS_2. The lighter spheres represent molybdenum atoms and the darker spheres sulfur.*

1.2.5 Pour Point Depressants

Pour point depressants (PPDs), also called low-temperature flow improvers, are polymeric molecules which are added to base oils to improve their flow properties at low temperatures. Without this additive, at cold temperatures, the lubricants could become too viscous to flow since the aliphatic linear long-chain components of the paraffinic oils (waxes), tend to aggregate and precipitate out of the solution.[21] As a result, the flow of the lubricant through the system could be too slow or, in the worst cases, oil lines could be clogged by waxes deposits.

Before the use of PPDs in the early 1930s, few options were available to control the lubricant viscosity at low-temperature. For example, kerosene was first added to lubricants to increase the oil solvency. However kerosene did not show a good performance due to its high volatility. An alternative used at those times was also to add natural materials such as asphalt resins. Although these additives were somehow effective, they were often used for specific applications. This idea, however, stimulated the investigation of synthetic PPDs with structures based on hydrocarbon arrangements similar to those of the asphalt resins. As a result, the general chemical structure of a PPD polymer is similar to that of a comb and it is characterized by long chains grafted onto the polymer backbone and interspaced by shorter chains (Figure 1.5).

The long aliphatic chains can interact with the wax in the oil, whereas

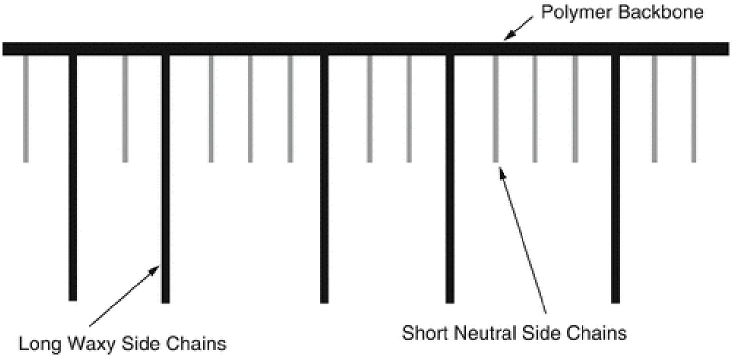

Figure (1.5): *PPD comb polymer diagram*

the shorter side chains act as "inert diluents" helping to control the extent of interactions with the wax. Indeed, the intensity of this interactions is a function of the types and number of side chains. In this way, the PPD can prevent the wax aggregation, maintaining the system fluid also at low temperatures.[22]

Historically, polymethacrylates have been the first polymeric PPD since 1937.[23] Over the years the number of different polymers used as PPDs have gradually increased. Nowadays they include, but they are not limited to, acrylates[24], methacrylates[25], alkylated styrenes[26], alpha olefins[27], ethylene vinyl acetates (EVA) and vinyl acetate-maleic anhydride[28].

1.2.6 Viscosity Index Improvers

Viscosity index (VI) is a common method used to measure the viscosity changes of fluids, as a conseguence of temperature change. The higher is the VI, the smaller is the change in viscosity with temperature. VI improvers (also known as Viscosity Modifiers, VMs) are additives able to keep the viscosity of the fluid high throughout the whole temperature range used.[29]

They are widely used in engine oils where large temperature variations are observed during oparation. For instance, in the crankcase, an oil characterized by low viscosity at low temperature is needed to allow the oil pump to push the oil up to the top of the engine during start up in cold days. On the other hand, the same oil must be viscous enough to protect the engine at the operating temperature (with peaks over 300 °C).

VI additives are also used in transmissions and hydraulic fluids.

This type of lubricant additives consists of polymeric molecules whose coil size in the lubricating oil is sensitive to the temperature. At low temperatures the molecule chains contract and do not impact significantly on the fluid viscosity; at high temperatures the polymer chains expand. At the increase of the hydrodynamic volume of the polymer coils, corresponds an increase of the fluid resistance to flow, increasing the lubricant viscosity (Figure 1.6).

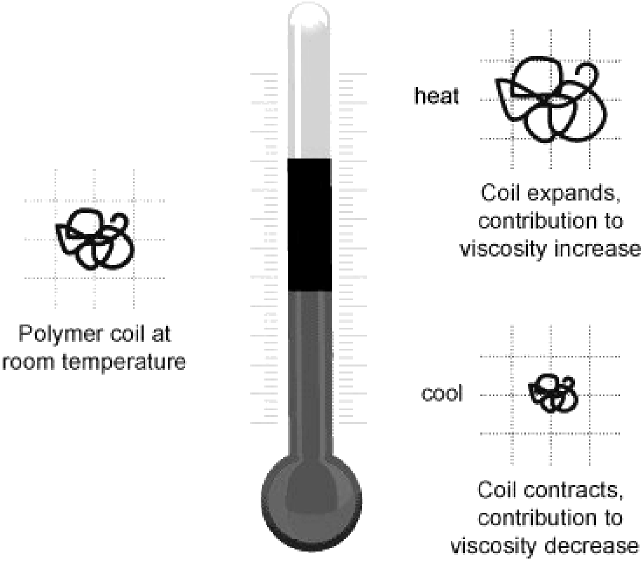

Figure (1.6): *Temperature effect on the polymer coil size*

The net result is a relatively constant fluid viscosity over a wide temperature range.[30]

VI improvers are polymeric materials taken from the following class of polymers: olefin copolymers (OCPs), polyalkyl methacrylates (PAMAs), polyisobutylenes (PIBs), styrene block polymers (such as styrene isoprene, styrene butadiene) and ethylene alphaolefin copolymers. They are prepared by the polymerization of the appropriate monomers.

The chemical types of the monomers, their relative proportions, their sequence of distribution, the overall molecular weight and the molecular weight distribution are the specific polymer properties which affect lubricant performance. By tuning these properties, the performance of the VI improvers additives can be changed. Using a variety of monomer combinations and processing techniques, the production of different polymer architectures can be achieved. They can be linear, branched, star or comb polymers, each of which can be made of homopolymers, block copolymers or random copolymers.

While the synthetic processes of ethylene-based copolymers involve the use of Ziegler-Natta or metallocene catalysts, the styrene-diene copolymers are prepared by anionic polymerization of styrene with either butadiene or isoprene. The residual unsaturation of the backbone is subsequently removed by hydrogenation. For the purpose of synthetizing A-B block copolymers, the monomers are added sequentially. Anionic polymerization yields polymers with very narrow molecular weight distributions, especially when compared to those obtained by radical polymerization.

During operation, the lubricant can be exposed to high mechanical shear stress that can cause the modification of the polymer chain size. When it happens, the additive partially loses its ability to act as a viscosity improver.

Shear breakdown takes place via two mechanisms. Temporary shear breakdown occurs under certain conditions of moderate shear stress and it results in a temporary loss of viscosity. Under these conditions the long molecules of the VI improver align themselves in the direction of the stress, thus reducing resistance to flow. When the stress is removed, the molecules return to their usual random arrangement and the temporary viscosity loss is recovered. Permanent shear breakdown takes place when the shear stresses actually break the long molecules, converting them into lower molecular weight polymers, which are less effective VI improvers. This phenomenon leads to a permanent viscosity loss, which can be significant.

In relation to the polymer mechanical stability, a narrow molecular weight distribution of the VI improvers always maximize the ratio of shear stability to thickening efficiency[1].

Higher molecular weight polymers are better thickeners, nevertheless they tend to have less resistance towards mechanical shear.

On the other hand, lower molecular weight polymers are more shear resistant, but they are less able to improve the viscosity at higher temperatures (they have a lower thickening efficiency). Therefore, they have to be used in larger quantities.

The shear stability of VI improvers is evaluated using laboratory shear test equipments. The viscosity of VI improved lubricants is measured before

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[1] With "thickening efficiency" we mean the viscosity increase that a given amount of VI additive imparts to the base oil

and after being subjected to standard shear conditions (Figure 1.7).

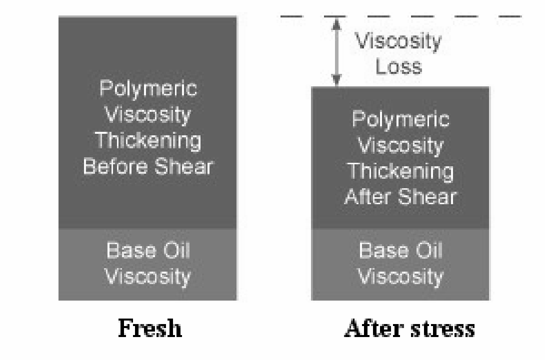


Figure (1.7): *Polymeric viscosity thickening before and after shear stress*

The results are rated as Shear Stability Index (SSI): the lower the value, the better, or more resistant to mechanical stress, the VI improver is. Therefore, the SSI is a measure of the VI improver resistance to mechanical degradation.

$$\text{SSI} = \frac{\text{Viscosity loss}}{\text{Pol. viscosity thickening before shear}} * 100$$

Viscosity loss = Solution viscosity before shear – Solution viscosity after shear

Absolute thickening efficiency = Solution viscosity – Base blend viscosity.

Star polymers as VI improvers

To overcome the shear stability problems, without loss in terms of thickening efficiency, some additive producers use some multi-branch polymer structures. Compared to linear polymers of same molecular weight, this kind of materials allows to reach the same thickening efficiency, by putting together in a single molecule, multiple branches of limited lenght.[31] This impart to the multi-branches polymers greater shear stability and consequently low SSI values.

The shear stress effects are shown in Figure 1.8. Both polymer structure morphologies have the same molecular weight (30 KDa) and before shearing the oil viscosities are approximately the same for both the oils (see the left part of Figure 1.8). Due to the different chain length of the two polymers, the degradation is more likely on the linear one and the effect of the chain rupture more severe. For these reasons, the multi-branch polymers may

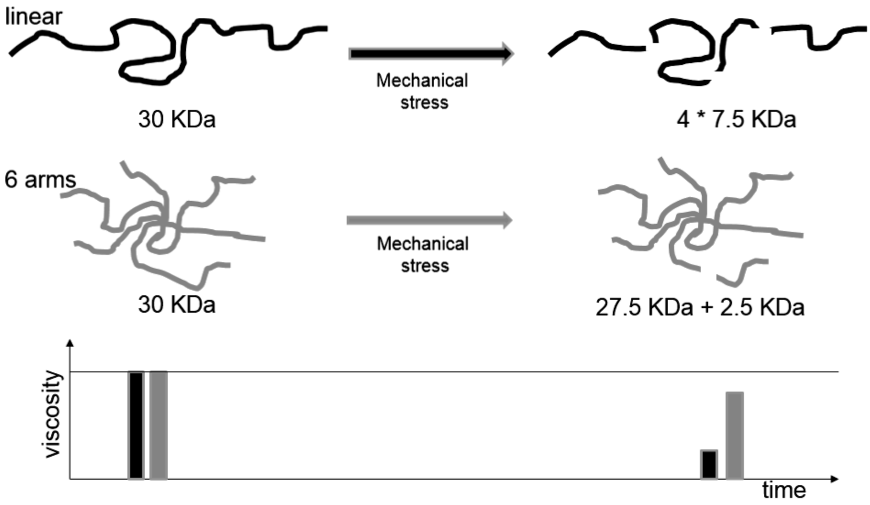


Figure (1.8): *Mechanical degradation under shearing stress for multi-branches (green) and linear (blue) polymers*

have in the future more and more importance as VI improvers. In this field, the most promising polymer structures are the star-shaped polymers (SP). They consist of a multifunctional center from which at least three polymer branches radiate.

SP can be synthesized through various approaches. The most common syntheses include an arm-first approach (or convergent approach), in which the living chains are used as the initiators. The monofunctional living polymers are used as precursors in the reaction. The active site at the end of their chain can be directly reacted with an appropriately reactive multifunctional polymer core (also known as a “linking agent”) to produce a star-shaped polymer.

Another method is the core-first approach (or divergent approach), which involves a multifunctional core as the simultaneous initiator for several arms. This one is more complicated than the arm-first approach, and finding an appropriate and stable core is more challenging.

The research and development areas of many companies are trying to produce star-shaped polymers with very low dispersity. This result can only be obtained having a high control of the living polymer chain length and the number of reactive sites within the core.

1.2.7 Detergents

One of the most important properties of the lubricants is their ability to suspend undesirable products coming from thermal and oxidative degradation processes. These insoluble materials could lead to malfunctioning of the closely fitted surfaces and clog small openings. In the internal combustion engines, the final products of combustion of fuel and those arising from lubricant decomposition include organic and inorganic acids, aldehydes, ketones and other oxygenated materials.[32,33] Among these, acids have in addition the propensity to attack metal surfaces and cause corrosive wear.

With the purpose of limiting all these phenomena, detergents are added to the lubricants.

The detergents are based on metal compounds of organic acids. They are classified as "neutral detergents" if they contain only the metal salts of organic acids and as "overbased detergents" if the contain, associated to the metal salts, also an excess of base, usually in the carbonate form.

Common metal ions which can be used to make neutral or overbased detergents include sodium, potassium, magnesium, calcium, and barium.[34] Calcium and magnesium detergents find most extensive use as lubricant additives, with a preference for those of calcium due to their lower cost. The use of barium-derived detergents is being suppressed due to concern for barium toxicity.[18]

These metals are conveyed in the lubricant environment as colloidal nanoparticles stabilised by a surfactant layer.

The nanoparticles can be composed by metal oxides, hydroxides, and carbonates.

Oxides and hydroxides are usually the preferred bases used in the production of detergents. In the case of sodium, calcium, and barium detergents, hydroxide forms are often used. However, for magnesium detergents, magnesium oxide is the preferred base.

The metal salts of organic acids (commonly called "soaps"), contained in the detergents, keep in suspension nonacidic oxygenated products such as alcohols, aldehydes and others oxygenated species.[32] In this way, detergents prevent the build-up of harmful deposits, and in internal combustion engines, help in keeping clean the hottest parts of the engine, like piston rings and grooves. For this reason, detergents belong to the deposit control agents.

The reserve of alkalinity contained in the overbased detergents has the function to neutralize the organic and inorganic acidity resulting from the thermo-oxidative decomposition of the lubricant and from the fuel combustion, thus controlling the wear and corrosion phenomena on the metal surfaces.

Detergent substrates

The nature of the detergents depends on the type of metal and of the surfactant used in the synthesis. The most common surfactants used are alkyl-benzene sulfonates, sulfurised alkylphenates, salicylates and phosphates.[35]

Sulfonate detergents are perhaps the most widely employed detergent additives and they have been extensively studied. Two different sources of sulfonates have been used: petroleum and synthetic sulfonates. The overbased detergents are synthesized by reacting the sulfonic acids with a metal hydroxide and subsequently carbonating the excess of metal hydroxide with carbon dioxide. The TEM[36–38] and SANS[39,40] particle size studies give a particle diameter in the range of 3-10 nm with an organic stabilising shell thickness of 2 nm. The shape of the inverse micelles is close to spherical, as supported by molecular dynamics computer simulation[40] and TEM studies[36–38].

Phenates detergents are produced from alkyl-phenols or sulfurized alkyl phenols (SAP) using a similar process to that used for the sulfonates. The SAP are produced by means of two steps: in the first one an olefin is used to alkylate the phenol, whereas in the subsequent step this material is sulfurized using sulfur halides or sulfur itself. The surfactant produced is made in average of two or more phenol molecules bridged by one or more sulfur atoms.[41] The alkyl tails can be straight or branched with a backbone length of typically 12 carbon atoms. Once synthesizing the organic acid precursor, the detergent can be obtained by reaction with a metal hydroxide, eventually carbonating the excess of metal hydroxide with carbon dioxide.

The salicylate detergents are synthesized from alkyl salicylic acids, derived from alkyl phenols by the Kolbe-Schmitt reaction.[42] As in the case of phenates and sulfonates, the alkyl tail of the surfactant can be branched or linear and the chain length is C_8 or greater. A spherical shape structure centered on the mineral core has been suggested by molecular dynamics computer simulation performed on overbased salycilate detergents.[43]

The phosphonate surfactants can be produced by reacting poly-isobutene with phosphorous pentasulfide. The phosphonate detergents are much less common than all the others detergents.[41] The overbased phosphonate detergents are characterized by a lower alkalinity than the other overbased detergents due to poor ability of phosphonates to incorporate an inorganic base.[44]

Synthesis

As mentioned above, the overbased calcium detergents are based on colloidal nanoparticles of calcium carbonate (and calcium hydroxide) stabilized by a surfactant layer. These materials are usually made by an inorganic core (15–40 % by weight) stabilized by oil-soluble surfactants (20–45 % by weight) incorporated into a base oil.[45]

The industrial synthesis of stable colloidal metal carbonates is known as the "oxide/hydroxide" process. The mechanism of formation proceeds through a micro-emulsion route.[46]

For the overbased detergents, the reaction system consists of an excess of metal hydroxide, an appropriate surfactant and a mixture of different solvents: normally polar and non-polar solvents. The polar solvents are usually methanol and/or water: these ones, in the presence of the surfactant, form swollen reverse micelles, which contain dispersed particles of $Ca(OH)_2$.

The surfactants are made *in-situ* by the reaction of the corresponding organic acid with the metal base.

The subsequent diffusion of gaseous CO_2, which is bubbled through the system, generates $CaCO_3$ in the reverse micellar cores, which then nucleate at supersaturation.[46] The micellar cores grow not only by absorption of $CaCO_3$ but also through coalescence with other reverse micelles containing $CaCO_3$. Literature suggests that a stable system requires a certain amount of residual calcium hydroxide, which ensures that the inorganic core is amorphous.[46] If carbonation is driven to completion, the cores are transformed into crystalline calcite, which can agglomerate to form larger particles, which eventually sediment during the reaction.[47]

The polar solvents are then stripped off at high temperature and low pressure. The resulting products are then filtered under high pressure and temperature to remove unreacted inorganic material and, eventually, agglomerated particles. The initial water-in-oil micro-emulsion reaction system results in the formation of nanometer-sized particles, with a narrow particle size distribution. Although the mechanisms involved in these reactions are not fully understood yet,[46,48] Jacquet and co-workers[47] have studied the oxide/hydroxide reaction and have drawn some general conclusions on the behavior of promoters and determination of the factors controlling the overbasing reaction.

Bibliography

[1] A. Schilling, *Motor Oils and Engine Lubrication: Automobile Engine Lubrication*, Scientific Publ., 1972.

[2] S. Q. Rizvi, *Lubricant Chemistry, Technology, Selection, and Design*, ASTM International: West Conshohocken, PA, USA, 2009.

[3] R. G. Anderson, A. Y. Drummond and F. A. Stuart, *Lubricating oil compositions containing alkenyl succinimides of tetraethylene pentamine*, 1968, US Patent 3,361,673.

[4] E. E. Klaus, J. L. Duda and J. C. Wang, *Tribology Transactions*, 1992, **35**, 316 – 324.

[5] P. A. MacFaul, K. U. Ingold and J. Lusztyk, *The Journal of Organic Chemistry*, 1996, **61**, 1316 – 1321.

[6] P. R. Paolino, *Marcel Dekker, Thermoplastic Polymer Additives. Theory and Practice,*, 1989, 1 – 35.

[7] A. J. Bridgewater and M. D. Sexton, *Journal of the Chemical Society, Perkin Transactions 2*, 1978, 530 – 536.

[8] H. Berger, T. A. B. M. Bolsman and D. M. Brouwer, *Developments in Polymer Stabilisation*, 1983, **6**, 1.

[9] J. Pospíšil, in *Polysoaps/Stabilizers/Nitrogen-15 NMR*, Springer, 1995, pp. 87 – 189.

[10] M. Rasberger, in *Chemistry and technology of lubricants*, Springer, 1997, pp. 98 – 143.

[11] D. G. L. Holt and M. A. Francisco, *Multiring aromatics for enhanced deposit control*, 1996, EP Patent App. EP19,950,307,523.

[12] A. G. Horodysky, *Borated hydroxyl-containing compositions and lubricants containing same*, 1988, US Patent 4,788,340.

[13] H. R. Baker and W. A. Zisman, *Industrial & Engineering Chemistry*, 1948, **40**, 2338 – 2347.

[14] H. R. Baker, D. T. Jones and W. A. Zisman, *Industrial & Engineering Chemistry*, 1949, **41**, 137 – 144.

[15] O. N. Ananhd, V. P. Malik, K. D. Neemla and V. Kumar, *Anti-Corrosion Methods and Materials*, 1986, **33**, 12 – 18.

[16] H. E. Ries and J. Gabor, *Chemistry & Industry*, 1967, 1561.

[17] H. Montgomerie, A. Naraghi and N. U. Obeyesekere, *Corrosion inhibitors with low environmental toxicity*, 2002, EP Patent App. EP20,000,302,904.

[18] R. F. Baker, *NLGI spokesman*, 1994, **57**, 15 – 18.

[19] A. H. Battez, J. L. Viesca, R. González, D. Blanco, E. Asedegbega and A. Osorio, *Wear*, 2010, **268**, 325 – 328.

[20] V. Mel'nikov, *Chemistry and technology of fuels and oils*, 1997, **33**, 286 – 295.

[21] ASTM International, West Conshohocken, PA, *ASTM D 2500 – Test Method for Cloud Point of Petroleum Products*, 2011.

[22] F. Yanga, Y. Zhaob, J. Sjoblomb, C. Lib and K. G. Pasob, *Journal of Dispersion Science and Technology*, 2015, **36**, 213 – 225.

[23] C. Cheape, *The Pennsylvania Magazine of History and Biography*, 1987, **111**, 415 – 417.

[24] J. C. Wang, J. T. Zhao, Z. H. Du, C. M. Liu and X. Dong, *Advances in Environmental Science and Engineering*, 2012, **518-523**, 884 – 887.

[25] P. Ghosha, M. Hoquea and D. Nandia, *Petroleum Science and Technology*, 2015, **33**, 920 – 927.

[26] W. C. Hollyday, *Alkylated polystyrene pour-point depressants for lubricating oils*, 1956, US Patent 2,756,265.

[27] V. Bagheri, L. D. Moore, P. M. DiGiacinto and M. Sanchezrivas, *Low viscosity oligomer oil product, process and composition*, 2013, US Patent 20130225459 A1.

[28] H. Zhu and Z. Liu, *Preparation of wax containing crude oil pour point depressant*, 2015, CN 104693352 A.

[29] J. B. Gardiner, J. Zielinski, R. L. Elliott and S. J. Brois, *Viscosity index improvers*, 1979, US Patent 4,137,185.

[30] H. H. Horowitz, *Industrial & Engineering Chemistry*, 1958, **50**, 1089 – 1094.

[31] T. E. Kiovsky, *Star-shaped dispersant viscosity index improver*, 1978, US Patent 4,077,893.

[32] S. Q. Rizvi, *Materials Park, OH: ASM International*, 1992, 98 – 112.

[33] K. U. Ingold, *Chemical Reviews*, 1961, **61**, 563 – 589.

[34] C. R. Dickey and P. M. Williamson, *Overbased magnesium sulfonate process*, 1980, US Patent 4,192,758.

[35] L. K. Hudson, J. Eastoe and P. J. Dowding, *Advances in colloid and interface science*, 2006, **123**, 425 – 431.

[36] J. L. Mansot, M. Hallouis and J. M. Martin, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1993, **71**, 123 – 134.

[37] J. L. Mansot, J. Wéry and P. Lagarde, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1994, **90**, 167 – 182.

[38] J. M. Martin, J. L. Mansot and M. Hallouis, *Ultramicroscopy*, 1989, **30**, 321 – 328.

[39] R. H. Ottewill, E. Sinagra, I. P. MacDonald, J. F. Marsh and R. K. Heenan, *Colloid and Polymer Science*, 1992, **270**, 602 – 608.

[40] J. A. Griffiths and D. M. Heyes, *Langmuir*, 1996, **12**, 2418 – 2424.

[41] S. P. O'Connor, J. Crawford and C. Cane, *Lubrication Science*, 1994, **6**, 297 – 325.

[42] A. S. Lindsey and H. Jeskey, *Chemical Reviews*, 1957, **57**, 583 – 620.

[43] C. A. Bearchell, J. A. Edgar, D. M. Heyes and S. E. Taylor, *Journal of Colloid and Interface Science*, 1999, **210**, 231 – 240.

[44] H. Hong, F. D. S. Marquis and J. A. Waynick, *Carbon nanoparticle-containing lubricant and grease*, 2007, US Patent 20,070,158,609.

[45] C. A. Bearchell, D. M. Heyes, D. J. Moreton and S. E. Taylor, *Physical Chemistry Chemical Physics*, 2001, **3**, 4774 – 4783.

[46] R. Bandyopadhyaya, R. Kumar and K. S. Gandhi, *Langmuir*, 2001, **17**, 1015 – 1029.

[47] J.-P. Roman, P. Hoornaert, D. Faure, C. Biver, F. Jacquet and J.-M. Martin, *Journal of Colloid and Interface Science*, 1991, **144**, 324 – 339.

[48] J. Galsworthy, S. Hammond and D. Hone, *Current opinion in colloid & interface science*, 2000, **5**, 274 – 279.

CHAPTER 2

CALIXARENES

Calixarenes are among the most important macrocycles. They are obtained from the condensation of phenol and formaldehyde in basic conditions and with procedures that allow their isolation in different ring size. Mainly, they contain 4, 6 or 8 phenol residues.

The name "calixarene" was originally conceived for their resemblance with the vase-like shape that these phenol-derived macrocycles assume when they are in the conformation where all aryl groups are oriented in the same direction.[1] Actually, their name derives from the Greek "calix" (meaning "vase") and "arene", which indicates the presence of aryl residues in the macrocyclic structure. The number of the repeating o-methylenephenol units is defined by a bracketed number between the words calix and arene in the name of the compound. For instance, p-tert-butylcalix[4]arene is composed by four repeating units.

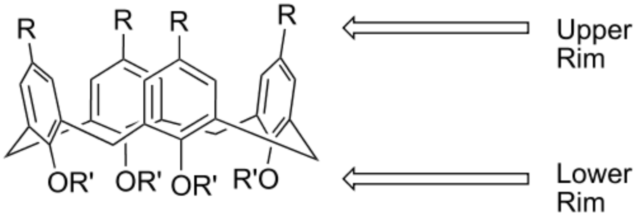


Figure (2.1): *Calix[4]arene in cone conformation*

Two different regions can be identified in these structures, as outlined in Figure 2.1: the phenolic hydroxy groups region (also called "lower rim") and the para-position of the phenols (named "upper rim").

Calix[4]arene derivatives can adopt four different structures which are called cone, partial cone, 1,2-alternate and 1,3-alternate (Figure 2.2). Stability and dynamic properties of these four structures depend strictly on the substituents present on the phenolic O-atom. For tetrahydroxy calix[4]arenes the most thermodynamically stable conformer is the cone one, as a result of strong homodromic intramolecular hydrogen bonds among the hydroxyl groups. Moreover these intramolecular interactions entail a significant increase of OH acidity in comparison to analogous monomeric phenols, even to 6 orders of magnitude.

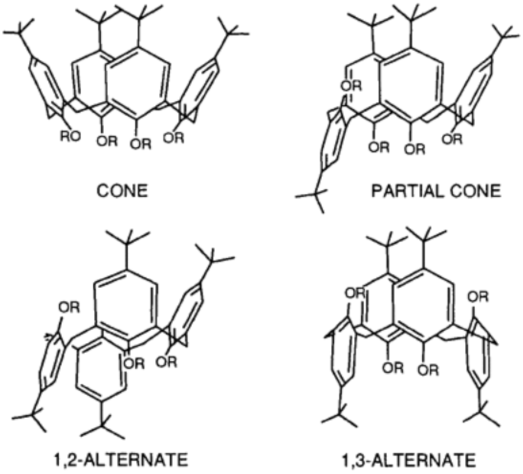


Figure (2.2): *Different conformations of the calix[4]arene derivatives*

For tetramethoxy- and tetraethoxy- derivatives, the absence of H-bonding and the presence of small alkyl groups (compared to the size of the annulus of the macrocycle) allow a fast interconversions among the four different conformations. On the other hand, groups larger than ethoxy present at the lower rim completely block conformational interconversion in one of the four structures (atropoisomers).

In the simplest cases, these isomers may be separated and characterized or obtained pure through well-consolidated stereoselective tetraalkylation reactions.[2] Calix[6]- and calix[8]arenes on the other hand are quite difficult to be blocked conformationally via alkylation of the phenolic O-atoms and different strategies should be used (bridging of two or more phenol units,[3] self-inclusion of pendant groups,[4] etc. . .).

2.1 Synthesis of Calixarenes

For many years, the preparation of p-tert-butylcalix[4]arene (one of the milestone of this class of compounds) remained a scarcely reproducible event. Although the target product could be obtained, its yields were often functions of unpredictable variables even though the reaction conditions were apparently quite similar one to the others.

The investigations carried out by D. Gutsche in the 1970's on the influence of base catalyst concentration at various temperatures on the condensation reaction permitted to set some conditions which are adequately reliable to ensure reproducibility.[5]

However already in 1872, many years before the macrocyclic nature of calixarene structure could be proved, Baeyer took the first steps towards the synthesis of calixarenes by studying the resins originated by the condensation of formaldehyde and different phenol derivatives in the presence of a mineral acid.[6] The resulting tars were not characterized, but this research represents the first chapter of what the field of phenol-formaldehyde chemistry was going to become. At a later stage, researchers discovered that these materials could be transformed into a hard material, called "Bakelite", which was the first commercial synthetic polymer. Other scientists worked on the base induced reaction between formaldehyde and phenols, obtaining o-(hydroxymethyl)phenols and p-(hydroxymethyl)phenols.[7,8] As it will be discussed in the following of this thesis, the ortho-derivatives are important intermediates in the synthesis of calixarenes. Thus, the discovery of their formation under these reaction conditions was extremely important for the further development of calixarenes.

Thereafter, a very important improvement was achieved by Zinke. In fact, he was able to simplify the reaction mixtures and to reduce the number of possible products by working with para-substituted phenols, which avoids the formation of cross-linked products in favor of linear ones.[9]

In 1956 Hayes and Hunter (Bakelite Ltd researchers) published a short report[10] about the "cyclic tetranuclear p-cresol novolak" synthesis, followed by a more detailed full account in 1958.[11] This synthesis, outlined in Figure 2.3, exploits a bromine atom as protecting group of a reactive site (ortho-

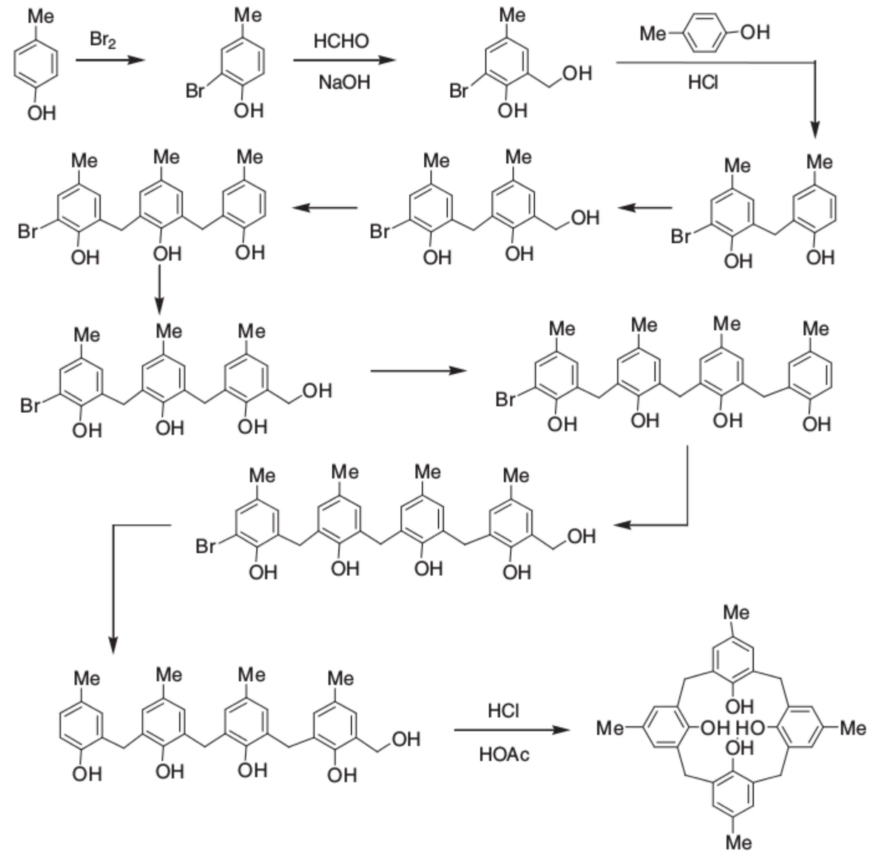


Figure (2.3): *Hayes and Hunter stepwise synthesis of a calix[4]arene*

position of p-cresol residues) and subsequently removes it at a later point of the synthetic pathway by catalytic hydrogenation. To introduce an hydroxyl methyl group into the phenol, a base-induced metal-templated reaction with formaldehyde was used. The intermediate was subsequently reacted with a large excess of p-cresol under acid conditions to yield a dimer. The subsequent iterations of these two steps could lead firstly to a trimer, and then to a tetramer. The bromine removal by catalytic hydrogenation afforded the mono-hydroxymethylated linear tetramer and the final acid-catalyzed cyclization reaction under high dilution led to a calix[4]arene.

The 1,2,4,6-tetrasubstitution pattern on the aromatic rings observed by IR analysis and a proper elemental analysis allowed to propose a cyclic tetrameric structure. In this way, these evidence allowed to confirm the formation of cyclic structures during the basic catalyzed condensation of para-substituted phenol and formaldehyde.

Another important target was achieved by Cornforth and coworkers[12] which repeated the Zinke reaction using p-tert-butylphenol. In this study, they could isolate two different compounds instead of a single one. Both of them were crystalline products but having different melting points. The elemental analysis performed on these products indicated the presence of the same ratio between CH_2 groups (methylene bridges) and phenolic residues in both these isolated compounds. Also, these compounds did not react with p-nitrobenzenediazonium chloride, indicating the absence of any reactive positions on the aromatic rings. Finally, they had apparently the same molecular weight (but this result subsequently revealed to be wrong).

In order to explain the reason of such different melting points, Cornforth proposed the existence of two different conformers for these molecules, arising from hindered rotation of the phenol nuclei around the $Ph-CH_2-Ph$ bonds. The Cornforth's hypothesis was also supported by examination of molecular models.[13] However, subsequent NMR studies showed that, in this case, the conformational energy barriers in solution can be overcome easily increasing the temperature above room temperature.[14]

Some experimental data obtained at the end of the last century led scientists to agree on the hypothesis of the presence of two different compounds in the mixture obtained from Cornforth and co-workers but with the assignment to the cyclic tetramer and the cyclic octamer.

Nowadays, the most used procedure for calixarene synthesis is the "base-promoted one-step synthesis". Base-induced condensations of p-substituted phenols and formaldehyde always result in a mixture of linear and cyclic oligomers (among which, however, the cyclic derivatives are normally by far the most abundant).[1]

The mechanism of the methylene-bridged dimer formation is reported in Figure 2.4.[15] In detail, the acid-base reaction between p-substituted phenol and a base (normally NaOH, KOH or RbOH) yields a p-substituted phenolate. The phenolate can then react with a formaldehyde molecule, envolving into an ortho-methylolderivative. Elimination of an hydroxide ion from the methylol derivatives gives an ortho-methylene quinone, an extremely strong electrophile which immediately reacts with another phenolate moiety yielding a dimeric species with a methylene bridge. The repetition of this cycle of reactions leads to the formation of oligomeric species, which can

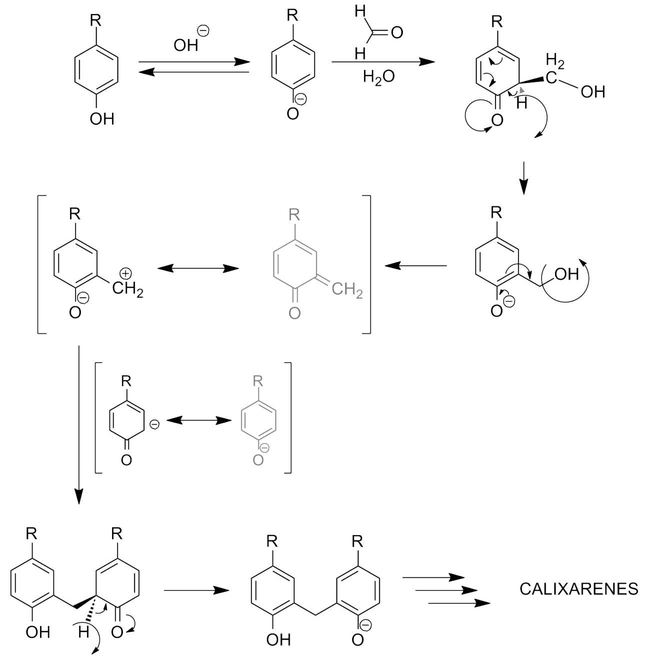


Figure (2.4): *The first steps of the mechanism of formation of calixarene base induced catalysis*

subsequently cyclize to form the calixarene compounds.

In the case of p-tert-butylphenol, mainly the tetrameric, hexameric and octameric cyclic products are formed. In the ′70s and ′80s, a careful investigation of this reaction by Gutsche, involving changes in the type of base, reactant ratios and reaction temperatures, resulted in the development of reproducible procedures for the synthesis of each of these single macrocyclic structures with excellent yields.[5,16,17] This investigation quite nicely demonstrates that these processes can be easily carried out also on a large scale. From these studies, Gutsche determined that the cyclic octamer is the product obtained under kinetic control, whereas the cyclic tetramer is the product of thermodynamic control. On the other hand, it was also proposed that the cyclic hexamer is the compound synthesized under kinetic control where the counterion (metal ion) of the base, K^+ or Rb^+, act as a template.

Despite the extensive experimental efforts, the exact synthetic mechanism for the formation of these macrocycles is still not completely known and understood.

In 1996 Vocanson and Lamartine got evidence of the existence of inter-

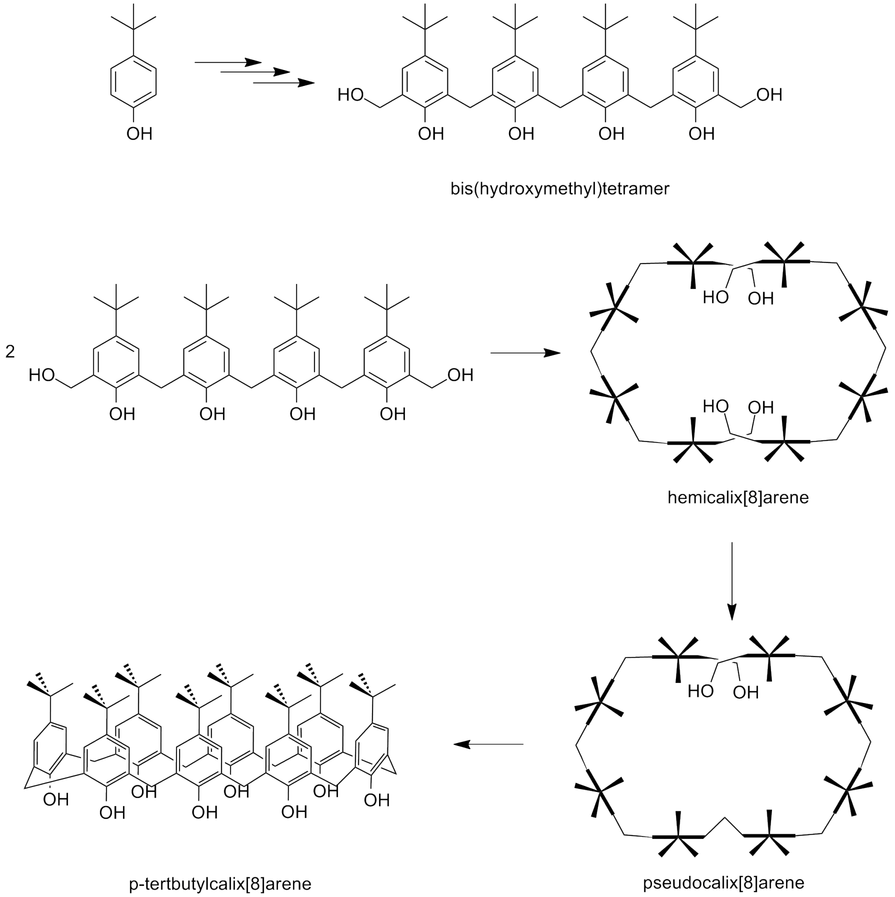


Figure (2.5): *Proposed mechanism of formation of p-tert-butylcalix[8]arene*

mediate hemicalixarene (see Figure 2.5) in the reaction mixture.[9,18] In detail, for the synthesis of p-tert-butylcalix[8]arene they suggested a mechanism involving the reaction of a hemicalixarene (formed by two tetramers) to give an open octamer named pseudocalixarene (Figure 2.5). After the extrusion of a molecule of formaldehyde and water, this intermediate pseudocalixarene may cyclize to yield the p-tert-butylcalix[8]arene.

Another compound, which is obtained with lower yields in the synthesis of this type of calixarenes, is the bis(homooxa)-p-tert-butylcalix[4]arene (Figure 2.6). This co-product can be easily isolated due to its higher solubility in common organic solvents than the main products.[19] Moreover, "homooxa" compounds can be prepared in higher yields also in quite different conditions,[20] demonstrating the complexity and variability of these

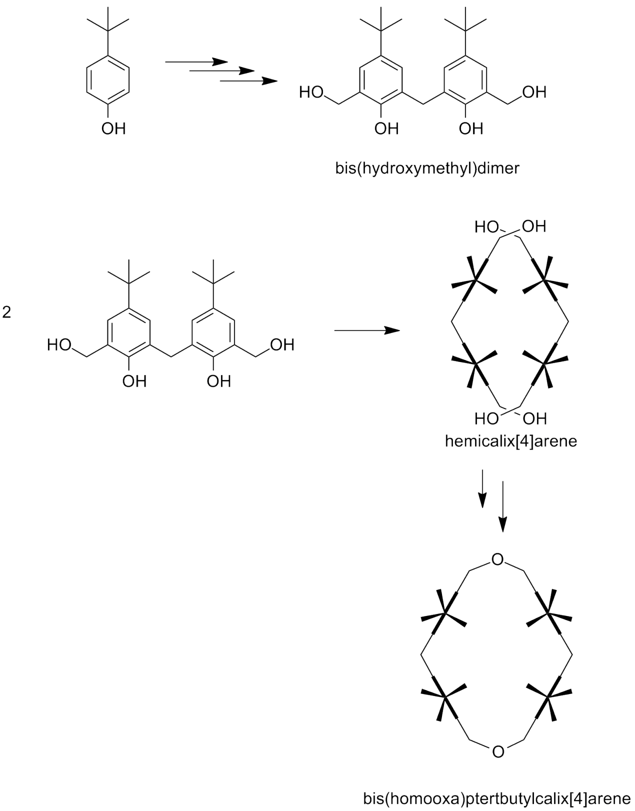


Figure (2.6): *Proposed mechanism of formation of bis(homooxa)-p-tert-butylcalix[4]arene*

syntheses.

Whatever is the synthetic mechanism that gives calixarenes, the calixarene library obtained by direct synthesis is actually rather limited, despite the huge amount of potential applications of such macrocyclic compounds in basic and applied chemistry and the large variability of p-substituted phenols available. In fact, the compounds synthesized by the "one-step" procedure can only be obtained from seven phenols: p-isopropylphenol, p-tert-butylphenol, p-tert-pentylphenol, p-tert-octylphenol, p-phenylphenol, p-benzylphenol and p-adamantylphenol. Moreover, these facts clearly show how it could still be interesting to expand the calixarene library to other p-substituted phenols, especially for bulk uses for industrial applications.

2.2 Functionalization at the lower rim

The functionalization of phenolic OH groups has been extensively used to introduce different groups into the lower rim of the calixarene structure. Many examples were reported in the literature: the most important processes are the alkylation and acylation reactions.[9,21–23] Procedures are known for a partial functionalization (only few of the OH groups modified) or exhaustive functionalization (all the OH groups modified). For instance, in the case of the calix[4]arene series, the mono-, di- (1,2 and 1,3), tri- and tetra-derivatives might be prepared. In the exhaustive functionalisation of calix[4]arenes, stereoselective syntheses allow also to obtain pure cone, partial cone, 1,2-alternate or 1,3-alternate structures.

If the introduced group is larger than the ethyl group, the interconversion energy barrier between these structures cannot be overcome, blocking the conformational isomers of calix[4]arene derivatives into atropoisomers.[23]

2.2.1 Alkylation

Extensive experimental studies allowed to develop stereoselective synthesis (alkyl halides groups larger than ethyl) for three (cone, partial cone and 1,3-alternate) tetra-alkylated calix[4]arenes, which can be obtained in high yields and purity.

The exhaustive alkylation of calix[4]arenes using NaH as base generally affords only the tetra-alkylated cone calix[4]arenes,[24,25] while the use of $^{t}BuO^{-}K^{+}$ gives the tetraethers-calix[4]arenes in the partial cone structure, and Cs_2CO_3 in acetonitrile the 1,3-alternate isomers.[26] Until nowadays, general and direct procedures have not been yet established for the selective synthesis of tetra-functionalized calix[4]arenes in the 1,2-alternate structures, forcing scientists to follow indirect multistep synthetic strategies.[24,27]

The ether formation reaction on calixarene OH groups is probably the most important functionalization process, and it is extremely useful since it allows to easily introduce a wide variety of different moieties on the calixarenes structure.

Many types of alkylating reagents (generally indicated as RX, where X is a leaving group) have been used, but the most common class of reagents are chloroalkanes and bromoalkanes.[28]

The direct alkylation of calix[4]arenes can be achieved by using either a strong base (as NaH[27] or $CH_3O^-Na^+$[29]) or a weak one (as K_2CO_3 or CsF)[24], depending on whether one would like to obtain an exhaustive or partial alkylation of the lower rim, respectively.

As reported in the literature, the selective mono-alkylation processes were achieved with more difficulties due to the comparable values of the first acidity constant of both not-alkylated and monoalkylated calixarenes.[24]

1,3-dialkylation is generally more easily achieved than 1,2-dialkylation due to selective anion formation at the distal OH position in mono-alkylated calix[4]arenes.[30] Trismethylation of p-tert-butylcalix[4]arene can normally be obtained with a small excess of the alkylating agent in the presence of stoichiometric NaH.[27]

Other possible strategies to achieve partially functionalized macrocycles, exploit the selective cleavage of ether bonds starting from tetra-substituted calixarenes. In detail, one way to obtain monoalkylated calix[4]arenes is the dealkylation processes of the tetra-alkylated calixarenes with stoichiometric amounts (3 eq) of Me_3SiI.[31] The 1,2-dimethyl ether of p-tert-butylcalix[4]arene was obtained in good yield by a selective dealkylation of its tetra-methyl ether with 2 equivalents of $TiBr_4$ in $CHCl_3$.[32]

Furthermore, the alkylation of calix[4]-, calix[5]- and calix[8]arenes were studied. However, as soon as the size and mobility of the macrocycle increase, the degree of control in the alkylation reaction decreases. For this reason, alkylation processes are less selective, giving complex mixtures of products. In details, procedures for the partial alkylation of calix[6]arenes were also studied, taking advantage of the know-how developed with the calix[4]arene series. Most of the possible methyl ethers of this macrocycle could be synthesized and isolated.[3,33–36] In order to have calixarenes more soluble in organic solvents, also octyl[37] and benzyl[38] derivatives were prepared.

The calix[8]arenes is an even more complicated substrate due to the particularly high number of possible partially alkylated derivatives, which could be present.[39–41] Up to date, no significant selective alkylation of such compounds are present in the literature.

For these reasons, the most studied functionalization of calix[8]arenes is the complete alkylation. The octa-alkyl ethers can be synthesized using strong bases and a large excess of alkylating reagent.[42]

Polyfunctional alkylating reagents

The use of alkylating reagents containing further functional groups permits an easy introduction of such functional groups on the calixarene structure and their further modifications. There are many different types of these reagents (generally indicated as X−R−Y, where X is the leaving group and Y is a different functionality.

Allyl- and propargyl- halides are the first examples. These ones can react under basic conditions with calixarenes species forming the ethers derivatives.[43,44]

The most useful and common of these alkylating agents have general formula X−R−C(=O)−Z, where Z could be alkyl-,[45] alcoholate-[46] or amine-derivatives[47]. Alpha-halo carbonyl compounds are quite reactive, being the alpha-carbon particularly electrophile, and therefore it easily undergoes nucleophilic aliphatic substitution. Their high reactivity favors their introduction on the macrocyclic scaffold.

These halo-carbonyl compounds are also quite crucial due to the possibility, once on the calixarene scaffold, to subsequently be converted in other functional groups by using the classical functional group transformation reactions. For instance, the ester group grafted onto the calixarene could be easily hydrolyzed under basic conditions to obtain an acidic functionality[48] or it could be reacted with organometallic compounds to give a tertiary alcohol.[49]

2.2.2 Acylation

The esterification reactions of the phenolic OH groups is another possible reaction exploited for the functionalization of the lower rim. However its use is mainly limited to the exhaustive acylation of all the hydroxy groups, since the reaction of partial functionalization possess a lower degree of selectivity. Also, the tetra-acylation reactions of calix[4]arenes generally yield complex mixtures of the different stereoisomers (cone, partial cone and alternate structures).

Both acyl halides or anhydrides and a base such as NaH, AcO^-Na^+ or pyridine have been used. If the acylating agent is used in excess, the products obtained from p-tert-butylcalix[4]arene are often completely functionalized with different and sometimes not predictable conformational outcomes.[50]

Similar results are achieved by using p-tert-butylcalix[6]- and -[8]arene as substrates.[15,51]

The complete acylation of the lower rim was often used to easily increase the solubility of “native” calixarenes. An important example was shown in 1997 by Casnati and coworker[52] which completely acetylated p-(benzyloxy)calix[8]arene, increasing its solubility in common organic solvents.

From the ’90s, the researchers concentrated their attention on partial functionalizations in order to modulate both physical and chemical properties of the calixarenes. These ones could be carried out using, for instance, limiting amounts of the acylating reagents. In order to control the functionalization degree, bulky acylating reagents were also tested.[53,54]

A further strategy to allow the control of the acylation processes exploits the use of weak bases, such as pyridine,[55] in order to have a smaller amount of activated hydroxyl groups per calixarene.

2.3 Functionalization at the upper rim

As previously underlined (Section 2.1), the use of p-alkyl phenols allows the regioselective control of the phenol/formaldehyde reactions, preventing the formation of cross-linked polymers. However, this strategy results in the presence of alkyl chains on the calixarene upper rim as in the case of p-tert-butylcalix[n]arenes.

In order to exploit the upper rim for the introduction of additional functional groups, the reaction of removal of p-alkyl chains has been extensively studied. Fortunately, the de-alkylation reaction can be carried out quite effectively by a reverse Friedel–Crafts process, using a Lewis’ acid as catalyst (normally $AlCl_3$). Thus this reaction allows to remove the tert-butyl groups and to make the upper rim accessible to further modifications.[53]

Quite interestingly, the removal of tert-butyl groups from phenol bearing unfunctionalized OH groups is much faster that removal of tert-butyls from alkyl phenol ethers.[56] This remarkably different reactivity thus allows to selectively remove alkyl groups from the upper rim of calixarenes partially functionalized at the lower rim and therefore also to selectively introduce functional groups at the upper rim.

In the ’80s, a lot of procedures for the upper rim modifications were developed, generally exploiting electrophilic aromatic substitution reactions. Following this approach, many different functional groups can be introduced at the upper rim. Some examples are the halogens,[57,58] $-NO_2$,[59] $-SO_3H$,[60,61] $-CHO$,[62] $-COR$,[63] and $-CH_2Cl$ groups.[64]

Most of these calixarenes are quite crucial intermediate due to their possibility to be subsequently converted in other derivatives by using the classical organic chemistry reactions of the functional groups transformation. For istance, NO_2 can be transformed into NH_2 group by reduction with H_2 or NH_2NH_2 in the presence of a metal catalyst.[65–67] The CH_2Cl groups are other interesting compounds due to their capability to react with nucleophiles in the SN2 processes.[68,69] Formyl groups ($-CHO$) can also be easily converted to various other groups, including COOH (oxidation),[70,71] $R-OH$ (reduction),[70] azomethines (amination)[72] and alkenes (Wittig).[73,74]

2.4 Industrial application of calixarenes

Due to the different type of properties shown by calixarenes and their derivatives, there is a wide range of possible applications for such kind of compounds. This is demonstrated by the large number of patents on calixarenes since 1980s.

Some of the main characteristics that make calixarenes interesting for various types of applications are that they:

- are not expensive materials;
- are well defined oligomers;
- can be prepared with different sizes of their cavities;
- can be easily functionalized inserting even quite different groups;
- large calixarenes (hexamer and octamers) are endowed of high conformational freedom, while, on the other hand, the smaller calix[4]arene can be used as a rigid and preorganized scaffols;
- show exceptionally high and selective complexation capacity of metal ions and neutral molecules;
- show remarkably high chemical and thermal stability.

Their possible applications range from nanomedicine to biochemical and material science fields. For instance, patents were filed that claim the use of calixarenes in cosmetic and pharmaceutical formulation,[75] cell transfection[76] and as antibacterial agents.[77] They have also been proposed as dental materials,[78] adhesion promoter,[79] hair dyes,[80] photographic toners,[81,82] glass photoresists[83] and antioxidants.[84] In addition to these uses, calixarenes were also suggested for industrial applications like metal colloids stabilizers[85] and temperature sensing devices.[86]

In material science, in order to achieve homogeneous dispersion of these macrocycles in the final material, the solubility is a critical issue. For this reason, one of the major difficulties regarding the use of these compounds is related to the possibility to increase their solubility in organic solvents, which is usually pretty low at least for the native (free phenolic OH) calixarenes.

Their functionalization can sometimes solve this problem but, in any case, a general approach aiming at decreasing the remarkable affinity to crystallize shown by these compounds would be highly desirable, at least for certain applications. Moreover, the functionalization may change some physicochemical properties of the final materials, making them more effective for the specific application.

2.4.1 Calixarene-based VI improvers

To the best of our knowledge, calixarene derivatives have never been marketed as Viscosity Index improvers.

The literature reports only few examples of calixarene functionalization for the synthesis of star polymer (SP).

A patent was filed in 1998 by Kennedy and coworkers of the University of Akron (Ohio, USA),[87] where the SP synthesis was achieved using the "core first" method and multifunctional calix[n]arene derivatives are used as initiators. Under these polymerization conditions, the cationic living polymerization of isobutylene was carried out. In detail, this "core first" approach is divided into two steps. A tertiary alkyl chloride group in the calixarene structure first reacts with BCl_3, forming an ion pair between the tertiary alkyl carbocation and the BCl_4^-. In a second step, the generated carbocationic species induces the living polymerization of isobutylene. In this way, SP structures were obtained.

A disadvantage of this process is the large number of synthetic steps (nine) to obtain the calixarene precursor. Moreover, the use of dangerous or very labile reagents (such as CH_3I, CH_3COCl and CH_3MgBr) further limits the application of this process to an industrial scale.

In the same year, Angot and coworker have proposed the use of bromo calixarene derivatives for the Atom Transfer Radical Polymerization (ATRP) of styrene monomers in the presence of CuBr/2,2'-bipyridyl as activator.[88] Polystyrene (PS) polymers of narrow polydispersity with exactly eight arms could be synthesized by restricting the polymerization to low conversion, typically below 15–20 %. Unfortunately, irreversible cross-coupling occurred between stars at higher conversions. In agreement with these results, this synthetic approach is not applicable to industrial level due to the high cost of the process, which is determined by the low conversion of monomers.

The use of calixarene cores for the SP synthesis shows interesting perspectives, but more work needs to be done in order to achieve a high control in the synthetic processes.

To improve these processes, the number of synthetic steps have to be reduced. Moreover, as described in Section 1.2.6, the use of a living anionic polymerization should ensure the required control on the process. For these reasons, the activity on star polymers in this thesis will be focused on the synthesis of appropriate calixarenes for the living anionic polymerization processes.

2.4.2 Calixarene-based detergents

There are only few examples of calixarene-based detergents. According to our knowledge, only one academic group showed interest for this topic.

In the early 2000s, Heyes and coworkers have studied the behavior of calixarenes based detergents in lubricant oils. Such research activity was funded by private companies (BP Oil, Lubrizol) leader in the sector of lubricant additives. They proposed calixarates (phenolate salts made up of deprotonated calixarene and calcium carbonate) as active component of detergents for lubricants.

An article published in 2003 reports a calixarate/stearate calcium carbonate overbased detergent, which was prepared and characterised by ^{1}H-NMR, ^{13}C-NMR, IR, Raman and UV-Vis spectroscopic methods.[89] In this work, p-tert-butylcalix[8]arene was proposed as novel sulfur-free surfactant for the synthesis of overbased detergents. This compound was found to allow the preparation of high TBN detergents, while the addition of a carboxylic acid co-surfactant permits to reduce the amount of the more expensive calixarene used.[90]

Whereas for the sulfonate-based detergents (the most common detergents on the market) the deprotonation of the sulfonic acids results essentially complete (due to their high acidity), the analogue deprotonation for the phenolic OH of the calixarenes is much less important. The pKa values are not readily available for the p-tert-butylcalix[8]arene and therefore, when present, they are strongly dependent from the mixture of solvents used.[9,91] However, calixarenes can complex Ca^{2+} ion especially in the (partially) deprotonated forms, and this could result interesting for the stabilization of the overbased detergents.

Through the UV-Vis studies reported in the paper, evidence of partial deprotonation in 2-ethylhexanol/ethylene glycol mixture was collected. In detail, the scientists assumed a maximum of 25 % of deprotonated hydroxy groups as conseguence of the "neutralization" step with $Ca(OH)_2$.[89] Even though $CaCO_3$ is a weaker base than $Ca(OH)_2$, the absence of significant changes in the UV-Vis spectra between the "neutralized" and the "carbonatated" material seems to indicate a rather similar deprotonation degree.[89]

According to these results, the use of calixarenes could adversely affect the properties of the final detergent due to their low acidity. This fact could result in a low detergent effectiveness, in addition to some possible stability problems of these additives and of the reverse micelles they form.

Despite the important results achieved by the group of Hayes, in order to overcome these problems, more work needs to be done. For these reasons, the activities of this thesis were focused on increasing the degree of deprotonation of calixarene structures, increase the ability of the macrocycle to bind calcium, to stabilize the reverse micelles, and to improve the detergent solubility in non-polar solvents, such as the base oils.

Bibliography

[1] C. D. Gutsche and R. Muthukrishnan, *The Journal of Organic Chemistry*, 1978, **43**, 4905 – 4906.

[2] L. C. Groenen, B. H. M. Ruël, A. Casnati, P. Timmerman, W. Verboom, S. Harkema, A. Pochini, R. Ungaro and D. N. Reinhoudt, *Tetrahedron Letters*, 1991, **32**, 2675 – 2678.

[3] A. Casnati, P. Minari, A. Pochini and R. Ungaro, *Journal of the Chemical Society, Chemical Communications*, 1991, 1413 – 1414.

[4] A. Casnati, P. Jacopozzi, A. Pochini, F. Ugozzoli, R. Cacciapaglia, L. Mandolini and R. Ungaro, *Tetrahedron*, 1995, **51**, 591 – 598.

[5] C. D. Gutsche, M. Iqbal and D. Stewart, *The Journal of Organic Chemistry*, 1986, **51**, 742 – 745.

[6] A. Baeyer, *Berichte der Deutschen Chemischen Gesellschaft*, 1872, **5**, 280.

[7] L. Lederer, *Journal für Praktische Chemie*, 1894, **50**, 223 – 226.

[8] O. Manasse, *Berichte der deutschen chemischen Gesellschaft*, 1894, **27**, 2409 – 2413.

[9] C. D. Gutsche, *Monographs in Supramolecular Chemistry, The Royal Society of Chemistry, Cambridge*, 1989, **1**, year.

[10] B. T. Hayes and R. F. Hunter, *Chemistry & Industry*, 1956, 193.

[11] B. T. Hayes and R. F. Hunter, *Journal of Applied Chemistry*, 1958, **8**, 743 – 748.

[12] J. W. Cornforth, P. D. Hart, G. A. Nicholls, R. J. W. Rees and J. A. Stock, *British Journal of Pharmacology and Chemotherapy*, 1955, **10**, 73 – 86.

[13] J. L. Ballard, W. B. Kay and E. I. Kropa, *Journal of Paint Technology*, 1966, **38**, 251.

[14] J. H. Munch, *Die Makromolekulare Chemie*, 1977, **178**, 69 – 74.

[15] C. D. Gutsche, B. Dhawan, K. H. No and R. Muthukrishnan, *Journal of the American Chemical Society*, 1981, **103**, 3782 – 3792.

[16] C. D. Gutsche, B. Dhawan, M. Leonis and D. Stewart, *Organic Syntheses*, 1993, 77.

[17] J. H. Munch and C. D. Gutsche, *Organic Syntheses*, 1993, 80.

[18] F. Vocanson and R. Lamartine, *Supramolecular Chemistry*, 1996, **7**, 19 – 25.

[19] J. M. Harrowfield, M. I. Ogden and A. H. White, *Journal of the Chemical Society, Dalton Transactions*, 1991, 979 – 985.

[20] B. Dhawan and C. D. Gutsche, *The Journal of Organic Chemistry*, 1983, **48**, 1536 – 1539.

[21] V. Böhmer, *Angewandte Chemie*, 1995, **107**, 785 – 818.

[22] C. D. Gutsche, *Accounts of Chemical Research*, 1983, **16**, 161 – 170.

[23] S. Shinkai, *Tetrahedron*, 1993, **49**, 8933 – 8968.

[24] L. C. Groenen, B. H. M. Ruel, A. Casnati, W. Verboom, A. Pochini, R. Ungaro and D. N. Reinhoudt, *Tetrahedron*, 1991, **47**, 8379 – 8384.

[25] J. A. J. Brunink, J. R. Haak, J. G. Bomer, D. N. Reinhoudt, M. A. McKervey and S. J. Harris, *Analytica Chimica Acta*, 1991, **254**, 75 – 80.

[26] J. D. Van Loon, W. Verboom and D. N. Reinhoudt, *Organic Preparations and Procedures International*, 1992, **24**, 437 – 462.

[27] K. Iwamoto, K. Araki and S. Shinkai, *Tetrahedron*, 1991, **47**, 4325 – 4342.

[28] C. D. Gutsche and J. A. Levine, *Journal of the American Chemical Society*, 1982, **104**, 2652 – 2653.

[29] C.-M. Shu, W.-S. Chung, S.-H. Wu, Z.-C. Ho and L.-G. Lin, *The Journal of Organic Chemistry*, 1999, **64**, 2673 – 2679.

[30] A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M.-J. Schwing, R. J. M. Egberink, F. De Jong and D. N. Reinhoudt, *Journal of the American Chemical Society*, 1995, **117**, 2767 – 2777.

[31] A. Casnati, A. Arduini, E. Ghidini, A. Pochini and R. Ungaro, *Tetrahedron*, 1991, **47**, 2221 – 2228.

[32] A. Arduini, A. Casnati, L. Dodi, A. Pochini and R. Ungaro, *Journal of the Chemical Society, Chemical Communications*, 1990, 1597 – 1598.

[33] R. G. Janssen, W. Verboom, D. N. Reinhoudt, A. Casnati, M. Freriks, A. Pochini, F. Ugozzoli, R. Ungaro, P. M. Nieto, M. Carramolino *et al.*, *Synthesis*, 1993, **1993**, 380 – 386.

[34] H. Otsuka, K. Araki and S. Shinkai, *The Journal of Organic Chemistry*, 1994, **59**, 1542 – 1547.

[35] H. Otsuka, K. Araki and S. Shinkai, *Tetrahedron*, 1995, **51**, 8757 – 8770.

[36] P. Neri and S. Pappalardo, *The Journal of Organic Chemistry*, 1993, **58**, 1048 – 1053.

[37] M. Conner, V. Janout and S. L. Regen, *Journal of the American Chemical Society*, 1993, **115**, 1178 – 1180.

[38] S. Kanamathareddy and C. D. Gutsche, *The Journal of Organic Chemistry*, 1992, **57**, 3160 – 3166.

[39] P. Neri, C. Geraci and M. Piattelli, *The Journal of Organic Chemistry*, 1995, **60**, 4126 – 4135.

[40] P. Neri, G. M. L. Consoli, F. Cunsolo, C. Rocco and M. Piattelli, *The Journal of Organic Chemistry*, 1997, **62**, 4236 – 4239.

[41] C. Geraci, M. Piattelli and P. Neri, *Tetrahedron letters*, 1996, **37**, 3899 – 3902.

[42] P. Neri, E. Battocolo, F. Cunsolo, C. Geraci and M. Piattelli, *The Journal of Organic Chemistry*, 1994, **59**, 3880 – 3889.

[43] C. D. Gutsche, J. A. Levine and P. K. Sujeeth, *The Journal of Organic Chemistry*, 1985, **50**, 5802 – 5806.

[44] W. Xu, J. J. Vittal and R. J. Puddephatt, *Canadian Journal of Chemistry*, 1996, **74**, 766 – 774.

[45] F. Arnaud-Neu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. McKervey and E. Marques, *Journal of the American Chemical Society*, 1989, **111**, 8681 – 8691.

[46] M. A. McKervey, E. M. Seward, G. Ferguson, B. Ruhl and S. J. Harris, *Journal of the Chemical Society, Chemical Communications*, 1985, 388 – 390.

[47] A. Casnati, P. Minari, A. Pochini, R. Ungaro, W. F. Nijenhuis, F. De Jong and D. N. Reinhoudt, *Israel Journal of Chemistry*, 1992, **32**, 79 – 87.

[48] A. Arduini, L. Domiano, L. Ogliosi, A. Pochini, A. Secchi and R. Ungaro, *The Journal of Organic Chemistry*, 1997, **62**, 7866 – 7868.

[49] D. J. Cram, *Fundamentals of carbanion chemistry*, Elsevier, 2012.

[50] K. No and H. J. Koo, *Bulletin of the Korean Chemical Society*, 1994, **15**, 483 – 488.

[51] J. S. Rogers and C. D. Gutsche, *The Journal of Organic Chemistry*, 1992, **57**, 3152 – 3159.

[52] A. Casnati, R. Ferdani, A. Pochini and R. Ungaro, *The Journal of Organic Chemistry*, 1997, **62**, 6236 – 6239.

[53] C. D. Gutsche and L.-G. Lin, *Tetrahedron*, 1986, **42**, 1633 – 1640.

[54] K. A. See, F. R. Fronczek, W. H. Watson, R. P. Kashyap and C. D. Gutsche, *The Journal of Organic Chemistry*, 1991, **56**, 7256 – 7268.

[55] G. M. L. Consoli, F. Cunsolo, M. Piattelli and P. Neri, *The Journal of Organic Chemistry*, 1996, **61**, 2195 – 2198.

[56] J. D. Van Loon, A. Arduini, W. Verboom, R. Ungaro, G. J. Van Hummel, S. Harkema and D. N. Reinhoudt, *Tetrahedron Letters*, 1989, **30**, 2681 – 2684.

[57] P. Linnane, T. D. James and S. Shinkai, *Journal of the Chemical Society, Chemical Communications*, 1995, 1997 – 1998.

[58] P. Timmerman, W. Verboom, D. N. Reinhoudt, A. Arduini, S. Grandi, A. R. Sicuri, A. Pochini and R. Ungaro, *Synthesis*, 1994, **1994**, 185 – 189.

[59] S. Kumar, R. Varadarajan, H. M. Chawla, G. Hundal and M. S. Hundal, *Tetrahedron*, 2004, **60**, 1001 – 1005.

[60] S. Shinkai, H. Koreishi, K. Ueda, T. Arimura and O. Manabe, *Journal of the American Chemical Society*, 1987, **109**, 6371 – 6376.

[61] S. Shinkai, K. Araki and O. Manabe, *Journal of the Chemical Society, Chemical Communications*, 1988, 187 – 189.

[62] K. No, Y. Noh and Y. Kim, *Bulletin of the Korean Chemical Society*, 1986, **7**, 442 – 444.

[63] T. Arimura, S. Shinkai, T. Matsuda, Y. Hirata, H. Satoh and O. Manabe, *Bulletin of the Chemical Society of Japan*, 1988, **61**, 3733 – 3734.

[64] M. Almi, A. Arduini, A. Casnati, A. Pochini and R. Ungaro, *Tetrahedron*, 1989, **45**, 2177 – 2182.

[65] R. A. Jakobi, V. Böhmer, C. Gruttner, D. Kraft and W. Vogt, *New Journal of Chemistry*, 1996, **20**, 493 – 501.

[66] S. Shinkai, T. Arimura, K. Araki, H. Kawabata, H. Satoh, T. Tsubaki, O. Manabe and J. Sunamoto, *Journal of the Chemical Society, Perkin Transactions 1*, 1989, 2039 – 2045.

[67] W. Verboom, P. J. Bodewes, G. Van Essen, P. Timmerman, G. J. Van Hummel, S. Harkema and D. N. Reinhoudt, *Tetrahedron*, 1995, **51**, 499 – 512.

[68] A. Arduini, A. Pochini, A. Sicuri, A. Secchi and R. Ungaro, *Gazzetta Chimica Italiana*, 1994, **124**, 129 – 132.

[69] M. D. Conner, V. Janout, I. Kudelka, P. Dedek, J. Zhu and S. L. Regen, *Langmuir*, 1993, **9**, 2389 – 2397.

[70] J. D. Van Loon, A. Arduini, L. Coppi, W. Verboom, A. Pochini, R. Ungaro, S. Harkema and D. N. Reinhoudt, *The Journal of Organic Chemistry*, 1990, **55**, 5639 – 5646.

[71] C. D. Gutsche and P. F. Pagoria, *The Journal of Organic Chemistry*, 1985, **50**, 5795 – 5802.

[72] T. Komori and S. Shinkai, *Chemistry Letters*, 1992, 901 – 904.

[73] E. Kelderman, L. Derhaeg, W. Verboom, J. F. J. Engbersen, S. Harkema, A. Persoons and D. N. Reinhoudt, *Supramolecular Chemistry*, 1993, **2**, 183 – 190.

[74] J.-B. Regnouf-de Vains and R. Lamartine, *Tetrahedron Letters*, 1996, **37**, 6311 – 6314.

[75] A. Spagnul, F. Rebiere, G. Phan, C. Bouvier-Capely and E. Fattal, *Cosmetic and pharmaceutical formulations of calixarene molecules*, 2015, US Patent 8,987,334.

[76] R. Ungaro, A. Casnati, G. Donofrio, F. Sansone and V. Bagnacani, *Functionalized calixarene derivatives for cell transfection*, 2013, WO Patent App. PCT/IB2012/054,041.

[77] S. J. Harris, *Calixarene-based compounds having antibacterial, antifungal, anticancer-hiv activity*, 1995, WO Patent App. PCT/IE1995/000,008.

[78] U. K. Fischer, N. Moszner, H. Ritter, M. Schaub, M. Tabatabai and A. Utterodt, *Verwendung von polymerisierbaren Calix[n]arenen als Dentalmaterialien*, 2011, EP Patent 1,970,042.

[79] S. J. Harris, M. A. McKervey, D. P. Melody, J. Woods and J. M. Rooney, *Instant adhesive composition utilizing calixarene accelerators*, 1987, US Patent 4,636,539.

[80] H. O. D. De Noack, H. D. O. L. De Weinelt and B. D. O. W. De Noll, *Neues haarfaerbemittel*, 1993, DE Patent App. DE19,914,135,760.

[81] S. Yamanaka, K. Sukata and S. Sugawara, *Charge control agent and toner for developing electrostatic images*, 1992, EP Patent App. EP19,920,108,518.

[82] K. Sukata and S. Yamanaka, *Calixarenes as charge control agents and toner*, 2001, EP Patent 0,712,049.

[83] L. D. Bozano, H. Ito and L. K. Sundberg, *Calixarene blended molecular glass photoresists and processes of use*, 2011, US Patent 7,993,812.

[84] L. P. J. Burton, *Phenolic phosphite antioxidant for polymers*, 1984, US Patent 4,474,917.

[85] A. Katz, N. De Silva, A. Solovyov, A. Kuperman, C. Y. Chen, P. Nandi, A. Okrut and I. Busygin, *Calixarene-bound iridium-containing metal colloids*, 2015, US Patent 8,969,607.

[86] S. Asher and C. Reese, *Colorimetric reagent*, 2001, US Patent App. 09/865,348.

[87] J. P. Kennedy, I. J. Majoros and S. Jacob, *Star polymers having multiple polyisobutylene arms emanating from a calixarene core, initiators therefor, and method for the synthesis thereof*, 1998, US Patent 5,844,056.

[88] S. Angot, K. S. Murthy, D. Taton and Y. Gnanou, *Macromolecules*, 1998, **31**, 7218 – 7225.

[89] I. D. Cunningham, J.-P. Courtois, T. N. Danks, D. M. Heyes, D. J. Moreton and S. E. Taylor, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2003, **229**, 137 – 147.

[90] S. J. Cook, S. P. O'Conner and A. Pearce, *Process for the production of overbased calixarates*, 1993, US Patent 5,205,946.

[91] U. Lüning, Academic Press, 1995, vol. 30, pp. 63 – 116.

Part II

Star polymer core precursors

CHAPTER 3

AIMS OF RESEARCH

The aim of the research carried out in this part of Thesis concerns the use of calixarenes as cores of star polymers which can be utilized as viscosity index improvers for lubricants.

The use of calixarene derivatives will enable the production of star polymers with a high and well-defined number of branches and endowed with a very low dispersivity of molecular weight that can, hopefully, originate better performances than the current commercially available viscosity index improvers of the major competitor.

The calix[8]arene derivatives will be ideal candidates due to their peculiar properties such as well defined molecular weight, easy of functionalization and high number (8) of sites to be used to attach polymer chains. Quite interestingly, this number of branches can even be easily extended to multiple of 8 (16, 24, …).

Several functional groups, such as alkyl chlorides, alkenes and esters, will be considered to prepare reactive p-tert-butylcalix[8]arene cores to be used in living anionic polymerization.

n-butyllithium will be used as model of the living anionic polymer to test the outcome of the reaction of polymer insertion on the calixarene core, facilitating the analyses of the products.

The calixarene derivatives, which will easier react with n-BuLi, will be selected for the preparation of star polymers by using a isoprene/styrene living anionic polymer.

Finally, the lubricant formulations, including the calixarene based star polymers or commercially available products as viscosity index improvers, will be prepared and comparatively tested.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The viscosity index (VI) improvers consist of polymers whose behavior in solution is affected by the temperature. On one hand, at low temperatures the polymer chains contract and do not impact significantly on the fluid viscosity. On the other hand, at high temperatures the chains expand and an increase in fluid viscosity occurs.

During service, the lubricant can be exposed to high mechanical shear stress that can cause the cleavage of the polymer chains. When this happens, the additive partially loses its ability to act as a viscosity index improver.

In order to limit the shear stability problems, some manufacturers of lubricant additives introduced on the market viscosity index improvers based on multi-branched polymer structures, among which the star-shaped polymers are the most common ones (for more details see Section 1.2.6).

The most used method to prepare star polymers (SPs) is the convergent approach, where monofunctional linear polymers are used as precursors of the SPs. The reactive groups at the end of these linear polymers can be directly reacted with an appropriate multifunctional core (also known as a "linking agent") to produce the SPs.

To obtain viscosity index improvers with high thickening power and good shear stability, the SPs need to have a low molecular weight dispersion. This result can be obtained having an high control on the molecular weight of the linear polymer chains and on the number of reactive sites within the core.

The most common polymerization technique to prepare linear polymers precursors of SPs is the living anionic polymerization.

The living anionic polymerization, introduced in the ′60, has been the first synthetic technique to prepare polymers with narrow molecular weight distribution. Nowadays, despite the continuing development of new strategies for the synthesis of well-defined polymers and copolymers (some examples could be the group transfer polymerization,[1] ring-opening metathesis polymerization[2] and the living radical polymerization[3]), anionic polymerization is still the most reliable and versatile method for the synthesis of a wide variety of polymers.

The main reason of the success of the living anionic polymerization is the high efficiency in the generation of the growing polyanions. During this process, termination or chain transfer reactions are limited, allowing to obtain polymers with a narrow distribution of the molecular weights.[4]

Besides, to obtain SPs with low molecular weight dispersion, the multifunctional core must have a narrow distribution of the reactive sites number. Divinylbenzene (DVB) and chlorosilane derivatives, due to their multiple electrophilic sites, were extensively used as linking agents.[5–7] The use of these derivatives allows a good control on the distribution of the molecular weight of the final SPs due to their relatively low reactive site number. However, when the number of reactive sites increases significantly, the control on the molecular weight distribution of the final polymers fades.

To overcome this problem, a different approach is proposed in this thesis. The use of calixarene-based derivatives as precursors of the core should enable the production of highly branched polymers with an high and defined number of functional groups which should result in a SP with very low dispersion.

4.2 The calixarene platform

The calix[8]arene derivatives are good candidates as cores of SPs, due to their peculiar properties. Their well-defined structure with 8 units of phenol allows to have an high and defined number of reactive sites. Moreover, the simple synthetic procedure of p-tert-butylcalix[8]arene (also indicated as

"HBC"), the possibility to carry out its preparation even on kilo-scale, its easy of purification by fractional precipitation as well as the simple functionalization procedures make the "HBC" derivatives among the most interesting scaffolds for the preparation of SPs.

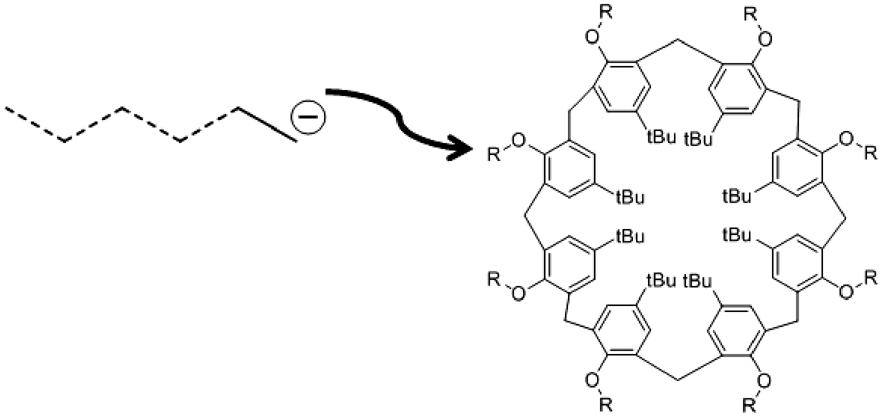


Figure (4.1): *Addition of an anionic polymer to a generic p-tert-calix[8]arene core*

Another important advantage of the p-tert-butylcalix[8]arene derivatives it that they are flexible molecules able of minimizing the steric hindrance effect arising during the grafting processes (Figure 4.1) and thus maximizing also the number of linear polymer chains which can be linked to the core.

The introduction on the p-tert-butylcalix[8]arene structure of specific electrophilic functional groups allows their reaction (addition or substitution) with anionic polymeric chains. It could be also planned to introduce on each of the phenolic O-atoms groups able to react with two or more chains (such as ester or trichlorosilane) or chains presenting branches along their structure. In this way, the total potential number of attached arms could even reach multiples of 8.

However, to obtain SPs with an high number of arms it is necessary that all the phenolic hydroxy groups in the p-tert-butylcalix[8]arene structure are completely functionalized with groups reactive towards the anionic polymer. Besides, the presence of residual unfunctionalized hydroxy groups in the calixarene structure not only decreases the possible number of sites of attachment onto the central core, but also causes the quenching of the polymeric anionic chains to unreactive alkanes.

4.2.1 Synthesis of p-tert-butylcalix[8]arene

First of all, the synthesis of p-tert-butylcalix[8]arene had to be achieved as reported in the literature by Munch and Gutsche.[8]

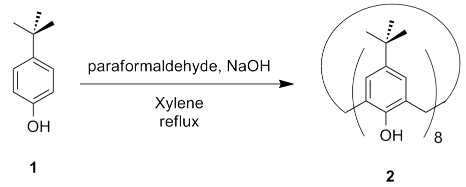


Figure (4.2): *Synthesis of p-tert-butylcalix[8]arene (***2***)*

After re-precipitation in chloroform, the calixarene **2** was obtained in good yield as a colorless powder.

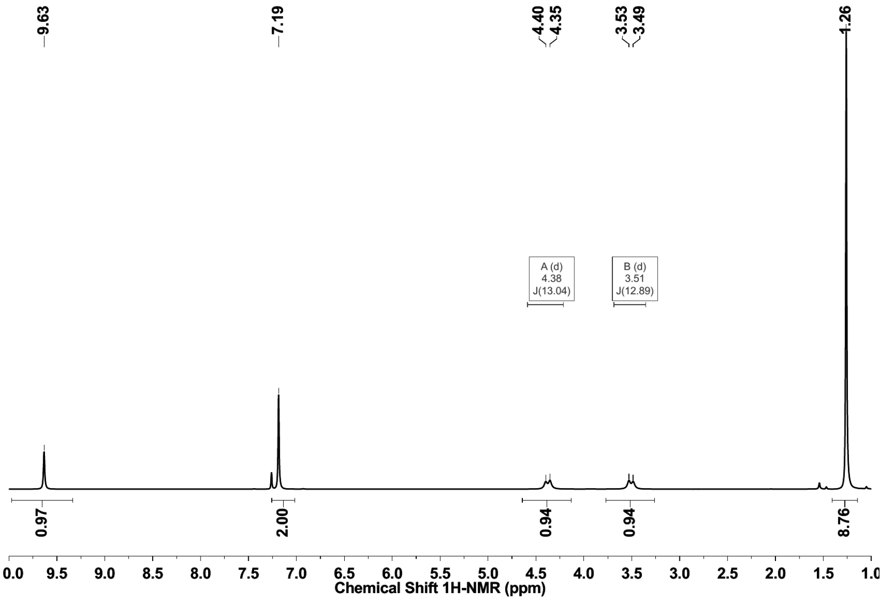


Figure (4.3): *^{1}H-NMR (CDCl$_3$, 300 MHz) of p-tert-butylcalix[8]arene*

The ^{1}H-NMR analysis (Figure 4.3) shows at 4.38 and 3.51 ppm the two doublets due to the protons (axial and equatorial ones, respectively) of the methylene bridge and at 9.63 ppm the broad signal of hydroxyl groups. The shape of the methylene-bridge peaks suggests that the macrocycle is in slow exchange on the NMR time-scale and that, on the average a cone conformation stabilized by intramolecular hydrogen bonds is present.

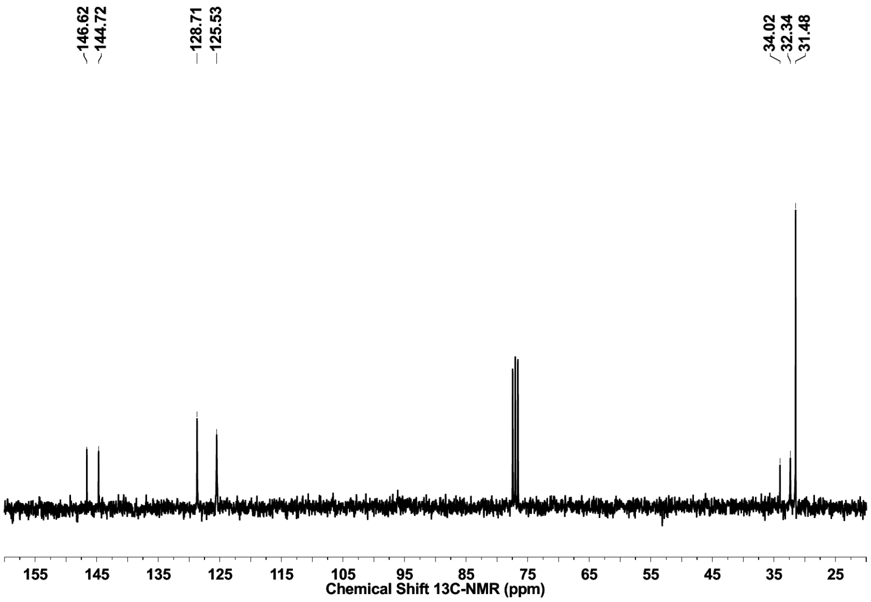


Figure (4.4): *^{13}C-NMR (CDCl$_3$, 75 MHz) of p-tert-butylcalix[8]arene*

The ^{13}C-NMR spectum (Figure 4.4) shows the methylene bridge carbon peak at 32.3 ppm, whereas the signal at 146.6 ppm is due to the benzene carbon atom bonded to the OH group.

As shown in the following sections of this chapter, the aromatic signal at 146.6 ppm is very important to evaluate the functionalization degree of p-tert-butylcalix[8]arene. In fact, the ^{13}C-NMR spectrum of the functionalized derivatives always presents these signals over 150 ppm.

4.3 Functional groups

In the work carried out during this thesis, several functional groups, such as alkyl chlorides, alkenes and esters, where considered to prepare p-tert-butylcalix[8]arene cores for SP preparation.

The alkylating agents used to introduce these functional groups at the lower rim of p-tert-butylcalix[8]arene need also to be commercially available and cheap, especially taking into account the final possible industrialization of these products.

For this reason, all the synthetic approaches explored start from commercial reactants and exploit fractional precipitations for the purification of the intermediates or final products.

4.3.1 Alkyl chlorides

Alkyl chlorides are usually able to react with a polymeric carbanion species.[9] p-tert-butylcalix[8]arenes functionalized with ω-chloro-alkyl groups, should therefore react with the anionic arms (Figure 4.5) via aliphatic substitution, elimination of Cl^- and formation of a SPs with eight polymeric arms.

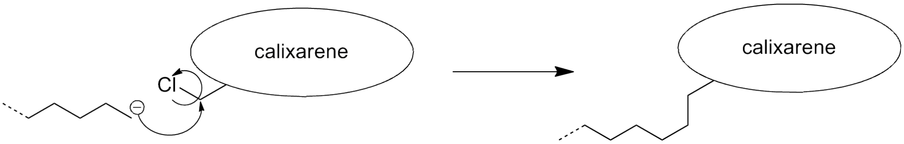
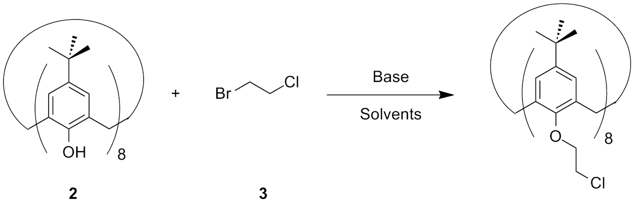


Figure (4.5): *Nucleophilic substitution of an anionic polymer chain to a generic alkyl chloride*

2-chloroethyl derivative

A first attempt to introduce $-CH_2Cl$ groups onto the calixarene structure exploited the reaction of p-tert-butylcalix[8]arene (**2**) with 1-bromo-2-chloroethane (**3**) (Figure 4.6).

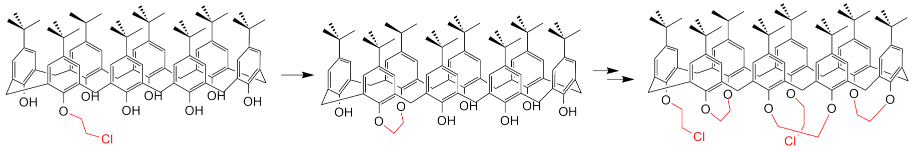


2 **3** **4**

Figure (4.6): *Synthesis of the product **4** from **2***

The reaction was carried out under different basic conditions, but no satisfactory results could be obtained. In fact, a mixture of products was always detected by ESI-MS analysis.

The phenomenon that limits the formation of the desired product was identified in the occurrence of intramolecular reactions (Figure 4.7), where bridges between different phenolic O-atoms take place.



4'   4''   4'''

Figure (4.7): *Example of intramolecular reactions during the reaction of calix[8]arene with 1-bromo-2-chloro ethane*

As soon as the first chloroethyl groups are inserted onto the calixarene (e.g. **4'** in Figure 4.7) they find a high local concentration of phenol/phenoxide O-atoms in close proximity which strongly favor the intramolecular bridging reaction (**4''** in Figure 4.7). Probably also due to solubility issue, even in the presence of huge excess of alkylating agents, the intramolecular reaction is high favored compared to the intermolecular one. An example of these products is indicated as **4'''** in Figure 4.7.

Using a strong base for the deprotonation of the calixarene (for example NaH instead of K_2CO_3), the outcome of the reaction even got worse. This result was correlated to the occurrence of simultaneous multiple deprotonations on the calixarene O-atoms which further promote the intramolecular reactions. On the other hand, the use of a weak base resulted in a very low conversion due to the inability to deprotonate the calixarene O-atoms and therefore to activate the nucleophiles.

Even the reduction of the reaction temperature did not give better results probably due to the reduction of the solubility of p-tert-butylcalix[8]arene in the reaction mixture.

Changing the nature of the counterion of the base (for example from K^+ to Cs^+) could eventually increase separation of ion-pairs, but this effect had no significant effect on the outcome of the reactions.

As an example, Figure 4.8 reports the ESI-MS analysis of the best reaction mixture obtained. The signal at 1832 m/z was due to the complex formed by the octafunctionalized calix[8]arene and Na^+. All the other signals are related to different species in which a variable number of ethylene bridges are present.

Because of the complexity of the reaction mixture, the isolation of the desired product by chromatographic separation was not possible. In this way, only fractions containing mixtures of different products could be obtained.

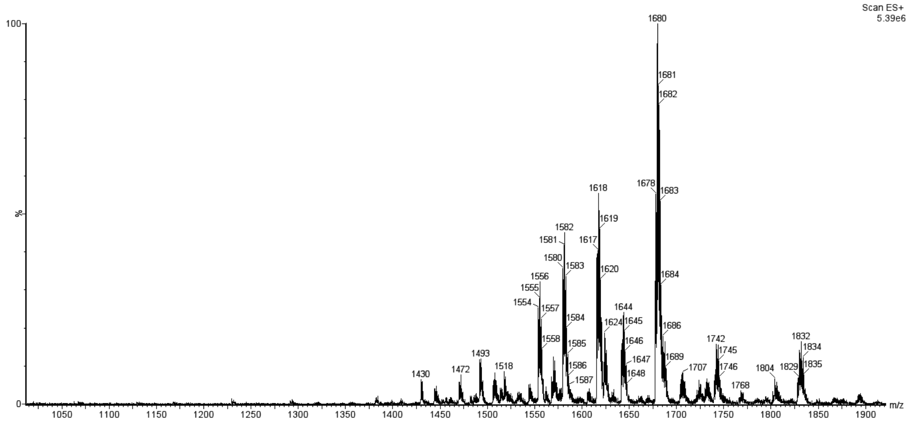


Figure (4.8): *ESI-MS spectrum of a crude of the alkylation reaction with 1-bromo-2-chloroethane*

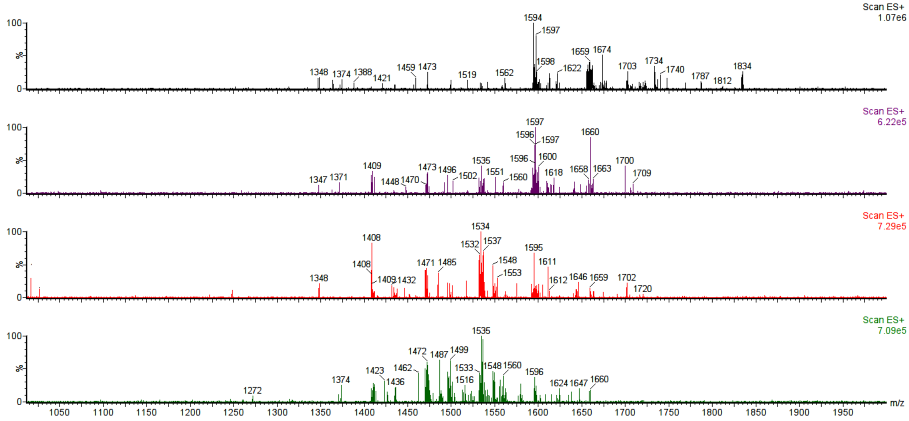


Figure (4.9): *ESI-MS spectra of different chromatographic fractions (crude of the alkylation reaction with 1-bromo-2-chloroethane)*

In Figure 4.9 the ESI-MS analysis of subsequent chromatographic fractions (eluent: hexane/DCM 9/1) are reported. Comparing the faster eluting fraction (black) with the slowest one (green), a gradual decrease of the average molecular weights can be observed. The octafunctionalised product was only present in the fastest eluting fraction, but in mixture with other products.

As soon as the retention time of the eluted products increases, a progressive increase of ethylene intramolecular bridges was also observed. Unfortunately, none of the fractions collected contained only pure single products, but always quite complicated mixtures of different compounds.

In conclusion, the difficulty in the synthesis and purification of the products obtained by the reaction of Figure 4.6 did not allow its use for our purposes.

Considering the unsatisfactory results of this first approach, a new one was planned. This new approach is based on a multistep strategy which considers the use of an halogenoalkane bearing a functional group that can be converted to halogen but only in a subsequent step, when all the phenolic O-atoms are already alkylated.

At first, p-tert-butylcalix[8]arene is totally functionalized by using an α-bromoacetate ester as alkylating agent (for more detail see Section 4.3.3). Subsequently the octa-ester derivative (**15**) is reduced to octa-alcohol (**5**), as shown in Figure 4.10. Finally, in the last step the replacement of the OH group with a Cl atom by reaction with $SOCl_2$ is planned to take place.

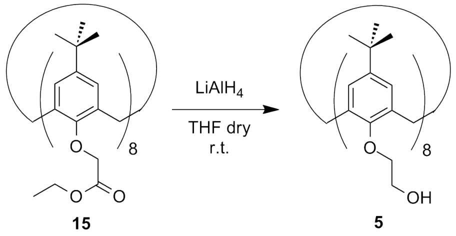


Figure (4.10): *Synthesis of the product* **5** *from* **15**

The compound **15** was reduced by $LiAlH_4$ in THF at room temperature. After 4 h CH_3OH was added dropwise, the solvents were removed at reduced pressure and the product was recovered in toluene. After recrystallization in CH_3Cl, the desired product **5** was obtained as a white solid.

The positive outcome of this reaction was confirmed by ESI-MS analysis (Figure 4.11) which indicates the presence of the signal at 1673 m/z due to the adduct of **5** with Na^+.

In this spectrum also the adducts of **5** with two ions Na^+ (848 m/z) and with one Li^+ and one Na^+ were detected. The compound **5** was subsequently treated with $SOCl_2$ to synthesize the chloroethyl derivative (**4** in Figure 4.12).

The reaction was studied using several experimental procedures and conditions to maximize the yield. Unfortunately, all the attempts failed, once again due to intramolecular reactions.

As shown in Figure 4.13, an alcohol group of **5** could react with a molecule

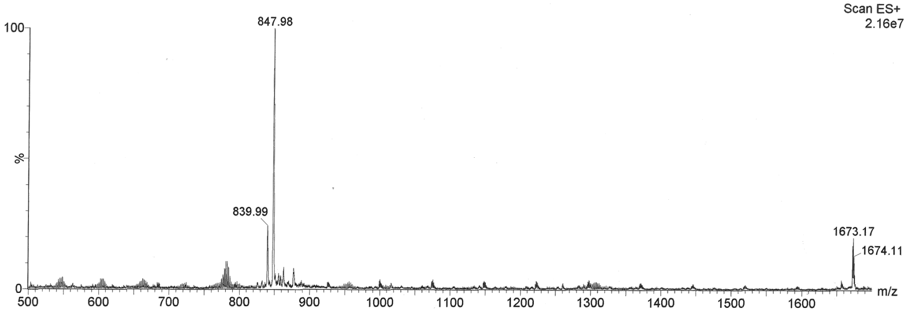
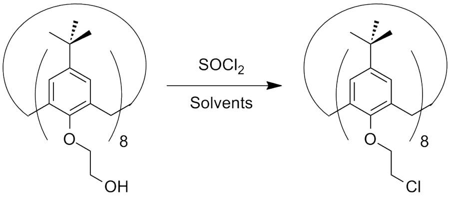


Figure (4.11): *ESI-MS spectrum of product **5***



5 **4**

Figure (4.12): *Synthesis of the product **4** from **5***

of $SOCl_2$ to give the intermediate chlorosulfonic ester reported in the center of the figure. The elimination from this intermediate of a molecule of SO_2 to give the chloroethyl group is in competition with an undesired intramolecular reaction with a second OH group spatially close, giving rise to a bridging sulfite diester shown on the right of Figure 4.13.

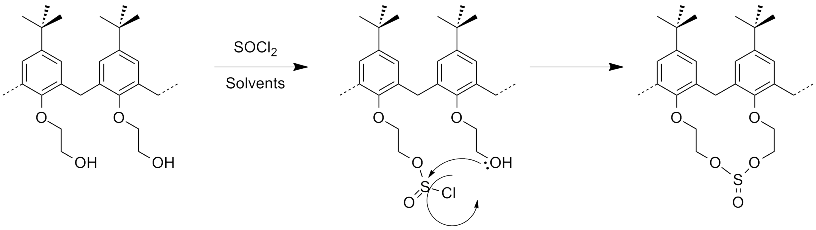
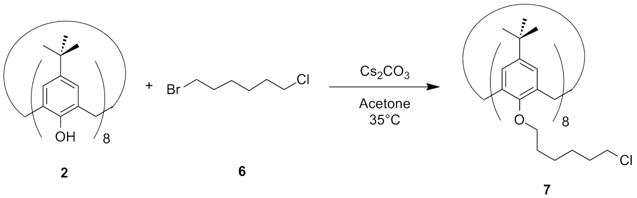


Figure (4.13): *Intramolecular reactions during the process in Figure 4.12*

The ESI-MS spectra of the reaction mixtures always showed the presence of various distributions of molecular weights. From these results it can therefore be concluded that also a multistep synthesis cannot be used to obtain the desired product.

6-chlorohexyl derivative

Due to the negative results obtained in the previous syntheses, we tried to disfavor intramolecular reactions by increasing the distance between the bromo and chloro atoms in the alkylating agent. For this purpose, the calixarene **2** was reacted with 1-bromo-6-chlorohexane (**6**). This strategy resulted to be particularly successful since, allowing the formation of the desired product **7**.



2

6

7

Figure (4.14): *Synthesis of the product* **7**

As shown in Figure 4.14, Cs_2CO_3 was used as base to allow the deprotonation of calixarene **2**. As reported in literature,[10] the counter ion Cs^+ can form loose ion pairs with the calixarene, allowing a higher reactivity of the calixarate-cesium salt with 1-bromo-6-chlorohexane.

After precipitation in CH_3OH, the desired product **7** was obtained.

The ^1H-NMR spectrum of the product (Figure 4.15) shows singlets for the aromatic protons around 7 ppm and for the CH_2 bridges at 3.6 ppm. The success of the functionalization was also confirmed by the signal at 4.07 ppm due to the $PhO-CH_2$ group. Furthermore, the presence of the signal related to CH_2-Cl residue (triplet at 3.46 ppm) confirms the hypothesis that the substitution takes place only at the CH_2-Br groups of the alkylating agent.

Further evidences of the complete functionalization are visible in the ^{13}C-NMR spectrum (Figure 4.16), which shows a single signal for the carbon of $PhO-CH_2$ at 72.9 ppm and the aromatic $C-OR$ at 153.3 ppm. Moreover, the peak at 45 ppm confirms the presence of CH_2-Cl residue in the product (and not of the CH_2-Br).

Due to the success of this functionalization, the behavior of this calixarene derivative was subsequently evaluated as SPs core precursor. The results of the reaction between the derivative **7** and a model carboanionic compound (n-butyllithium) are reported in Section 4.5.1 of this thesis.

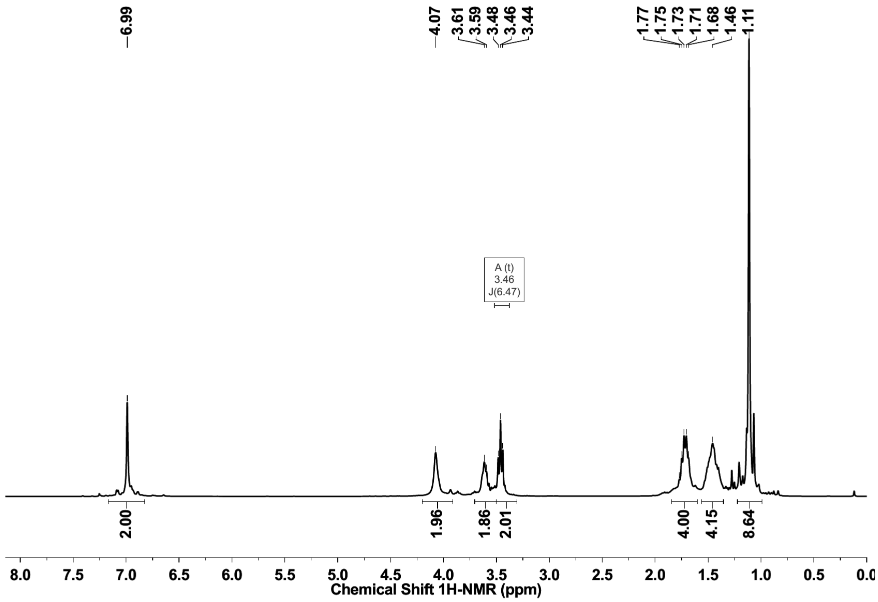


Figure (4.15): *^{1}H-NMR of the derivative* **7**

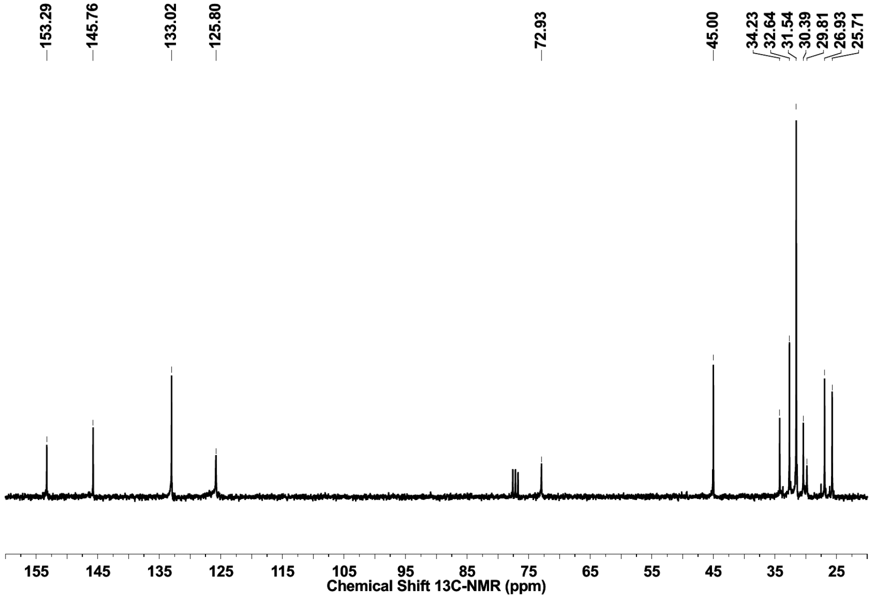


Figure (4.16): *^{13}C-NMR of the derivative* **7**

p-(chloromethyl)benzyl derivative

The use of a new alkylating agent was considered to increase the possibilities of introducing halide functionalities on the calixarene. As previously discussed, the alkylating agent should introduce a spacer between the calixarene backbone and the C−Cl bond. For this purpose, 1,4-bis(chloromethyl)benzene (**8** in Figure 4.17) was chosen.

As reported in the literature,[11] the benzyl-chloride group is quite reactive in SN2 reactions even when anionic living polymers are used. For this reason, the calixarene derivative bearing benzyl-chloride groups could be tested for SP preparation.

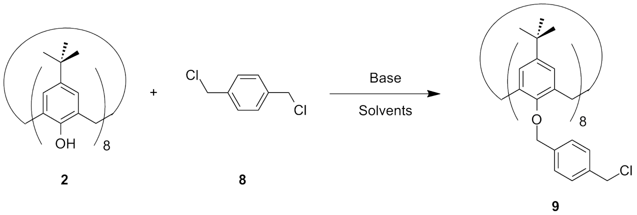


Figure (4.17): *Synthesis of the product **9***

On the other hand, the alkylating agent **8** (Figure 4.17), having two identical C−Cl groups, is more symmetrical compared to the bromo-chloro alkylating agents discussed so far (**3** and **6** in the previous paragraphs). This resulted in a low discrimination of the two ends during reaction with calix[8]arene **2** that results in a tight competition between intermolecular and intramolecular reactions. In fact, in all the experiments attempted it was never possible to isolate or even have evidence of the product of octafunctionalization while ESI-MS suggested the formation of products where xylene-bridges are present due to intramolecular reactions.[12]

4.3.2 Alkenes

The olefin double bond was the second type of functional group planned to be introduced onto the calixarene to produce calixarene-based core structure for the reaction with anionic living polymers. The literature reports the use of several compounds containing the C=C bond in the industrial synthesis of multi-branched polymer structures. For example, divinylbenzene (DVB) derivatives were extensively used as linking agents.

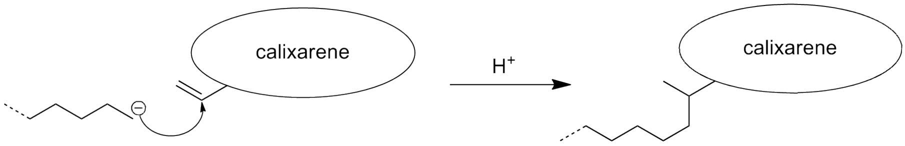


Figure (4.18): *Nucleophilic substitution of an anionic substrate to an olefine functionalized calixarene*

As shown in Figure 4.18, the olefin double bond on a calixarene core could react with carbanionic chains giving rise to a carbanion on the core, which can be subsequently quenched by an acid to terminate the polymerization process. In this way, eight polymer chains could be introduced for each calixarene core.

In order to study this approach, two calixarene derivatives have been considered and discussed in the following.

Allyl derivative

The first p-tert-butylcalix[8]arene olefin derivative considered for our purpose is the allyl derivative, whose synthesis of which was reported in 1999 by Wang and coworkers.[13]

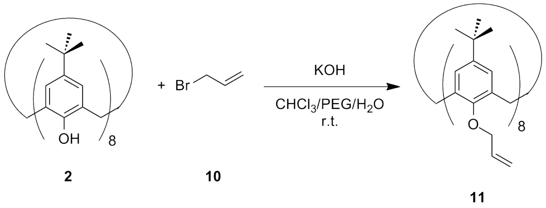


Figure (4.19): *Synthesis of the product **11***

As shown in Figure 4.19, the reaction was carried out in biphasic conditions using PEG400 as phase-transfer catalyst. After 24 h at room temperature, the product **11** was obtained in good yield.

The ^{1}H-NMR spectrum (Figure 4.20) of derivative **11** shows narrow signals, which means an high symmetry of the product structure. In detail, the peak of the methylene bridges is detected at 4.05 ppm, whereas the signals of allyl groups are shown between 5.80 and 4.00 ppm (inset "A" in Figure 4.20).

The Figure 4.21 displays the ^{13}C-NMR of the product **11**. In detail, the presence of $O-CH_2$ residue is confirmed by the peak at 73.6 ppm, whereas

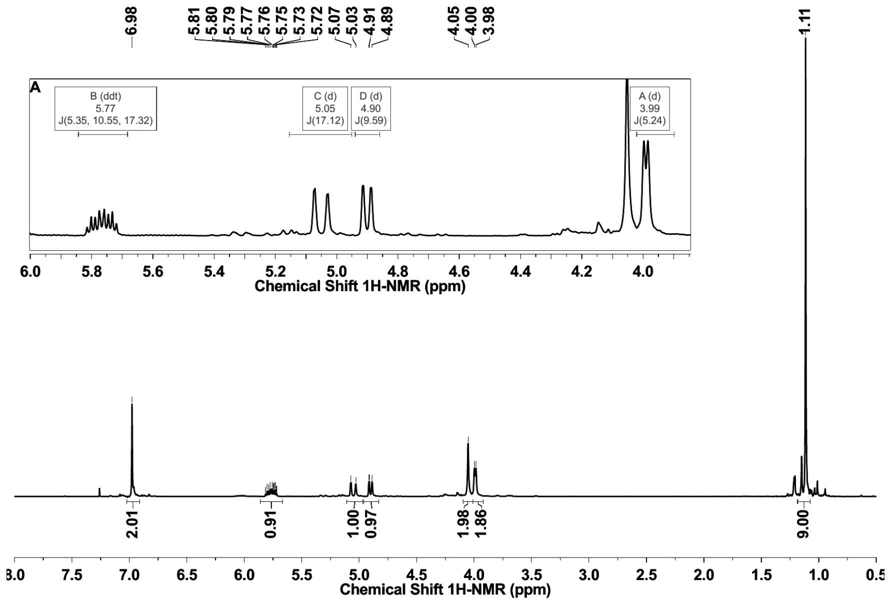


Figure (4.20): *^{1}H-NMR (CDCl$_3$, 400 MHz) of the derivative* ***11***

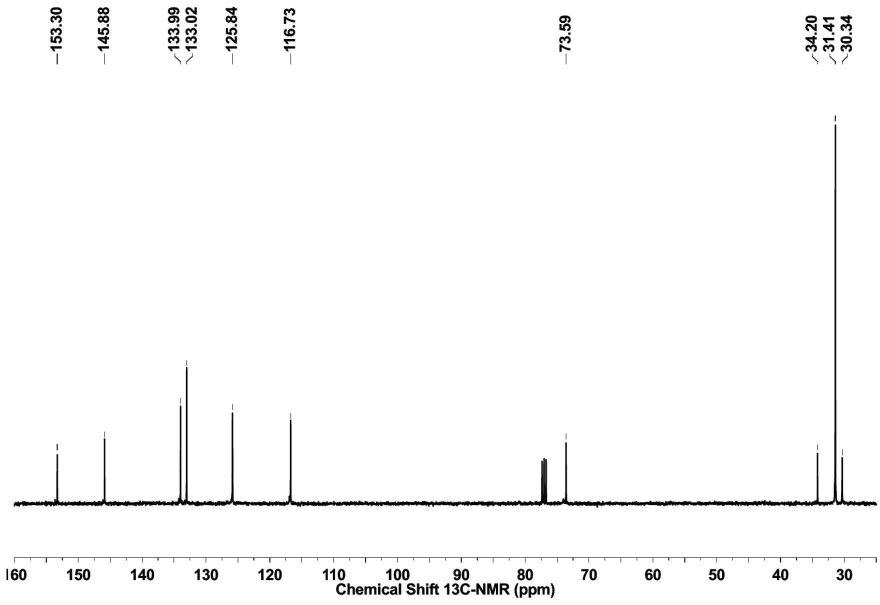


Figure (4.21): *^{13}C-NMR (CDCl$_3$, 100 MHz) of the derivative* ***11***

the C=C functionalization is detected by the signals at 116.7 and 134.0 ppm. Besides, the single peak at 153.3 ppm is due to the benzene carbon atom bonded to the OR group, demonstrating the complete functionalization of the starting calixarene.

Considering the positive outcome of this reaction and its potential applicability on an industrial scale, the product **11** was subsequently tested as SPs precursor. The results of the reaction of compound **11** with a model of the anionic living polymer (n-butyllithium) are reported in Section 4.5.2.

p-methylstyrene derivative

To obtain an olefine calixarene derivative with a highly reactive double bond, the reaction of p-tert-butylcalix[8]arene with p-(chloromethyl)styrene (**12** in Figure 4.22) was also attempted.

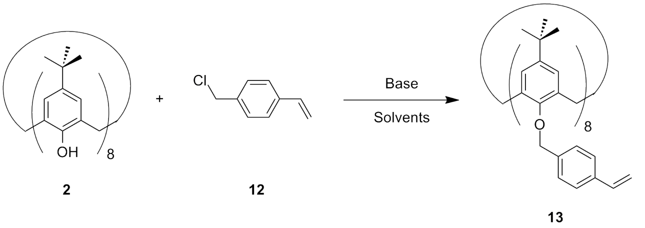


Figure (4.22): *Synthesis of the product **13***

As extensively reported in the literature, in fact, the styrene residues are highly reactive in anionic polymerization.[14] However, unfortunately, this high reactivity characterized also the functionalization with the calixarenes. The starting material itself (commercial source: Sigma-Aldrich) results quite impure (90 % w/w) due to the presence of products of oligomerization and as soon as the reactants are mixed together, a series of by-products due also to decomposition of the alkylating agent start to form. Although some products possibly attributable to alkylated calixarenes were identified by TLC analysis, their isolation resulted impossible, making this interesting intermediate unavailable for further use as SPs precursor.

4.3.3 Esters

The ester is the third type of functional group we planned to insert on the calixarene for SP preparation. According to our knowledge, the literature does not report relevant examples of ester derivatives as central cores for the living anionic polymerization.

As shown in Figure 4.23, an ester group can react with an anionic polymer chain forming, in a first reaction step, a ketone group by elimination of an alcoholate.

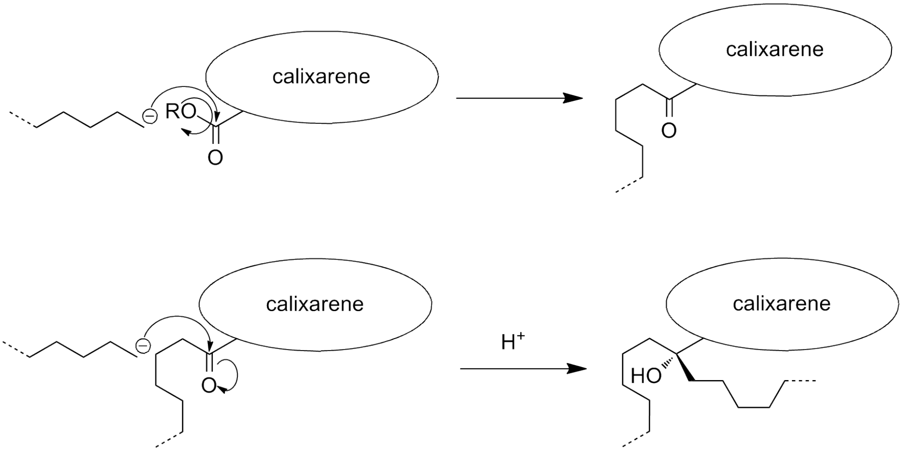


Figure (4.23): *Nucleophilic attack of two anionic chains to a generic ester derivative*

The ketone intermediate, being more electrophilic, should react even faster than the original ester with a second anionic chain to give a tertiary alcohol.[9] For this reason, the ester group is also particularly interesting than the other ones previously proposed, because it could allow to graft two polymer chains to every single core arms, allowing to double the number of final chains which constitute the star polymer. In this way, up to 16 polymeric arms could be theoretically grafted to a calix[8]arene core functionalized with 8 esters groups.

With the aim to evaluate this possibility, the synthesis of three different ester derivatives were studied.

Ethyl acetate derivative

The first example of ester derivative studied in this thesis was the calixarene **15** (Figure 4.24).

The procedure of product **15** synthesis is well known on calix[8]arenes since 1984, as reported in the literature.[15] By reaction of p-tert-butylcalix[8]arene

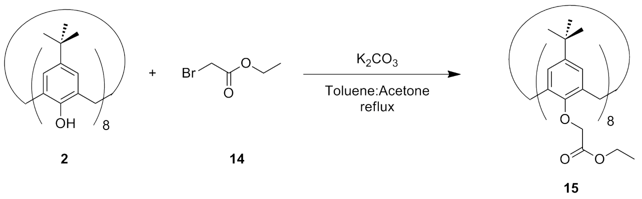


Figure (4.24): *Synthesis of the product* ***15***

(**2**) with ethyl α-bromoacetate (**14**), in the presence of K_2CO_3 as base, the desired product (**15**) was obtained as white solid with good yield.

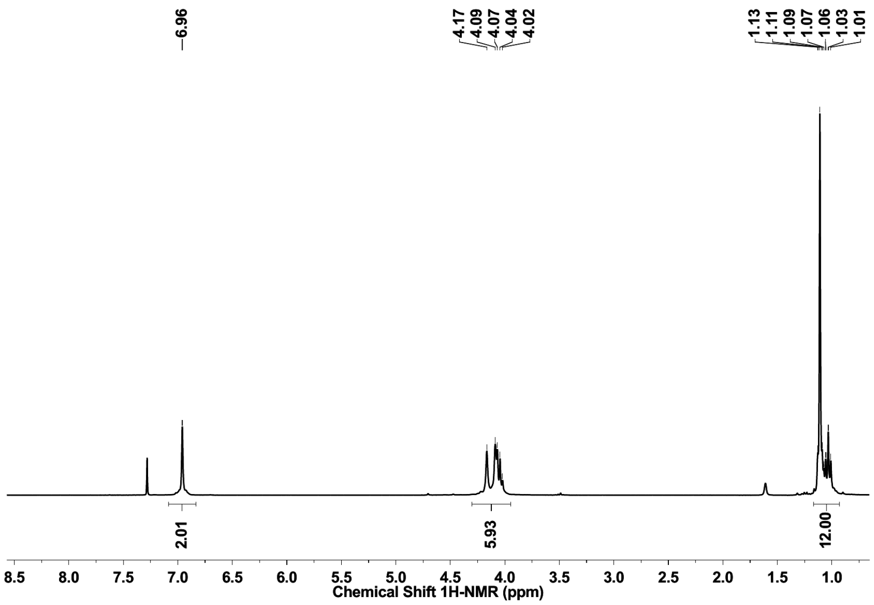


Figure (4.25): *^{1}H-NMR ($CDCl_3$, 400 MHz) of the derivative* ***15***

The NMR analyses confirm the positive outcome of this synthesis. In detail, the ^{1}H-NMR (Figure 4.25) shows a multiplet from 4.2 to 4.0 ppm, due to 6 protons. These signals can be correlated to different residues: 2 protons of methylene bridges, 2 protons of $PhOCH_2$ residues and 2 methylene protons of ethyl ester groups. The triplet due to methyl group of ethyl ester is partially hidden by tert-butyl peak close to 1 ppm.

In the ^{13}C-NMR spectrum (Figure 4.26) the following signals are in agreement with the proposed substitution: 168.8 ppm (COOR), 69.9 ppm ($PhOCH_2$), 61.0 ppm (OCH_2) and 13.9 ppm (OCH_2CH_3).

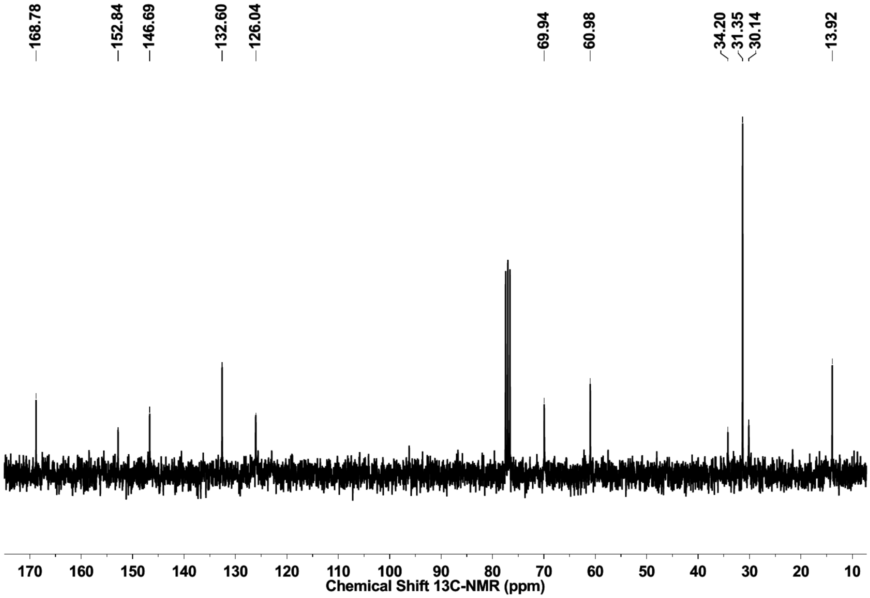


Figure (4.26): *^{13}C-NMR ($CDCl_3$, 100 MHz) of the derivative* ***15***

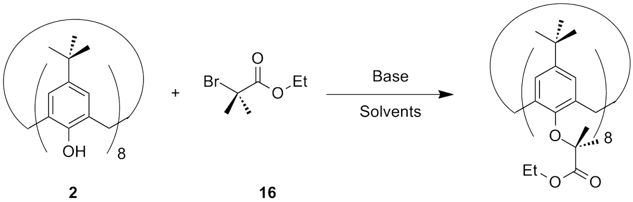
Considering the positive outcome of this reaction, the product **15** was subsequently tested as SPs precursor. The results of the reaction of compound **15** with n-butyllithium will be discussed in Section 4.5.3. In such paragraph we will explain that the presence of acidic hydrogen atoms in α position to carboxylic group of compound **15** causes the undesired consumption of n-butyllithium and prevents the formation of SPs with an high number of polymeric arms. For this reason new calixarene ester derivatives, lacking H in α-position to the carbonyl group were studied.

Ethyl isobutyrate derivative

The second ester calixarene derives from the reaction of p-tert-butylcalix[8]arene with ethyl α-bromoisobutyrate (**16** in Figure 4.27).

As shown in Figure 4.27, the reactive site of the alkylating agent **17** is a tertiary carbon which is known to be less reactive than primary one. This characteristic is due to the steric hindrance of CH_3 groups.[9]

Despite the use of strong bases (for example KH), high reaction temperatures (over 100 °C) and long reaction time (over 10 days), the product **17** could not be obtained.



2 **16** **17**

Figure (4.27): *Synthesis of the product* ***17***

The reaction however afforded a mixture of products with different functionalization degrees (between 3 and 6) as could be evidenced from ESI-MS analysis of the crude material (Figure 4.28).

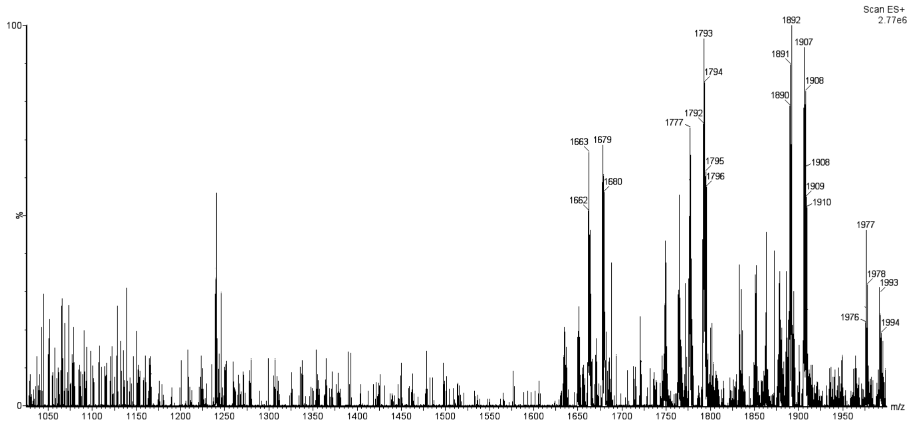


Figure (4.28): *ESI-MS spectrum of the crude material (synthesis of the product* ***17****)*

In ESI-MS spectrum the peaks at 1663 and 1679 m/z are due to the adducts between the tri-functionalized calixarene and respectively the Na^+ and K^+ cation. The complexes of tetra-functionalized products are outlines by the signals at 1777 and 1793 m/z, whereas the penta-functionalized ones are revealed by the peaks at 1892 and 1907 m/z. Finally, the signals at 1977 and 1993 m/z indicate also the presence of the adduct of the hexa-functionalized calixarene.

The absence of the desired product in the reaction mixture prevented its use in the subsequent step of SPs polymers synthesis.

Methyl p-methylbenzoate derivative

The last example of calixarene ester derivative studied in this Thesis is the product **19** (Figure 4.29).

On the basis of the results and the explanations outlined in the preceding paragraphs, for the synthesis of a new ester derivative without acid α hydrogen atoms and bearing an halogen atom on a primary carbon atom was desired. Besides, a conjugation between the reactive site and the ester group was desirable in the alkylating agent to slightly enhance its reactivity. Following these criteria, the alkylating agent that has been chosen was methyl p-(bromomethyl)benzoate (**18** in Figure 4.29).

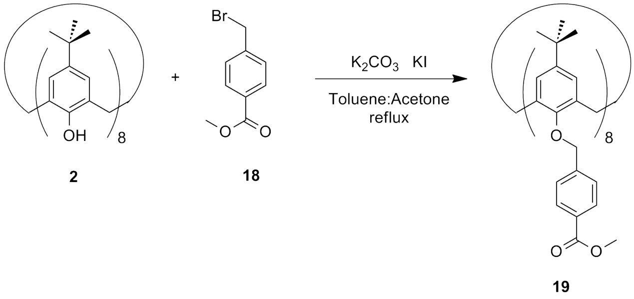


Figure (4.29): *Synthesis of the product* ***19***

By reaction of p-tert-butylcalix[8]arene (**2**) with the alkylating agent (**18**), in the presence of K_2CO_3 and catalytic amount of KI, the product **19** was obtained with good yield after 2 days at 70 °C in acetone and toluene mixture.

NMR spectra (Figure 4.30 and Figure 4.31) confirm the completion of the reaction.

The ^{1}H-NMR spectrum (Figure 4.30) reveals the doublets due to aromatic protons of benzylic residue at 7.75 and 7.14 ppm, the singlet of $PhO-CH_2$ at 4.55 ppm and the singlet at 3.90 ppm due to methoxy residue of the ester group. Moreover, the singlets at 6.94, 3.98 and 0.98 ppm are the other signals expected for the desired product **19**.

The most significant peaks of ^{13}C-NMR spectrum due to the functionalization are at 166.9 ppm (COOR), 73.9 ppm ($PhOCH_2$) and 52.1 ppm (OCH_3).

Due to the success of this functionalization, the behavior of the calixarene **19** as star polymer precursor was studied. The results of the reaction of compound **19** with n-butyllithium are reported in Section 4.5.4. Compared to the product **15**, previously discussed, the product **19** should give better

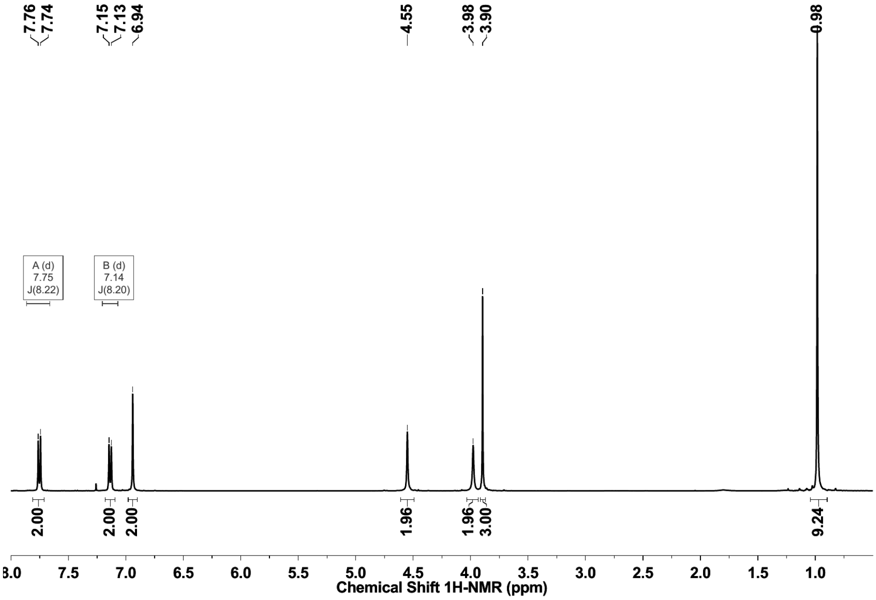


Figure (4.30): *^{1}H-NMR ($CDCl_3$, 300 MHz) of the derivative* ***19***

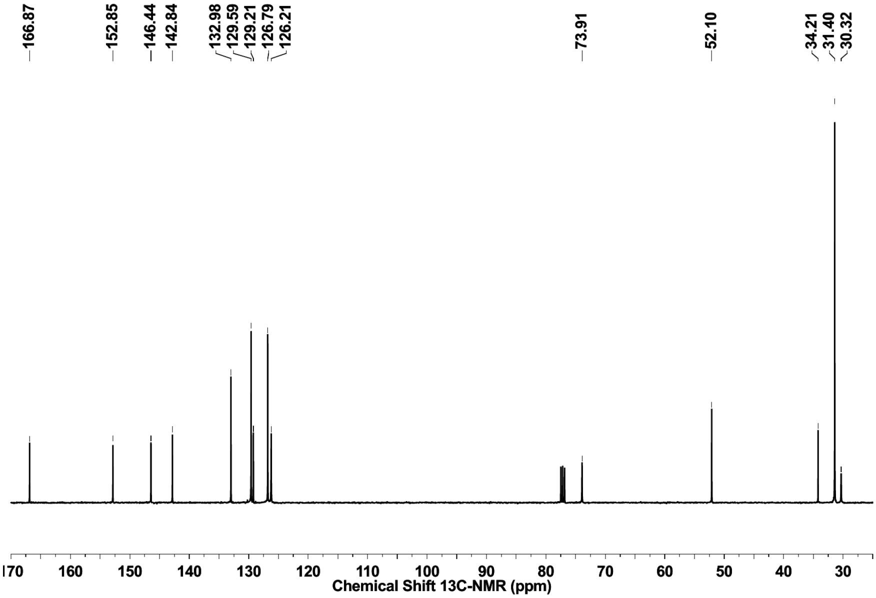


Figure (4.31): *^{13}C-NMR ($CDCl_3$, 75 MHz) of the derivative* ***19***

results in SPs formation both for the absence of acidic hydrogen and for lower steric hindrance effects in the grafting process, which should be due to the longer distance between the ester group and the calixarene backbone.

4.4 A carbanionic model system

After the synthesis of the calixarene derivatives described in Section 4.3, the study of their reactivity towards living anionic polymer chains became necessary.

To overcome the possible low reactivity of carbanionic polymer chains due to their steric hindrance and to have products of low molecular weight easier to be characterized, the use of a simple model reactant was necessary.

This model reactant must be a carboanionic species with a reactivity similar to that of the anionic living polymer lithium salts. Furthermore, it has to be preferably commercial and with a known purity. These characteristics are necessary for a fast and simple preliminary evaluation of the functionalized calixarenes reactivity towards carbanionic reactants.

A good candidate for our purpose was identified in n-butyllithium (n-BuLi).

4.4.1 n-butyllithium

n-butyllithium is available from Sigma Aldrich as a solution in hydrocarbon solvents such as pentane, hexane, cyclohexane or toluene, at a concentration in the range between 1.4 and 11.0 M. For reasons of cost and availability, the chosen solution of n-BuLi was 1.6 M in hexane.

The determination of the exact n-BuLi solution concentration was performed by volumetric titration,[16] using the procedure described in Section 6.1.1.

The calixarene derivatives were then reacted with n-BuLi solution. The reaction was carried out in a Schlenk tube under inert atmosphere at a temperature of 40 °C, using dry cyclohexane containing 1000 ppm of dry THF as reaction solvent, identical to the one used in living anionic polymerization carried out in an industrial plant.

After solubilization of the calixarene derivative (about 100 mg) in 10 mL of solvent mixture, the n-BuLi solution was added under inert atmosphere. Unless otherwise stated, 1 equivalent of n-BuLi per reactive site was added.

Certainly reactions could give better yields in shorter times by using large excesses of n-BuLi, but we wanted to reproduce as close as possible the conditions to be used in the SP preparation. In this case, excesses of anionic species cannot be used because they cannot be separated by the desired star polymers at the end of the reaction.

The standard reaction time was 20 min, even if the time could be changed in function of the reactivity of the calixarene derivatives.

4.5 Reactions between calixarene derivatives and n-BuLi

4.5.1 i-(6-hexyloxy)-p-tert-butylcalix[8]arene

The first candidate as polymer core precursor was the derivative **7**, whose synthesis has already been discussed in Section 4.3.1.

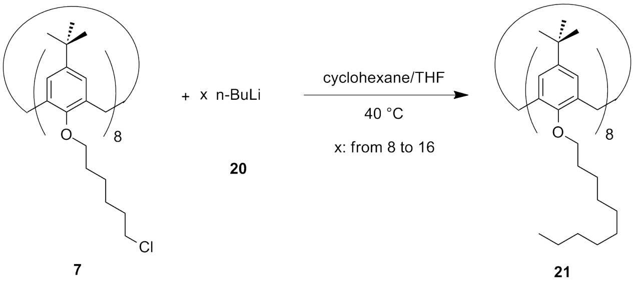


Figure (4.32): *Reaction of product **7** with n-BuLi; [n-BuLi]/[arm$_{calix}$] ratio: from 1/1 to 2/1*

The low solubility of this calixarene in the standard solvent mixture forced us to change its composition.

The new solvent mixture was constituted by 5 mL of dry toluene, 5 mL of dry cyclohexane and 1 μL of dry THF. The reaction was carried out at 40 °C for 12 h. At the end a 1 M solution of HCl_{aq} was added to quench the reaction.

Unfortunately, the ^{1}H-NMR analysis (Figure 4.33) shows the non-completeness of the reaction. The presence of broad signals in the spectrum are symptom of symmetry decrease due to an incomplete functionalization. Besides, the area ratio between aliphatic and aromatic hydrogen signals confirms a low

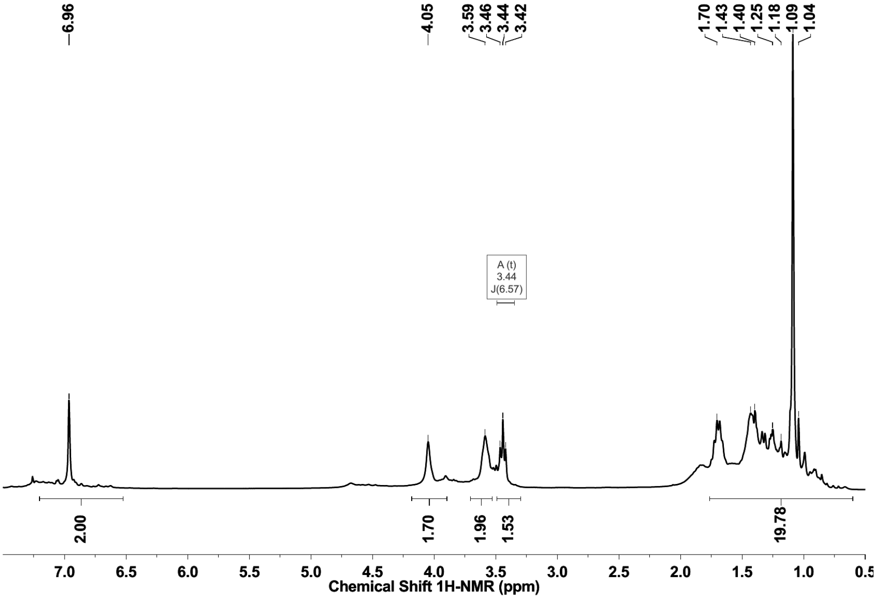


Figure (4.33): *^{1}H-NMR (CDCl$_3$, 400 MHz) of crude material (synthesis of* ***21****)*

functionalization degree. On the average, these area ratios correspond to a functionalization degree of about 30 %.

As a further confirmation, the ^{13}C-NMR in Figure 4.34 shows the presence of a signal at 45 ppm due to C−Cl bond, which is correlated to the ^{1}H-NMR signal at 3.47 ppm.

The increase in the reaction mixture of n-BuLi amount (2 eq per chloroalkyl chain) did not lead to any significant increase of the functionalization degree. As a result of these experimental evidences, the calixarene **7** is not suitable to be used as polymer core precursor.

Further studies are needed to understand if the low reactivity of calixarene **7** is due to a low reactivity of C−Cl bond or to steric hindrance of calixarene structure. In the first case, the class of alkyl chlorides must be discarded in favor of other more reactive functional groups. In the second case, a greater distance between the calixarene backbone and the reactive sites could be a way to improve the reactivity of the C−Cl bonds.

To answer to this question, the same type of reaction was carried out using a model of calixarene **7**, which is the analogue monomeric phenol

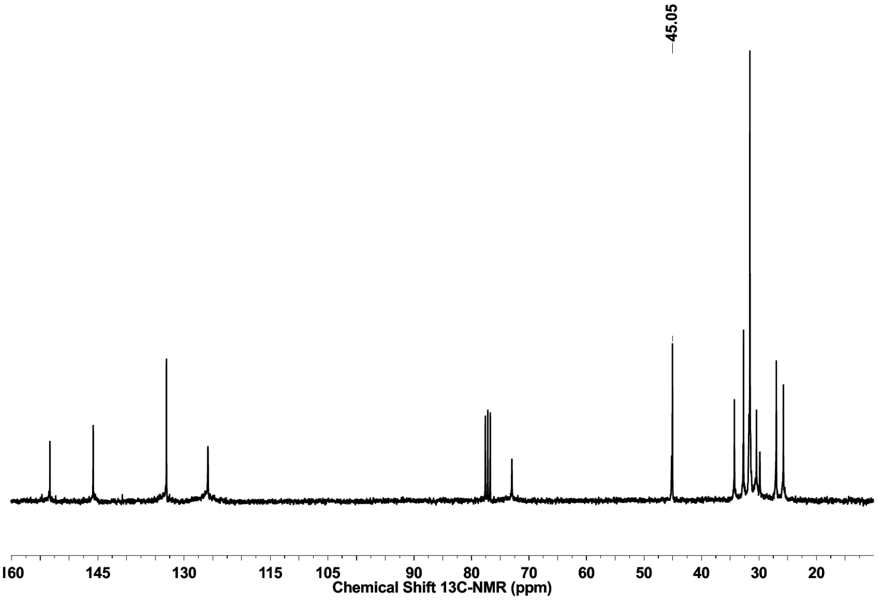


Figure (4.34): *^{13}C-NMR ($CDCl_3$, 100 MHz) of crude material (synthesis of* ***21****)*

derivative (**25** in Figure 4.45). The results are reported in Section 4.6.1.

4.5.2 i-(allyloxy)-p-tert-butylcalix[8]arene

The second candidate as polymer core precursor was the calixarene **11**. This derivative was soluble in the standard reaction solvent mixture (cyclohexane/THF) and so the studies of its reactivity with n-BuLi were performed using the standard reaction parameters, as indicated in Figure 4.35.

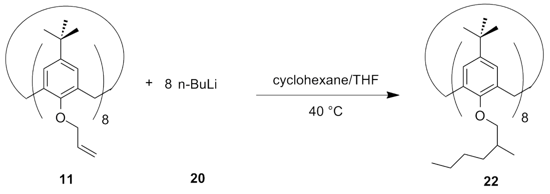


Figure (4.35): *Reaction of product* ***11*** *with n-BuLi; [n-BuLi]/[arm$_{calix}$] ratio: 1/1*

A low grafting degree was evidenced by NMR analyses in all experiments carried out by reacting the calixarene **11** with n-BuLi. After the standard reaction time (20 min), the addition at room temperature of 1 M HCl_{aq} led to the formation of gas bubbles (n-butane) indicating the presence of unreacted n-BuLi in the reaction mixture.

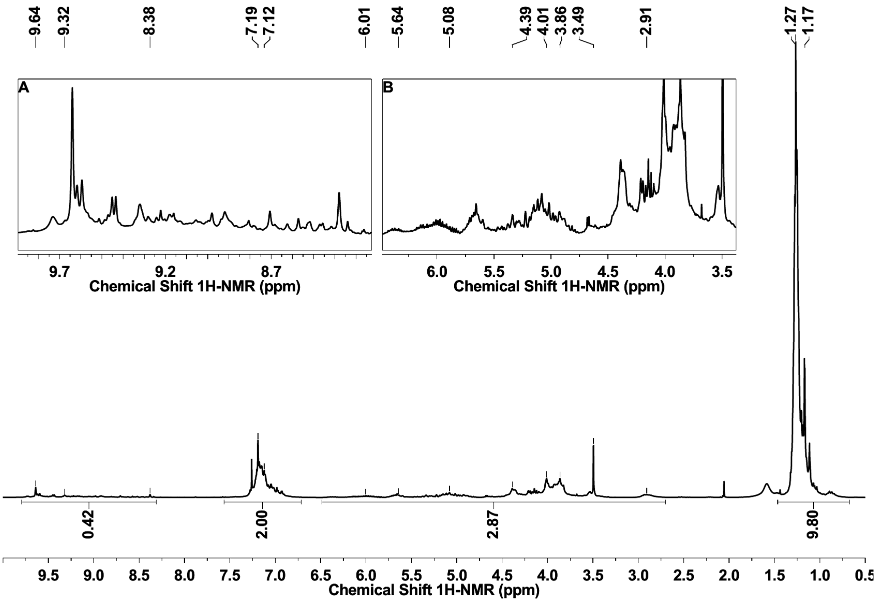


Figure (4.36): *^{1}H-NMR ($CDCl_3$, 400 MHz) of crude material (synthesis of* ***22****)*

The presence of broad signals in ^{1}H-NMR spectrum of the reaction mixture (Figure 4.36) are indication of symmetry loss due to an incomplete functionalization. Such evidence is confirmed by the area ratio between aliphatic and aromatic hydrogen signals. In particular, this ratio corresponds to a functionalization degree lower than 10 %.

The low grafting degree may be caused by the elimination reaction that can take place after the nucleophilic attack of n-BuLi on the terminal carbon of allyl group, as reported in Figure 4.37. This hypothesis was supported by the presence of signals over 8 ppm (inset "A" in Figure 4.36)), which might be due to hydroxyl groups in the calixarene structure. However, the product of complete elimination (p-tert-butylcalix[8]arene) could never be obtained.

Another possible explanation could be the formation of a carbanionic species which subsequently attacks another vicinal allyl group, causing an "intramolecular oligomerization", after an initial nucleophilic attack of n-

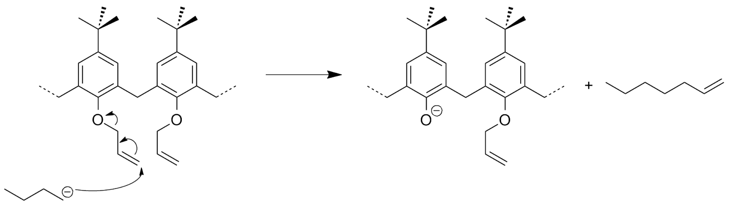


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Figure (4.37): *Elimination mechanism involving the allyl group*

BuLi on a first allyl group (Figure 4.38).

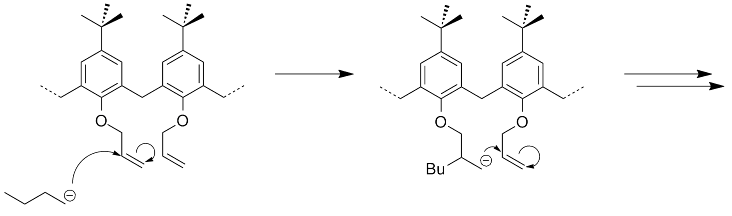

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Figure (4.38): *Intramolecular oligomerization mechanism involving the allyl group*

With the aim of understanding the reason of the failure of this coupling and of the low functionalization degree, the same type of reaction was carried out using the analogue monomeric phenol derivative (**27** in Figure 4.48) instead of calixarene **11**. The results are reported in Section 4.6.2.

4.5.3 i-(ethyloxycarbonylmethyloxy)-p-tert-butylcalix[8]arene

The third candidate as polymer core precursor was the calixarene **15**. The good solubility of this derivative in the reaction mixture (cyclohexane/THF) in combination with the possibility of linking two polymeric chains for each ester group, make this derivative a potentially attractive candidate for our purposes.

The study of the reactivity of calixarene **15** with n-BuLi was conducted using the reaction parameters indicated in Figure 4.39.

Several experiments were carried out, varying the ratio between the equivalents of n-BuLi and those of calixarene ester derivative. Unfortunately, a lower functionalization degree than the expected was always highlighted by ESI-MS analysis.

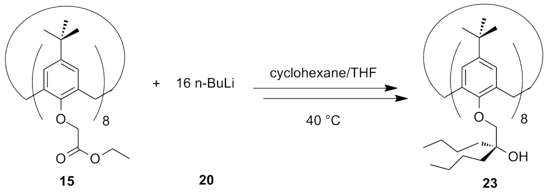

Figure (4.39): *Reaction of product **15** with n-BuLi; [n-BuLi]/[arm$_{calix}$] ratio: 2/1*

For instance, Figure 4.40 reports the ESI-MS analysis of a reaction mixture obtained using an equivalent ratio [n-BuLi]/[ester group] of 2. In case of successful reaction the product should be a calixarene with 8 tertiary alcoholic functionalities and 2 butyl groups linked to each of them (**23** in Figure 4.39).

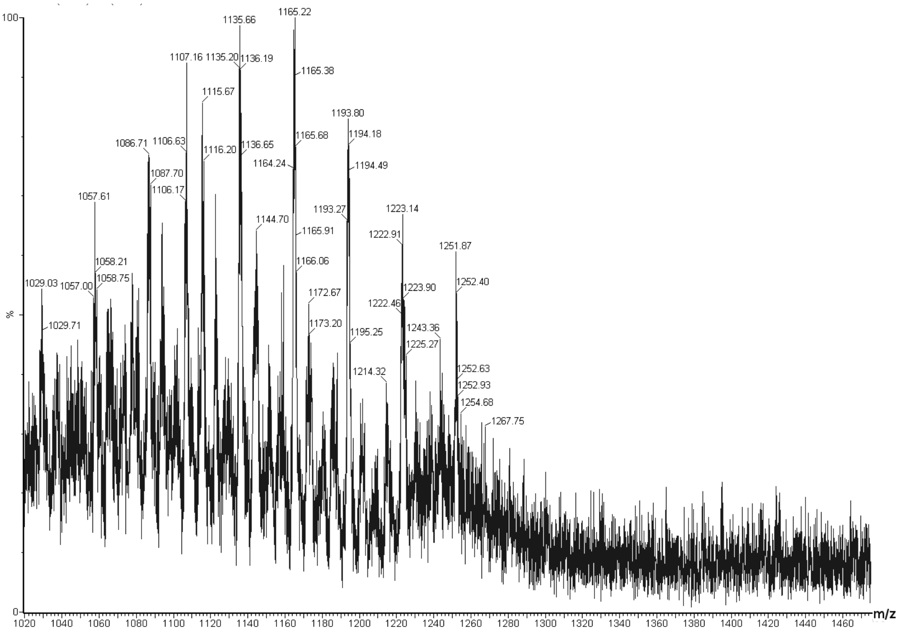

Figure (4.40): *ESI-MS spectrum of crude material (synthesis of **23**)*

The ESI-MS spectrum in Figure 4.40 clearly shows the presence of a mixture of compounds, characterized by different functionalization degree and with a different number of ester, ketone and alcohol groups. Moreover, the addition of 1 M HCl_{aq} to the reaction mixture did not led to the formation of appreciable amount of gas bubbles (n-butane), indicating the total consumption of n-BuLi.

A possible explanation of these experimental results are the reaction of the hydrogen atoms in α position to the carboxyl group with n-BuLi partially quenching the carbanionic species (Figure 4.41).[17]

Furthermore, similar functionalization degrees were also obtained using an excess of n-BuLi. These phenomena could be correlated to the generation of enolate-like compounds, which prevent the reaction of the ester group with n-BuLi carbanion, perhaps because of charge repulsion between groups.

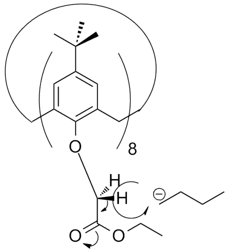

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Figure (4.41): *Deprotonation mechanism of the hydrogens atoms in α to the carboxyl groups*

As a result of these experimental evidences, the calixarene **15** is not suitable to be used for reactions with living anionic polymer chains. Also in this case, to better study the reason of the partial functionalization of derivative **15**, the same type of reaction was carried out using the analogue monomeric phenol derivative (**29** in Figure 4.51) instead of calixarene **15**. The results are reported in Section 4.6.3.

4.5.4 i-(p-(methyloxycarbonyl)benzyloxy)-p-tert-butylcalix[8]arene

The last candidate as polymer core precursor was the calixarene **19**.

An advantage of this ester derivative compared to **15** is the absence of acid α hydrogens to the carboxyl group, which should avoid acid-base reactions with the carbanionic species. Another advantage is a longer distance between ester group and calixarene backbone, that could make more available the ester reactive site for the reaction with carbanions.

The experimental results of the reaction between calixarene **19** and n-BuLi are in agreement with those expected. In fact, using a ratio [n-BuLi]/[ester] equal to 2, the desired compound **24** was obtained (Figure 4.42).

The product **24** (alcohol derivative) has solubility characteristics quite different from the reactant **19** (ester derivative). In fact, while the product

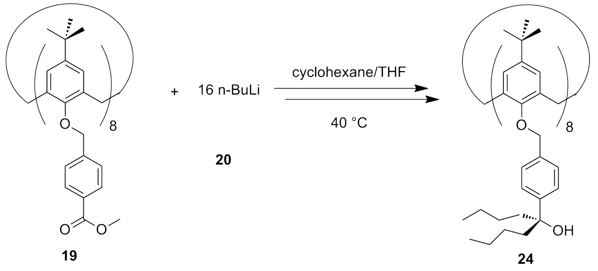

Figure (4.42): *Reaction of product **19** with n-BuLi; [n-BuLi]/[arm$_{calix}$] ratio: 2/1*

24 was perfectly soluble in polar organic solvents and sparingly soluble in $CHCl_3$, the ester derivative has an opposite behavior. For this reason, the NMR analyses of the product **24** were performed in a solution in $(CD_3)_2C{=}O$.

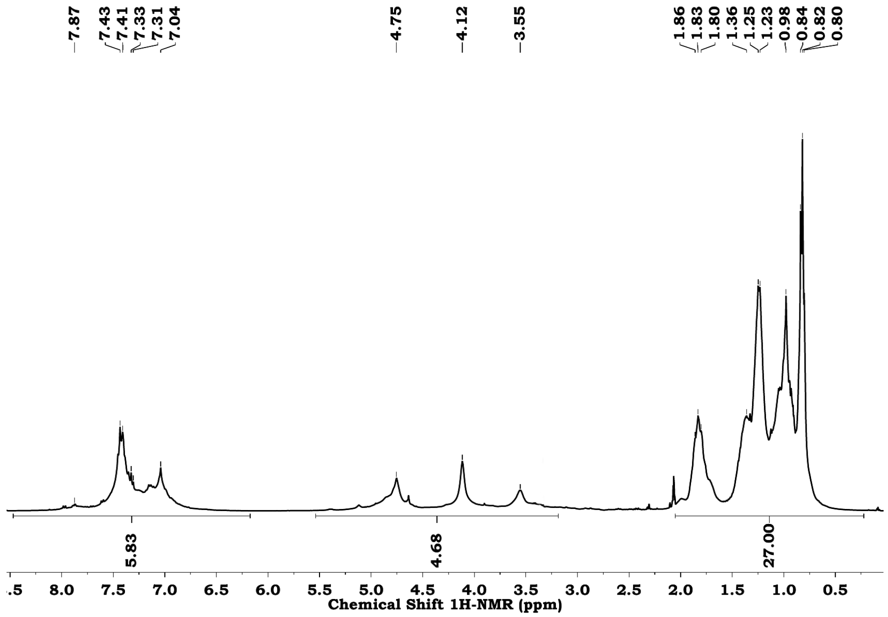

Figure (4.43): *^{1}H-NMR ($(CD_3)_2CO$, 400 MHz) of crude material (synthesis of **24**)*

The Figure 4.43 shows the ^{1}H-NMR spectrum of the reaction mixture. The ratio between the area of aliphatic protons with that of aromatic protons is in agreement with the expectations. Therefore, the signals attributable to the functionalization (PhO$-$CH$_2$ and OH) and the methylene bridges were reported at 4.75, 3.55 and 4.12 ppm, respectively.

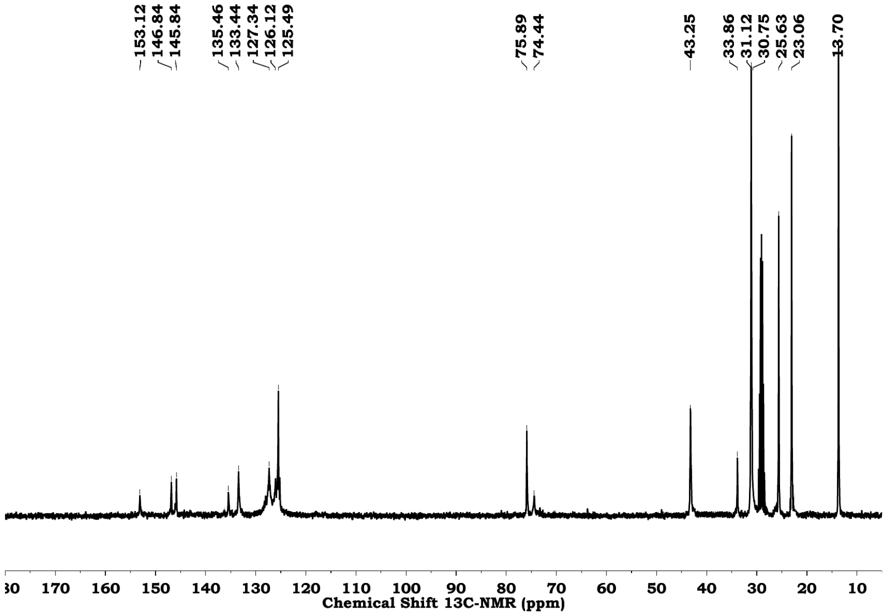

Figure (4.44): *^{13}C-NMR ((CD_3)$_2$CO, 100 MHz) of crude material (synthesis of **24**)*

The ^{13}C-NMR analysis (Figure 4.44) supported these good results. In detail, the disappearance of the carboxylic signal (166.9 ppm in Figure 4.31) and the presence of the pick at 75.9 ppm (attributable to the tertiary C$-$OH) confirm the reaction occurred. Furthermore, the signals at 43.2, 25.6, 23.1 and 13.7 ppm established the presence of residues n-butyl grafted to the tertiary C$-$OH in the derivative **24**.

However, to obtain a further confirmation of the results presented in this section, the same type of reaction was carried out using the analogue monomeric phenol derivative (**31** in Figure 4.55) instead of calixarene **19**. These results are reported in Section 4.6.4.

Considering the good results obtained with the derivative **19** in the reaction with n-BuLi, such calixarene was tested in the grafting reaction with living anionic polymer chains, as discussed in Section 4.7.

4.6 BuLi studies with monofunctionalizated derivatives

The studies of the reactions between monomeric phenol derivatives and n-BuLi were needed to better understand the reactivity of the calixarene derivatives under the same reaction conditions but on a simpler substrate.

The synthesis of monomeric phenol derivatives and the results of their reactions with n-BuLi are described in the following Sections.

The results of the studies on chloro-alkyl derivative (**25**) are discussed within Section 4.6.1. The Section 4.6.2 deals with allyl derivative (**27**) and in Sections 4.6.3 and 4.6.4 the results on ester derivatives (**29** and **31**, respectively) are reported.

4.6.1 1-(chlorohexyloxy)-4-tert-butylbenzene

The procedure for the synthesis of 1-(chlorohexyloxy)-4-tert-butylbenzene was derived from the literature.[18]

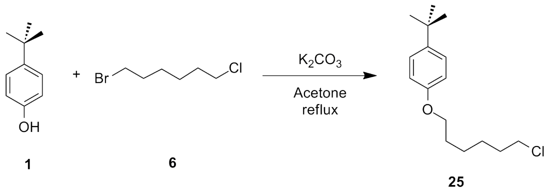

Figure (4.45): *Synthesis of the product* **25**

The product **25** was synthesized using an excess of 1-bromo-6-chlorohexane (**6** in Figure 4.45) in the presence of K_2CO_3 as base.

After chromatographic purification (eluent: hexane/toluene 1/1), the derivative **25** was obtained in good yield. The reaction between **25** and n-BuLi was carried out using the same solvent mixture (cyclohexane/toluene/THF mixture) and operative conditions (40 °C) already used for the calixarene derivative (Section 4.5.1). After 1 h a 1 M solution of HCl_{aq} was added to quench the reaction.

The negative outcome of the reaction was confirmed by ^{1}H-NMR analysis, from which the presence of unreacted reactant **25** is confirmed. Also the ^{13}C-NMR analysis (Figure 4.47) shows the peak at 45.0 ppm due to C−Cl.

This experimental evidence on the monomer analogue thus confirms the

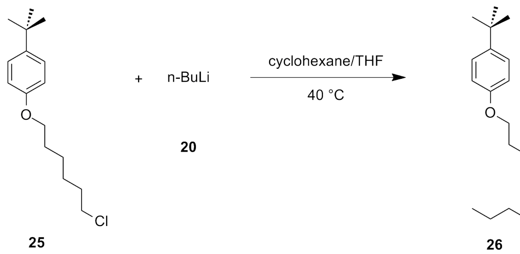

Figure (4.46): *Reaction of product **25** with n-BuLi; [n-BuLi]/[**25**] ratio: 1/1*

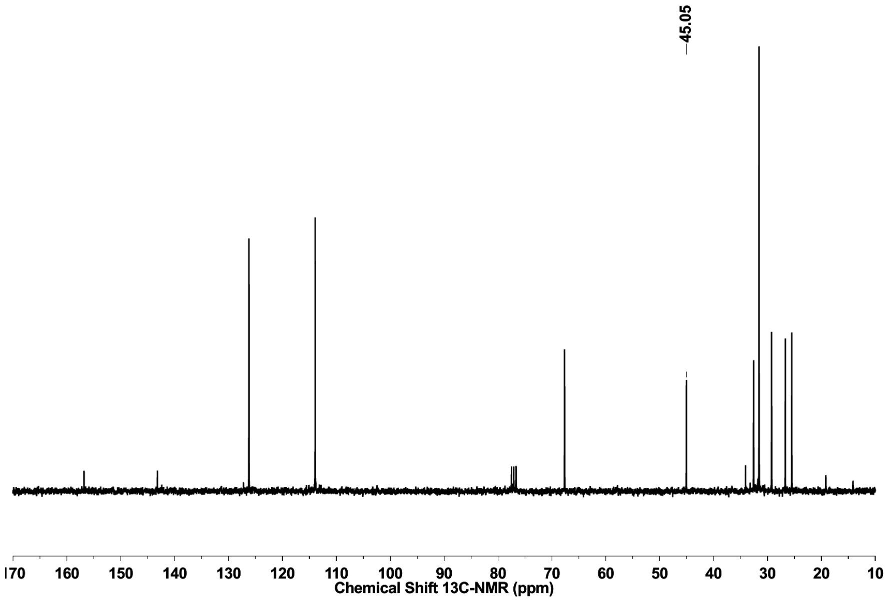

Figure (4.47): *^{13}C-NMR ($CDCl_3$, 100 MHz) of crude material (synthesis of **26**)*

results obtained with the calixarene derivative **7** (Section 4.5.1), suggesting that the lack of reactivity is intrinsic in the chloroalkyl derivative and not caused by the presence of the calixarene macrocycle.

4.6.2 1-(allyloxy)-4-tert-butylbenzene

The procedure for the synthesis of 1-(allyloxy)-4-tert-butylbenzene (**27**) is already reported in literature.[19]

The product **27** was synthesized using an excess of 3-bromoallyl (**10** in

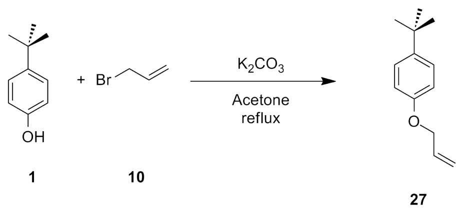

Figure (4.48): *Synthesis of the product* ***27***

Figure 4.48) in presence of K_2CO_3 as base.

At the end of reaction a 1 M solution of HCl_{aq} was added, the organic phase was separated and the solvent was removed under reduced pressure. The derivative **27** was obtained in good yield after chromatographic purification (eluent: hexane/toluene 1/1).

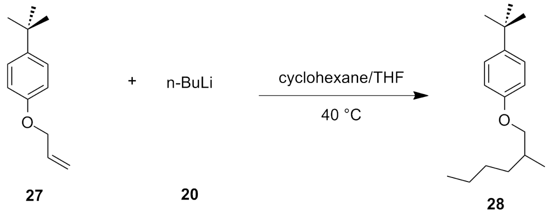

Figure (4.49): *Reaction of product* ***27*** *with n-BuLi; [n-BuLi]/[**27**] ratio: 1/1*

The reaction between **27** and n-BuLi was carried out using the same solvent mixture (cyclohexane/THF mixture) and operative conditions (40 °C) already used for the calixarene derivative (Figure 4.49). After 15 min a 1 M solution of HCl_{aq} was added to quench the reaction. The organic phase was separated and the solvent was removed under reduced pressure.

As shown by ^{1}H-NMR in Figure 4.50, a de-alkylation process takes place. In fact, about 75 % of the derivative **27** reacted with n-BuLi, forming p-tert-butylphenol (**1** in Figure 4.48) and 1-heptene, which was removed under reduced pressure. In the inset “A” of Figure 4.50 compound **1** can be identified from the aromatic signals at 7.3 and 6.8 ppm and from the broad signal of OH at 5.6 ppm. Furthermore, the presence of two phenolic structures was confirmed by two signals at 1.39 and 1.37 ppm, which were due to different p-tert-butyl derivatives (**27** and **1**, respectively).

The results obtained suggest therefore that the failure of the reaction between the calixarene **11** with n-BuLi (Figure 4.35) might be caused by a similar elimination mechanism.

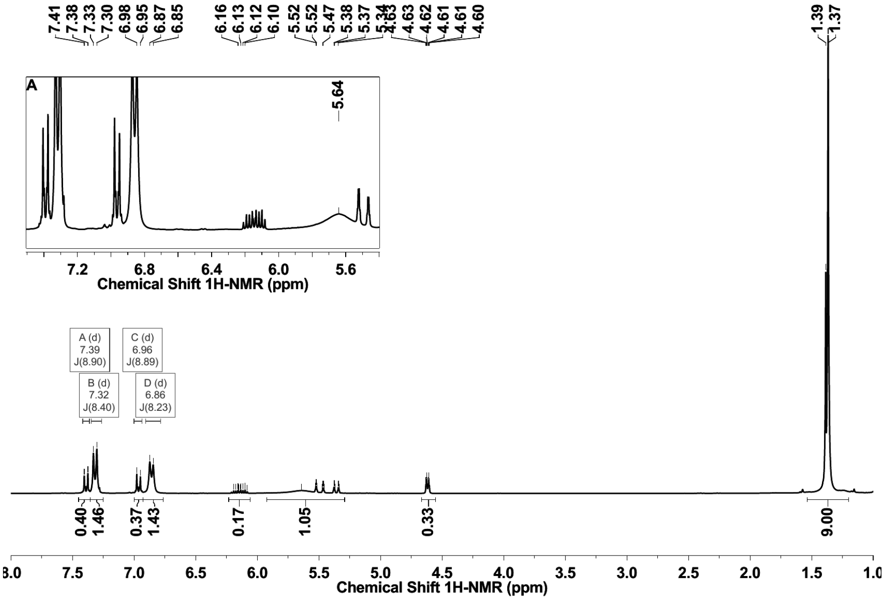

Figure (4.50): *^{1}H-NMR (CDCl$_3$, 400 MHz) of crude material (synthesis of 22)*

4.6.3 1-(ethyloxycarbonylmethyloxy)-4-tert-butylbenzene

The product **29** was synthesized as reported in literature,[20] in presence of K_2CO_3 as base and using an excess of ethyl α-bromoacetate (**14** in Figure 4.51).

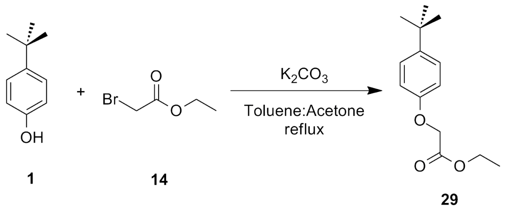

Figure (4.51): *Synthesis of the product **29***

At the end of reaction a 1 м solution of HCl_{aq} was added, the organic phase was separated and the solvent was removed under reduced pressure. The derivative **29** was then obtained in good yield after chromatographic purification (eluent: AcOEt/toluene 1/9) in order to remove the excess of ethyl α-bromoacetate, which was present from the synthesis.

The reaction between the ester **29** and n-BuLi was carried out using the same solvent mixture (cyclohexane/THF mixture) and operative conditions (40 °C) already used for the calixarene derivative (Figure 4.52). After 15 min a 1 M solution of HCl_{aq} was added to stop the reaction. The disappearance of the derivative **29** was monitored by TLC analysis.

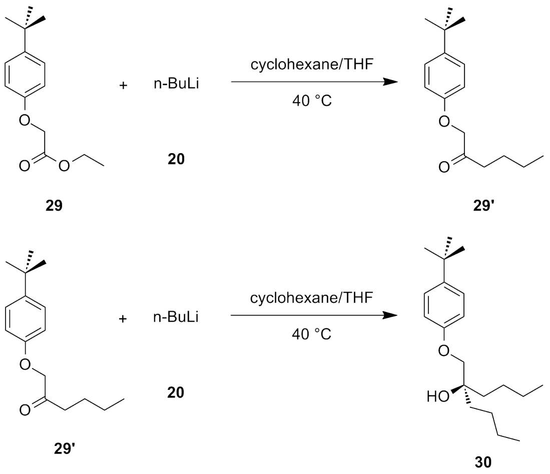

Figure (4.52): *Reaction of product **29** with n-BuLi; [n-BuLi]/[**29**] ratio: 2/1*

The incomplete functionalization of the monomer **29** was visible from the NMR analyses. The ^{1}H-NMR spectrum in Figure 4.53 shows the signals of two different phenolic derivatives in the reaction mixture. The ester **29** is not detected by ^{1}H-NMR spectrum and therefore it reacted completely to give firstly the ketone intermediate (**29′**), which then partly reacted to give the alcohol derivative (**30**). The presence of unreacted ketone intermediate is detected by the signals at 4.58 and 2.65 ppm, as well as by doublets at 7.26 and 6.85 ppm. By the ratio between the integrals of aliphatic and aromatic signals it was possible to calculate an alcohol content of about three times of that of the ketone.

The ^{13}C-NMR spectrum in Figure 4.54 confirms what previously evinced. In fact, the presence of the ketone derivative is detected by the peak at 208.7 ppm due to ketone carbonyl and by the peak at 74.0 ppm due to ketone $PhOCH_2$ residue. The two signals close to 73 ppm are, on the other side, due to alcohol (**30**).

The simultaneous presence in the reaction mixture of the desired product (**30**) and the ketone intermediate (**29′**) was the proof of an incomplete functionalization of the reactant **29** with n-BuLi.

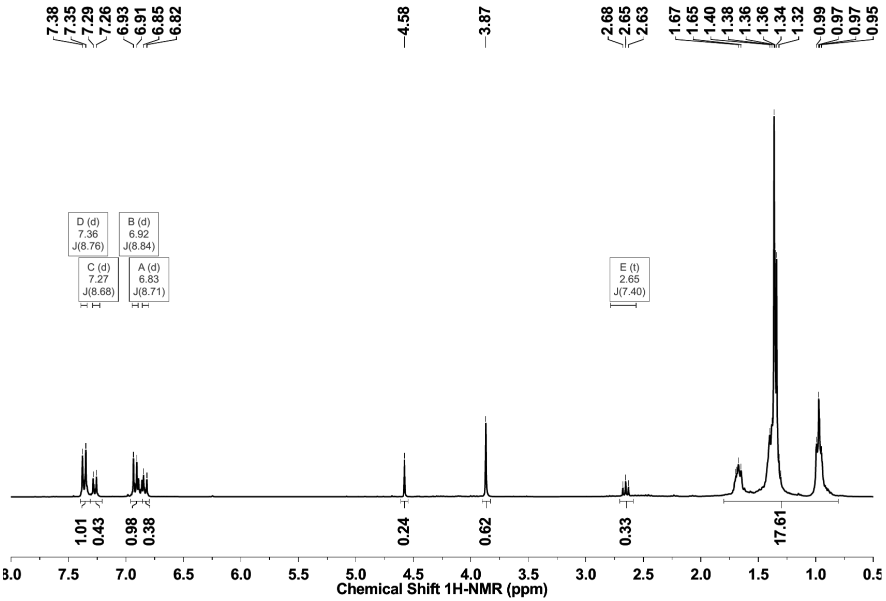

Figure (4.53): *^{1}H-NMR ($CDCl_3$, 400 MHz) of crude material (synthesis of **30**)*

These results confirms our hypothesis (Section 4.5.3), stating that these type of calixarene esters are not suitable for the star polymer preparation because of the presence of acid hydrogen atoms, which react with the carbanionic reactants preventing the complete functionalization of the calixarene, as shown in Figure 4.41.

4.6.4 1-(4-(methyloxycarbonyl)benzyloxy)-4-tert-butylbenzene

The compound **31** is the last monomeric phenol derivative discussed in this Section.

The product **31** was synthesized in the presence of K_2CO_3 as base and using an excess of methyl 4-(bromomethyl)benzoate as alkylating agent (**18** in Figure 4.55).

As for the previously monomeric phenol derivatives, the reaction of the ester **31** with n-BuLi was carried out at 40 °C in cyclohexane/THF as solvent mixture. After 15 min a 1 M solution of HCl_{aq} was added to quench the reaction.

The complete functionalization of the phenolic derivative was visible

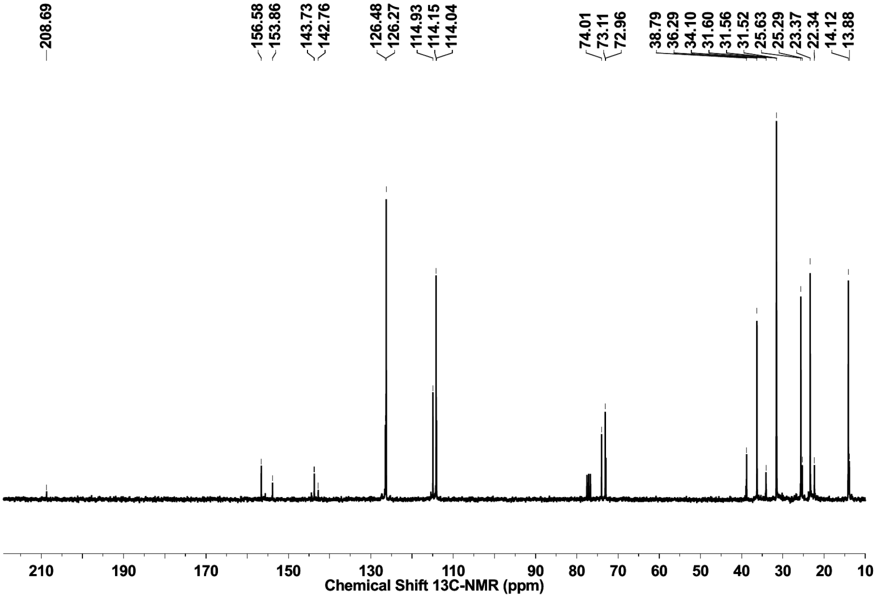

Figure (4.54): *^{13}C-NMR ($CDCl_3$, 100 MHz) of crude material (synthesis of* ***30****)*

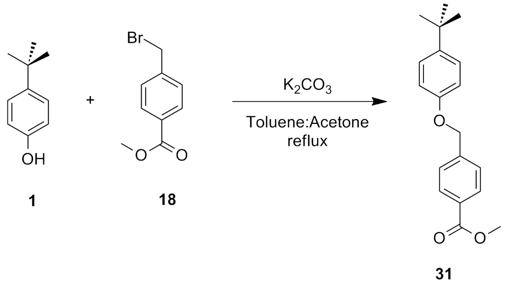

Figure (4.55): *Synthesis of the product* ***31***

by NMR analyses of the mixture obtained after extraction and removal at reduced pressure of organic solvents. In fact, in ^{1}H-NMR spectrum (Figure 4.57) are present only signals of the desired product **32**.

The confirmation of the complete functionalization also comes from ^{13}C-NMR analysis (Figure 4.58). In fact, the signal related to the carbon of alcohol residue is detected at 77.0 ppm, whereas the peaks at 42.8, 25.7, 23.2 and 14.1 ppm are due to n-butyl groups.

These results confirmed those obtained with the calixarene **19** (Sec-

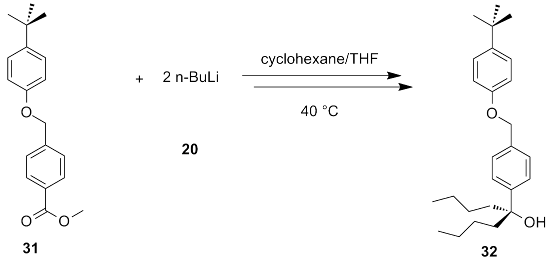

Figure (4.56): *Reaction of product **31** with n-BuLi; [n-BuLi]/[**31**] ratio: 2/1*

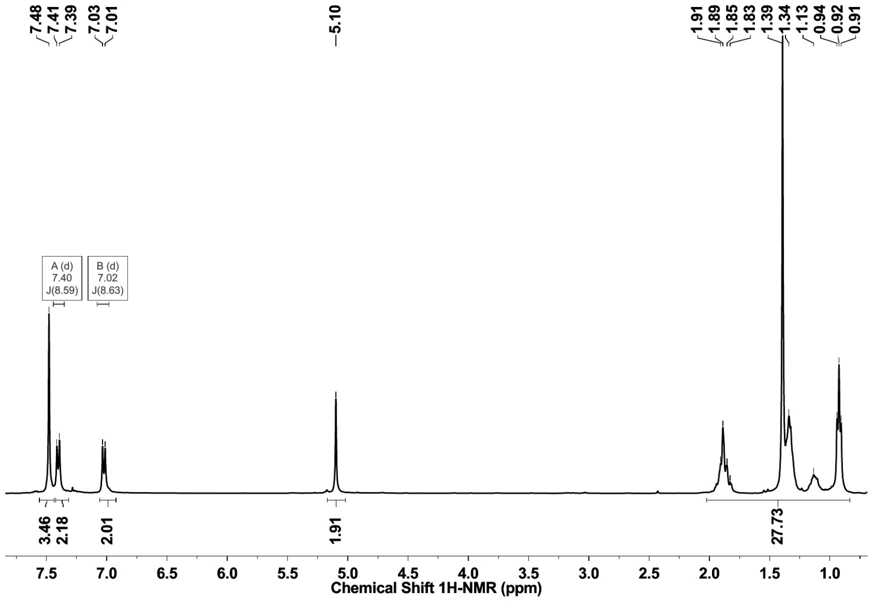

Figure (4.57): *^{1}H-NMR (CDCl$_3$, 400 MHz) of crude material (synthesis of **32**)*

tion 4.5.4) and supported the conclusion that such calixarene, having benzoate groups, is an excellent candidate for the synthesis of star polymers by grafting living anionic polymer chains on the calixarene structure. The results of this grafting process using the calixarene derivative **19** are discussed in Section 4.7.

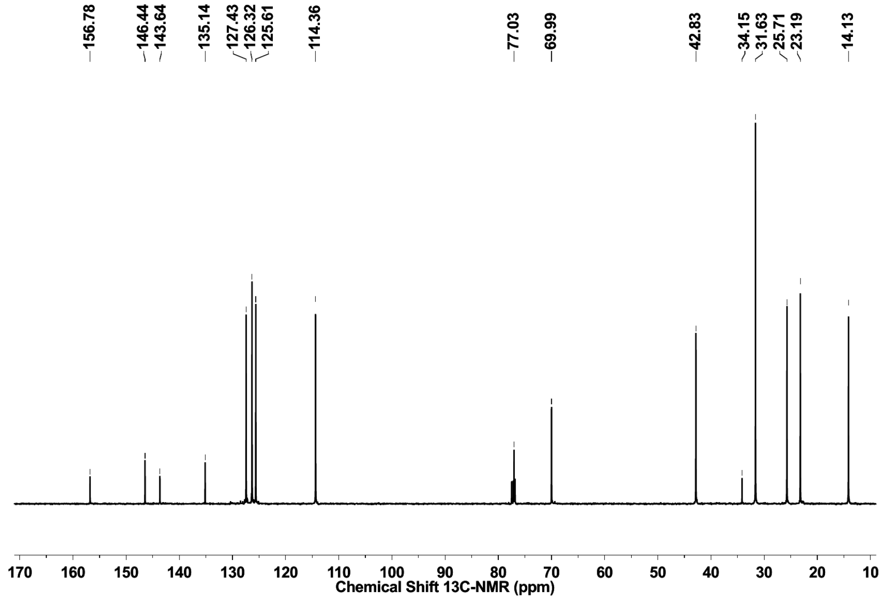

Figure (4.58): *^{13}C-NMR (CDCl$_3$, 100 MHz) of crude material (synthesis of 32)*

4.7 Calixarene-based SP as VI improver

In the previous Sections of this Chapter some potential SPs core precursors based on calixarene derivatives were presented and also the reactivity of their functional groups with n-BuLi was discussed.

The topics of this section are the synthesis of a calixarene based star polymer and its use as VI improver additive for lubricants.

The selected precursor for SPs synthesis was the calixarene derivative **19** (Section 4.5.4), which was characterized by the best reactivity towards n-BuLi. With the purpose of comparing the new calixarene based polymer with the commercial product Infineum Shellvis 260 (SV 260), the linear block copolymer segments to be grafted on calixarene structure were obtained by living polymerization of isoprene/styrene (90/10 % by weight). In fact, SV 260 is a star polymer having a PDVB core to which are linked block copolymer arms based on isoprene and styrene (about 90/10 % by weight).

Nowadays, according to our knowledge, SV 260 is one of the best viscosity index improvers, both in terms of performances and costs, available into the marketplace and for this reason this product was chosen as commercial reference to compare the characteristics of the newly synthesized calixarene-based VI improvers.

4.7.1 Synthesis of the calixarene-based star polymer

The preparation of the calixarene-based star polymer was carried out using the “arm-first” approach. In this way, the synthesis of the polymer chains was performed before the addition of the calixarene derivative. In detail, styrene was added in an inert atmosphere to a mixture of anhydrous cyclohexane and tetrahydrofuran. After thermostatation of the solution at 40 °C, a cyclohexane solution of n-BuLi was added. After 20 min, once styrene conversion was complete, isoprene was added. The living anionic polymer chains were then reacted with the calixarene **19**, which was added to the reaction mixture as a tetrahydrofuran solution (Figure 4.59).

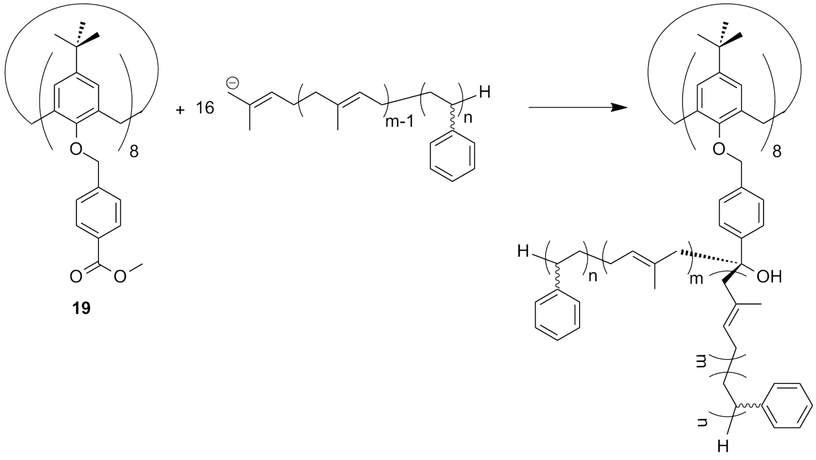

Figure (4.59): *Reaction of calixarene **19** with styrene-isoprene polymer chains*

After 45 min, at the end of the reaction between the calixarene and the anionic polymer chains, the mixture was subjected to a hydrogenation process in order to reduce the olefine C=C bonds of the polymer structure. This process is necessary to obtain a product with the desired thermo-oxidative stability. The catalyst used for the hydrogenation process is a mixture of butylethylmagnesium in heptane solution and cyclopentadienyl-titanium dichloride in cyclohexane solution.

To perform the hydrogenation process, after the addition of the catalysts, the mixture was placed under hydrogen pressure (15 bar) and maintained at 120 °C for 90 min, while being stirred (Figure 4.60).

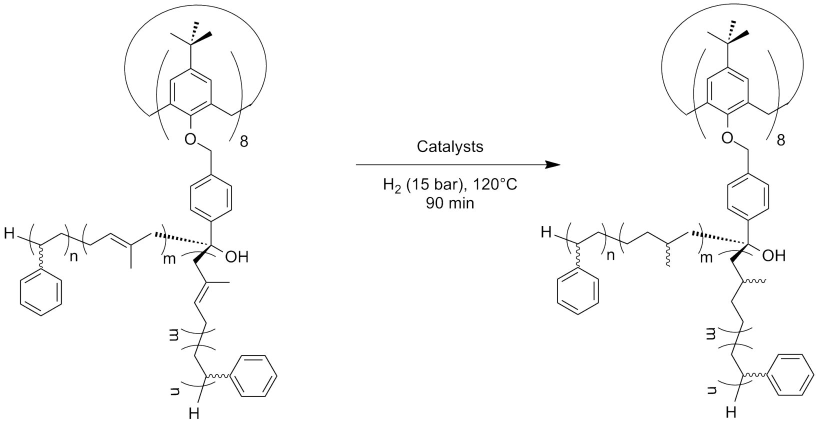

Figure (4.60): *Hydrogenation process of calixarene-based star polymer*

After the addition of antioxidants, the mixture was moved into a stripping system, in which the solvents were removed. The resultant granular product was dried in a vacuum oven.

The analysis carried out on the final product showed the almost complete addition of the polymer chains to the calixarene core. In detail, the calculated average number of linear polymer chains grafted to the calixarene core was 15.6, which was very close to the theoretical value of 16. Moreover, a hydrogenation degree of 93 % was obtained.

The Table 4.1 shows the characteristics of the star polymer determined by GPC analysis.

Table (4.1): *Hydrogenated isoprene-styrene calixarene-based star polymer*

Polymer properties	
M_w (KDa)	671
M_n (KDa)	541
M_w polymer segments (KDa)	43
M_w/M_n	1.24

With the aim of comparing the calixarene based star polymer with SV 260 (commercial reference), different lubricant formulations were prepared and tested. The results are discussed in Section 4.7.2.

4.7.2 Lubricant formulations with star polymers

With the purpose of testing the star polymers as viscosity index improver additives for lubricants, their solutions in a base oil were prepared. The base oil used for the star polymers dissolution was a Group I Solvent Neutral 150 (ENI SN 150S). Dissolution was carried out by heating the base oil at 130 °C, adding the polymer (calixarene based star polymer or Infineum Shellvis 260) and stirring at this temperature until complete dissolution. Some rheological characteristics, such as thickening power and shear stability index were determined on the solutions of the polymers in base oil. These characteristics are reported in Table 4.3.

Thickening power was calculated as the difference between the kinematic viscosity value at 100 °C of the 1 % by weight polymer solution in SN 150S and the kinematic viscosity value at 100 °C of SN 150S base oil.

The shear stability index was determined on a solution made up of 10 % by weight of a concentrated polymer solution in base oil and by 90 % by weight of base oil SN 150S.

The concentrated solutions of the two different polymers are prepared in such a way that their further dilutions (for example 10 % by weight of concentrated polymer solution and 90 % by weight of base oil SN 150S) give solutions with very similar kinematic viscosity values at 100 °C.

Using the concentrated solutions of polymers as viscosity index improver additives, automotive lubricant formulations were prepared. The selected viscosity grade of the lubricants was SAE 10W-40, which corresponds to a range of operating temperatures from 40 °C to -25 °C (Figure 4.61).

A lubricant with a SAE grade 10W-40 is called “multigrade” as it can be used both in cold and hot weather. The number before the letter “W” is related to the winter grade of the oil, while the last number designates the summer grade. The classification of the lubricant winter grade is made by determining the CCS viscosity, while the classification of the summer grade is made evaluating the kinematic viscosity at 100 °C (Table 4.2). CCS (Cold Cranking Simulator) is the low-temperature dynamic viscosity that simulates the engine start up at low temperature. Oils with high CCS viscosity can make it difficult for the starter motor in a vehicle to turn the engine over.

The lubricants object of this study were prepared adding to a mixture containing base oils and the concentrated solution of star polymer (viscosity index improver additive) and other additives, most of which contained into

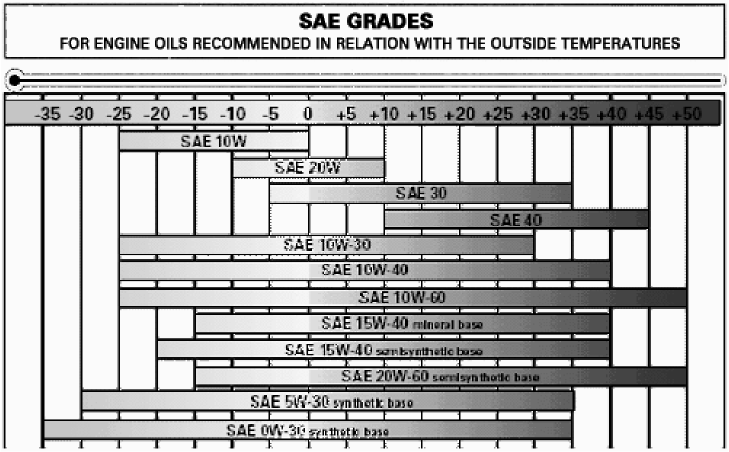

Figure (4.61): *SAE grades*

an "additive package".

The lubricants had the following composition:

- base oils: 79.1 % by weight;
- viscosity index improver: 7 % by weight;
- additive package: 13.8 % by weight;
- pour point depressant (PPD) additive: 0.1 % by weight.

The additive package used was a mixture of the following additives: dispersants, detergents, antioxidants and antiwear additives.

The lubricants were subsequently characterized determining the following parameters: kinematic viscosity at 100 °C and 40 °C, viscosity index, CCS (Cold Cranking Simulator) viscosity at -25 °C and the percentage viscosity loss by depolymerization. The latter parameter was calculated as a result of a shear test. The lubricating oil containing the viscosity index improver additive was pumped under pressure 30 times through a Bosch injector in an apparatus (Bosch injector rig). The results of the test were two kinematic viscosity values at 100 °C: (i) kinematic viscosity of the fluid prior of shear test and (ii) kinematic viscosity of the sheared oil after the test. Using these results, the percentage viscosity loss was calculated.

The characteristics of the tested lubricating oils are reported in Table 4.3.

On the basis of the results shown in Table 4.3, the radial polymer with a central core made up of calixarene (calixarene-based SP) has characteristics,

Table (4.2): *SAE viscosity classification for engine oils*

	Low temp. viscosity	High temp. viscosity	
	CCS	KV at 100 °C (cSt)	
SAE Grade	(cP max)	min	max
0W	6200 at -35 °C	3.8	
5W	6600 at -30 °C	3.8	
10W	7000 at -25 °C	4.1	
15W	7000 at -20 °C	5.6	
20W	9500 at -15 °C	5.6	
25W	13000 at -10 °C	9.3	
15		6.1	< 8.2
20		6.9	< 9.3
30		9.3	< 12.5
40		12.5	< 16.3
50		16.3	< 21.9
60		21.9	< 26.1

Table (4.3): *Comparison between calixarene-based SP and SV 260*

Property	Calix-based SP	SV 260
Thickening power at 100 °C (cSt) (1 % by weight polymer in SN 150S)	7.6	7.5
Concentrated solution		
Polymer content (w/w)	10.45	10.55
Shear stability index (%)	7	10
Final lubricant with other additives		
Viscosity (40 °C)	92.26	91.28
Viscosity (100 °C)	13.78	13.69
Viscosity index	152	152
CCS viscosity -25 °C (cSt)	6650	6671
Viscosity loss by depolym. (%)	3.6	5.2

such as thickening power, mechanical shear stability and low-temperature behavior (CCS viscosity), which make it highly suitable as viscosity index improver additive for lubricant oils. In particular, this new star polymer exhibited mechanical shear stability (shear stability index and viscosity loss by depolymerization) which is better than that of the commercial reference SV 260 (made up of the same type of polymer segments but with a PDVB core).

Bibliography

[1] T. E. Patten, J. Xia, T. Abernathy and K. Matyjaszewski, *Science*, 1996, **272**, 866 – 868.

[2] R. R. Schrock, *Accounts of Chemical Research*, 1990, **23**, 158 – 165.

[3] M. Kamigaito, T. Ando and M. Sawamoto, *Chemical Reviews*, 2001, **101**, 3689 – 3746.

[4] H. Hsieh and R. P. Quirk, *Anionic polymerization: principles and practical applications*, CRC Press, 1996.

[5] N. Hadjichristidis, *Journal of Polymer Science Part A: Polymer Chemistry*, 1999, **37**, 857 – 871.

[6] N. Hadjichristidis, S. Pispas, M. Pitsikalis, H. Iatrou and C. Vlahos, in *Branched polymers I*, Springer, 1999, pp. 71 – 127.

[7] M. Pitsikalis, S. Pispas, J. W. Mays and N. Hadjichristidis, in *Blockcopolymers-Polyelectrolytes-Biodegradation*, Springer, 1998, pp. 1 – 137.

[8] J. H. Munch and C. D. Gutsche, *Organic Syntheses*, 1990, **68**, 243 – 246.

[9] F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry: Part A: Structure and Mechanisms*, Springer Science & Business Media, 2007.

[10] F. C. J. M. Van Veggel, W. Verboom and D. N. Reinhoudt, *Chemical reviews*, 1994, **94**, 279 – 299.

[11] S. W. Ryu and A. Hirao, *Macromolecules*, 2000, **33**, 4765 – 4771.

[12] S. Kanamathareddy and C. D. Gutsche, *Journal of the American Chemical Society*, 1993, **115**, 6572 – 6579.

[13] W.-G. Wang, Q.-Y. Zheng and Z.-T. Huang, *Synthetic Communications*, 1999, **29**, 3711 – 3718.

[14] D. M. Knauss, H. A. Al-Muallem, T. Huang and D. T. Wu, *Macromolecules*, 2000, **33**, 3557 – 3568.

[15] S.-K. Chang and I. Cho, *Chemistry Letters*, 1984, **13**, 477 – 478.

[16] R. E. Ireland and R. S. Meissner, *The Journal of Organic Chemistry*, 1991, **56**, 4566 – 4568.

[17] L. Xie, K. M. Isenberger, G. Held and L. M. Dahl, *The Journal of Organic Chemistry*, 1997, **62**, 7516 – 7519.

[18] R. C. Griffith and J. J. Napier, *Containing a piperidine and phenyl ring in structure*, 1990, US Patent 4,912,222.

[19] D. R. Vutukuri, P. Bharathi, Z. Yu, K. Rajasekaran, M.-H. Tran and S. Thayumanavan, *The Journal of Organic Chemistry*, 2003, **68**, 1146 – 1149.

[20] X. Li, S.-L. Gong, W.-P. Yang, Y.-Y. Chen and X.-G. Meng, *Tetrahedron*, 2008, **64**, 6230 – 6237.

CHAPTER 5

CONCLUSIONS

In this part of Thesis, we have successfully found that p-tert-butylcalixarenes functionalized at the lower rim with methyl-4-bromomethyl benzoate originates an octaester **19**, which can be used as core for the attachment of isoprene-styrene living anionic polymers. Interestingly, the use of this derivatives allows from one side to increase to 16 the total number of potential branches to attach on the calixarene structure.

Test reaction with the model n-BuLi on octaester **19** allowed, in fact, to obtain the attachment of two butyl groups per ester moieties.

The preparation of the calixarene-based star polymer was carried out using the "arm-first" approach. In this way, the synthesis of the isoprene/styrene chains was performed before the addition of the calixarene derivative. In order to obtain a product with the desired thermo-oxidative stability, an hydrogenation step (hydrogenation degree of 93 %) was introduced to reduce the C=C double bonds to alkanes.

With the aim of comparing the calixarene based star polymers with SV 260 (commercial reference), also different lubricant formulations were prepared and tested. From the results obtained, we could demonstrate that the radial polymers having a central core made up of calixarene (calixarene-based SP) have characteristics such as thickening power, mechanical shear stability and low-temperature behavior (CCS viscosity), which make them highly promising viscosity index improver additives for lubricating oils. In particular, this new star polymer exhibits mechanical shear stability (shear stability index and viscosity loss by depolymerization) better than that of the commercial reference SV 260 (made up of the same type of polymer segments but with a PDVB core).

Once we could prove the importance of the use of calixarene-based star polymers as viscosity index improvers, the following steps of this research could be:

1. to synthesize new calixarene derivatives which ensure a higher number of branches on the central core of the star polymer;
2. to prepare star polymers with different types of block copolymers, in order to change, as desired, the final properties of the star polymer.

CHAPTER 6

EXPERIMENTAL SECTION

6.1 General information

All moisture sensitive reactions were carried out under nitrogen atmosphere, using previously oven-dried glassware.

Dry solvents were prepared according to standard procedures, distilled before use and stored over 3 or 4 Å molecular sieves.

Most of the solvents and reagents were obtained from commercial sources and used without further purification.

Analytical TLC were performed using prepared plates of silica gel (Merck 60 F-254 on aluminum) and then, according to the functional groups present on the molecules, revealed with UV light or using staining reagents: H_2SO_4 (5 % in EtOH) or basic solution of $KMnO_4$ (0.75 % in H_2O).

Merck silica gel 60 (70–230 mesh) was used for flash chromatography and for preparative TLC plates.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker AV300 and Bruker AV400 spectrometers (observation of ^{1}H nucleus at 300 MHz and 400 MHz, respectively, and of ^{13}C nucleus at 75 MHz and 100 MHz, respectively). All chemical shifts are reported in part per million (ppm) using the residual peak of the deuterated solvent, whose values are referred to tetramethylsilane (TMS, $\delta_{TMS} = 0$), as internal standard.

For descriptions of the multiplicity of ^{1}H-NMR spectra was used the following terminology: s = singlet, d = doublet, t = triplet, q = quartet, m =

multiplet, b = broadened signal.

All ^{13}C-NMR spectra were performed with proton decoupling. The identification of the carbon atoms in the residues of functionalization was performed indicating sequence numbers in according to the proximity of the carbon to the oxygen of the phenol or calixarene derivative.

The spectra were processed with the software MestreNova®.

Electrospray ionization (ESI) mass analyses were performed on a Waters ZMD spectrometer equipped with an electrospray interface.

The nomenclature used for the calixarene derivatives is in accordance with that discussed in the Appendix of this Thesis at pag. 191.

In the case of calixarene derivatives, their millimoles were reported in reference to their monomeric units ($mmol_{m.u.}$).

Compounds **2**[1], **11**[2], **15**[3], **27**[4] and **29**[5] were synthesized according to literature procedures.

6.1.1 Titration of n-butyllithium

The titration of n-butyllithium was carried out as reported in the literature from Ireland and Meissner.[6]

In detail, 2,2′-bipyridine (5 mg) was dissolved in 3 mL of dry ethyl ether under nitrogen atmosphere. n-BuLi in hexane (50 µL) was added, so that a deep red color persisted. A 1.00 M solution of dry 2-butanol in benzene was added dropwise until the color disappeared, forming the yellow dihydropyridine indicator.

n-BuLi in hexane (100 µL) was added to the indicator solution, which turn red. This red solution was then titrated with the 1.00 M 2-butanol solution until the solution turned back to yellow.

The concentration of n-BuLi can be determined by dividing the volume (in µL) of 2-butanol solution used in the titration of 100 µL (the amount of the second batch of n-BuLi solution used).

In our case, the concentration of n-BuLi was 1.56 M, quite similar to the nominal one reported by Sigma-Aldrich (1.6 M).

6.2 Synthesis of the calixarene structure

p-tert-butylcalix[8]arene (2)

The synthesis of p-tert-butylcalix[8]arene was achieved as reported in the literature by Munch and Gutsche[1] to give the desired product as a white solid in 70.4 % yield (65.8 g, 405 $\mathrm{mmol}_{m.u.}$)[1].

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 9.63 (b, 1 H, OH); 7.19 (s, 2 H, H_{cal}); 4.38 (d, 1 H, $^2J = 13.0$ Hz, $H_{\mathrm{br,ax}}$); 3.51 (d, 1 H, $^2J = 12.9$ Hz, $H_{\mathrm{br,eq}}$); 1.26 (s, 9 H, $C(CH_3)_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 146.6 ($C_{\mathrm{cal,i}}$OH); 144.7 ($C_{\mathrm{cal,p}}$); 128.7 ($C_{\mathrm{cal,o}}$); 125.5 ($C_{\mathrm{cal,m}}$H); 34.0 ($C(CH_3)_3$); 32.3 (C_{br}), 31.5 ($C(CH_3)_3$).

The product **2** showed the same physico-chemical properties reported in the literature.

6.3 Synthesis of calixarene derivatives

i-(2-hydroxyethyloxy)-p-tert-butylcalix[8]arene (5)[2]

In a round bottom flask a solution of $LiAlH_4$ (1.00 g, 26.3 mmol) in dry THF (200 mL) was added dropwise to a solution of **15** (9.87 g, 39.7 $\mathrm{mmol}_{m.u.}$) in dry THF (200 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 4 h and checked via TLC (eluent: hexane/AcOEt 1/1). When completed, firstly MeOH was added dropwise and then a 0.1 M solution of HCl_{aq} was dripped in the flask. The product was extracted in AcOEt, the organic phase was separated and the solvent removed under reduced pressure to give a yellowish solid. The crude solid was purified by precipitation in $CHCl_3$ to give the product **5** as a white solid in 97.5 % yield (8.00 g, 38.8 $\mathrm{mmol}_{m.u.}$).

ESI-MS: m/z 1673.17 $[M+Na]^+$, 847.98 $[M+2Na]^{2+}$ and 839.99 $[M+Li+Na]^{2+}$.

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[1] $\mathrm{mmol}_{m.u.}$: mmol of monomer unit in the sample; in this case mmol of monomer unit are 8 times mmol of p-tert-butylcalix[8]arene. For more details, see 194.

[2] Numenclature of Gutsche for derivative **5**: 5,11,17,23,29,35,41,47-Octakis(2-hydroxyethyloxy)-p-tert-butylcalix[8]arene.

i-(6-chlorohexyloxy)-p-tert-butylcalix[8]arene (7)[3]

In a round bottom flask **2** (3.497 g, 21.5 mmol$_{m.u.}$), Cs_2CO_3 (7.111 g, 21.8 mmol) and 1-bromo-6-chlorohexane (7.01 mL, 47.0 mmol) were dissolved in acetone (10 mL). The mixture was stirred at 35 °C for 4 d and checked via TLC (eluent: hexane/DCM 1/2). When completed, the suspension was filtered on Buchner funnel and then the solvent of the filtrate was removed under reduced pressure to give a yellowish solid. This solid was dissolved in DCM and washed twice with a 1 M solution of HCl_{aq}. The organic phase was separated and the solvent removed under reduced pressure. The crude solid was purified by precipitation in MeOH to give the product **7** as a white solid in 56.1 % yield (3.41 g, 12.1 mmol$_{m.u.}$).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.99 (s, 2 H, H_{cal}); 4.07 (s, 2 H, $CH_{2\,br}$); 3.60 (m, 2 H, OCH_2); 3.46 (t, 2 H, ^3J = 6.5 Hz, CH_2Cl); 1.7 (m, 4 H, OCH_2CH_2 and CH_2CH_2Cl); 1.46 (m, 4 H, $O(CH_2)_2CH_2CH_2(CH_2)_2Cl$); 1.11 (s, 9 H, $C(CH_3)_3$).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.2 ($C_{cal,i}OR$); 145.7 ($C_{cal,p}$); 133.0 ($C_{cal,o}$); 125.8 ($C_{cal,m}H$); 72.9 ($C_{hex,1}O$); 45.0 ($C_{hex,6}Cl$); 34.2 ($C(CH_3)_3$); 32.6 ($C_{hex,2}$); 31.5 ($C(CH_3)_3$); 30.4 ($C_{hex,5}$); 29.8 (C_{br}); 26.9 ($C_{hex,3}$); 25.7 ($C_{hex,4}$).

i-(allyloxy)-p-tert-butylcalix[8]arene (11)[4]

The synthesis of compound **11** was achieved as reported in the literature by Wang and coworkers[2] to give the desired product as white solid in 58.0 % yield (0.288 g, 1.42 mmol$_{m.u.}$).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.98 (s, 2 H, H_{cal}); 5.77 (ddt, 1 H, $^3J_1$ = 5.3 Hz, $^3J_2$ = 10.5 Hz, $^3J_3$ = 17.3 Hz, $H_{all,2}$); 5.05 (d, 1 H, ^3J = 17.1 Hz, $H_{all,3}$); 4.90 (d, 1 H, ^3J = 9.6 Hz, $H_{all,3}$); 4.05 (s, 2 H, $CH_{2\,br}$); 3.99 (d, 2 H, ^3J = 5.2 Hz, $H_{all,1}$); 1.11 (s, 9 H, $C(CH_3)_3$).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.3 ($C_{cal,i}OR$); 145.9 ($C_{cal,p}$); 134.0 ($C_{all,2}$); 133.0 ($C_{cal,o}$); 125.8 ($C_{cal,m}H$); 116.7 ($C_{all,3}$); 73.6 ($C_{all,1}$); 34.2 ($C(CH_3)_3$); 31.4 ($C(CH_3)_3$); 30.3 (C_{br}).

The product **11** showed the same physico-chemical properties reported in the literature.

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[3] Numenclature of Gutsche for derivative **7**: 5,11,17,23,29,35,41,47-Octakis(6-chlorohexyloxy)-p-tert-butylcalix[8]arene.

[4] Numenclature of Gutsche for derivative **11**: 5,11,17,23,29,35,41,47-Octakis(allyloxy)-p-tert-butylcalix[8]arene.

i-(ethyloxycarbonylmethyloxy)-p-tert-butylcalix[8]arene (15)[5]

The synthesis of the derivative **15** was achieved as reported in the literature by Chang and Cho[3] to give the derivative **15** as white solid in 75.0 % yield (17.1 g, 68.9 $\text{mmol}_{m.u.}$).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.96 (s, 2 H, H_{cal}); 4.17 (s, 2 H, $OCH_{2\,est,1}$); 4.1–4.0 (m, 4 H, $CH_{2\,br}$ and $OCH_{2\,est,3}$); 1.2–1.0 (m, 12 H, $C(CH_3)_3$ and $CH_{3\,est,4}$).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 168.8 ($C_{est,2}OOR$); 152.8 ($C_{cal,i}OR$); 146.7 ($C_{cal,p}$); 132.6 ($C_{cal,o}$); 126.0 ($C_{cal,m}H$); 69.9 ($C_{est,1}$); 61.0 ($C_{est,3}$); 34.2 ($C(CH_3)_3$); 31.4 ($C(CH_3)_3$); 30.1 (C_{br}); 13.9 ($C_{est,4}$).

The product **15** showed the same physico-chemical properties reported in the literature.

i-(p-(methyloxycarbonyl)benzyloxy)-p-tert-butylcalix[8]arene (19)[6]

In a round bottom flask **2** (8.248 g, 50.84 $\text{mmol}_{m.u.}$), K_2CO_3 (13.258 g, 95.93 mmol) KI (1.027 g, 6.19 mmol) and methyl 4-(bromomethyl)benzoate (16.452 g, 71.82 mmol) were dissolved in acetone (60 mL) and toluene (40 mL). The mixture was stirred at reflux for 2 d and checked via TLC (eluent: hexane/AcOEt 4/1). When completed, the suspension was filtered on Buchner funnel and then the solvent of the filtrate was removed under reduced pressure to give a yellowish solid. This solid was dissolved in AcOEt and washed twice with a 1 M solution of HCl_{aq}. After separation, the organic solvent was removed under reduced pressure. The crude solid was purified by precipitation in MeOH to give the product **19** as a white solid in 51.3 % yield (8.10 g, 26.1 $\text{mmol}_{m.u.}$).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.75 (d, 2 H, ^3J = 8.2 Hz, $H_{Bz,4}$); 7.14 (d, 2 H, ^3J = 8.2 Hz, $H_{Bz,3}$); 6.94 (s, 2 H, H_{cal}); 4.55 (s, 2 H, $OCH_{2\,Bz,1}$); 3.98 (s, 2 H, $CH_{2\,br}$); 3.90 (s, 3 H, $CH_{3\,Bz,7}$); 0.98 (s, 9 H, $C(CH_3)_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 166.9 ($C_{bz,6}OOMe$); 152.8 ($C_{cal,i}OR$); 146.4 ($C_{cal,p}$); 142.8 ($C_{bz,2}$); 133.0 ($C_{cal,o}$); 129.6 ($C_{bz,5}$); 129.2 ($C_{bz,4}H$); 126.8 ($C_{bz,3}H$); 126.2 ($C_{cal,m}H$); 73.9 ($OC_{bz,1}$); 52.1 ($OC_{bz,7}$); 34.2 ($C(CH_3)_3$); 31.4 ($C(CH_3)_3$); 30.3 (C_{br}).

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[5] Numenclature of Gutsche for derivative **15**: 5,11,17,23,29,35,41,47-Octakis(ethyloxycarbonylmethyloxy)-p-tert-butylcalix[8]arene.

[6] Numenclature of Gutsche for derivative **19**: 5,11,17,23,29,35,41,47-Octakis(p-(methyloxycarbonyl)benzyloxy)-p-tert-butylcalix[8]arene.

6.4 Functionalization of p-tert-butylphenol

1-(6-chlorohexyloxy)-4-tert-butylbenzene (25)

In a round bottom flask p-tert-butylphenol (500 mg, 3.33 mmol), K_2CO_3 (690 mg, 4.99 mmol) and 1-bromo-6-chlorohexane (0.78 mL, 4.99 mmol) were dissolved in acetone (30 mL). The mixture was stirred at reflux for 4 h and checked via TLC (eluent: hexane/toluene 1/1). When completed, the suspension was filtered on Buchner funnel and then the solvent of the filtrate was removed under reduced pressure to give a yellowish liquid. This liquid was diluted in toluene and washed twice with a 1 M solution of HCl_{aq}. The organic phase was separated and its solvent removed under reduced pressure. The crude liquid was purified via flash column chromatography (eluent: hexane/toluene 1/1) to give the product as a colorless liquid in 86.0 % yield (769 mg, 2.86 mmol).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.40 (d, 2 H, ^3J = 8.8 Hz, $H_{ph,m}$); 6.94 (d, 2 H, ^3J = 8.8 Hz, $H_{ph,o}$); 4.04 (t, 2 H, ^3J = 6.4 Hz, $OC_{hex,1}H_2$); 3.63 (t, 2 H, ^3J = 6.7 Hz, $C_{hex,6}H_2Cl$); 1.89 (m, 4 H, $C_{hex,2}H_2$ and $C_{hex,5}H_2$); 1.60 (m, 4 H, $C_{hex,3}H_2$ and $C_{hex,4}H_2$), 1.41 (s, 9 H, $C(CH_3)_3$).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 156.9 ($C_{ph,i}OR$); 143.2 ($C_{ph,p}$); 126.3 ($C_{ph,m}H$); 114.0 ($C_{ph,o}H$); 67.7 ($C_{hex,1}O$); 45.0 ($C_{hex,6}Cl$); 34.1 ($\mathit{C}(CH_3)_3$); 32.6 ($C_{hex,2}$); 31.6 ($C(CH_3)_3$); 30.3 ($C_{hex,5}$); 26.8 ($C_{hex,3}$); 25.6 ($C_{hex,4}$).

1-(allyloxy)-4-tert-butylbenzene (27)

The synthesis of p-tert-butyl(allyloxy)phenol was achieved as reported in the literature by Vutukuri and coworkers[4] to give the product **27** as a colorless liquid in 90.5 % yield (574 mg, 3.02 mmol).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.40 (d, 2 H, ^3J = 8.8 Hz, $H_{ph,m}$); 6.97 (d, 2 H, ^3J = 8.8 Hz, $H_{ph,o}$); 6.16 (ddt, 1 H, $^3J_1$ = 5.3 Hz, $^3J_2$ = 10.5 Hz, $^3J_3$ = 17.2 Hz, $C_{all,2}H$); 5.51 (dq, 1 H, $^3J_1$ = 1.6 Hz, $^3J_2$ = 17.3 Hz, $C_{all,3}H$); 5.37 (dq, 1 H, $^3J_1$ = 1.5 Hz, $^3J_2$ = 10.5 Hz, $C_{all,3}H$); 4.61 (dt, 2 H, $^3J_1$ = 1.5 Hz, $^3J_2$ = 5.3 Hz, $C_{all,1}H_2$); 1.41 (s, 9 H, $C(CH_3)_3$).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 156.5 ($C_{ph,i}OR$); 143.5 ($C_{ph,p}$); 133.7 ($C_{all,2}$); 126.3 ($C_{ph,m}H$); 117.5 ($C_{all,3}$); 114.3 ($C_{ph,o}H$); 68.9 ($C_{all,1}$); 34.2 ($\mathit{C}(CH_3)_3$); 31.7 ($C(CH_3)_3$).

The product **27** showed the same physico-chemical properties reported in the literature.

1-(ethyloxycarbonylmethyloxy)-4-tert-butylbenzene (29)

The synthesis of compound **29** was achieved as reported in the literature by Li and coworkers[5] to give the desired product as a colorless liquid with 87.2 % yield (685 mg, 2.90 mmol).

^{1}H-NMR (**$CDCl_3$, 400 MHz**): δ (ppm) 7.32 (d, 2 H, ^3J = 8.8 Hz, $H_{ph,m}$); 6.87 (d, 2 H, ^3J = 8.8 Hz, $H_{ph,o}$); 4.60 (s, 2 H, $OC_{est,1}H_2$); 4.27 (q, 2 H, ^3J = 7.1 Hz, $OC_{est,3}H_2$); 1.35–1.25 (m, 12 H, $C(CH_3)_3$) and $C_{est,4}H_3$).

^{13}C-NMR (**$CDCl_3$, 100 MHz**): δ (ppm) 169.1 ($C_{est,2}OOEt$); 155.7 ($C_{ph,i}OR$); 144.3 ($C_{ph,p}$); 126.3 ($C_{ph,m}H$); 114.2 ($C_{ph,o}H$); 65.5 ($OC_{est,1}H_2$); 61.2 ($OC_{est,3}H_2$); 34.1 ($\mathit{C}(CH_3)_3$); 31.5 ($C(CH_3)_3$); 14.2 ($C_{est,4}H_3$).

The product **29** showed the same physico-chemical properties reported in the literature.

1-(p-(methyloxycarbonyl)benzyloxy)-4-tert-butylbenzene (31)

In a round bottom flask p-tert-butylphenol (500 mg, 3.33 mmol), K_2CO_3 (690 mg, 4.99 mmol) and 1-bromo-6-chlorohexane (0.78 mL, 4.99 mmol) were dissolved in acetone (30 mL). The mixture was stirred at reflux for 4 h and checked via TLC (eluent: hexane/AcOEt 9/1). When completed, the suspension was filtered on Buchner funnel and then the solvent of the filtrate was removed under reduced pressure to give a yellowish solid. This solid was dissolved in toluene and washed twice with a 1 M solution of HCl_{aq}. The organic phase was separated and its solvent was removed under reduced pressure. The compound **31** was purified by precipitation from MeOH as a white solid in 79.2 % yield (787 mg, 2.64 mmol).

^{1}H-NMR (**$CDCl_3$, 400 MHz**): δ (ppm) 8.07 (d, 2 H, ^3J = 8.0 Hz, $C_{bz,4}H$); 7.51 (d, 2 H, ^3J = 8.0 Hz, $C_{bz,3}H$); 7.32 (d, 2 H, ^3J = 8.6 Hz, $H_{ph,m}$); 6.92 (d, 2 H, ^3J = 8.6 Hz, $H_{ph,o}$); 5.12 (s, 2 H, $C_{bz,1}H_2$); 3.93 (s, 3 H, $C_{bz,7}H_3$); 1.31 (s, 9 H, $C(CH_3)_3$).

^{13}C-NMR (**$CDCl_3$, 100 MHz**): δ (ppm) 166.9 ($C_{bz,6}OOMe$); 156.3 ($C_{ph,i}OR$); 143.9 ($C_{ph,p}$); 142.6 ($C_{bz,2}$); 129.9 ($C_{bz,5}$); 129.6 ($C_{bz,4}H$); 127.0 ($C_{bz,3}H$); 126.3 ($C_{ph,m}H$); 114.3 ($C_{ph,o}H$); 69.4 ($C_{bz,1}H_2$); 52.1 ($C_{bz,7}H_3$); 34.1 ($\mathit{C}(CH_3)_3$); 31.5 ($C(CH_3)_3$).

6.5 Studies of reactivity between calix[8]arene- or phenol-derivatives and n-BuLi

A solution of calix[8]arene or phenol derivative (about 100 mg) in dry cyclohexane (10 mL) and dry THF (10 µL) was heated to 40 °C for 15 min. Then, a 1.6 M solution of n-BuLi in hexane (1 eq for olefin and chloro-alkyl groups or 2 eq for ester group) was added batchwise. The mixture was stirred at 40 °C for 20 min. Then, a 1 M solution of HCl_{aq} was added dropwise to the mixture. The organic phase was separated and the organic solvent removed under reduced pressure. The mixture thus obtained was directly characterized to verify the outcome of the reaction.

6.5.1 Calixarene derivatives

Derivative 21 from 7

Characteristic signals of the mixture:
^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.44 (t, 2 H, $^3J = 6.6$ Hz, $C_{hex,6}H_2Cl$).
^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 45.0 ($C_{hex,6}H_2Cl$)
These signals are due to the presence of the derivative **7**.

Derivative 22 from 11

The characteristic signals by ^{1}H-NMR analysis were reported:

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.8–8.3 (m, 0.4 H, OH); 7.5–6.5 (m, 2 H, H_{cal}); 6.3–3.3 (m, 3.3 H, $CH_{2\,br}$ and protons of functionalization); 1.7-0.7 (m, 10.1 H, $C(CH_3)_3$ and protons of functionalization).

These signals are not due to the presence of the derivative **22**.

Derivative 23 from 15

The characteristic signals by ESI-MS analysis were described:

ESI-MS: Calculated m/z 1288.0 $[M+Na+Li]^{2+}$, 1296.0 $[M+2Na]^{2+}$, 1304.0 $[M+Na+K]^{2+}$ and 1312.0 $[M+2K]^{2+}$. Found m/z 1029.0 $[(7_e, 1_k)+Na+K]^{2+}$, 1057.6 $[(6_e, 1_k, 1_a)+2Na]^{2+}$, 1086.7 $[(6_e, 2_a)+2Na]^{2+}$, 1107.2 $[(5_e, 1_k, 2_a)+2K]^{2+}$, 1115.7 $[(1_e, 5_k, 2_a)+2Na]^{2+}$, 1035.7 $[(4_e, 1_k, 3_a)+Na+K]^{2+}$, 1144.7 $[(1_e, 4_k, 3_a)+2Na]^{2+}$, 1165.2 $[(1_e, 3_k, 4_a)+Na+Li]^{2+}$, 1183.8 $[(2_e, 2_k, 4_a)+2K]^{2+}$, 1223.1 $[(1_e, 1_k, 6_a)+Na+Li]^{2+}$, 1243.4 $[(2_e, 6_a)+2K]^{2+}$, 1251.9 $[(1_k, 7_a)+2Li]^{2+}$

where "N_e" identifies the number of ester groups of calixarene derivative, whereas "N_k" reports the number of ketone groups and "N_a" the analogue for the alcohol groups.

No signal due to the product **23** was detected.

Derivative 24 from 19

Here the most important NMR signals of the mixture were reported:

^{1}H-NMR ($(CD_3)_2CO$, 400 MHz): δ (ppm) 7.7–6.7 (m, 6 H, H_{cal}, $H_{bz,3}$ and $H_{bz,4}$); 4.75 (s, 2 H, $OCH_{2bz,1}$); 4.12 (s, 2 H, $CH_{2\,br}$); 3.55 (s, 1 H, $C_{bz,6}OH$); 2.0-0.5 (m, 27 H, $C(CH_3)_3$ and protons of 2 n-butyl residues).

^{13}C-NMR ($(CD_3)_2CO$, 100 MHz): δ (ppm) 153.1 ($C_{cal,i}OR$); 146.8 ($C_{cal,p}$); 145.8 ($C_{bz,5}$); 135.5 ($C_{bz,2}$); 133.4 ($C_{cal,o}$); 127.4 ($C_{bz,3}H$); 126.1 ($C_{cal,m}H$); 125.5 ($C_{bz,4}H$); 75.9 ($C_{bz,6}OH$); 74.4 ($C_{bz,1}H_2$); 43.3 ($C_{bz,7}H_2$); 33.9 ($C(CH_3)_3$); 31.1 ($C(CH_3)_3$); 30.8 (C_{br}); 25.6 ($C_{bz,8}H_2$); 23.1 ($C_{bz,9}H_2$); 13.7 ($C_{bz,10}H_3$).

Relations between the integrals of the aliphatic and aromatic signals correspond to expectations for the derivative **24**.

6.5.2 Phenol derivatives

Derivative 26 from 25

Here the most important NMR signals of the mixture were reported:

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.46 (t, 2 H, $^3J = 6.6$ Hz, $C_{hex,6}H_2Cl$).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 45.0 ($C_{hex,6}H_2Cl$).

These signals are due to the presence of the derivative **25**.

Derivative 28 from 27

In addition to the signals due to the reactant **27**, the reaction mixture showed the presence of p-tert-butylphenol (**1**).

Detected signals of p-tertbutylphenol (**1**):

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.32 (d, 2 H, $^3J = 8.8$ Hz, $H_{ph,m}H$); 6.86 (d, 2 H, $^3J = 8.8$ Hz, $H_{ph,o}H$); 5.64 (b, 1 H, −OH), 1.37 (s, 9 H, $C(CH_3)_3$).

Derivative 30 from 29

Characteristic signals of product **30**:

^{1}H-NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.37 (d, 2 H, ^{3}J = 8.8 Hz, H$_{ph,m}$H); 6.92 (d, 2 H, ^{3}J = 8.8 Hz, H$_{ph,o}$H); 3.87 (s, 2 H, OC$_{alc,1}$H$_2$).

Characteristic signals of intermediate ketone:

^{1}H-NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.27 (d, 2 H, ^{3}J = 8.8 Hz, H$_{ph,m}$H); 6.83 (d, 2 H, ^{3}J = 8.8 Hz, H$_{ph,o}$H); 4.58 (s, 2 H, OC$_{ket,1}$H$_2$); 2.65 (t, 2 H, ^{3}J = 6.7 Hz, OC$_{ket,3}$H$_2$).

^{13}C-NMR (CDCl$_3$, 100 MHz): δ (ppm) 208.7 (Ç).

Through the ratio between the integrals in ^{1}H-NMR of these two compounds, the amount of alcohol **30** was calculated as about three times of the ketone species. Due to the presence of the ketone derivative, the reaction was not complete.

Derivative 32 from 31

Characterization of derivative **32**:

^{1}H-NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.48 (s, 4 H, H$_{bz,3}$ and H$_{bz,4}$); 7.40 (d, 2 H, ^{3}J = 8.6 Hz, H$_{ph,m}$H); 7.02 (d, 2 H, ^{3}J = 8.6 Hz, H$_{ph,o}$H); 5.10 (s, 2 H, OCH$_{2bz,1}$); 2.0–0.8 (m, 28.0 H, C(CH$_3$)$_3$, C$_{bz,6}$OH and protons of 2 n-butyl residues).

^{13}C-NMR (CDCl$_3$, 100 MHz): δ (ppm) 156.8 (C$_{ph,i}$OR); 146.4 (C$_{ph,p}$); 143.6 (C$_{bz,5}$); 135.1 (C$_{bz,2}$); 127.4 (C$_{bz,3}$H); 126.3 (C$_{ph,m}$H); 125.6 (C$_{bz,4}$H); 114.3 (C$_{ph,o}$H); 77.0 (C$_{bz,6}$OH); 70.0 (C$_{bz,1}$H$_2$); 42.8 (C$_{bz,7}$H$_2$); 34.1 (*C*(CH$_3$)$_3$); 31.6 (C(CH$_3$)$_3$); 25.7 (C$_{bz,8}$H$_2$); 23.2 (C$_{bz,9}$H$_2$); 14.1 (C$_{bz,10}$H$_3$).

Relations between the integrals of the aliphatic and aromatic signals correspond to expectations for the derivative **32**.

6.6 Synthesis of the calixarene-based star polymer

The synthesis of the isoprene-styrene calixarene-based star polymer was divided into three parts, each of which is discussed below. After the preparation of living anionic polymer segments, the calixarene **19** was added to the mixture. Subsequently the product was hydrogenated to leave the the final polymer.

Preparation of living anionic polymer segments

In the first step of this synthesis 8 kg of dry cyclohexane were introduced under nitrogen atmosphere into a 15 L reactor equipped with a heating jacket and stirrer. 47 g of styrene (0.45 mol) and 1.2 g of tetrahydrofuran were then added. The solution was thermostated to 40 °C. 0.82 g of n-butyllithium in a cyclohexane solution (12.80 mmol) were added. After 20 min, once styrene conversion was complete, 423 g of isoprene (6.21 mol) were added. After 30 min, living anionic polymer segments were formed.

Coupling reaction of living anionic polymers with calixarene

During the second phase, 1.99 g (6.40 $\text{mmol}_{m.u.}$) of the calixarene **19** were added in a dry THF solution. The reaction mixture was maintained at a temperature of 40 °C for 45 min.

Hydrogenation of the star polymer

The last step concerned the trasfer of the mixture under nitrogen atmosphere into another 15 L reactor, which was set up for hydrogenation. 1.61 g of butylethylmagnesium in a heptane solution and 1.22 g of bis-cyclopentadienyltitanium dichloride in a cyclohexane suspension were added. The solution was then placed under hydrogen pressure (15 bar) and maintained at a temperature of 120 °C for 90 min while being stirred.

Characterization of the star polymer

After the hydrogenation step, the solution was transferred into a tank and antioxidants (2.6 g of Irganox 565 and 17.0 g of Irgafos 168) were added. Subsequently the solvent of the mixture was removed by steam. The resultant granular product was then dried in a vacuum oven. The characteristics of the resultant hydrogenated star polymer are reported in Table 6.1.

Table (6.1): *Hydrogenated isoprene-styrene calixarene-based star polymer*

Property	**Value**
M_w (KDa)	671
M_n (KDa)	541
M_w polymer segments (KDa)	43
M_w/M_n	1.24

6.7 Lubricant formulations

The solution of the star polymer (Section 4.7) were prepared in Group I Solvent Neutral 150 base oil (ENI SN 150S). Dissolution was carried out by heating the base oil to a temperature of 130 °C, adding the polymer and stirring at this temperature until dissolution was complete.

Using the same operating conditions, a solution in base oil SN 150S were prepared of the commercial product Infineum Shellvis 260 (SV 260), which is a hydrogenated styrene-isoprene star polymer with a PDVB core.

The shear stability index and the thickening power were determined on the solutions of the polymers in the base oil. The shear stability index was determined on a solution made up of 10 % by weight of the polymer solution in base oil and by 90 % by weight of base oil SN 150S. Thickening power was calculated as the difference between the kinematic viscosity value at 100 °C of the 1 % by weight polymer solution in SN 150S and the kinematic viscosity value at 100 °C of the SN 150S oil.

Using the concentrated solutions of polymers as viscosity index improver additives, corresponding engine lubricating oils of viscosity grade SAE 10W–40 of the following composition were prepared:

- base oils: 79.1 % by weight;
- additive package: 13.8 % by weight;
- viscosity index improver: 7 % by weight;
- pour point depressant additive: 0.1 % by weight.
- foam inhibitor: 50 ppm.

In detail, the additive package was a mixture of the dispersants, detergents, antioxidants and antiwear additives. The following parameters were determined for the lubricating oils:

- kinematic viscosity at 100 °C (method ASTM D 445)[7];
- kinematic viscosity at 40 °C (method ASTM D 445)[7];
- viscosity index (method ASTM D 2270)[7];
- CCS viscosity at -25 °C (method ASTM D 5293)[8];

- percentage viscosity loss by depolymerization (method CEC L-14-93)[9].

Table 6.2 shows the results.

Table (6.2): *Comparison between calixarene-based SP and SV 260*

Property	Calix-based SP	SV 260
Thickening power at 100 °C (cSt) (1 % by weight polymer in SN 150S)	7.6	7.5
Concentrated solution		
Polymer content (w/w)	10.45	10.55
Shear stability index (%)	7	10
Final lubricant with other additives		
Viscosity (40 °C)	92.26	91.28
Viscosity (100 °C)	13.78	13.69
Viscosity index	152	152
CCS viscosity -25 °C (cSt)	6650	6671
Viscosity loss by depolym. (%)	3.6	5.2

Bibliography

[1] J. H. Munch and C. D. Gutsche, *Organic Syntheses*, 1990, **68**, 243 – 246.

[2] W.-G. Wang, Q.-Y. Zheng and Z.-T. Huang, *Synthetic Communications*, 1999, **29**, 3711 – 3718.

[3] S.-K. Chang and I. Cho, *Chemistry Letters*, 1984, **13**, 477 – 478.

[4] D. R. Vutukuri, P. Bharathi, Z. Yu, K. Rajasekaran, M.-H. Tran and S. Thayumanavan, *The Journal of Organic Chemistry*, 2003, **68**, 1146 – 1149.

[5] X. Li, S.-L. Gong, W.-P. Yang, Y.-Y. Chen and X.-G. Meng, *Tetrahedron*, 2008, **64**, 6230 – 6237.

[6] R. E. Ireland and R. S. Meissner, *The Journal of Organic Chemistry*, 1991, **56**, 4566 – 4568.

[7] ASTM International, West Conshohocken, PA, *ASTM D 445 – Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)*, 2006.

[8] ASTM International, West Conshohocken, PA, *ASTM D 5293 – Standard Test Method for Apparent Viscosity of Engine Oils and Base Stocks Between -10C and -35C Using Cold-Cranking Simulator*, 2015.

[9] *Evaluation of the Mechanical Shear Stability of Lubricating Oils Containing Polymers (Fuel Injection Pump)*, 2015.

Part III

Overbased detergents

CHAPTER 7

AIMS OF RESEARCH

The aim of the research carried out in this part of Thesis is the use of calixarenes as polycarboxylic acids to synthetize new sulfur-free detergents as lubricant additives. In this way, these detergents may be used for the formulation of new automotive lubricants with low content of ash, phosphorus and sulfur (low SAPS).

Due to their ability to form complexes with Ca^{2+} and their amphiphilic structures, the use of calixarene derivatives allow the preparation of high quality overbased calcium detergents. To increase the low deprotonation degree of OH groups and their capacity to complex calcium ions, a complete functionalization of the calixarene mixtures with acetic acid groups will be required. To introduce this kind of functional groups, a previous step of functionalization with ethyl α-bromoacetate will be necessary. Subsequent hydrolysis of the ester to the desired carboxylic acids will follow.

Futhermore, the "one-step" synthesis of new calixarenes with alkyl chains in para positions longer than the ones already known will be necessary to improve the oil solubility and stability of reverse micelles formed by the detergents. Moreover, the separation and characterization of the calixarenes will be carried out to optimize their synthetic process, also on pilot scale.

For our purpose, the use of p-tert-octylcalixarenes for the preparation of detergents will be carried out to compare the properties of the final detergents respect to the use of the p-dodecyl calixarenes.

Once achieved the functionalization of both calixarene mixtures with carboxylic acid groups, the synthesis of new calixarene-based detergents will be carried out to identify the best calixarene derivative for our purposes. The synthetic process for the preparation of calixarene-based detergent having very high basicity (TBN 400) will be investigated for applications in lubricants for marine engines.

Furthermore, with the purpose of testing the calixarene-based detergents in automotive lubricants, several additive packages (concentrated mixture of additives) containing our detergents will be prepared. Using these packages the corresponding automotive lubricants can be formulated. Besides, a lubricant containing commercial calcium alkylbenzene-sulfonates detergents will be prepared for the comparison of its detergency properties with those of the calixarene-based oils.

CHAPTER 8

RESULTS AND DISCUSSION

As mentioned in Section 2.4.2 of this Thesis, nowadays there are only very few examples of calixarene-based detergents.

Whereas for the sulfonate-based detergents (the most common ones) the deprotonation of the sulfonic acids results essentially complete (due to their high acid constant), the degree of deprotonation of free phenolic OH calixarenes is object of investigations. Evidence of an only partial deprotonation in 2-ethylhexanol/ethylene glycol mixture was indeed obtained. In detail, the chemists assumed a maximum of 25 % of the hydroxy groups in the deprotonated form upon treatment with $Ca(OH)_2$.[1] Calixarenes, in fact, do behave as polyprotic acids.[2] While the pKa for the first deprotonation is around 3.2-3.5 and hence quite lower than that of a monomeric phenol (pKa = 8.62),[3] the pKa values of the subsequent deprotonation steps rapidly increase. In fact, it has been measured that the 2^{nd} (for calix[4]arenes) and the 3^{rd} (for calix[6]- and [8]arenes) have pKa values higher than 11. Therefore, the use of calixarenes could adversely affect the properties of the final detergent due to their low degree of deprotonation. This fact could result in a low detergent effectiveness, in addition to possible problems of stability for these additives and their micelles.

Moreover, the length of p-alkyl chains of the known calixarenes could be not sufficient to ensure the necessary oil solubility of the calixarene-based detergents. For this reason, it was very important to synthesize new calixarenes bearing sufficiently long alkyl chains in para position to ensure their high compatibility in the lubricants. Unfortunately, the number of known calixarenes obtained by the "one-step" synthesis processes are actually rather low, as reported in Section 2.1 of this Thesis. These calixarenes bearing the longest alkyl chains are the p-tert-octylcalixarenes, which derivatives however are still solids with high crystallinity and reduced solubility in organic solvents.

The "one-step" syntheses reported in the literature to date are extremely efficient. In fact, they yield mainly a single oligomer and most of them use phenols substituted in para position with bulky groups: better if tertiary (tert-butyl and tert-octyl) or secondary (iso-propyl) alkyl groups.

A possible route to longer p-alkyl calixarenes is certainly represented by a multi-step process, consisting in the removal of p-tert-alkyl groups with a Lewis acid, followed by an alkylation of the para positions (for more details see Section 2.3 of this Thesis). Unfortunately, this stategy is certainly too expensive and time-demanding for a profitable industrialization.

All these considerations prompted us to study the synthesis of calixarene-based detergents, via the "one-step" synthesis and by starting from p-dodecylphenol.

With the term "dodecylphenol" it is intended any chemical compound resulting from the C-alkylation of phenol with the alkenes resulting from the tetramerization of propylene. Therefore, the alkyl groups in these chemical species are not univocal: they may be linear or branched, constituted of C_8-C_{15} atoms and be bonded in position 2 (ortho), 3 (meta) or 4 (para) on the phenol nucleus. This variability can generate an extremely large number of possible products and isomers, causing a significant difference in composition between batches of different manufacturers.

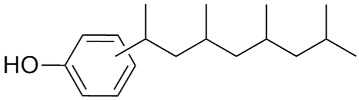

Figure (8.1): *One of the possible structures of dodecylphenol*

In addition, the common use of the wording "tetrapropylenphenol" is often associated not only to the structure with a main chain with eight carbon atoms and four methyl substituents (Figure 8.1), but also to a large number of isomers with alkyl chains "differently branched", in any position on the benzene ring. This variability originates from the synthesis of these compounds, which is based on a process of alkylation of the phenol via acid catalysis (Figure 8.2).

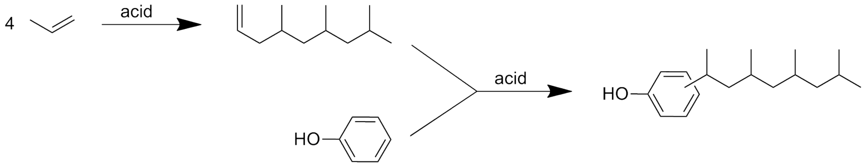

Figure (8.2): *Mechanism of phenol functionalization*

These compounds are normally produced in a continuous flow reactor with an acid solid phase to promote the alkylation of the phenol with the "tetrapropylene" reactant.[4] The conversion of the reaction is usually keep to a low degree to minimize polyalkylation products. The alkylated products are subsequently purified by fractional distillation to remove the unreacted olefins and phenol. These unreacted species are then normally re-inserted into the production cycle.

Due to a significant dispersity of molecular mass of the olefins, the obtained product is usually composed of similar chemical species, but having alkyl groups ranging from C_8 to C_{15}. To properly identify the quality of the raw materials employed in the synthesis of calixarenes, the batch of dodecylphenol used for the synthesis (bought from Sasol) was characterized.

8.1 Characterization of dodecylphenol

From the reported analyses carried out by the producer, the batches of "p-dodecylphenol" may be contain either monoalkylated compounds in the ortho position, but also dialkylated ones at the ortho and para position.[5] The presence of even traces of these co-products could adversely affect the reaction of formation of calixarenes. In fact, once olygophenolic chains react with o-alkylphenols or p-o-dialkylphenols, the products are no more able to form the calixarene structures (Figure 8.3).

The p-dodecylphenol used for our purposes had a high concentration of para substituted phenols (over 95 %), since the ortho-alkyl compounds are not detectable using nuclear magnetic resonance.

From the ^{1}H-NMR analysis, the ratio of aromatic over aliphatic protons was consistent with the expected one: 4 H_{Ar} over 25 H_{Alkyl} (Figure 8.4).

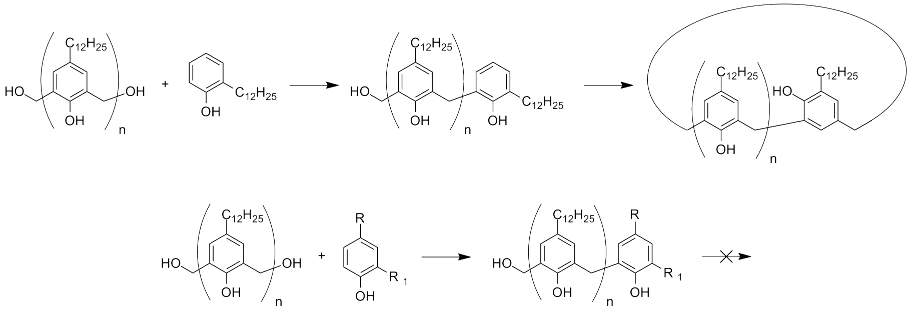

Figure (8.3): *Mechanism of interference of ortho- and para-ortho-substituted isomers*

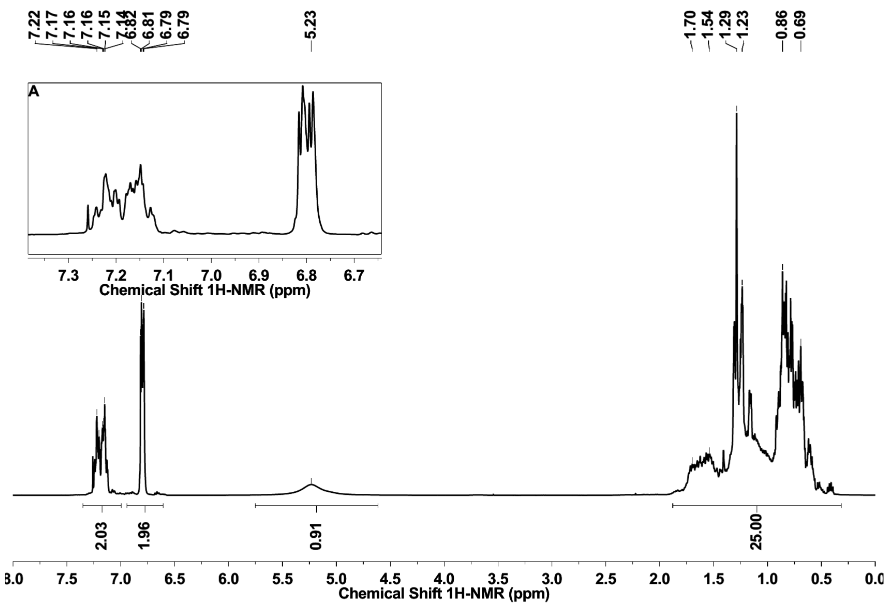

Figure (8.4): *^{1}H-NMR of dodecylphenol*

However, the presence of a wide multiplet at 7.25–7.10 ppm (which was due to the meta H_{Ar}) highlights the presence of not well-defined isomers of alkyl chains (inset "A" in Figure 8.4).

By the ^{13}C-NMR analysis in Figure 8.5, a structural variability of the compounds was confirmed. As for ^{1}H-NMR analysis, a greater variability of the aromatic reagion near the para-alkyl chain was detected. In detail, this significant difference in chemical shift could be attributable only to a great variability of the alkyl chain structures.

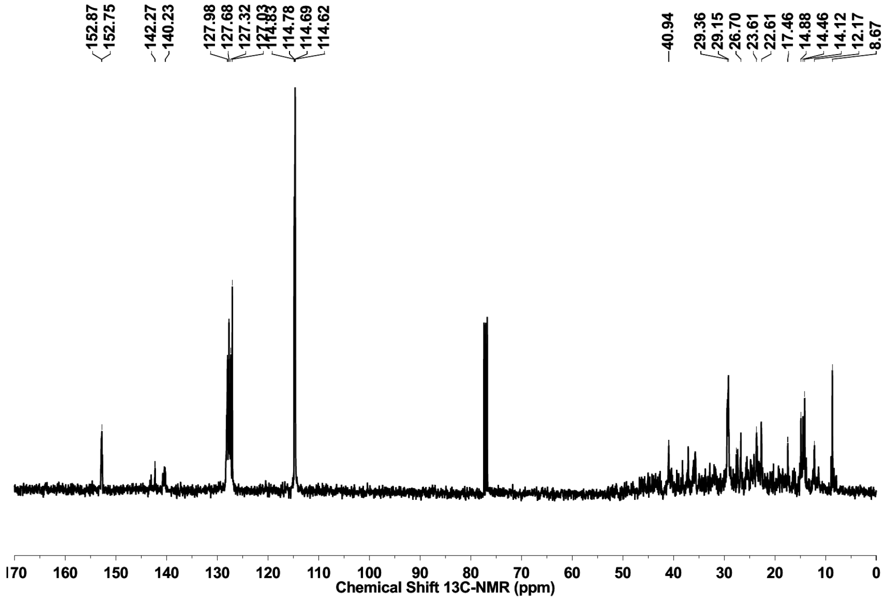

Figure (8.5): *^{13}C-NMR of dodecylphenol*

The structural variability was also confirmed by ESI-MS analysis of its acetylate derivative. In fact, the Figure 8.6 shows a large molecular weight distribution (Figure 8.6).

In detail, the presence of signals associated to phenols with alkyl chains of variable length between C_8H_{17} (271.4 m/z) and $C_{15}H_{29}$ (369.6 m/z) was observed. In Figure 8.6 the most relative abundance was identifiable for the phenols with a dodecyl chain (327.5 m/z), but further studies had to be done in order to determine the average molecular mass of this sample.

The titration of the hydroxyl groups was carried out to calculate the exact number of moles of phenol species present in a given mass of the sample. In this way, the average molecular mass of the phenol could be calculated. The procedures relating to these titrations were included in the Section 10.1.1 of this thesis. From the results obtained from five different titrations, a percentage weight of the hydroxyl groups on the sample of 6.41 % ± 0.02 % was obtained. With this datum the average molecular mass of 265.1 $\mathrm{g\,mol^{-1}}$ ± 1.0 $\mathrm{g\,mol^{-1}}$ was calculated, which was indeed rather close to the theoretical molecular mass of 262.43 $\mathrm{g\,mol^{-1}}$.

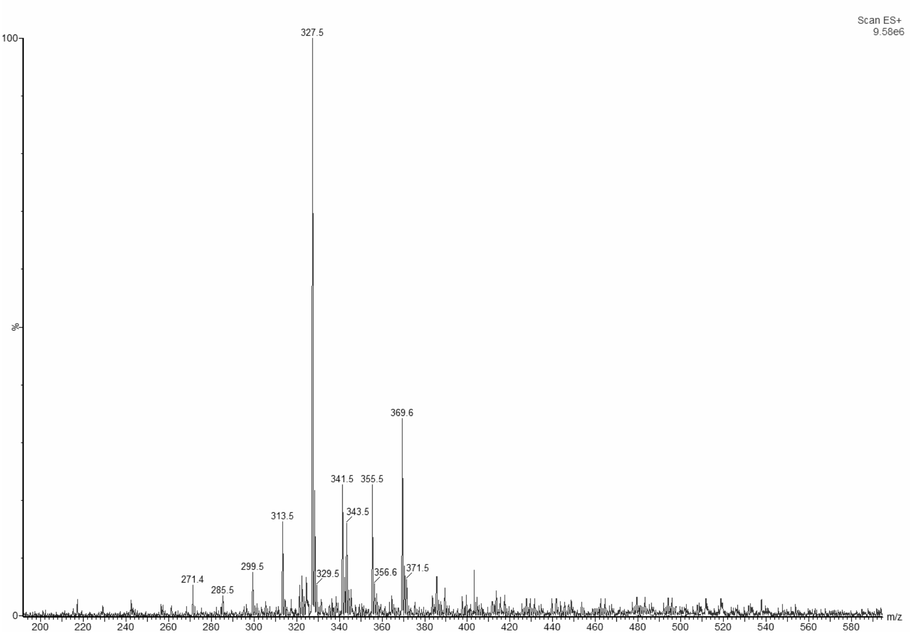

Figure (8.6): *ESI-MS analysis of dodecylphenyl acetate*

8.2 Characterization of p-tert-octylphenol

The analyses of p-tert-octylphenol are discussed in this Section because they are useful to compare this raw material with p-dodecylphenol.

The ^{1}H-NMR spectrum of p-tert-octylphenol (Figure 8.7) shows well-defined signals, unlike dodecylphenol (Figure 8.4). In fact, the doublets of the aromatic protons at 7.33 and 6.91 ppm are identified, in addition to the signal due to the OH group detected at 6.60 ppm. Finally, the singlets at 1.83, 1.47 and 0.87 ppm can be ascribed to the protons of the tert-octyl chain.

As for the ^{1}H-NMR spectrum, an unique structure of this material was confirmed by ^{13}C-NMR analysis in Figure 8.8. In detail, the aromatic carbons are detected at 152.7, 142.7, 127.4 and 115.0 ppm, whereas the signals of alkyl residue resonate at chemical shift lower than 60 ppm.

The well-defined structure of p-tert-octylphenol was also confirmed by ESI-MS analysis of its acetylated derivative. In fact, the Figure 8.9 shows only peaks at 271.5 and 287.4 m/z due to complexes between the acetated derivative and Na$^+$ or K$^+$, respectively.

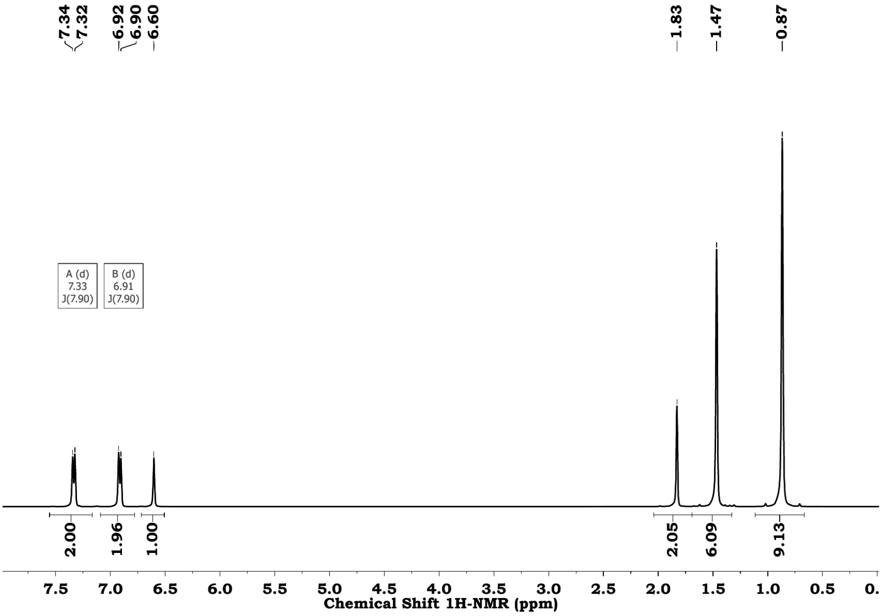

Figure (8.7): *^{1}H-NMR of p-tert-octylphenol*

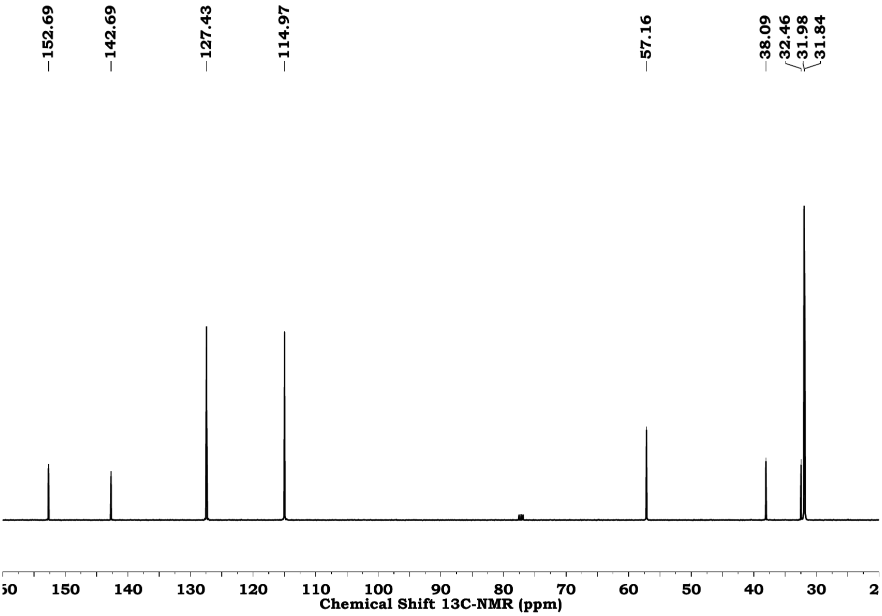

Figure (8.8): *^{13}C-NMR of p-tert-octylphenol*

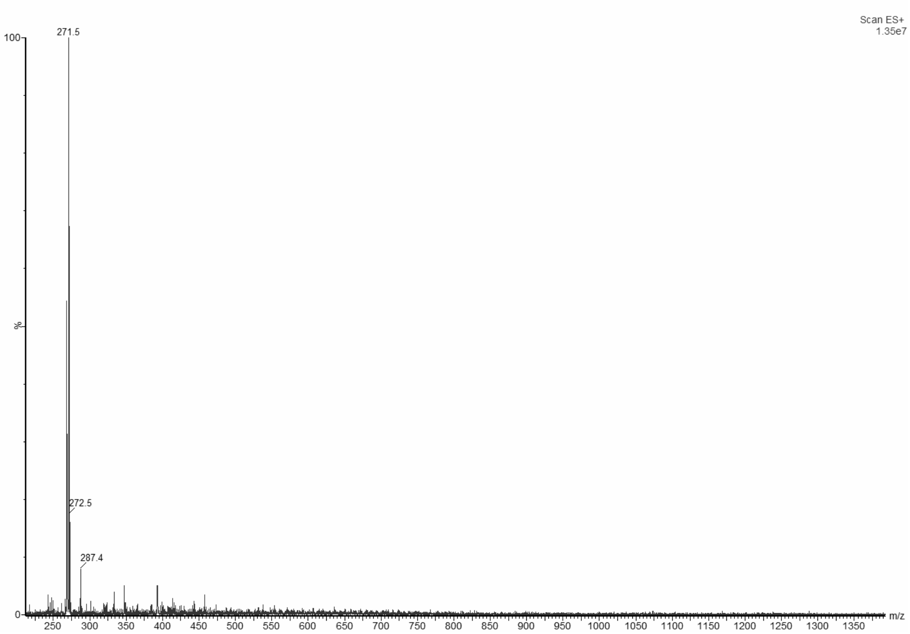

Figure (8.9): *ESI-MS analysis of p-tert-octylphenyl acetate*

8.3 Synthesis of calixarenes from dodecylphenol

The syntheses of p-dodecylcalixarenes were carried out by condensation of p-dodecylphenol with formaldehyde.

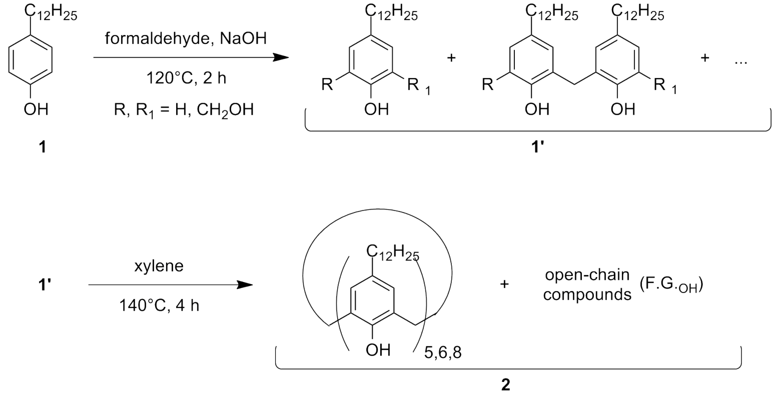

Figure (8.10): *Synthesis of calixarenes (**2**) from dodecylphenol (**1**)*

During these years the synthesis of cyclic oligomers was implemented to increase the formation yield of the calixarene structures. In this way, the optimized process could be carried out also on pilot scale on a 500 kg batch of phenol.

The synthesis was performed in two stages (Figure 8.10). In the first step the p-dodecylphenol was reacted with aqueous formaldehyde at 120 °C using sodium hydroxide as catalyst. At the end of this stage, mainly a mixture of linear oligomers with methylol groups could be obtained (**1'** in Figure 8.10). During the second part, carried out in xylene at 140 °C, the cyclization of the linear methylol-terminating oligomers takes place with the formation of calixarenes and water (which was removed as azeotrope mixture with xylene). Under these conditions, more than 97 % of yield could be obtained. By TLC, NMR and ESI-MS analyses, the disappearance of p-dodecylphenol and the formation of some calixarene compounds could be observed. In order to reduce the high viscosity of the mixture at room temperature, 22.5 % by weight of xylene was retained in the final product.

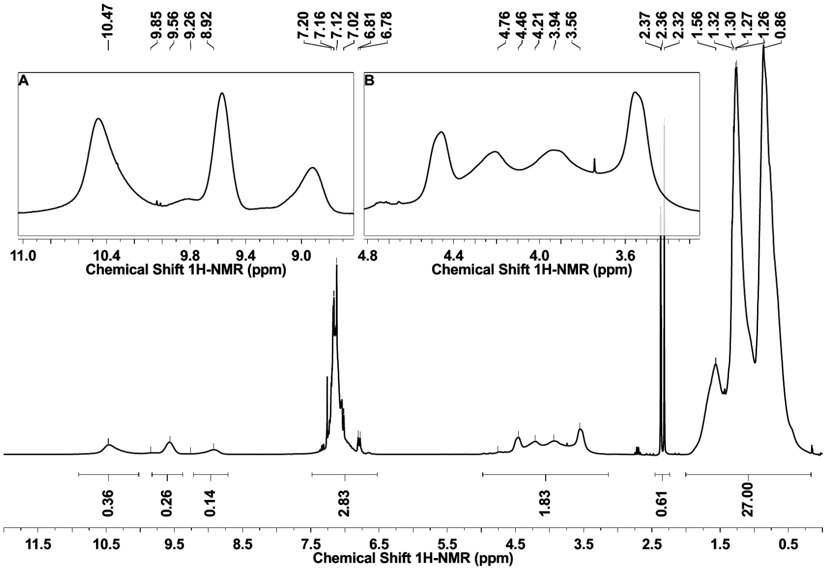

Figure (8.11): *^{1}H-NMR of the crude material (synthesis of* **2***)*

The ^{1}H-NMR analysis in Figure 8.11 shows the presence of different OH proton signals between 10.5 and 8.9 ppm. In detail, the inset "A" shows the presence of 3 main signals over 8 ppm: 10.44, 9.57 and 8.91 ppm. The aromatic region reports several signals due to cyclic and open compounds. The inset "B" shows clearly the signals also due to the methylene bridges on different open and cyclic oligomeric structures. Lastly, the signals due to alkyl chains results less splitted than in the spectrum of monomeric dodecylphenol (Figure 8.4).

8.3.1 Separation of the main products

The high solubility of these calixarene compounds presented in the reaction mixture and the high variability in length and branching of their alkyl chains resulted in considerably difficult separations of the cyclic calixarene species from the open-chain oligomers. Therefore, the selective precipitation of the individual calixarene species was not possible and the purification by chromatographic separation was necessary to characterize the different products of the obtained mixture.

Chromatographic separation

The chromatographic separation of the reaction mixture on a direct stationary phase was particularly difficult. This fact was due to an extremely small difference in polarity between different components. In addition, the variability in length and branching of their alkyl chains caused a significant broadening of the chromatographic peaks. In this way, rather small differences in retention times (ΔR_f) with low resolutions values between the chromatographic peaks were always observed.

After an initial screening by TLC analyses, the best eluent found for the separation of calixarene species was identified in a mixture formed by hexane (76 %), chloroform (19 %) and toluene (5 %). In this way, different fractions of the mixture could be obtained and a quantitative separation of the calixarene structures from the open-chain compounds was obtained.

In the following Section, the characterization of the main products was discussed.

8.3.2 Characterization of the main products of dodecylphenol-formaldehyde condensation reaction

A ratio in weight between calixarenes and open structures could be estimated by the preparative column chromatography and resulted to be approximately $\frac{70\ \%}{30\ \%}$, demonstrating good yields in the cyclization process.

Unfortunately, a mixture of different calixarenes was obtained, as shown below.

Characterization of p-dodecylcalixarenes

p-dodecylcalix[8]arenes

Following chromatographic purification, a product with lower affinity with the stationary phase (silica gel) was isolated. The product thus obtained was characterized by NMR and ESI-MS analyses.

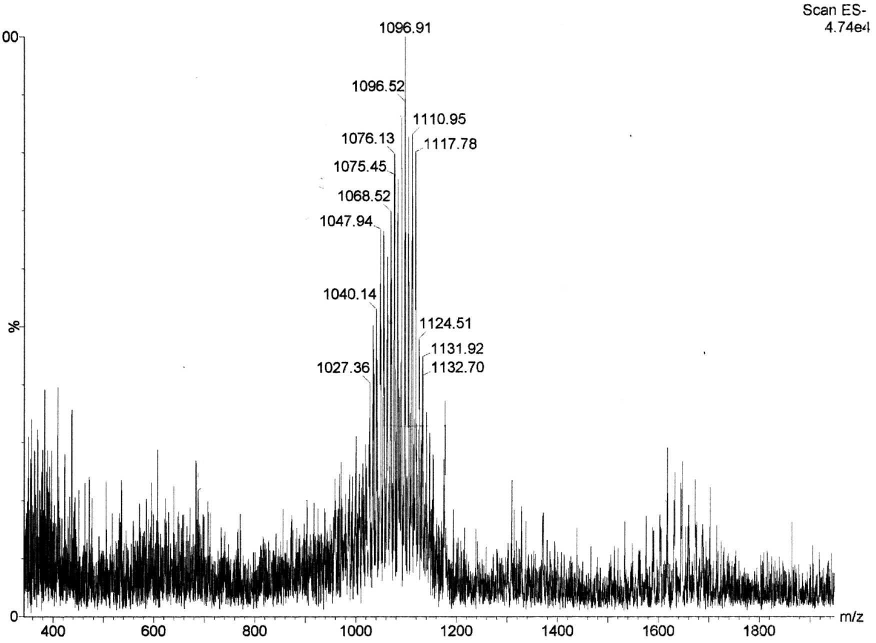

Figure (8.12): *ESI-MS analysis of p-dodecylcalix[8]arene*

In Figure 8.12 the ESI-MS analysis of this compound is shown. As expected from the characterization of p-dodecylphenol, this analysis showed a broad distribution of m/z values of these compounds. In detail, the distribution range was 1027.4–1154.1 m/z, with a maximum (1096.9 m/z) attributed to the doubly-charged deprotonation of the calix[8]arene derivative with an average length of alkyl chains of 12 carbon atoms. The other signals are due to calix[8]arenes with different lengths of the alkyl chains. In fact, the difference of 7 m/z between the different peaks of this distribution is caused by the addition or subtraction of a CH_2 residue (14 a.m.u.) within the alkyl chains in para position of the calix[8]arene species.

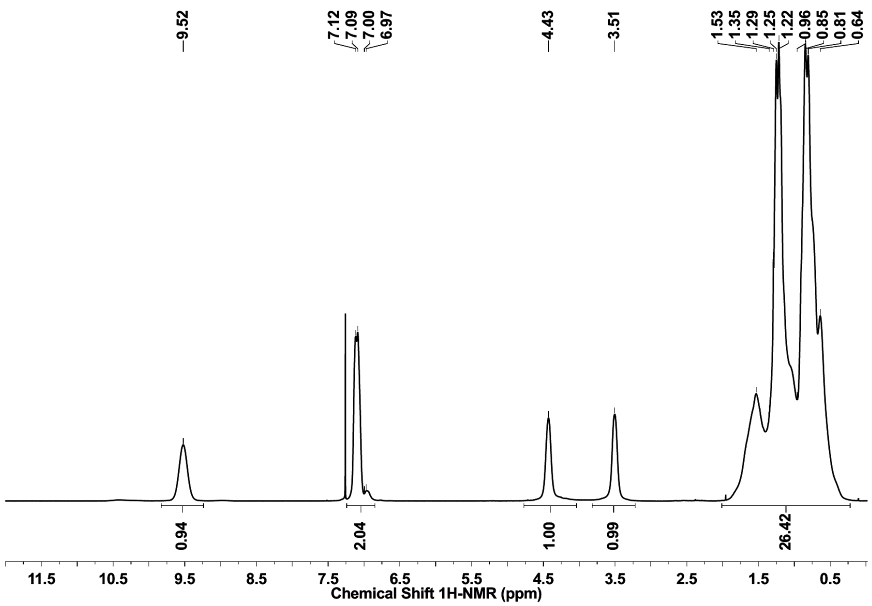

Figure (8.13): *^{1}H-NMR of p-dodecylcalix[8]arene*

In the ^{1}H-NMR spectrum (Figure 8.13) the signals of the alkyl chains can be observed between 2.0 and 0.3 ppm and their integral correspond to about 26 H. The aromatic protons are observed around 7.1 ppm with an area of 2 H. The evidence of the cyclic structure comes from the presence of two signals, respectively at 4.43 and 3.51 ppm. Each ones integrate for 1 H and they can be assigned to axial and equatorial protons of the methylene bridges in the calixarene. Further confirmation is also given by the detection of the hydroxyl proton at quite high chemical shift (9.52 ppm), as a consequence of the formation of intramolecular hydrogen bonds in the calixarene structure. As reported in Figure 8.11, the same signals are detected in the ^{1}H-NMR spectrum of the reaction mixture.

The ^{13}C-NMR spectrum (Figure 8.14) shows the peaks due to aromatic carbon atoms between 150 and 120 ppm. In detail, C−OH was detected at 146.6 ppm, whereas the carbons in para position resonate at 143.9 and 141.7 ppm. Finally, ortho and meta aromatic carbons were detected at 128.6 and 126.6 ppm respectively. Inhomogeneity of the alkyl chains is deduced by

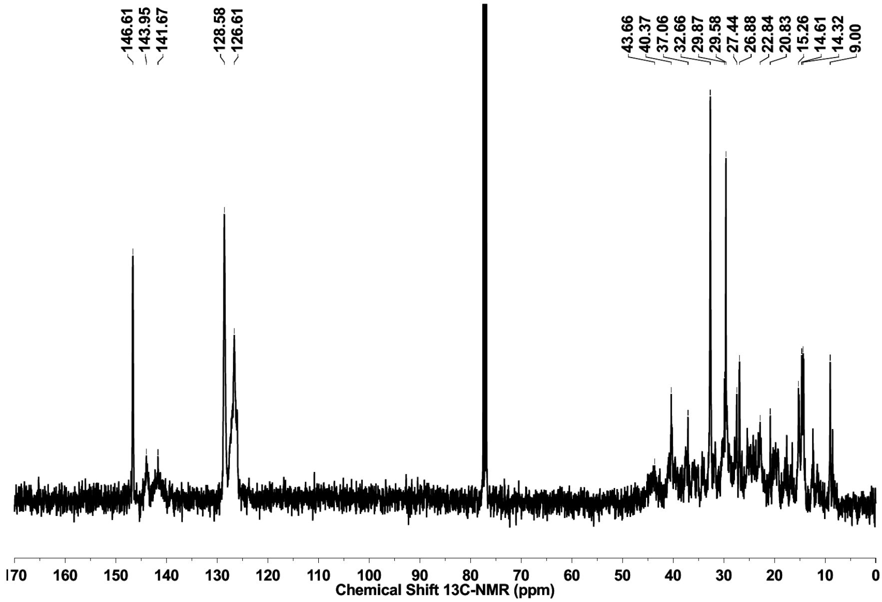

Figure (8.14): *^{13}C-NMR of p-dodecylcalix[8]arene*

progressive broadening of their signals as the correspondig carbon atoms are closer to the aromatic carbons of the chain.

As already observed for the p-dodecylphenol, the aliphatic region of the ^{13}C-NMR spectrum confirms the structural variability of the alkyl chains in para position to the calixarene structure.

In Figure 8.15 the ^{1}H-^{13}C HSQC (Heteronuclear Single Quantum Correlation) of p-dodecylcalix[8]arene is shown. Interestingly, the carbon of the methylene bridges is detected at 32.2 ppm and the meta aromatic carbon (C$-$H) is reported near 126 ppm.

In Figure 8.16 the ^{1}H-^{13}C HMBC (Heteronuclear Multiple Bond Correlation) of this sample is also reported. This experiment gives correlations between carbons and protons that are separated by at least two bonds. Therefore, direct one-bond correlations are suppressed.

Enriched mixture of p-dodecylcalix[5,6]arenes

Unlike the calix[8]arene, the other p-dodecylcalix[n]arenes were not separated each from the other. However, an enriched mixture of the other p-dodecylcalix[n]arenes was isolated and characterized by NMR and ESI-MS

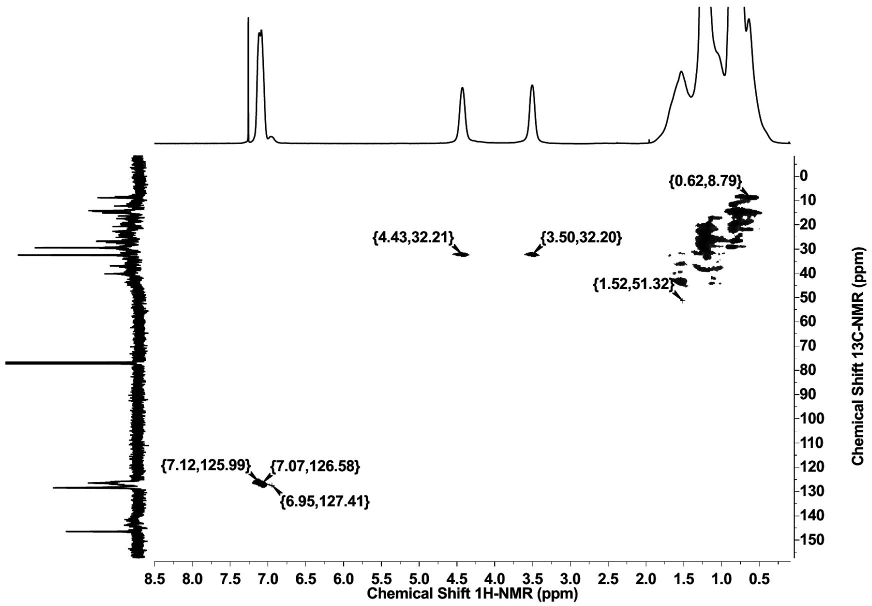

Figure (8.15): *^{1}H-^{13}C HSQC of p-dodecylcalix[8]arene*

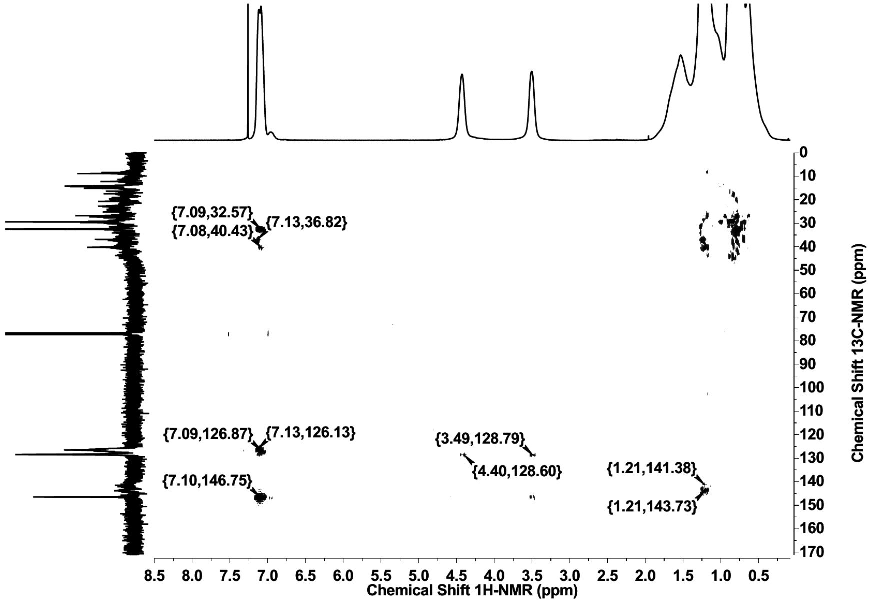

Figure (8.16): *^{1}H-^{13}C HMBC of p-dodecylcalix[8]arene* analyses.

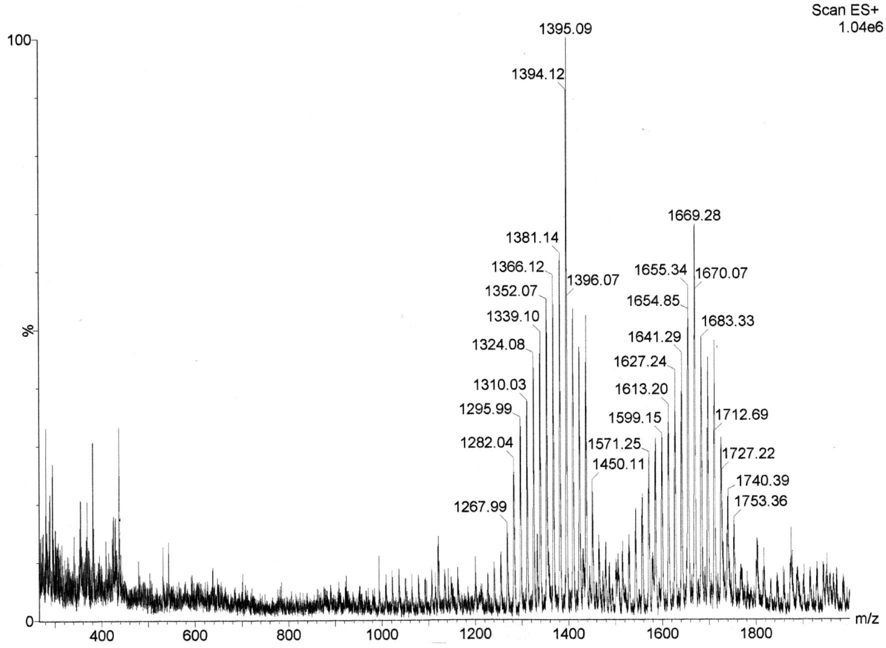

Figure (8.17): *ESI-MS analysis of p-dodecylcalix[5,6]arenes*

In Figure 8.17 two main distibutions are reported, which are due to single-charged complex between calixarene species and a Na^+ ion. The distribution of peaks on the left are attributed to calix[5]arenes, whereas the distribution on the right is given by calix[6]arenes. The most intense peaks of the two distributions (1395.1 and 1669.3 m/z) were related respectively to calix[5]- and -[6]arenes with an average length of alkyl chains of 12 carbon atoms.

In the ^{1}H-NMR spectrum (Figure 8.13) the signals of the alkyl chains were observed between 2.0 and 0.3 ppm and their integral is nearly 26 H. The aromatic protons are detected near 7.1 ppm with area of 2 H. The evidence of the cyclic structure are given by the presence of signals between 4.5 and 3.0 ppm with integral 2 H (inset "B" in Figure 8.13), although the peaks are not well resolved. Comparing these values with those obtained for the analogous calix[8]arene (Figure 8.13), a decrease in chemical shifts of the signals due to axial protons is shown, while the resonance frequency of the equatorial protons remained constant.

Further confirmation was given by the detection of the hydroxyl proton at quite high chemical shift (10.41 and 8.88 ppm), which is due to the formation

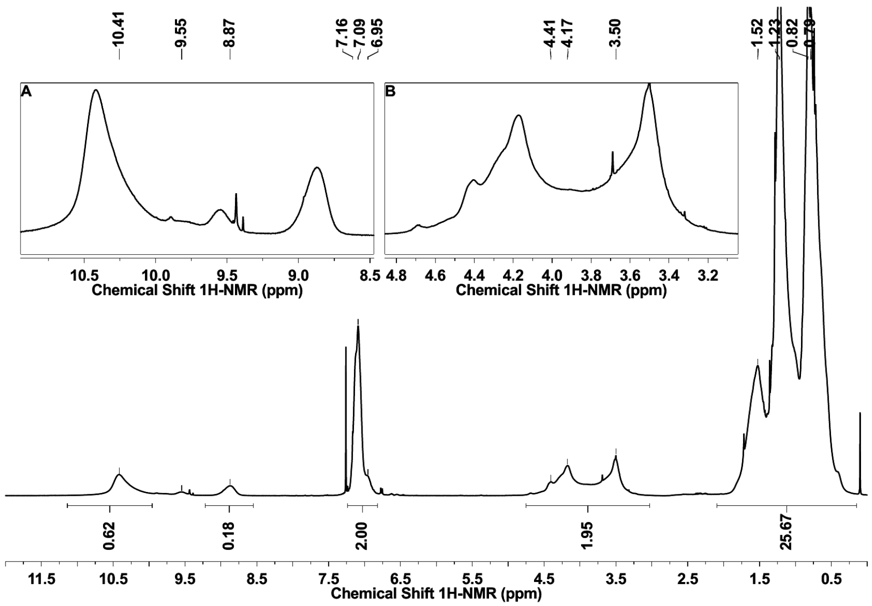

Figure (8.18): *^{1}H-NMR of p-dodecylcalix[5,6]arenes*

of intramolecular hydrogen bonds in the calixarene structures. The inset "A" in Figure 8.18 shows at least one more broadened signal at 9.55 ppm, which might be due to p-dodecylcalix[8]arenes (see Figure 8.13). The low intensity of this signal might be correlated to a low concentration of the calix[8]arene in this sample, not detected by ESI-MS analysis. Therefore, in the same inset of the Figure 8.18 two peaks can be detected near 9.5 ppm, maybe due to traces of linear structures present in the sample.

The ^{13}C-NMR spectrum of this sample (Figure 8.19) is very similar to the analogue of p-dodecylcalix[8]arenes (Figure 8.14). However, in Figure 8.19 the signal of C−OH residue is reported at 147.5 ppm, which is an higher value than that of the analogue chemical shift in p-dodecylcalix[8]arenes. An opposite effect occurs for the aromatic carbons bonded to the methylene bridges. In detail, they resonated at 127.2 ppm instead of 128.6 ppm (Figure 8.14). From these experimental data, an effect given by the magnitude of the calixarene cycle on the chemical shift of some aromatic carbons can be evidenced.

Finally, the ^{1}H-^{13}C HSQC analysis (Figure 8.20) allows to point out the peaks of the carbon atoms of the methylene bridges at 31.9 ppm.

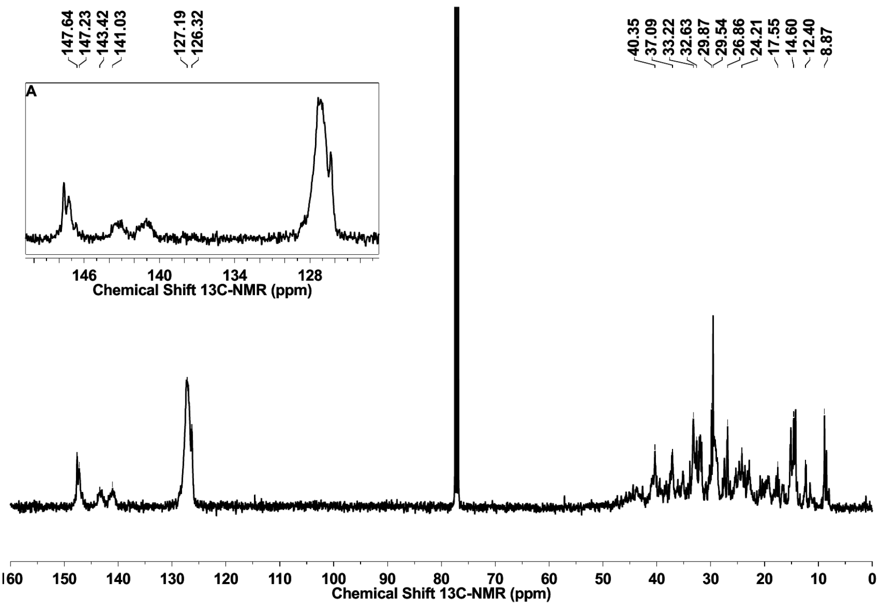

Figure (8.19): *^{13}C-NMR of p-dodecylcalix[5,6]arenes*

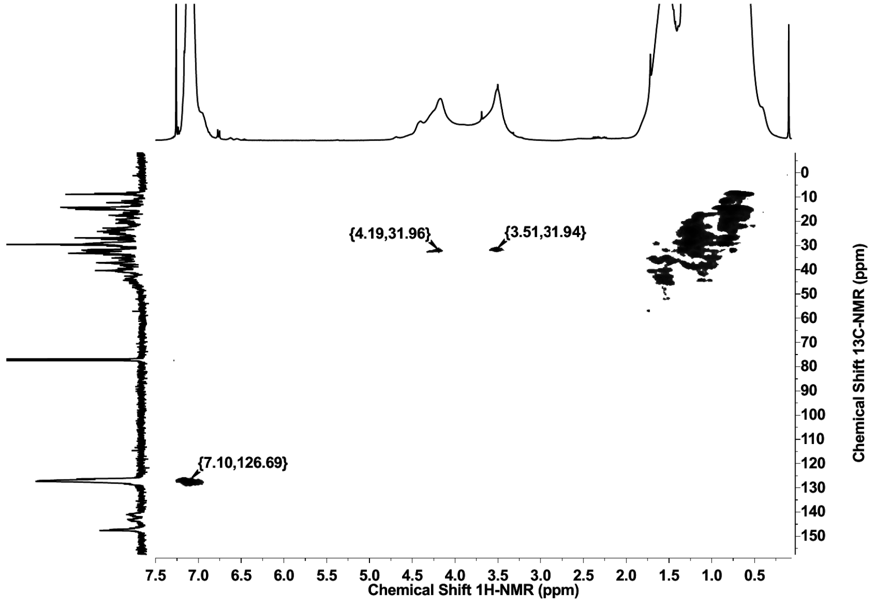

Figure (8.20): *^{1}H-^{13}C HSQC of p-dodecylcalix[5,6]arenes*

Open-chain compounds

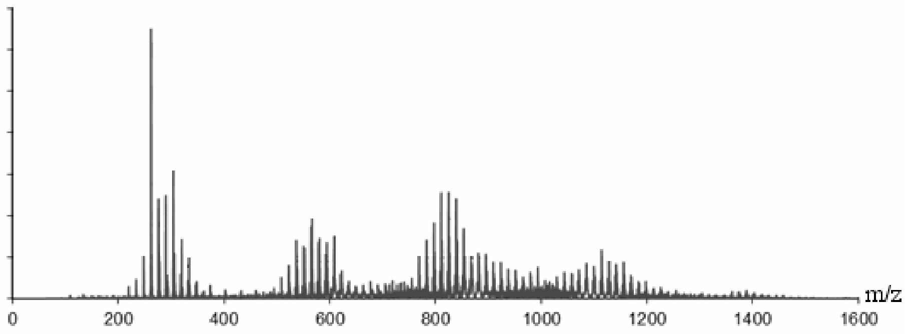

Figure (8.21): *ESI-MS analysis of the open-chain compounds*

In the ESI-MS spectrum (Figure 8.21) four main distributions can be identified and attributed to structures ranging from monomer to tetramer (respectively 247–333 m/z, 493–635 m/z, 769–937 m/z, 1029–1197 m/z).

Focusing on the m/z interval associated to monomer units, three distributions seems to be present, respectively due to the monomer as it is, to a monomer with a methylol unit ($-CH_2OH$) and to the one with two methylol units, respectively (for the $C_{12}H_{25}$ phenols) at 261, 291 and 321 m/z. Further, the analysis shows signals at 333 and 363 m/z, due to the functionalized pentadecylphenol, respectively with one and two methylol groups.

Similar distributions are found for the other open chain oligomers.

8.4 Synthesis of p-tert-octylcalix[6,8]arenes

We planned to synthesize detergents based on p-tert-octylcalixarenes to compare their properties with those of the detergents based on p-dodecylcalixarenes.

For this purpose, the synthesis of p-tert-octylcalix[6,8]arenes is reported in this Section.

In detail, this process was divided into two phases (Figure 8.22).

During the first step, the mixture of p-tert-octylphenol, aqueous formaldehyde and NaOH was heated to 120 °C, by removing the water from the reaction mixture. Subsequently, after 4 hours of reaction at 140 °C in xylene, a partial distillation of the solvent was achieved. After the addition of 2-propanol to the reaction mixture, a yellow solid was formed. This product

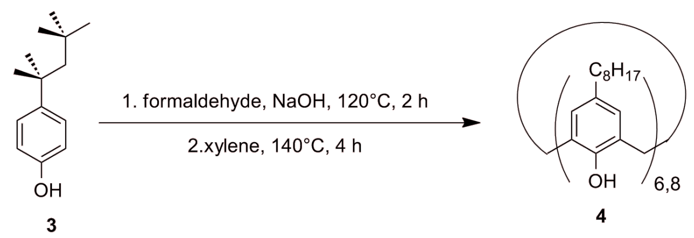

Figure (8.22): *Synthesis of calixarenes (**4**) from p-tert-octylphenol (**3**)*

was filtered and then characterized by ESI-MS analysis (Figure 8.23).

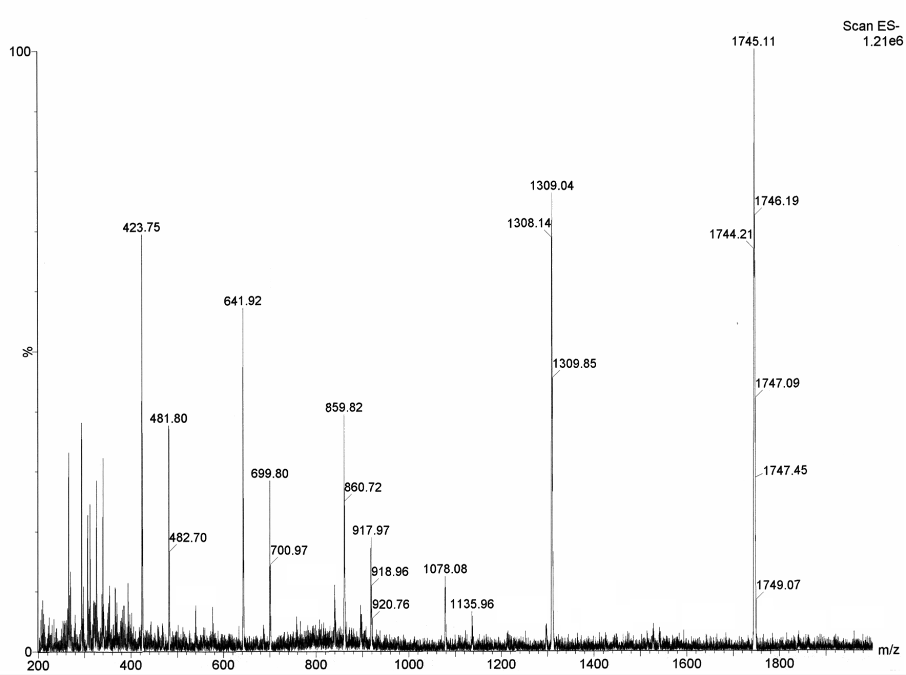

Figure (8.23): *ESI-MS analysis of the solid obtained as crude of the reaction (synthesis of **4**)*

This spectrum shows signals due to p-tert-octylcalix[6]arene (1309.0 m/z) and p-tert-octylcalix[8]arene (1745.1 m/z), whereas the peaks due to the open-chain compounds were detected under 1200 m/z. In detail, dimers with $-$H and $-CH_2OH$ residues in ortho positions were detected at 423.7 and 481.8 m/z, respectively. Analogue distributions were shown for trimers (641.9 and 699.8 m/z), tetramers (859.8 and 918.0 m/z) and pentamers (1078.1 and 1136.0 m/z) of the p-tert-octylphenol.

Having demonstrated the presence of cyclic structures in the sample, this yellow solid was washed with water, 2-propanol and xylene to isolate only calixarenes as a white solid. The purity of this product was checked by ^{1}H-NMR, ^{13}C-NMR and ESI-MS analyses, highlighting only the presence of cyclic structures.

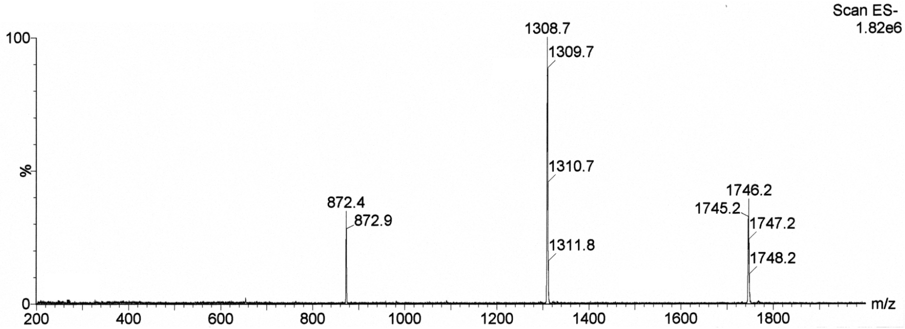

Figure (8.24): *ESI-MS analysis of p-tert-octylcalix[6,8]arenes (**4**)*

The ESI-MS spectrum (Figure 8.24) shows the presence of the only p-tert-octylcalix[6]- and -[8]arenes, highlighting the efficacy of the purification process. In detail, whereas the signals of the mono-deprotonated compounds are at 1308.7 and 1746.2 m/z, the signal of the bis-deprotonated p-tert-octylcalix[8]arene is shown at 872.4 m/z.

The ^{1}H-NMR spectrum (Figure 8.25) of this product reports the signals due to alkyl chains at 1.77, 1.38 and 0.80 ppm, whereas the doublets of the axial and equatorial protons appears between 4.5 and 3.5 ppm (inset "A" in Figure 8.25). The appearance of different broad signals in lack of homogeneity of this region is caused by the simultaneous presence of the two chemical species (cyclic hexamer and octamer), whose methylene bridges resonate at different chemical shifts.

The OH group of the cyclic species are detected at 10.35 and 9.49 ppm (respectively due to p-tert-octylcalix[6]- and -[8]arene). The aromatic protons give rise to signals perfectly superimposed at 7.22 ppm.

Further confirmation of the cyclic structures was provided by ^{13}C-NMR analysis in Figure 8.26. The aromatic peaks are reported at 146.5, 143.7, 128.3 and 126.3 ppm, whereas the carbons of alkyl chain are detected at 57.0, 38.0, 32.1, 31.7 and 31.6 ppm. Lastly, the methylene bridges can be identified by the peak at 32.5 ppm.

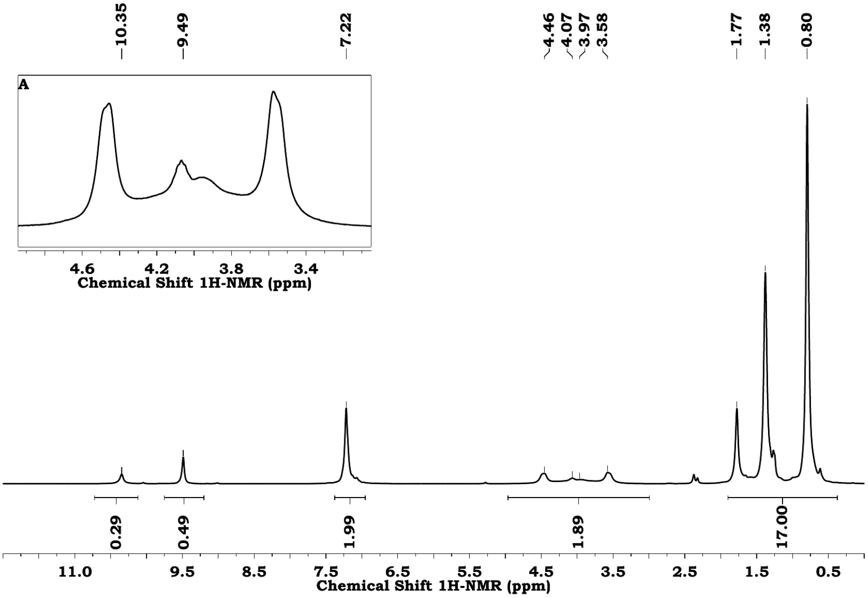

Figure (8.25): *^{1}H-NMR of p-tert-octylcalix[6,8]arenes (**4**)*

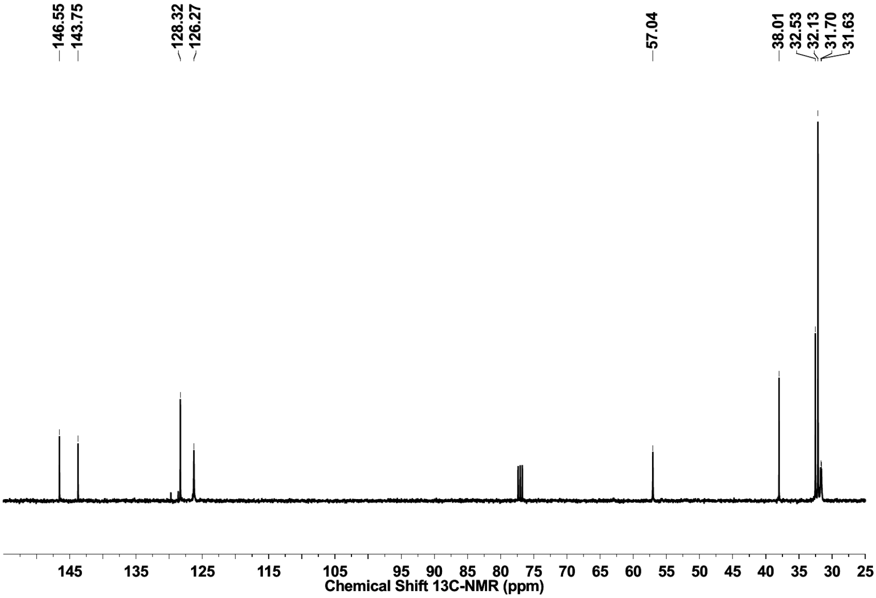

Figure (8.26): *^{13}C-NMR of p-tert-octylcalix[6,8]arenes (**4**)*

8.5 Functionalization with acid groups

The functionalization step of both p-tert-octyl and p-dodecylcalixarene mixtures (Section 8.3 and 8.4) was necessary to increase the capacity of the calixarene derivatives to complex calcium ions and to increase the amount of $CaCO_3$ incorporation in the final detergent. For these reasons, the functionalization of the mixtures with acetic acid moieties was required.

To introduce this kind of functional groups, a previous step of functionalization with ethyl α-bromoacetate was carried out. In the next Sections, the functionalizations of p-dodecyl- and p-tert-octylcalixarenes are described.

8.5.1 p-dodecylcalixarenes and analogous open-chain compounds

In Figure 8.27 the scheme of the first functionalization step is reported. As shown, the introduction of ester groups in the mixture of p-dodecylcalixarenes and analogous open-chain compounds was carried out using ethyl α-bromoacetate as alkylating agent.

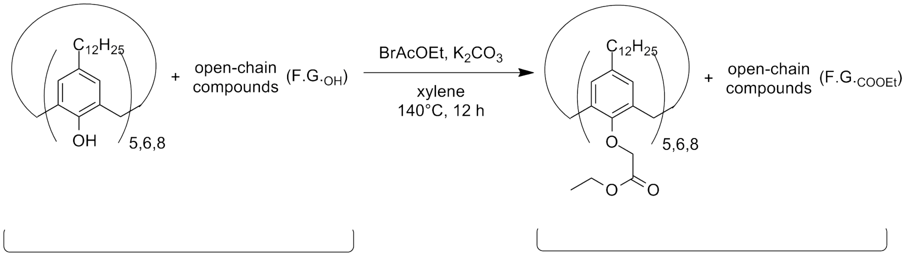

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Figure (8.27): *Functionalization of p-dodecylcalixarenes and analogous open-chain compounds with BrAcOEt*

In a 2.5 L reactor 232.7 g of p-dodecylcalix[5,6,8]arenes and analogous open-chain compounds at 77.5 % by weight in xylene (0.641 $\text{mol}_{m.u.}$)[1] were added to the mixture composed of 320.2 g of xylene, 123.8 g of K_2CO_3 (0.896 mol) and 141.9 g of ethyl α-bromoacetate (0.833 mol). The mixture was heated to 140 °C for 12 hours. At room temperature, a 10 M solution of HCl_{aq} was added, the organic phases were separated and the solvent removed under reduced pressure.

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[1] $\text{mol}_{m.u.}$: moles of monomer unit in the sample.

In this way, the exhaustive functionalization of the OH groups of the starting material was achieved, as already reported in the literature for similar calixarenes. This excellent result was confirmed by NMR analyses.

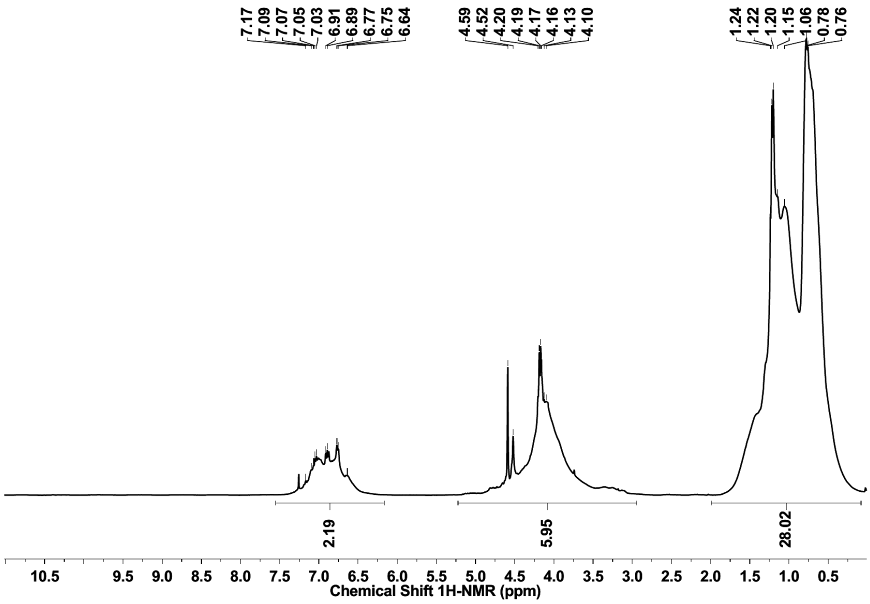

Figure (8.28): *^{1}H-NMR of p-dodecylcalixarenes and analogous open-chain compounds with ester groups*

The ^{1}H-NMR spectrum (Figure 8.28) shows three main groups of signals: (i) an aromatic region (7.5–6.5 ppm) with integral of roughly 2 H, (ii) an aliphatic multiplet (1.8–0 ppm) with area 28 H and (iii) a region around 4 ppm whose signals has an integral of 6 H. While multiplets on the left part of this spectrum are due to aromatic protons of the calixarene structures (2 H for each monomer unit) or open-chain compounds (2 H or more for each monomer unit), the aliphatic signals are associated to the alkyl chains ($C_{12}H_{25}$) and to the CH_3 groups of the ester residues. Finally, methylene bridges, CH_2OH residues (open-chain compounds) and four protons of the $PhO{-}CH_2COOCH_2CH_3$ groups are detected between 5.2 and 3.0 ppm. The absence of signals at chemical shift higher than 7.5 ppm confirms the complete functionalization of the starting mixture.

In the ^{13}C-NMR spectrum (Figure 8.29), broadened signals due to calixarenes are distinguised by the sharp peaks associated with open-chain

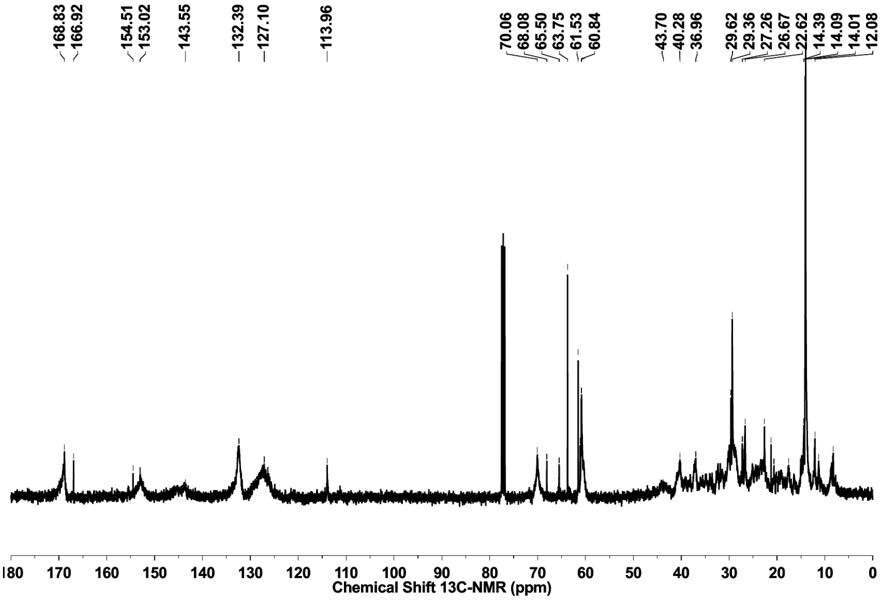

Figure (8.29): *^{13}C-NMR of p-dodecylcalixarenes and analogous open-chain compounds with ester groups*

compounds. In detail, the high degree of functionalization was also confirmed by signals at 168.8 and 166.9 ppm (COOEt of calixarenes and open-chain structures, respectively); 153.0 and 154.5 ppm (CO−R); 70.0, 68.1 and 65.5 ppm (PhO−CH_2); 60.8, 63.7 and 61.5 ppm (COO−CH_2) and 14.1 ppm (OCH_2−CH_3).

The presence of C−H residues in ortho positions on the phenolic rings (only due to open-chain compounds) was confirmed by a peak at 114.0 ppm (see ^{13}C-NMR in Figure 8.5).

The mixture of these ester intermediates was subsequently hydrolyzed according to the diagram in Figure 8.30.

This last step was achieved adding to the mixture 372.5 g of xylene, 10.2 g of PEG400, 250 g of water and 65.1 g of KOH at 85 % by weight (0.988 mol). The mixture was heated to 100 °C for 12 hours.

The correct outcome of the overall synthesis was confirmed by NMR analyses, where no signal due to ethyl group of the ester can be detected.

In detail, the inset "A" in Figure 8.31 shows aromatic signals between 7.2 and 6.5 ppm, whereas the broadened peak of acid proton are present at 7.62

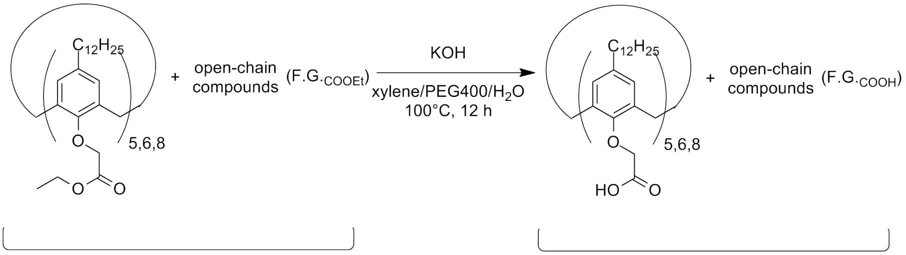

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Figure (8.30): *Synthesis of p-dodecylcalixarenes and analogous open-chain compounds with acid groups*

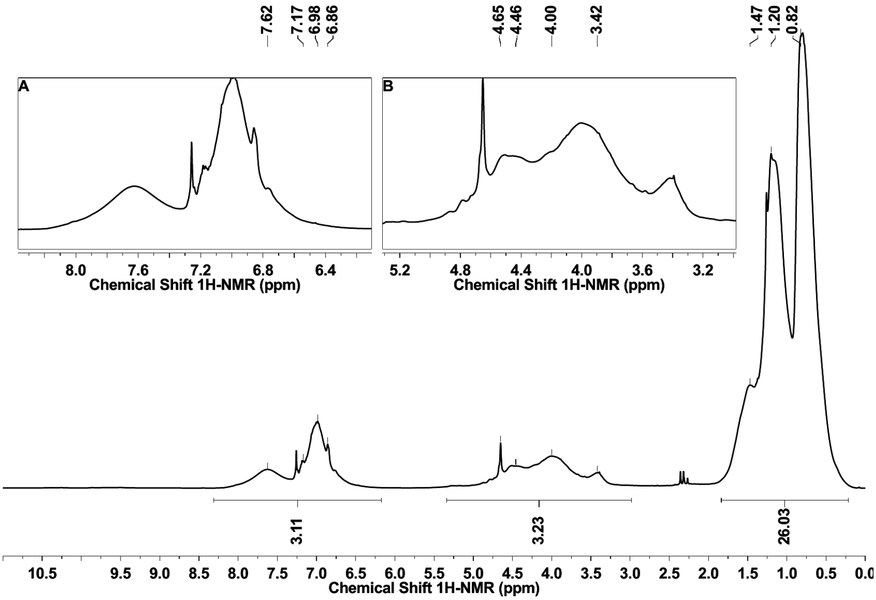

Figure (8.31): *^{1}H-NMR of p-dodecylcalixarenes and analogous open-chain compounds with acid groups*

ppm.

However, to confirm the absence of ester residue in the mixture, a ^{13}C-NMR analysis was also reported. For this purpose, ^{13}C APT (Attached Proton Test) NMR of this sample was performed. With this type of experiment, carbons unattached to protons and CH_2 signals can be distinguished from CH and CH_3 signals. Methine (CH) and methyl (CH_3) signals are positive, while quaternary (C) and methylene (CH_2) signals are negative.

In detail, the ^{13}C APT NMR spectrum reports the carboxylic acid signal at

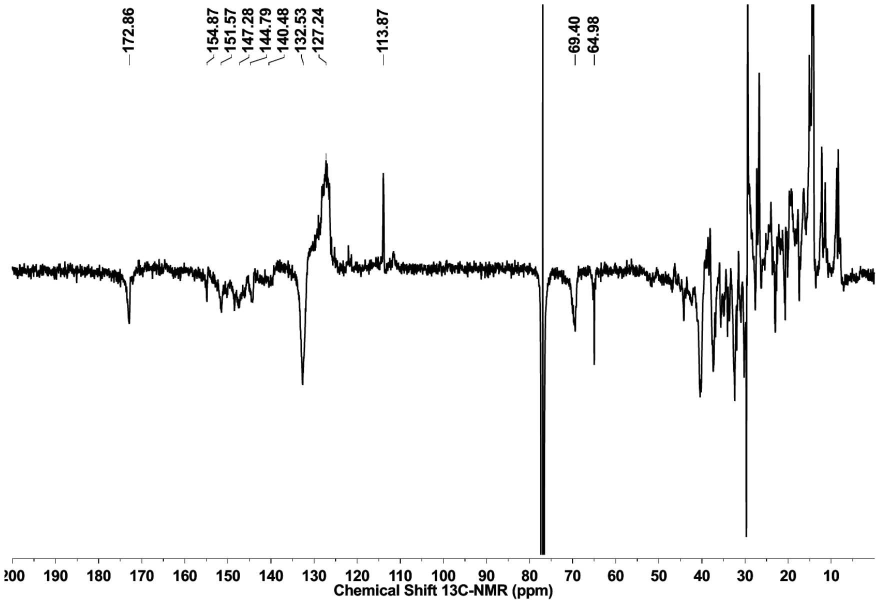

Figure (8.32): *^{13}C APT NMR of p-dodecylcalixarenes and analogous open-chain compounds with acid groups*

172.9 ppm, whereas PhO−CH_2 signals are shown at 69.4 ppm in calixarene structures and 65.0 ppm in open-chain compounds. Once more, the presence of C−H residues in ortho positions on the phenolic rings (only due to open-chain compounds) are confirmed by the peak at 113.8 ppm.

8.5.2 p-tert-octylcalix[6,8]arenes

A synthetic approach similar to that discussed in the Section 8.5.1 was also used in the analogous functionalization of p-tert-octylcalix[6,8]arenes (Figure 8.33).

The ^{1}H-NMR analysis (Figure 8.34) shows aproper ratio between integrals of the signals in the aromatic region, in the aliphatic portion of the spectrum and around 4 ppm. In detail, an integral of 2 H for the singlet close to 7 ppm is in agreement with the presence of two aromatic protons. The integral of 20 H in the aliphatic region is due to 17 protons in the alkyl chain and 3 protons in $OCH_2{-}CH_3$ of the ester moiety. Around 4 ppm, the 2 H of methylene bridge and 4 H of the acetate group (PhO−CH_2 and O−CH_2CH_3) resonate.

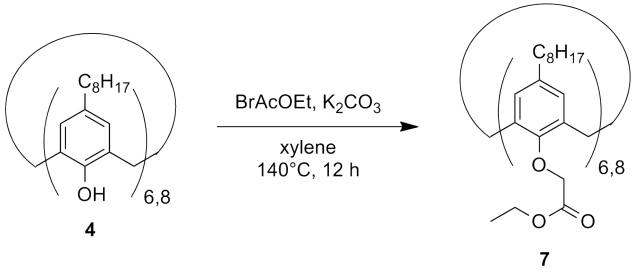

Figure (8.33): *Functionalization of p-tert-octylcalix[6,8]arenes with BrAcOEt*

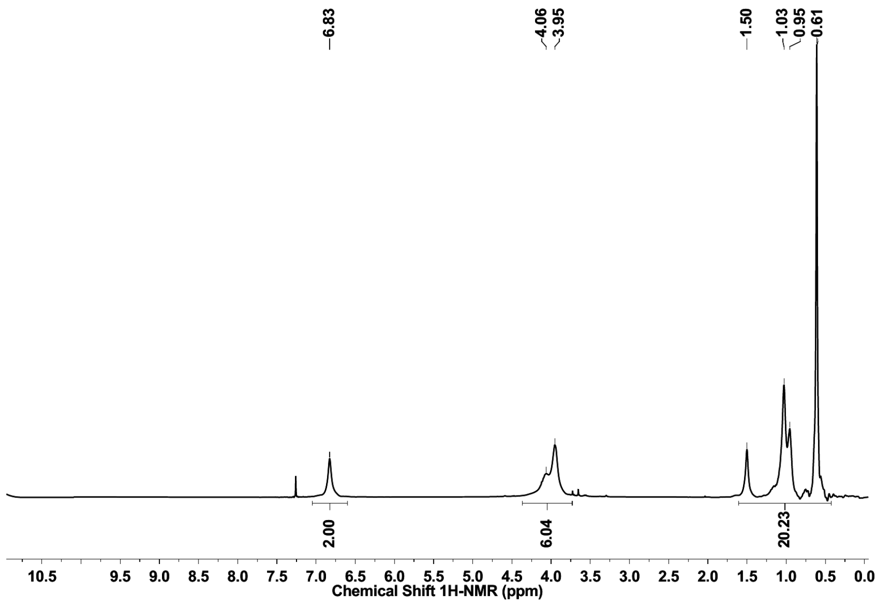

Figure (8.34): *^{1}H-NMR of p-tert-octylcalix[6,8]arenes with ester groups*

The ^{13}C-NMR analysis (Figure 8.35) shows the signals due to the ester residue at 168.7 (COOEt), 69.8 (PhO$-$CH$_2$), 60.8 (COOCH$_2$) and 13.9 ppm (OCH$_2-$CH$_3$).

These ester intermediates were subsequently submitted to a base-induced hydrolysis step to obtain the desired acid derivatives (Figure 8.36).

This last phase of the synthetic process was carried out adding 57.6 g of p-tert-octylcalix[6,8]arenes **7** (0.189 mol$_{m.u.}$) to a mixture of xylene, PEG400, water and 33.7 g of KOH 85 % by weight (0.511 mol). The mixture was heated to 100 °C for 12 hours.

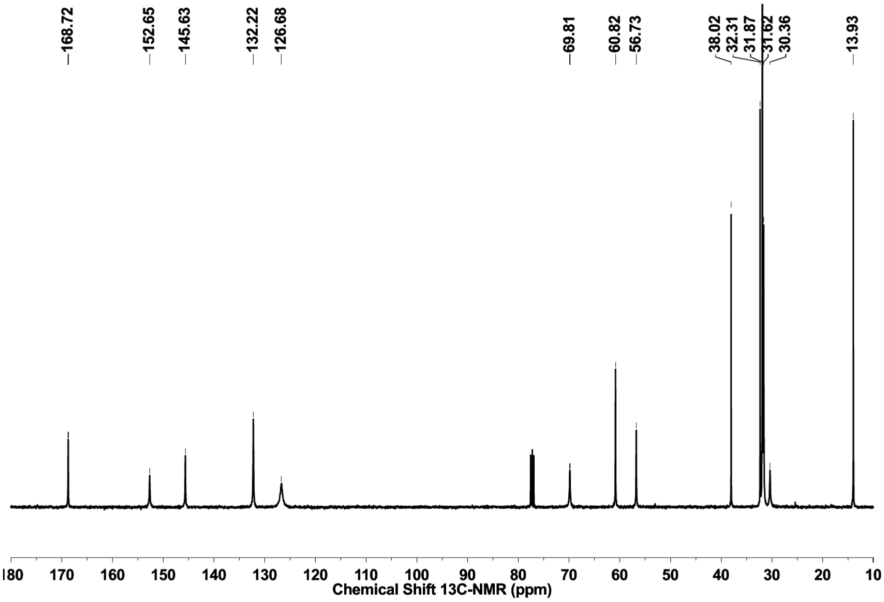

Figure (8.35): *^{13}C-NMR of p-tert-octylcalix[6,8]arenes with ester groups*

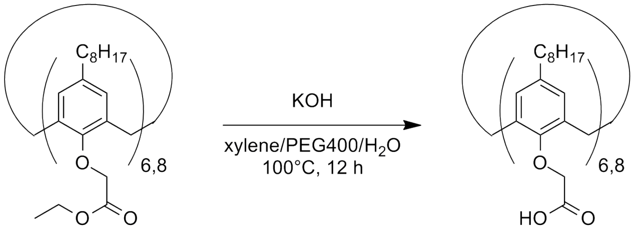

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Figure (8.36): *Synthesis of p-tert-octylcalix[6,8]arenes bearing acetic acid groups*

The NMR analyses, where no signals due to ethyl group of the ester can be detected, confirmed the proper outcome of the reaction.

In detail, the ^{1}H-NMR spectrum (Figure 8.37) reports the signal due to carboxylic acid proton at 10.34 ppm. Protons of methylene bridge and of the PhO−C*H*COO are detected between 5.5 and 3.5 ppm, whereas the singlet of aromatic protons is at 7.00 ppm.

In the ^{13}C-NMR spectrum analysis, inset "A" in Figure 8.38 shows the carboxylic acid signal at 172.5 ppm, whereas the signal at 69.5 ppm (PhO−CH_2COO) confirms the correct derivatization reaction.

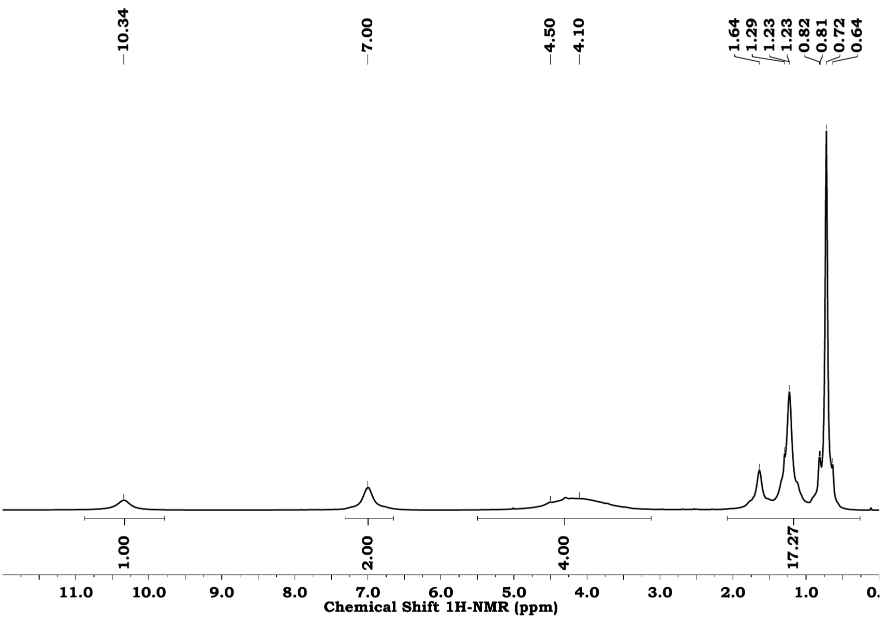


Figure (8.37): ^{1}H-NMR *of p-tert-octylcalix[6,8]arenes bearing acetic acid groups*

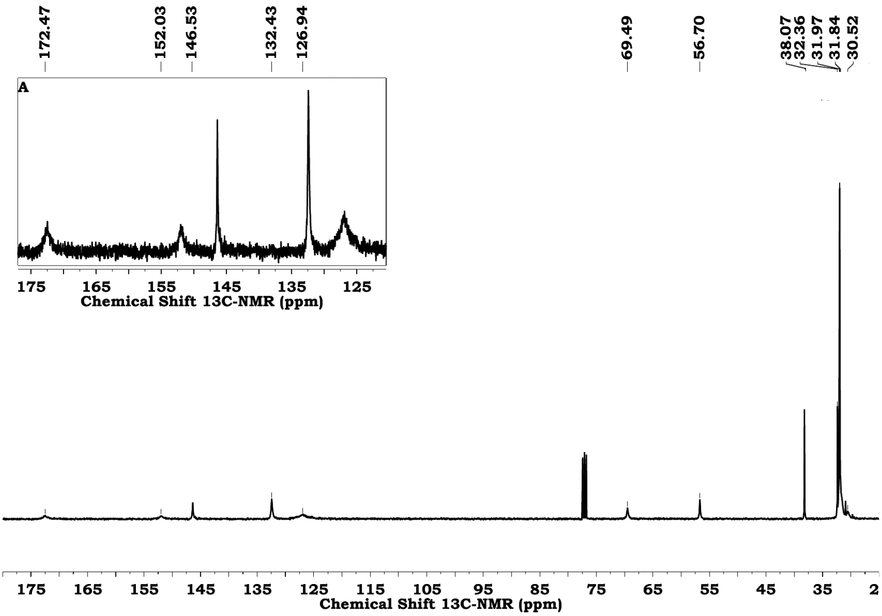


Figure (8.38): ^{13}C-NMR *of p-tert-octylcalix[6,8]arenes bearing acetic acid groups*

8.6 Synthesis of new calixarene-based detergents

The calixarene derivatives previously obtained (Sections 8.5.1 and 8.5.2) were used for the syntheses of calcium-based detergents. In the following Sections, the comparison among the obtained detergents is reported.

The full report on esperimental details of their synthetic processes is described in the Section 10.7 of this thesis. However, a brief summary is also given here.

The syntheses of calixarene-based detergents is a quite complicated and tricky process which need the careful compliance of a precise protocol consisting of different steps.

During the first step (salification), the base oil (SN 150S), organic acid compounds, $Ca(OH)_2$ (lime) and solvents (2-ethylhexanol and ethylene glycol) were mixed to form the corresponding organic acid calcium salts (soaps). The organic acids tested in this process were the calixarenes derivatives, alone or in mixture with alkylcarboxylic acids such as isostearic acid. The calixarene derivatives were added to the reaction vessel as solids or as xylene solutions. The salification was performed at a temperature of about 130 °C and, to increase the salification degree, the water formed in this phase was removed as H_2O/2-ethylhexanol azeotrope, using a Dean Stark apparatus.

The calixarene based detergents more studied in this Thesis are the "overbased" detergents, which contain a reserve of alkalinity in the form of $CaCO_3$. In these cases the process of salification was carried out using an excess of lime, the amount of which was in relation with the desired basicity of the final product. In a second step the calcium hydroxide in excess was transformed into calcium carbonate by bubbling a weighted amount of CO_2 into the reaction mixture.

Carbonation is a critical step of the detergents production process, as the success of this phase influences the alkalinity and the colloidal stability of the final product. The results of these studies show that, in the case of calixarene-based detergents with very high alkalinity, to perform a partial carbonation of the lime is necessary, in such a way to leave an optimal amount of free lime able to stabilize the colloidal structure of the product.

The carbonation step was performed at 130 °C in a time between 1 and 3 h, depending on the alkalinity of the final product. The CO_2 addition was performed with a feed rate sufficient to obtain its complete absorption in the reaction mixture and to ensure its desired dosage. Another factor that determines the success of the carbonation step is the presence of an adequate amount of ethylene glycol, which has the function of promoting the reaction making possible the complete absorption of the carbon dioxide. For this reason it is advisable to add 2 portions of ethylene glycol, one before the salification and the other before the carbonation, because a part of glycol could be removed with the water during the salification process.

The water formed during the carbonation step was then removed by distillation from the reaction mixture together with the solvents, operating at a temperature up to 200 °C and at reduced pressure. During this process, reverse micelles characterized by a $CaCO_3$ core are formed. Such cores are kept in oil solution by the organic acid soaps which direct the polar groups toward the inorganic nanoparticle and the lipophilic tails towards the base oil SN 150S.

Normally these mixtures were submitted to filtration and/or centrifugation processes to remove the insoluble inorganic particles not properly suspended, achieving the final detergent. The filtration could be a critical step in the industrial scale production of the common detergents and, in the worst cases, the production could be blocked, causing significant economic losses. For this reason, calixarene-based detergent with good filterability besides excellent detergent properties had to be synthetized. The products were then characterized by acid-base titrations, which give the corresponding values of TBN (Total Base Number) and of free alkalinity (DBN, Direct Base Number). These measurements of alkalinity are expressed in terms of the equivalent number of milligrams of KOH per gram of sample (mg_{KOH}/g). The value of DBN measures the alkalinity due only to the $Ca(OH)_2$ content in the detergent, whereas to the value of TBN contribute all the base species present in the detergent. In particular, the contribution to the TBN of detergents is given, in addition to $CaCO_3$ and $Ca(OH)_2$, by the calcium salts of the calixarene derivatives and by calcium isostearate.

As already mentioned, a small amount of free $Ca(OH)_2$ (measured as DBN) is desired to stabilize the detergent. On the other hand, too high value of DBN can lead to a not complete compatibility of the detergent with other lubricant additives (for example dispersants), limiting its use. For these reasons, the synthesis of detergents with relatively low value of DBN (lower than 60 mg_{KOH}/g) is desired.

The final detergents are characterized also by their kinematic viscosity at 100 °C. To have low values of viscosity is quite important to ensure a fair detergent ductility during subsequent blending processes with other additives. Furthermore, very high values of viscosity may affect negatively also the syntheses on an industrial scale, for example during the filtration step. For this reason, viscosity values at 100 °C under 300 cSt are preferable.

The quality of the detergent are also monitored as a function of its turbidity. This is the haziness of a fluid (in our case the detergent) and it is a measure of the numbers of individual particles that are generally invisible to the naked eye. Turbidity measurements are performed on a solution at 5 % by weight of detergent in base oil (SN 150S) and are based on the use of an instrument called "nephelometer", where the detector is positioned at a side of the light beam. If there are lots of small particles in the sample, the light beam is scattered and more light reaches the detector. The units of turbidity for a calibrated nephelometer are called Nephelometric Turbidity Units (NTU). The higher is the value of NTU, the worse (more cloudy) the detergent appears.

In the following part of this Chapter, comparisons among different calixarene-based detergents are discussed. The full description of the detergents synthesis procedures was reported in the Section 10.7 of this Thesis.

8.6.1 Effect of the calixarene acid functionalization on the salification degree

To verify the effect on the calixarene salification degree of their acid groups (PhOH or COOH groups), the comparison between the fully- (**6**) and non-functionalizated mixture (**2**) was done. In detail, the batches containing mixtures of p-dodecylcalixarenes and analogous open-chain compounds (Section 8.5.1) were used for this purpose. This comparison was made by preparing "neutral" detergents with an expected soap content of 51.5 % by weight. Such product was obtained by reaction of the calixarenes with a stoichiometric amount of $Ca(OH)_2$ (Table 8.1).

The incorporation efficiency of calcium, reported in Table 8.1, was calculated from the experimental and theoretical calcium contents in the detergent. The neutralization degree was calculated from experimental TBN (due to calixarene soap and $Ca(OH)_2$), DBN (due to $Ca(OH)_2$) and theoretical TBN (due to calixarene soap), while the soap content was calculated from theoretical soap content and neutralization degree.

As reported in Table 8.1, the functionalization with carboxylic acid groups

Table (8.1): *Effect of the calixarene acid functionalization on the salification degree*

ID detergent	**D1**	**D2**
Type of Calixarenes		
ID calixarene	**2**	**6**
Alkyl chain	$C_{12}H_{25}$	$C_{12}H_{25}$
Funct. degree (%)	0	100
Product features		
Calcium content (% w/w)	2.80	2.88
Viscosity 100 °C (cSt)	112.3	890.3
TBN (mg_{KOH}/g)	78.5	81.0
DBN (mg_{KOH}/g)	62.01	0
Turbidity (NTU)	11.6	5.0
Results		
Filtration	very slow	fast
Incorporation eff. of Ca (%, calc.)	81.4	100
Neutralization degree (%, calc.)	17.1	100
Soap content (% w/w, calc.)	8.8	51.5

determines the complete neutralization of the calixarenes, ensuring an efficient incorporation of calcium ions and a high soap content in the final detergent. Lastly, the full incorporation of calcium in the detergent ensures a high filterability of the final material, as shown by the comparison between detergent **D1** and **D2**. In fact, there were no insoluble particles able to plug the filter in detergent **D2** and so its filtration results fast and steady. From the results shown in the Table 8.1, the synthesis of calixarenes with carboxylic acid groups (**6**) was necessary to obtain detergents of high quality and high performance.

8.6.2 Effect of the length of the alkyl chains in calixarene structures

To verify the effect due to the length of the alkyl chains in calixarene structures on the final products, a comparison between the p-tert-octyl and p-dodecyl calixarene, both completely functionalizated, was carried out. Different overbased detergents were synthetized using these calixarene derivatives.

Detergents having TBN 300 and an expected total soap content of about 46 % were prepared, using roughly the same amount of isostearic acid as co-soap in the two preparations to decrease the viscosity and the final cost of the detergent. In particular, a 1:2.1 by weight ratio between calixarene and isostearic acid was used for the preparation of the detergents.

Table (8.2): *Effect of the length of the alkyl chains in calixarene structures*

ID detergent	**D3**	**D4**
Type of Calixarenes		
ID calixarene	**8**	**6**
Alkyl chain	C_8H_{17}	$C_{12}H_{25}$
Funct. degree (%)	100	100
Product features		
Calcium content (% w/w)	11.04	11.46
Viscosity 100 °C (cSt)	234.8	194.4
TBN (mg_{KOH}/g)	309.0	320.8
Turbidity (NTU)	5.6	6.0
Results		
Filtration	slow	slow
Incorporation eff. of Ca (%, calc.)	87.5	92.2
Calcium isostearate (% w/w, calc.)	32.2	31.9
Calcium calixarate (% w/w, calc.)	15.6	15.2
Soap content (% w/w, calc.)	47.8	47.1

The incorporation efficiency of calcium, reported in Table 8.2 was calculated as already explained in Section 8.6.1, while the soap content was calculated from the mass balance of the reactions and considering the calixarenes and the isostearic acid as completely salified by $Ca(OH)_2$.

As reported in Table 8.2, the use of a functionalized calixarene structure with longer alkyl chains ensures a higher quality of the final product. In fact, the detergent **D4** shows a higher calcium incorporation efficiency than the product **D3**. In this way, a greater value of TBN can be achieved. Moreover, the detergent **D4** has a lower viscosity than the product **D3**.

The performances of the two detergents were evaluated in an automotive lubricant formulation. The results of the evaluation were reported in Section 8.6.5.

8.6.3 Effect of the higher salification degree

To verify the effect of different salification degrees in the calixarene-based detergents, two products having TBN 300 were synthetized. In detail, the detergent **D5** was prepared using the non-functionalizated p-dodecylcalixarenes (**2**), whereas the synthesis of **D6** was achieved using the fully-functionalizated one (**6**). Both the detergents were prepared using the same amount of isostearic acid as co-soap, and a 1:1 weight ratio between calixarene and isostearic acid. This weight ratio was increased compared to the detergents **D3** and **D4** (Section 8.6.2) in order to evaluate if the increase of calixarene soap in the detergent leads to the improvement of its characteristics and performances.

Table (8.3): *Effect of the higher salification degree in detergents TBN 300*

ID detergent	**D5**	**D6**
Type of Calixarenes		
ID calixarene	**2**	**6**
Alkyl chain	$C_{12}H_{25}$	$C_{12}H_{25}$
Funct. degree (%)	0	100
Product features		
Calcium content (% w/w)	10.27	10.88
Viscosity 100 °C (cSt)	80.5	140.8
TBN (mg_{KOH}/g)	290.5	304.5
DBN (mg_{KOH}/g)	15.3	14.4
Turbidity (NTU)	4.2	5.1
Results		
Filtration	slow	medium
Incorporation eff. of Ca (%, calc.)	93.7	99.4
Carbonatation (%, calc.)	94	93.6
Calcium isostearate (% w/w, calc.)	23.1	23.2
Calcium calixarate (% w/w, calc.)	4.0	23.0
Soap content (% w/w, calc.)	27.1	46.2

The soap contents of Table 8.3 was calculated from the mass balance of the reactions and considering the functionalized calixarenes (**6**) and the isostearic acid as completely salified, while the non-functionalized calixarene (**2**) as partially salified (17.1 %, as shown by detergent **D1** in Section 8.6.1). As reported in Table 8.3, the fully-functionalizated p-dodecyl derivatives

(**6**) ensured a higher value of TBN. Since the values of DBN of the two products were quite similar, the lower value of TBN in the detergent **D5** has presumably to be ascribed to a loss of $CaCO_3$ during the filtration process. This result could be explained by an increase in the complexing power given by the functionalization of the calixarene structures, as planned by the design of our detergent. Besides, the increase of calixarene soap in detergent **D6** compared to detergent **D5** (Section 8.6.2) led to an improvement of the filterability and incorporation efficiency of calcium.

The detergents were evaluated in an automotive lubricant formulation. The results of the evaluation were reported in Section 8.6.5.

From these excellent results, the synthesis of a detergent having an even higher TBN (TBN 400) was planned, as discussed in the next Section.

8.6.4 Synthesis of calixarene-based detergent having TBN 400

The high alkalinity detergents (TBN 400) find application mainly in marine lubricants. The most common detergents used for this application are those based on calcium sulfonates, which, in some cases, do not ensure the requested detergency performances. For this reason, the development of new high alkalinity detergents is needed.

In this context we studied the synthesis of a calixarene based detergent having a TBN 400. Their synthesis was much more insidious than that of the detergents discussed so far. This was mainly due to the need of keeping an extremely high amount of $CaCO_3$ in the final detergent, decreasing the amount of base oil to be used. This fact could cause stability problems of the product and also a significant increase of its viscosity, which could cause serious problem during the synthesis of the detergent on a large scale. The use of the totally functionalized p-dodecylcalixarenes (**6**) allowed to overcome the viscosity problem, but also improvements of the synthesis process became necessary.

The improvements are related to the carbonation step and to the final purification step of the product. Relatively to carbonation step a partial carbonation of the lime (carbonation degree of about 85 %) is necessary to leave an optimal amount of free lime able to stabilize the colloidal structure of the product.

Relatively to the purification step, the direct filtration of the product, after the stripping of the solvents, was not possible, because the relatively high quantity of solid impurities plugged the filter. The problem was solved performing firstly the certrifugation of the product, after its dilution in xylene, to remove the coarse particles. Subsequentely the filtration of the liquid phase was performed to obtain, after removal of the solvent by distillation, the detergent with the desired characteristics.

Using the improved process and an acid mixture of functionalized p-dodecylcalixarenes (**6**) and isostearic acid in a 1:1 weight ratio, was possible to obtain a detergent whose characteristics were reported in Table 8.4.

Table (8.4): *Characterization of calixarene-based detergent having TBN 400*

ID detergent	**D7**
Type of Calixarenes	
ID calixarene	**6**
Alkyl chain	$C_{12}H_{25}$
Funct. degree (%)	100
Product features	
Calcium content (% w/w)	14.46
Viscosity 100 °C (cSt)	237.5
TBN (mg_{KOH}/g)	404.5
DBN (mg_{KOH}/g)	52.2
Turbidity (NTU)	7.5
Results	
Filtration	medium (after centrifugation)
Incorporation eff. of Ca (%, calc.)	98.3
Carbonatation (%, calc.)	85.0
Calcium isostearate (% w/w, calc.)	23.2
Calcium calixarate (% w/w, calc.)	23.0
Soap content (% w/w, calc.)	46.2

From the data of Table 8.4, TBN and DBN reach the desired values, while turbidity value are still very good and, in any case, much lower than that of commercial high alkalinity detergents based on calcium sulfonates, which normally have a turbidity of about 30 NTU. This characteristic, that indicates a high stability of the colloidal structure of the detergent, is important to obtain very clear and bright lubricants.

The viscosity at 100 °C was higher compared to the detergent **D6** in Table 8.3, but it is acceptable for a high alkalinity product.

All these good results support the conclusion that the detergent having TBN 400 has all the characteristics to be evaluated by engine tests. For this reason the pilot scale production of this detergent is ongoing to obtain an amount of product to perform the tests. The first results of pilot scale production studies were promising and similar to those obtained on laboratory scale, indicating the scale up feasibility of the production process.

8.6.5 Lubricant formulations with calixarene based detergents

With the purpose of testing the calixarene based detergents in automotive lubricants, 4 additive packages (concentrated mixture of additives) **P1**, **P2**, **P3** and **P4** (Table 8.5) containing respectively the detergents **D3**, **D4**, **D5** and **D6** (Table 8.2 and Table 8.1) at a concentration of 10.3 % by weight were prepared. Besides, a package (**P5** in Table 8.5) containing the commercial calcium alkylbenzenesulfonates detergents ENI MX 3280 and ENI MX 3245, at a total concentration of 13.1 % by weight, was prepared.

ENI MX 3280 is a low alkalinity detergent characterized by: TBN 24 mg_{KOH}/g, calcium content = 2.8 % by weight, soap content = 49 % by weight.

ENI MX 3245 is instead an overbased detergent characterized by: TBN = 308 mg_{KOH}/g, calcium content = 12 % by weight, soap content = 27 % by weight.

The packages from **P1** to **P5** contain other additives, which are the same and at the same concentration for all the packages. These additives are: dispersants, antioxidants, antiwear additives and friction modifiers.

Using the packages from **P1** to **P5**, we prepared the corresponding automotive lubricants (from **L1** to **L5**) of viscosity grade SAE 5W-30, which present the following composition:

- base oil (SN 150S): 78.8 % weight;
- additive package: 16 % by weight;
- viscosity index improver: 5 % by weight;
- pour point depressant additive: 0.2 % by weight.

All lubricants (from **L1** to **L5**) contain the same base oil, the same additive viscosity index improver and the same additive pour point depressant.

The lubricants were subsequently characterized by determining the following parameters: kinematic viscosity at 100 °C and 40 °C, viscosity index, total base number (TBN), calcium content and deposits at high temperature (method ASTM D 7097)[6]. The latter parameter is determined by the method TEOST MHT (Thermo-Oxidation Engine Oil Simulation Test), which is employed to evaluate the ability of an engine oil to control the formation of deposits at high temperatures. This method consists in the determination of the weight of deposits formed in oxidant conditions (air flow) as a result of recirculation of a sample of oil, containing a small amount of catalyst, through a special rod electrically heated at a temperature of 285 °C. The duration of the test is 24 hours. The method determines the total deposits as the sum of the deposits on the rod and those collected on a filter after washing of the rod with a solvent.

Table (8.5): *Lubricant formulations with calixarene based detergents*

Additives package

ID package	**P1**	**P2**	**P3**	**P4**	**P5**
ID detergent	**D3**	**D4**	**D5**	**D6**	ENI MX3245 + ENI MX3280
Detergent (% w/w)	10.3	10.3	10.3	10.3	13.1

Lubricant 5W-30: Composition

ID Lubricant	**L1**	**L2**	**L3**	**L4**	**L5**
Base oils (% w/w)	78.8	78.8	78.8	78.8	78.8
Additives package (% w/w)	16.0	16.0	16.0	16.0	16.0
Viscosity Index improver (% w/w)	5.0	5.0	5.0	5.0	5.0
Pour Point Depressant (% w/w)	0.2	0.2	0.2	0.2	0.2
Soap from detergents (% w/w)	0.79	0.78	0.76	0.45	0.76
Calcium isostearate (% w/w)	0.53	0.53	0.38	0.38	—
Calixarene calcium salt (% w/w)	0.26	0.25	0.38	0.07	—

Lubricant 5W-30: Characterization

KV 40°C (cSt)	75.95	75.40	74.23	71.43	76.23
KV 100°C (cSt)	11.90	11.79	11.64	11.31	11.93
Viscosity Index	153	153	152	153	153
TBN (mg$_{KOH}$/g)	9.4	9.6	9.40	9.10	8.2
Calcium content (% w/w)	0.183	0.188	0.178	0.168	0.162
Total deposits TEOST MHT (mg)	6.9	6.4	4.6	18.1	19.2

The results reported in Table 8.5 shows that the lubricants **L1**, **L2** and **L3**, containing detergents based on calixarenes completely functionalized with carboxylic acid groups (**6**), have better detergency properties in comparison to the lubricant **L4**, containing a detergent based on non-functionalized calixarenes (**2**) and in comparison to the lubricant **L5** formulated with conventional detergents based on calcium alkylbenzensulfonates. Such behavior was highlighted by TEOST MHT. In particular, the lubricants **L1**, **L2** and **L3** give a lower formation of deposits compared to the lubricant formulations **L4** and **L5**.

The best performance of the lubricant formulations containing detergents based on functionalized calixarenes compared to that based on non-functionalized calixarenes is principally due to a higher content of soap and in particular of calcium salts of calixarenes (see Table 8.5). Furthermore, between the lubricants **L2** and **L3**, both containing detergents based on functionalized p-dodecylcalixarenes (**6**) and with the same content of soap (calcium salts of calixarenes + calcium isostearate), the lower deposits formation was observed in the lubricant **L3**, which has a higher content of calixarene soap than the lubricant **L2**.

Bibliography

[1] I. D. Cunningham, J.-P. Courtois, T. N. Danks, D. M. Heyes, D. J. Moreton and S. E. Taylor, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2003, **229**, 137 – 147.

[2] A. Casnati, D. Sciotto and G. Arena, in *Calixarenes 2001*, Springer, 2001, pp. 440 – 456.

[3] A. E. Martell and R. M. Smith, *Critical stability constants*, Springer, 1974, vol. 1.

[4] F. Merger, M. Strohmeyer, G. Sandrock, H. Hohenschutz, L. Schroff and G. Nestler, *Manufacture of p-alkylphenols*, 1980, US Patent 4,198,531.

[5] SASOL, *Alkylphenols – Product range*, http://www.celsius.co.kr/chemicals/download/AlkylphenolsPRGB07.pdf.

[6] ASTM International, West Conshohocken, PA, *ASTM D 7097 – Standard Test Method for Determination of Moderately High Temperature Piston Deposits by Thermo-Oxidation Engine Oil Simulation Test-TEOST MHT*, 2009.

CHAPTER 9

CONCLUSIONS

In this part of Thesis, we have successfully synthetized a new type of calixarenes with long branched alkyl chains (p-dodecyl[n]arenes) for the production of calcium-based detergents with improved oil solubility and stability of reverse micelles of which the detergents are formed. In fact, these calixarenes were used as polycarboxylic acids to synthetize new sulfur-free detergents as lubricant additives. In this way, these detergents may be used for the formulation of new automotive lubricants with low content of ash, phosphorus and sulfur (low SAPS).

The "one-step" synthesis of p-dodecylcalixarenes, optimized in laboratory was subsequently carried out on a pilot scale for the production of 500 kg of sample containing about 70 % of calixarene structures. In particular, we identified cyclic pentamers, hexamers and octamers. These cyclic oligomers do not possess a unique molecular mass, but rather a distribution of molecular masses due to different lengths of the differently branched alkyl chains: from C_8H_{17} to $C_{15}H_{31}$ as demonstrated by ESI-MS analysis of the starting phenol. As a consequence of the long alkyl chains and of the lack of their structural homogeneity, these calixarenes are not solids, but are very viscous liquids. In addition, the lack of homogeneity and the modest difference in polarity between cyclic oligomers prevents effective purification both by direct phase chromatographic column (silica gel) and fractional precipitation. Despite this, the p-dodecyl[8]arene was isolated in small sample in laboratory by chromatographic separation, as evidenced by NMR and ESI-MS analyses.

However, for our purpose the use of well-known p-tert-octylcalixarenes for the preparation of detergents was also necessary to compare its properties to those of the p-dodecylcalixarene derivatives.

To favour the deprotonation degree of OH groups and their capacity to complex calcium ions, the complete functionalization of both mixtures (p-tert-octyl- and p-dodecyl calixarenes) with acetic acid groups was achieved. In this way, the synthesis of new calixarene-based detergents was carried out. In detail, overbased detergents at TBN 300 and TBN 400 were obtained.

Furthermore, with the purpose of testing the calixarene based detergents in automotive lubricants, several additive packages (and corresponding automotive lubricants) containing our detergents were prepared. Besides, a lubricant containing commercial calcium alkylbenzene-sulfonates detergents was prepared for comparison of detergency properties with the calixarene-based oils. From these studies, the new sulfur-free detergents based on p-dodecylcalixarenes completely functionalized with carboxylic acid groups present excellent detergency performance, and therefore can be used for the formulation of the new automotive lubricants with low content of ash, phosphorus and sulfur (low SAPS).

CHAPTER 10

EXPERIMENTAL SECTION

10.1 General information

Most of the solvents and reagents were obtained from commercial sources and used without further purification.

Analytical TLC were performed using prepared plates of silica gel (Merck 60 F-254 on aluminum) and then, according to the functional groups present on the molecules, revealed with UV light or using staining reagents: H_2SO_4 (5 % in EtOH) or basic solution of $KMnO_4$ (0.75 % in H_2O).

Merck silica gel 60 (70–230 mesh) was used for flash chromatography and for preparative TLC plates.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker AV300 and Bruker AV400 spectrometers (observation of ^{1}H nucleus at 300 MHz and 400 MHz, respectively, and of ^{13}C nucleus at 75 MHz and 100 MHz, respectively). All chemical shifts are reported in part per million (ppm) using the residual peak of the deuterated solvent, whose values are referred to tetramethylsilane (TMS, $\delta_{TMS} = 0$), as internal standard.

For descriptions of the multiplicity of ^{1}H-NMR spectra was used the following terminology: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broadened signal.

All ^{13}C-NMR spectra were performed with proton decoupling. The identification of the carbon atoms in the residues of functionalization was performed indicating sequence numbers in according to the proximity of the carbon to the oxygen of the phenol or calixarene derivative.

The spectra were processed with the software MestreNova®.

Electrospray ionization (ESI) mass analyses were performed on a Waters ZMD spectrometer equipped with an electrospray interface.

The nomenclature used for the calixarene derivatives is in accordance with that discussed in the Appendix of this Thesis at pag. 191.

In the case of calixarene derivatives, their millimoles were reported in reference to their monomeric units ($\text{mmol}_{m.u.}$).

10.1.1 Standard test methods for OH groups using acetic anhydride acetylation

The procedure discussed in this Section was obtained from the Annual Book of ASTM Standards.[1]

Procedure

The sample is acetylated using a solution of acetic anhydride in pyridine in a flask at 98 °C for 2 h. Subsequently, the mixture is cooled to room temperature and the excess of acetic anhydride is hydrolyzed by addition of distilled water.

The mixture is poured into a conical flask and the traces of solution in the first flask are retrieved with pyridine. After addition of phenolphthalein (about 3 drops), the acetic acid formed is titrated by a 0.5 M standard solution NaOH_{aq}. The equivalence point is confirmed by a pale pink color of the solution for at least 15 s.

The content of hydroxyl groups is calculated by difference of titrant of white and the solution containing the sample under examination.

Calculation

The calculation of the hydroxyl content in the sample in terms of mass percentage is calculated according to the equation:

$$m_{\%} = \frac{(A - B) * N_t * MM * 100}{W * n * 1000}$$

where:

- A indicates mL of standard solution NaOH_{aq} used for the blank;

- B indicates mL of standard solution $NaOH_{aq}$ used for the sample;
- N_t indicates $meq\,mL^{-1}$ of the solution of titrant (in this circumstance $N_t = 0.5\ meq\,mL^{-1}$);
- n indicates the number of OH groups per molecule (or monomer unit) of the compound (in our case $n = 1$);
- MM indicates the molecular mass of the compound (or monomer unit) in the sample;
- W is the mass of the sample.

10.2 Analytical methods of overbased detergent characterization

10.2.1 Filterability

The products obtained at the end of stripping from synthesis, were filtered in a jacketed filter made of stainless steel at 160 °C and 5 atm. We detect the volume filtered as a function of time. By correlating times and volumes, the filterability was calculated as $L\,h^{-1}\,m^{-2}$. Based on these values, in this thesis the filterability was expressed such as "fast", "medium", "slow" and "very slow".

Procedure

The procedure of filtration was divided in several parts, which were listed below.

1. Prepare the filter, entering the bottom of the filter mesh stainless steel;
2. Replace the filter and heat it to 160 °C;
3. Prepare 100 g of SN 150S oil with addition of 10 g of filtration aid;
4. Open the cover of the filter and pour the suspension of oil in the ground previously prepared;
5. Close the filter and put it in nitrogen pressure in order to filter the oil and forming the filtration panel;

6. When the reaction of preparation of detergents was completed, prepare in the synthesis reactor a suspension constituted by the product (amount of between 500–1000 g) and the adjuvant added in an amount, calculated on the weight of the product to be filtered, of 4 % by weight;
7. Reopen the filter and load the suspension of the adjuvant in the product;
8. Replace the filter, place a graduated beaker of 500 mL under the drain, and apply a pressure of 5 atm;
9. As soon as the product begins to filter, discard the first 50 mL and then measure the time of filtration;
10. Detecting the filtration time for each 100 mL;
11. Extrapolating the values obtained ($\frac{Volume}{Time}$), calculate the volume filtered after 60 min ($V_{60\ min}$);
12. Calculate the filterability (F) as $F = \dfrac{V_{60\ min}}{A_{Filter}\,(dm^3)}$, where A_{Filter} is the filtering surface.

10.2.2 TBN

The procedure discussed in this Section was obtained from the Annual Book of ASTM Standards.[2] In detail, this test method covers the determination of basic constituents in petroleum products by titration with perchloric acid in glacial acetic acid.

TBN (Total Base Number) is the quantity of a specified acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide per gram of sample (mg_{KOH}/g), required to titrate a sample in a specified solvent to a specified endpoint using a specified detection system.

The sample was dissolved in an essentially anhydrous mixture of chlorobenzene and glacial acetic acid and titrated with a solution of perchloric acid in glacial acetic acid using potentiometric titrimeter. A glass indicating electrode and a reference electrode were used, the latter being connected with the sample solution by means of a salt bridge. The meter readings were plotted against the respective volumes of titrating solution, and the end point was taken at the inflection in the resulting curve.

Preferably, the approximate amount of sample ($m_{sample,approx}$) for titration is calculated as $m_{sample,approx}\left(g\right) = \frac{10}{TBN_{expected}}$.

Procedure

1. After addition of 60 mL of titration solvent to the sample, place the sample on the titration stand and stir the solution until the sample is dissolved;
2. position the electrodes in the solution;
3. adjust the instrument in accordance with the manufacturer's instructions and set the titration speed at 1.0 $\mathrm{mL\,min^{-1}}$ maximum;
4. on completion of the titration, remove the beaker and rinse the electrodes with titration solvent, then with water, then again with titration solvent.

10.2.3 DBN

Unlike TBN (Section 10.2.2), DBN (Direct Base Number) the quantity of a specified acid required to titrate the content of $Ca(OH)_2$ in a sample in a specified solvent to a specified endpoint using a specified detection system. As for TBN, DBN is expressed as the equivalent number of milligrams of potassium hydroxide per gram of sample (mg_{KOH}/g).

Procedure

1. The sample (0.1–0.5 g) is mixed well and then weighed into a 250 mL erlenmeyer flask;
2. add 15 mL of SN 150S to the flask and heat on a hot plate;
3. after the organic phase was dissolved in SN 150S, 80 mL of titration solvent (50 % toluene, 49.5 % isopropyl alcohol, 0.5 % water) were added and warmed slightly to dissolve the organic phase;
4. then 25 mL of the sucrose solution (20 % by weight in water) were added and the contents of the flask were heated to a gentle reflux on the hot plate for a few minutes;

5. a magnetic stirbar and 5 drops of phenolphthalein indicator were added;
6. the sample was mixed thoroughly on a magnetic stirrer prior to titration while avoiding physical loss of material;
7. the hot contents of the flask were titrated with 0.1 M HCl_{aq} to the phenolphthalein end point in the aqueous phase. The flask contents were mixed vigorously after each addition.

Warming slightly on a hot plate aided the phase separation.

The base number titration was considered complete when the aqueous phase remained colorless for at least 30 sec on standing.

10.2.4 HAZE

The presence of turbidity (haze) in lubricating oils can be due to a component of the additive, which does not dissolve completely or it is not dispersed as a stable colloid.

The method reported in this thesis gave this glaze using a nephelometer, and it is applicable to all additives, dispersants, detergents and also the finished lubricants.

Procedure

1. Dilute the sample at 5 % in SN 150S;
2. heat the mixture to 60 °C, stirring until complete mixing;
3. fill the measuring cell with the mixture still warm. If the mixture is viscous can be found air bubbles that might affect the misure;
    (a) in this case, put the cell without lid in a stove until the disappearance of the air;
    (b) close the cell and allow it to cool to room temperature.
4. Place the cell with the sample in the compartment of the nephelometer;
5. wait 5 minutes to allow the stabilization of the signal;
6. the HAZE value can be read on the instrument display.

10.2.5 Viscosity

The procedure discussed in this Section was obtained from the Annual Book of ASTM Standards.[3] In detail, this test method covers and specifies a procedure for the concurrent measurement of both the dynamic viscosity (η) and the density (ρ) of liquid petroleum products and crude oils, both transparent and opaque. The kinematic viscosity (ν) can be obtained by dividing the dynamic viscosity by the density obtained at the same test temperature.

The Stabinger viscometer uses a rotational coaxial cylinder measuring system. The outer cylinder (tube) is driven by a motor at a constant and known rotational speed. The low-density inner cylinder (rotor) is held in the axis of rotation by the centrifugal forces of the higher density sample and in its longitudinal position by the magnet and the soft iron ring. Consequently, the system works free of bearing friction as found in rotational viscometers. A permanent magnet in the inner cylinder induces eddy currents in the surrounding copper casing. The rotational speed of the inner cylinder establishes itself as the result of the equilibrium between the driving torque of the viscous forces and the retarding eddy current torque. This rotational speed is measured by an electronic system (Hall effect sensor) by counting the frequency of the rotating magnetic field.

The result obtained from this test method is dependent upon the behavior of the sample and is intended for application to liquids for which the shear stress and shear rate are proportional (Newtonian flow behavior), as for the lubricants.

1. Set the internal temperature control to the desired measuring temperature;
2. make sure that the measuring cells are clean and dry;
3. load a minimum of 3 mL of the sample to the syringe; if enough sample is available it is recommended to fill the entire syringe;
4. leave the syringe in the inlet opening and start the measurement;
5. wait for the instrument to indicate that the determination is valid and record the values;
6. inject a further 1 mL without taking off the syringe and repeat the measurement.

7. If the deviation between two consecutive determinations exceeds the 0.1 % , repeat the measurement until the deviation is within this limit;

8. then remove the syringe, rinse and dry the measuring cell.

10.2.6 TEOST

The thermo-oxidation engine oil simulation test (TEOST®-MHT) protocol[4] was used to obtain information on deposits and the formation of polar volatile organic compounds and, in this way, to evaluate the ability of an engine oil to control the formation of deposits at high temperatures.

This method consists in the determination of the weight of deposits formed in oxidant conditions (dry air flow, 10 $\mathrm{mL\,min^{-1}}$) as a result of recirculation of 8.4 g of sample, containing 0.1 g of Fe-based organo-metallic catalyst, through a special rod electrically heated at a temperature of 285 °C. The duration of the test is 24 hours. The method determines the total deposits as the sum of the deposits on the rod and those collected on a filter after washing of the rod with n-eptane.

10.3 Characterization of raw phenols

10.3.1 p-dodecylphenol (1)

p-dodecylphenol was bought from Sasol and it was used without further purification.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.3–7.1 (m, 2 H, H_m); 6.9–6.8 (m, 2 H, H_o); 5.23 (b, 1 H, OH); 1.9–0.3 (m, 25 H, $C_{12}H_{25}$).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 152.9–152.7 (C_iOH); 142.3–140.2 (C_p); 128.0–127.0 (C_m); 114.8–114.6 (C_o); 50–8 ($C_{12}H_{25}$).

ESI-MS (acetylated derivative): Calculated m/z 327.5. Found m/z 271.4 $[M_8+Na]^+$, 285.5 $[M_9+Na]^+$, 299.5 $[M_{10}+Na]^+$, 313.5 $[M_{11}+Na]^+$, *327.5* $[M_{12}+Na]^+$, 341.5 $[M_{13}+Na]^+$, 355.5 $[M_{14}+Na]^+$, 369.6 $[M_{15}+Na]^+$; where “x” in M_x identifies the number of carbons contained in the alkyl chain: for example M_{10} identifies all the phenols with $C_{10}H_{21}$ as alkyl chain.

10.3.2 p-tert-octylphenol (3)

p-tert-octylphenol was bought from Sigma-Aldrich and it was used without further purification.

^{1}H-NMR (CDCl$_3$, 300 MHz): δ (ppm) 7.33 (d, 2 H, ^{3}J = 7.9 Hz, H_m); 6.91 (d, 2 H, ^{3}J = 7.9 Hz, H_o); 6.60 (b, 1 H, OH); 1.83 (s, 2 H, CH_2); 1.47 (s, 6 H, $C(CH_3)_2$); 0.87 (s, 9 H, $C(CH_3)_3$).

^{13}C-NMR (CDCl$_3$, 75 MHz): δ (ppm) 152.7 (C_iOH); 142.7 (C_p); 127.4 (C_m); 115.0 (C_o); 57.2 (CH_2); 38.1 ($C(CH_3)_2$); 32.5 ($C(CH_3)_3$); 32.0 ($C(CH_3)_3$); 31.8 ($C(CH_3)_2$).

ESI-MS (acetylated derivative): Found m/z 271.5 $[M+Na]^+$, 287.4 $[M+K]^+$

10.4 Synthesis of calixarene mixtures

10.4.1 p-dodecylcalix[5,6,8]arenes and open-chain compounds (2)

In a 3 L reactor equipped with mechanical stirrer, thermometer and condenser, p-dodecylphenol (364.7 g 1.39 mol) was added to a mixture of aqueous formaldehyde (37 % w/w, 139.9 g, 1.723 mol) and NaOH 10 M (6.46 mL, 0.065 mmol). The mixture was heated under nitrogen pressure at 120 °C. Water was gathered in a Dean and Stark condenser. After 2 h, xylene (1.6 L) was added. The mixture was heated to reflux under nitrogen pressure. After 4 h, water (500 mL) was added to the mixture. The organic phase was extracted and the product was concentrated to 77.5 % by weight in xylene under reduced pressure. The product was obtained as an amber solution.

The relative abundance of calixarene structures was determined by chromatographic separation and subsequent characterization by ^{1}H-NMR, ^{13}C-NMR and ESI-MS analyses of the product without xylene. The calixarenes were about 60 % w/w of the active part, while the remaining 40 % was due to open oligophenolic chains.

p-dodecylcalix[8]arene

p-dodecylcalix[8]arene was purified from the reaction mixture by chromatographic purification (eluent: hexane/CHCl$_3$/toluene 76/19/5).

^{1}H-NMR (CDCl$_3$, 400 MHz): δ (ppm) 9.52 (b, 1 H, OH); 7.2–6.9 (m, 2 H, H_{cal}); 4.43 (b, 1 H, $H_{br,ax}$); 3.51 (b, 1 H, $H_{br,eq}$); 2.0–0.3 (m, 25 H, $C_{12}H_{25}$).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 146.6 ($C_{cal,i}OH$); 144.0–141.0 ($C_{cal,p}$); 128.6 ($C_{cal,o}$); 126.6 ($C_{cal,m}H$); 50–8 ($C_{12}H_{25}$); 32.2 ($CH_{2\,br}$).

ESI-MS ([calix[8]arene - 2H]$^{2-}$): Calculated m/z 1096.9. Found m/z 1027.4, 1034.3, 1040.1, 1047.9, 1054.7, 1061.6, 1068.5, 1076.1, 1083.2, 1090.6, *1096.9*, 1103.9, 1110.9, 1117.8, 1124.5, 1131.9, 1139.0, 1145.9, 1154.1.

Enriched mixture of p-dodecylcalix[5,6]arenes

This sample was purified from the reaction mixture by chromatographic purification (eluent: hexane/$CHCl_3$/toluene 76/19/5).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 10.41 (b, 0.62 H, OH_{cal6}); 8.87 (b, 0.18 H, OH_{cal5}); 7.2–6.9 (m, 2 H, H_{cal}); 4.5–3.3 (m, 2 H, $CH_{2\,br}$); 2.0–0.3 (m, 25 H, $C_{12}H_{25}$).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 147.6–147.2 ($C_{cal,i}OH$); 143.7–140.5 ($C_{cal,p}$); 129.0–126.0 ($C_{cal,m}H$ and $C_{cal,o}$); 50–8 ($C_{12}H_{25}$); 32.0 ($CH_{2\,br}$).

ESI-MS ([calix[5]arene + Na]$^+$): Calculated m/z 1395. Found m/z 1268.0, 1282.0, 1296.0, 1310.0, 1324.1, 1339.1, 1352.1, 1366.1, 1381.1, *1395.1*, 1409.1, 1423.1, 1437.1, 1451.1, 1465.1.

ESI-MS ([calix[6]arene + Na]$^+$): Calculated m/z 1669.3. Found m/z 1515.2, 1529.2, 1543.2, 1557.2, 1571.2, 1585.2, 1599.1, 1613.2, 1627.2, 1641.3, 1655.3, *1669.3*, 1683.3, 1697.3, 1711.3, 1726.4, 1740.4, 1753.4.

Open oligophenolic chains

The open oligophenolic chains were obtained from the reaction mixture by chromatographic purification (eluent: hexane/$CHCl_3$/toluene 76/19/5).

10.4.2 p-tert-octylcalix[6,8]arenes (4)

The procedure followed for the synthesis of p-tert-octylcalix[6]- and -[8]arenes was derived from the literature.[5] In detail, the mixture of p-tert-octylphenol (160 g, 0.77 mol), aqueous formaldehyde (37 %, 80 mL, 1.07 mol) and NaOH (2.00 g, 50 mmol) was heated to 120 °C, removing the water from the reaction. Subsequently, after 4 hours of reaction at 140 °C in xylene (600 mL, a partial distillation of the solvent was performed (400 mL). After the addition of 2-propanol (600 mL) to the reaction mixture, a yellow solid was formed. The product was filtered and washed with water, 2-propanol and xylene in order to obtain the product as a white solid (146.8 g, 0.672 mol$_{m.u.}$, 87.3 %).

^{1}H-NMR (CDCl$_3$, 400 MHz): δ (ppm) 10.35 (b, 0.3 H, OH$_{cal6}$); 9.49 (b, 0.49 H, OH$_{cal5}$); 7.22 (s, 2 H, H$_{cal}$); 4.5–3.5 (m, 2 H, CH$_{2\,br}$); 1.77 (s, 2 H, CH$_2$); 1.38 (s, 6 H, C(CH$_3$)$_2$); 0.80 (s, 9 H, C(CH$_3$)$_3$).

^{13}C-NMR (CDCl$_3$, 100 MHz): δ (ppm) 146.5 (C$_{cal,i}$OH); 143.7 (C$_{cal,p}$); 128.3 (C$_{cal,o}$); 126.3 (C$_{cal,m}$H); 57.0 (CH$_2$); 38.0 (C(CH$_3$)$_2$); 32.5 (*C*(CH$_3$)$_3$); 32.1 (C(CH$_3$)$_3$); 31.7 (C(CH$_3$)$_2$); 31.6 (CH$_{2\,br}$).

ESI-MS: Found m/z 1309.0 [M$_{calix[6]}$-H]$^-$, 1745.1 [M$_{calix[8]}$-H]$^-$.

10.5 Ester functionalization of the mixtures

10.5.1 i-(ethyloxycarbonylmethyloxy)-p-dodecylcalix[5,6,8]arenes and open-chain compounds (5)

In a 2.5 L reactor equipped with mechanical stirrer, thermometer and condenser, **2** (77.5 %, 227.0 g, 0.641 mol$_{m.u.}$) was added to a mixture of xylene (320.2 g), K$_2$CO$_3$ (93.15 g, 0.674 mol) and BrAcOEt (191.3 g, 1.123 mol). The mixture was heated to reflux under nitrogen pressure. After 12 h, the mixture was cooled at room temperature and a 5 M solution of HCl$_{aq}$ (150 mL, 0.75 mol) was added. The organic phase was separated and washed with water (100 mL). The solvent and the excess of BrAcOEt were removed under reduced pressure. The product was obtained as an amber oil in 98.9 % yield (410.8 g, 0.634 mol$_{m.u.}$).

^{1}H-NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.5–6.5 (m, 2 H, H$_{cal}$); 5.2–3.0 (m, 6 H, CH$_{2\,br}$ and OCH$_{2est,1}$ and OCH$_{2est,3}$); 1.8–0.0 (m, 28 H, C$_{12}$H$_{25}$ and CH$_{3est,4}$).

^{13}C-NMR (CDCl$_3$, 100 MHz): δ (ppm) 168.8–166.7 (C$_{est,2}$OOR); 154.5–153.0 (C$_{cal,i}$OR); 145.0–143.0 (C$_{cal,p}$); 132.4 (C$_{cal,o}$); 127.1 (C$_{cal,m}$H); 114.0 (C$_{open,o}$); 70.0, 68.1 and 65.5 (C$_{est,1}$); 60.8, 63.7 and 61.5 ppm (C$_{est,3}$); 50–8 (C$_{12}$H$_{25}$); 32.2 (CH$_{2\,br}$); 14.1 (C$_{est,4}$).

10.5.2 i-(ethyloxycarbonylmethyloxy)-p-tert-octylcalix[6,8]arenes (7)

In a 2.5 L reactor equipped with mechanical stirrer, thermometer and condenser, **4** (140.0 g, 0.641 mol$_{u.m.}$) was added to a mixture of xylene (320.2 g),

K_2CO_3 (93.15 g, 0.674 mol) and BrAcOEt (191.3 g, 1.123 mol). The mixture was heated to reflux under nitrogen pressure. After 12 h, the mixture was cooled at room temperature and a 5 M solution of HCl_{aq} (150 mL, 0.75 mol) was added. The organic phase was separated and washed with water (100 mL). The solvent and the excess of BrAcOEt were removed under reduced pressure. The product was obtained as a white solid in 99.5 % yield (194.2 g, 0.638 $mol_{m.u.}$).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.83 (s, 2 H, H_{cal}); 4.4–3.7 (m, 6 H, $CH_{2\,br}$ and $OCH_{2\,est,1}$ and $OCH_{2\,est,3}$); 1.50 (s, 2 H, CH_2); 1.1–0.9 (s, 9 H, $C(CH_3)_2$ and $CH_{3\,est,4}$); 0.61 (s, 9 H, $C(CH_3)_3$).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 168.7 ($C_{est,2}OOR$); 152.6 ($C_{cal,i}OR$); 145.6 ($C_{cal,p}$); 132.2 ($C_{cal,o}$); 126.7 ($C_{cal,m}H$); 69.8 ($C_{est,1}$); 60.8 ($C_{est,3}$); 56.7 (CH_2); 38.0 ($C(CH_3)_2$); 32.3 ($C(CH_3)_3$); 31.8 ($C(CH_3)_3$); 31.6 ($C(CH_3)_2$); 30.4 ($CH_{2\,br}$); 13.9 ($C_{est,4}$).

10.6 Hydrolysis of the ester mixtures

10.6.1 i-(hydroxycarbonylmethyloxy)-p-dodecylcalix[5,6,8]arenes and open-chain compounds (6)

In a 2.5 L reactor equipped with mechanical stirrer, thermometer and condenser, **5** (226.8 g, 0.629 $mol_{m.u.}$) was added to a mixture of xylene (361.4 g), PEG400 (19 g), water (330 g) and KOH (85 %, 158.8 g, 2.406 mol). The mixture was heated to reflux under nitrogen pressure. After 13 h, the mixture was cooled at room temperature and a solution of HCl_{aq} (37 %, 264.1 g, 2.68 mol) was added. The mixture was stirred at 50 °C for 30 min. The organic phase was separated and washed with a 0.5 M solution of HCl_{aq} (2 * 150 mL). The excess of organic solvent was removed under reduced pressure to obtain the desired product in 96.0 % yield as an amber solution (53 % in xylene, 200.8 g, 0.604 $mol_{m.u.}$).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.62 (b, 1 H, $C_{ac,2}OOH$); 7.2–6.5 (m, 2 H, H_{cal}); 5.2–3.0 (m, 3.2 H, $CH_{2\,br}$ and $OCH_{2ac,1}$); 1.8–0.0 (m, 26 H, $C_{12}H_{25}$).

^{13}C-NMR ($CDCl_3$, 100 MHz): δ (ppm) 173.0 ($C_{ac,2}OOR$); 155.0–140.5 ($C_{cal,i}OR$ and $C_{cal,p}$); 132.5 ($C_{cal,o}$); 127.2 ($C_{cal,m}H$); 114.0 ($C_{open,o}$); 69.5 ($C_{cal,ac,1}$); 65.1 ($C_{open,ac,1}$); 50–8 ($C_{12}H_{25}$); 30.2 ($CH_{2\,br}$).

10.6.2 i-(hydroxycarbonylmethyloxy)-p-tert-octylcalix[6,8]arenes (8)

In a 2.5 L reactor equipped with mechanical stirrer, thermometer and condenser, **7** (191.5 g, 0.629 $mol_{m.u.}$) was added to a mixture of xylene (361.4 g), PEG400 (19 g), water (330 g) and KOH (85 %, 158.8 g, 2.406 mol). The mixture was heated to reflux under nitrogen pressure. After 13 h, the mixture was cooled at room temperature and a solution of HCl_{aq} (37 %, 264.1 g, 2.68 mol) was added. The mixture was stirred at 50 °C for 30 min. The organic phase was separated and washed with a 0.5 M solution of HCl_{aq} (2 $*$ 150 mL). The organic solvent was removed under reduced pressure to obtain the desired product in 94.7 % yield as a white solid (164.6 g, 0.595 $mol_{m.u.}$).

^{1}H-NMR (CDCl$_3$, 400 MHz): δ (ppm) 10.34 (b, 1 H, $C_{ac,2}OOH$); 7.00 (s, 2 H, H_{cal}); 5.0–3.0 (b, 4 H, $CH_{2\,br}$ and $OCH_{2ac,1}$); 1.64 (s, 2 H, CH_2); 1.23 (s, 6 H, $C(CH_3)_2$); 0.72 (s, 9 H, $C(CH_3)_3$).

^{13}C-NMR (CDCl$_3$, 100 MHz): δ (ppm) 172.5 ($C_{ac,2}OOH$); 152.0 ($C_{cal,i}OR$); 146.5 ($C_{cal,p}$); 132.4 ($C_{cal,o}$); 126.9 ($C_{cal,m}H$); 69.5 ($C_{ac,1}$); 56.7 (CH_2); 38.1 ($C(CH_3)_2$); 32.4 ($C(CH_3)_3$); 32.0 ($C(CH_3)_3$); 31.8 ($C(CH_3)_2$); 30.5 ($CH_{2\,br}$).

10.7 Synthesis of new calixarene-based detergents

The reactions for the preparation of detergents were conducted in a calorimeter RC-1 Mettler composed by a 0.5 L jacketed glass reactor thermostated for movement of a fluid coming from a thermostatic bath inside the instrument.

The reactor was equipped with:

- a mechanical agitator;
- a “Dean and Stark” condenser cooled with water, connected both to a vacuum and a nitrogen line, and with a flask for the collection of the distillate;
- a bottom outlet fitted with a tap of teflon;
- a thermocouple for measuring the temperature.

The system was controlled by a computer that allowed to set desired heating and cooling programs.

10.7.1 Detergent D1

In the RC-1 Mettler reactor, the derivative **2** (77.5 % in xylene, 120.60 g, 0.338 $\text{mol}_{m.u.}$) and SN 150S (94.82 g) were added under nitrogen atmosphere. The mixture was heated to 130 °C and xylene was removed by flash distillation by gradually decrease of pressure up to 20 mbar. Then, $Ca(OH)_2$ (12.54 g, 0.169 mol), ethylene glycol (25.65 g) and 2-ethylhexanol (157.07 g) were added to the mixture under nitrogen atmosphere. After 15 min, the pressure was gradually decreased up to 70 mbar. In 3 h, water was distilled through azeotropic mixture 2-ethylhexanol/water in the "Dean and Stark" condenser. Maintaining the pressure at 70 mbar, the mixture of reaction was heated up to 210 °C (rate: 1 $°C\,min^{-1}$). Finally, the pressure was lowered below 10 mbar for 1 h.

During this time, a panel of an inert filtering agent was made in a 0.4 L jacketed stainless filter.

The temperature of the reaction mixture was lowered to 160 °C and the same inert filtering agent of the filter (6 g) was added to this mixture. After 15 min, the mixture was filtered through the pre-formed panel at 160 °C with a pressure of 5 bar.

The product withheld in the filter was recovered in xylene and this organic solvent was then removed under reduced pressure.

After the fractions containing the product were combined, detergent **D1** (197 g) was obtained.

The characterizations of product **D1** are reported in Table 10.1.

10.7.2 Detergent D2

In the RC-1 Mettler reactor, the derivative **6** (53 % in xylene, 174.73 g, 0.273 $\text{mol}_{m.u.}$) and SN 150S (91.58 g) were added under nitrogen atmosphere. The mixture was heated to 130 °C and xylene was removed by flash distillation by gradually decrease of pressure up to 20 mbar. Then, $Ca(OH)_2$ (10.13 g, 0.1365 mol), ethylene glycol (25.02 g) and 2-ethylhexanol (153.40 g) were added to the mixture under nitrogen atmosphere. After 15 min, the pressure was gradually decreased up to 70 mbar. In 3 h, water was distilled through azeotropic mixture 2-ethylhexanol/water in the "Dean and Stark" condenser. Maintaining the pressure at 70 mbar, the mixture of reaction was heated up to 210 °C (rate: 1 $°C\,min^{-1}$). Finally, the pressure was lowered below 10 mbar for 1 h.

Table (10.1): *Characterization of detergent* ***D1***

Type of Calixarenes	
ID calixarene	**2**
Alkyl chain	$C_{12}H_{25}$
Funct. degree (%)	0

Product features	
Calcium content (% w/w)	2.80
Viscosity 100 °C (cSt)	112.3
TBN (mg_{KOH}/g)	78.5
DBN (mg_{KOH}/g)	62.01
Turbidity (NTU)	11.6

Results	
Filtration	very slow
Incorporation eff. of Ca (%, calc.)	81.4
Neutralization degree (%, calc.)	17.1
Soap content (% w/w, calc.)	8.8

During this time, a panel of an inert filtering agent was made in a 0.4 L jacketed stainless filter.

The temperature of the reaction mixture was lowered to 160 °C and the same inert filtering agent of the filter (6 g) was added to this mixture. After 15 min, the mixture was filtered through the pre-formed panel at 160 °C with a pressure of 5 bar.

The product withheld in the filter was recovered in xylene and this organic solvent was then removed under reduced pressure.

After the fractions containing the product were combined, detergent **D2** (190 g) was obtained.

The characterizations of product **D2** are reported in Table 10.2.

10.7.3 Detergent D3

In the RC-1 Mettler reactor, the derivative **8** (8.68 g, 0.0314 mol), isostearic acid (18.03 g, 0.0636 $mol_{m.u.}$) and SN 150S (19.22 g) were added under nitrogen atmosphere. The mixture was heated to 130 °C and xylene was removed by flash distillation by gradually decrease of pressure up to 20 mbar. Then, $Ca(OH)_2$ (13.92 g, 0.188 mol), ethylene glycol (6.66 g) and 2-ethylhexanol (51.09 g) were added to the mixture under nitrogen atmosphere. After 15 min, the pressure was gradually decreased up to 70 mbar. In 3 h, water

Table (10.2): *Characterization of detergent* **D2**

Type of Calixarenes	
ID calixarene	**6**
Alkyl chain	$C_{12}H_{25}$
Funct. degree (%)	100

Product features	
Calcium content (% w/w)	2.88
Viscosity 100 °C (cSt)	890.3
TBN (mg_{KOH}/g)	81.0
DBN (mg_{KOH}/g)	0
Turbidity (NTU)	5.0

Results	
Filtration	fast
Incorporation eff. of Ca (%, calc.)	100
Neutralization degree (%, calc.)	100
Soap content (% w/w, calc.)	51.5

was distilled through azeotropic mixture 2-ethylhexanol/water in the "Dean and Stark" condenser. Ethylene glycol (1.97 g) was added to the mixture and CO_2 (14.5 g, 0.329 mol) was bubbled into the reactor for 1 h. Then the pressure was gradually decreased up to 70 mbar and the mixture of reaction was heated up to 210 °C (rate: 1 °C min^{-1}). Finally, the pressure was lowered below 10 mbar for 1 h.

During this time, a panel of an inert filtering agent was made in a 0.4 L jacketed stainless filter.

The temperature of the reaction mixture was lowered to 160 °C and the same inert filtering agent of the filter (6 g) was added to this mixture. After 15 min, the mixture was filtered through the pre-formed panel at 160 °C with a pressure of 5 bar.

The product withheld in the filter was recovered in xylene and this organic solvent was then removed under reduced pressure.

After the fractions containing the product were combined, detergent **D3** (59.7 g) was obtained.

The characterizations of product **D3** are reported in Table 10.3.

Table (10.3): *Characterization of detergent* ***D3***

Type of Calixarenes	
ID calixarene	**8**
Alkyl chain	C_8H_{17}
Funct. degree (%)	100

Product features	
Calcium content (% w/w)	11.04
Viscosity 100 °C (cSt)	234.8
TBN (mg_{KOH}/g)	309.0
Turbidity (NTU)	5.6

Results	
Filtration	slow
Incorporation eff. of Ca (%, calc.)	87.5
Calcium isostearate (% w/w, calc.)	32.2
Calcium calixarate (% w/w, calc.)	15.6
Soap content (% w/w, calc.)	47.8

10.7.4 Detergent D4

In the RC-1 Mettler reactor, the derivative **6** (53 % in xylene, 16.44 g, 0.0257 $mol_{m.u.}$), isostearic acid (18.10 g, 0.0636 mol) and SN 150S (18.95 g) were added under nitrogen atmosphere. The mixture was heated to 130 °C and xylene was removed by flash distillation by gradually decrease of pressure up to 20 mbar. Then, $Ca(OH)_2$ (13.92 g, 0.188 mol), ethylene glycol (6.68 g) and 2-ethylhexanol (52.75 g) were added to the mixture under nitrogen atmosphere. After 15 min, the pressure was gradually decreased up to 70 mbar. In 3 h, water was distilled through azeotropic mixture 2-ethylhexanol/water in the "Dean and Stark" condenser. Ethylene glycol (2.11 g) was added to the mixture and CO_2 (14.5 g, 0.329 mol) was bubbled into the reactor for 1 h. Then the pressure was gradually decreased up to 70 mbar and the mixture of reaction was heated up to 210 °C (rate: 1 °C min^{-1}). Finally, the pressure was lowered below 10 mbar for 1 h.

During this time, a panel of an inert filtering agent was made in a 0.4 L jacketed stainless filter.

The temperature of the reaction mixture was lowered to 160 °C and the same inert filtering agent of the filter (6 g) was added to this mixture. After 15 min, the mixture was filtered through the pre-formed panel at 160 °C with a pressure of 5 bar.

The product withheld in the filter was recovered in xylene and this organic solvent was then removed under reduced pressure.

After the fractions containing the product were combined, detergent **D4** (60.6 g) was obtained.

The characterizations of product **D4** are reported in Table 10.4.

Table (10.4): *Characterization of detergent* ***D4***

Type of Calixarenes	
ID calixarene	**6**
Alkyl chain	$C_{12}H_{25}$
Funct. degree (%)	100

Product features	
Calcium content (% w/w)	11.46
Viscosity 100 °C (cSt)	194.4
TBN (mg_{KOH}/g)	320.8
Turbidity (NTU)	6.0

Results	
Filtration	slow
Incorporation eff. of Ca (%, calc.)	92.2
Calcium isostearate (% w/w, calc.)	31.9
Calcium calixarate (% w/w, calc.)	15.2
Soap content (% w/w, calc.)	47.1

10.7.5 Detergent D5

In the RC-1 Mettler reactor, the derivative **2** (77.5 % in xylene, 52.83 g, 0.146 $mol_{m.u.}$), isostearic acid (41.02 g, 0.144 mol) and SN 150S (64.79 g) were added under nitrogen atmosphere. The mixture was heated to 130 °C and xylene was removed by flash distillation by gradually decrease of pressure up to 20 mbar. Then, $Ca(OH)_2$ (38.28 g, 0.517 mol), ethylene glycol (20.50 g) and 2-ethylhexanol (137.01 g) were added to the mixture under nitrogen atmosphere. After 15 min, the pressure was gradually decreased up to 70 mbar. In 3 h, water was distilled through azeotropic mixture 2-ethylhexanol/water in the "Dean and Stark" condenser. Ethylene glycol (14.84 g) was added to the mixture and CO_2 (36.3 g, 0.834 mol) was bubbled into the reactor for 90 min. Then the pressure was gradually decreased up to 70 mbar and the mixture of reaction was heated up to 210 °C (rate: 1 $°C\,min^{-1}$). Finally, the pressure was lowered below 10 mbar for 1 h.

During this time, a panel of an inert filtering agent was made in a 0.4 L jacketed stainless filter.

The temperature of the reaction mixture was lowered to 160 °C and the same inert filtering agent of the filter (6 g) was added to this mixture. After 15 min, the mixture was filtered through the pre-formed panel at 160 °C with a pressure of 5 bar.

The product withheld in the filter was recovered in xylene and this organic solvent was then removed under reduced pressure.

After the fractions containing the product were combined, detergent **D5** (188.9 g) was obtained.

The characterizations of product **D5** are reported in Table 10.5.

Table (10.5): *Characterization of detergent* ***D5***

Type of Calixarenes	
ID calixarene	**2**
Alkyl chain	$C_{12}H_{25}$
Funct. degree (%)	0

Product features	
Calcium content (% w/w)	10.27
Viscosity 100 °C (cSt)	80.5
TBN (mg_{KOH}/g)	290.5
DBN (mg_{KOH}/g)	15.3
Turbidity (NTU)	4.2

Results	
Filtration	slow
Incorporation eff. of Ca (%, calc.)	93.7
Carbonatation (%, calc.)	94
Calcium isostearate (% w/w, calc.)	23.1
Calcium calixarate (% w/w, calc.)	4.0
Soap content (% w/w, calc.)	27.1

10.7.6 Detergent D6

In the RC-1 Mettler reactor, the derivative **6** (53 % in xylene, 77.67 g, 0.121 $mol_{m.u.}$), isostearic acid (41.25 g, 0.145 mol) and SN 150S (63.61 g) were added under nitrogen atmosphere. The mixture was heated to 130 °C and xylene was removed by flash distillation by gradually decrease of pressure up to 20 mbar. Then, $Ca(OH)_2$ (38.28 g, 0.517 mol), ethylene glycol (20.59 g) and

2-ethylhexanol (137.57 g) were added to the mixture under nitrogen atmosphere. After 15 min, the pressure was gradually decreased up to 70 mbar. In 3 h, water was distilled through azeotropic mixture 2-ethylhexanol/water in the "Dean and Stark" condenser. Ethylene glycol (14.91 g) was added to the mixture and CO_2 (37.5 g, 0.852 mol) was bubbled into the reactor for 90 min. Then the pressure was gradually decreased up to 70 mbar and the mixture of reaction was heated up to 210 °C (rate: $1\ °C\,min^{-1}$). Finally, the pressure was lowered below 10 mbar for 1 h.

During this time, a panel of an inert filtering agent was made in a 0.4 L jacketed stainless filter.

The temperature of the reaction mixture was lowered to 160 °C and the same inert filtering agent of the filter (6 g) was added to this mixture. After 15 min, the mixture was filtered through the pre-formed panel at 160 °C with a pressure of 5 bar.

The product withheld in the filter was recovered in xylene and this organic solvent was then removed under reduced pressure.

After the fractions containing the product were combined, detergent **D6** (189.2 g) was obtained.

The characterizations of product **D6** are reported in Table 10.6.

Table (10.6): *Characterization of detergent* ***D6***

Type of Calixarenes	
ID calixarene	**6**
Alkyl chain	$C_{12}H_{25}$
Funct. degree (%)	100

Product features	
Calcium content (% w/w)	10.88
Viscosity 100 °C (cSt)	140.8
TBN (mg_{KOH}/g)	304.5
DBN (mg_{KOH}/g)	14.4
Turbidity (NTU)	5.1

Results	
Filtration	medium
Incorporation eff. of Ca (%, calc.)	99.4
Carbonatation (%, calc.)	93.6
Calcium isostearate (% w/w, calc.)	23.2
Calcium calixarate (% w/w, calc.)	23.0
Soap content (% w/w, calc.)	46.2

10.7.7 Detergent D7

In the RC-1 Mettler reactor, the derivative **6** (53 % in xylene, 55.99 g, 0.088 mol$_{m.u.}$), isostearic acid (29.73 g, 0.105 mol) and SN 150S (62.90 g) were added under nitrogen atmosphere. The mixture was heated to 130 °C and xylene was removed by flash distillation by gradually decrease of pressure up to 20 mbar. Then, $Ca(OH)_2$ (48.74 g, 0.658 mol), ethylene glycol (14.86 g) and 2-ethylhexanol (102.5 g) were added to the mixture under nitrogen atmosphere. After 15 min, the pressure was gradually decreased up to 70 mbar. In 3 h, water was distilled through azeotropic mixture 2-ethylhexanol/water in the "Dean and Stark" condenser. Ethylene glycol (10.76 g) was added to the mixture and CO_2 (20.1 g, 0.457 mol) was bubbled into the reactor for 90 min. Then the pressure was gradually decreased up to 70 mbar and the mixture of reaction was heated up to 210 °C (rate: 1 $°C\,min^{-1}$). Finally, the pressure was lowered below 10 mbar for 1 h.

During this time, a panel of an inert filtering agent was made in a 0.4 L jacketed stainless filter.

The temperature of the reaction mixture was lowered to 100 °C, 2-ethylhexanol (180 g) was added to the mixture. Then, the mixture was discharged from the reactor and centrifuged at 2000 rpm for 20 min. The supernatant was collected and heated to 100 °C. The same inert filtering agent of the filter (6 g) was added to this mixture. After 15 min, the mixture was filtered through the pre-formed panel at 100 °C with a pressure of 5 bar.

The product withheld in the filter was recovered in 2-ethylhexanol and this organic solvent was then removed under reduced pressure.

After the fractions containing the product were combined, detergent **D7** (179.5 g) was obtained.

The characterizations of product **D7** are reported in Table 10.7.

10.7.8 Packages and Engine lubricant formulations

Using these detergents, the corresponding additive packages were prepared (from **P1** to **P4**). These last ones contained the detergents to a concentration of 10.3 %. A comparative package (**P5**) containing sulfur-based detergents (ENI MX 3280 and ENI MX 3245) was also prepared.

All packages also contained other additives, which are the same with the same concentration for all packages. These additives are dispersants, antioxidants, antiwear, friction modifiers and foam inhibitors.

Table (10.7): *Characterization of detergent* ***D7***

Type of Calixarenes	
ID calixarene	**6**
Alkyl chain	$C_{12}H_{25}$
Funct. degree (%)	100

Product features	
Calcium content (% w/w)	14.46
Viscosity 100 °C (cSt)	237.5
TBN (mg_{KOH}/g)	404.5
DBN (mg_{KOH}/g)	52.2
Turbidity (NTU)	7.5

Results	
Filtration	medium (after centrifugation)
Incorporation eff. of Ca (%, calc.)	98.3
Carbonatation (%, calc.)	85.0
Calcium isostearate (% w/w, calc.)	23.2
Calcium calixarate (% w/w, calc.)	23.0
Soap content (% w/w, calc.)	46.2

Using these packages, the corresponding engine lubricant formulations with SAE 5W-30 were prepared, comprising:

- base oils: 78.8 % weight;
- additive package: 16 % by weight;
- viscosity index improver: 5 % by weight;
- pour point depressant additive: 0.2 % by weight.

All lubricants (from **L1** to **L5**) contain the same base oil, the same additive viscosity index improver and the same additive pour point depressant.

The lubricants were subsequently characterized by determining the following parameters: kinematic viscosity at 100 °C and 40 °C, viscosity index, total base number (TBN), calcium content and deposits at high temperature (method ASTM D 7097)[4]. The latter parameter is determined by the method TEOST MHT (Thermo-Oxidation Engine Oil Simulation Test), which is employed to evaluate the ability of an engine oil to control the formation of deposits at high temperatures.

Table (10.8): *Lubricant formulations with calixarene based detergents*

Additives package

ID package	**P1**	**P2**	**P3**	**P4**	**P5**
ID detergent	**D3**	**D4**	**D5**	**D6**	ENI MX3245 + ENI MX3280
Detergent (% w/w)	10.3	10.3	10.3	10.3	13.1

Lubricant 5W-30: Composition

ID Lubricant	**L1**	**L2**	**L3**	**L4**	**L5**
Base oils (% w/w)	78.8	78.8	78.8	78.8	78.8
Additives package (% w/w)	16.0	16.0	16.0	16.0	16.0
Viscosity Index improver (% w/w)	5.0	5.0	5.0	5.0	5.0
Pour Point Depressant (% w/w)	0.2	0.2	0.2	0.2	0.2
Soap from detergents (% w/w)	0.79	0.78	0.76	0.45	0.76
Calcium isostearate (% w/w)	0.53	0.53	0.38	0.38	—
Calixarene calcium salt (% w/w)	0.26	0.25	0.38	0.07	—

Lubricant 5W-30: Characterization

KV 40°C (cSt)	75.95	75.40	74.23	71.43	76.23
KV 100°C (cSt)	11.90	11.79	11.64	11.31	11.93
Viscosity Index	153	153	152	153	153
TBN (mg_{KOH}/g)	9.4	9.6	9.40	9.10	8.2
Calcium content (% w/w)	0.183	0.188	0.178	0.168	0.162
Total deposits TEOST MHT (mg)	6.9	6.4	4.6	18.1	19.2

Bibliography

[1] ASTM International, West Conshohocken, PA, *ASTM E 222 – Standard test methods for hydroxyl groups using acetic anhydride acetylation*, 2010.

[2] ASTM International, West Conshohocken, PA, *ASTM 2896 – Standard test method for base number of petroleum products by potentiometric perchloric acid titration*, 1988.

[3] ASTM International, West Conshohocken, PA, *ASTM D 7042 – Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)*, 2004.

[4] ASTM International, West Conshohocken, PA, *ASTM D 7097 – Standard Test Method for Determination of Moderately High Temperature Piston Deposits by Thermo-Oxidation Engine Oil Simulation Test-TEOST MHT*, 2009.

[5] V. Bocchi, D. Foina, A. Pochini, R. Ungaro and G. D. Andreetti, *Tetrahedron*, 1982, **38**, 373 – 378.

Appendices

SUPPORTING INFO ABOUT CALIXARENES

1.1 Nomenclature of Calixarenes

As mentioned in the introductory chapters of this thesis, David Gutsche called the compound reported in Figure 1.1 as "calixarene", because of its resemblance to the Greek calix.[1] Since 1995, the term "calixarene" has been accepted by the IUPAC,[2] although previously the researchers used it because of its simplicity.

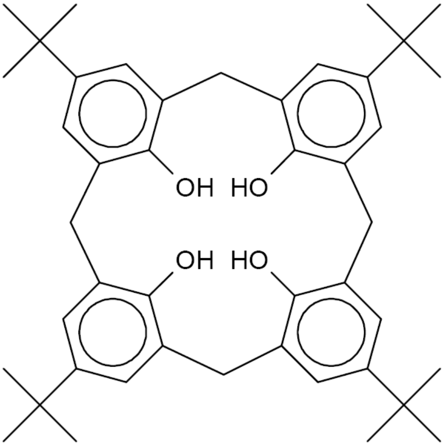


Figure (1.1): *p-tert-butylcalix[4]arene*

According to this nomenclature, a bracketed number is inserted between calix and arene, thus giving "calix[*n*]arene", where *n* denotes the number of phenolic groups. Therefore, a cyclic tetramer is called as "calix[4]arene", a cyclic hexamer is a "calix[6]arene", and a cyclic octamer is a "calix[8]arene".

For calixarenes with more substituents the general name "calix[n]arene" is maintained, the substituents are listed and their positions numbered as reported in Figure 1.2.

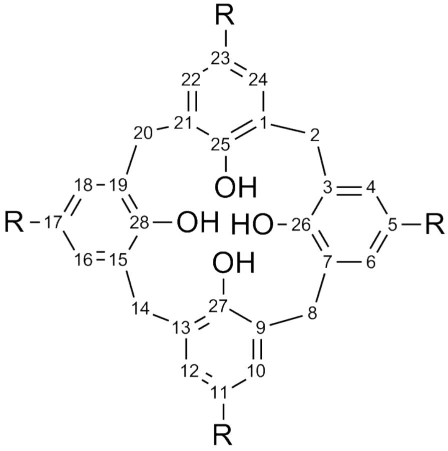


Figure (1.2): *Structure and numbering of calix[4]arene*

For instance, the calix[4]arene with R = ^{t}Bu at the upper rim becomes 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26,27,28-tetrahydroxycalix[4]arene. Since all of the R groups at the para-positions are the same (^{t}Bu), it can be frequently abbreviated as p-tert-butyl-25,26,27,28-tetrahydroxycalix[4]arene. When at the lower rim there are only hydroxyl groups, the compound can be named simply as p-tert-butylcalix[4]arene. The same rules can be applied to calix[6]arene and calix[8]arene.

In detail, the numbers of the positions in the calix[8]arene backbone are shown in Figure 1.3. As reported, the positions of hydroxyl groups are from 49 to 56, whereas the alkyl chains are bonded to the calixarene structure at 5,11,17,23,29,35,41 and 47.

The old IUPAC system of nomenclature was more difficult. Following this last system, the Chemical Abstracts[3] names the basic ring structure of the cyclic tetramer (Figure 1.2) as pentacyclo-[19.3.1.$1^{3,7}$.$1^{9,13}$.$1^{15,19}$]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene.

When this thesis was being written, use the Chemical Abstract nomenclature was not chosen, whereas the numenclature of Gutsche has been taken as a reference due to its more simplicity.

When the calix[8]arene was total functionalizated at its lower rim, the positions from 49 to 56 will be omitted from the name of the compound obtained.

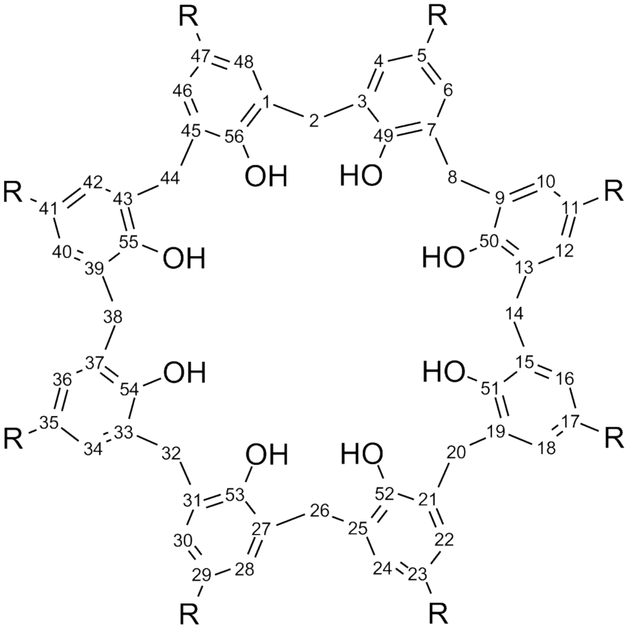


Figure (1.3): *Structure and numbering of calix[8]arene*

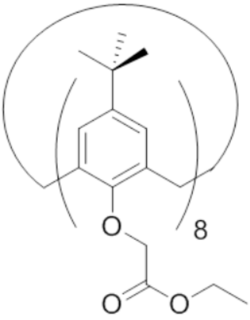


Figure (1.4): *p-tertbutyl(ethyloxycarbonylmethyloxy)calix[8]arene*

For example, in the case shown in Figure 1.4, in this thesis the name used for this molecule is:

i-(ethyloxycarbonilmethyloxy)-p-tertbutylcalix[8]arene

1.2 Representation of Calixarenes

The representations used in this thesis for the calixarene derivatives are commonly employed in supramolecular chemistry. In detail, the number of phenolic units belonged to the calixarene were indicated in the lower right of the parentheses around representations of these phenolic units (8 in Figure 1.4). Besides, in order to point out the cyclic nature of these compounds, an arc of an ellipse was used to connect the two endings of the repeating phenoxymethylene unit, as previously shown in Figure 1.4.

1.3 Criteria for the discussion on calixarenes

In this elaborate, the discussions of some procedures or analyses (such as ^{1}H-NMR, ^{13}C-NMR and FT-IR) on calixarene derivatives were often related to the monomer unit and not to the calixarene as a whole molecule. This approach was mainly used when all the phenolic nuclei are equally substituted.

This choise was especially taken since we considered calixarenes more as materials than as single molecule. Besides, the material often isolated was not homogeneous but it was a mixtures of homologs: compounds having the same basic structure but repeated a different number of times.

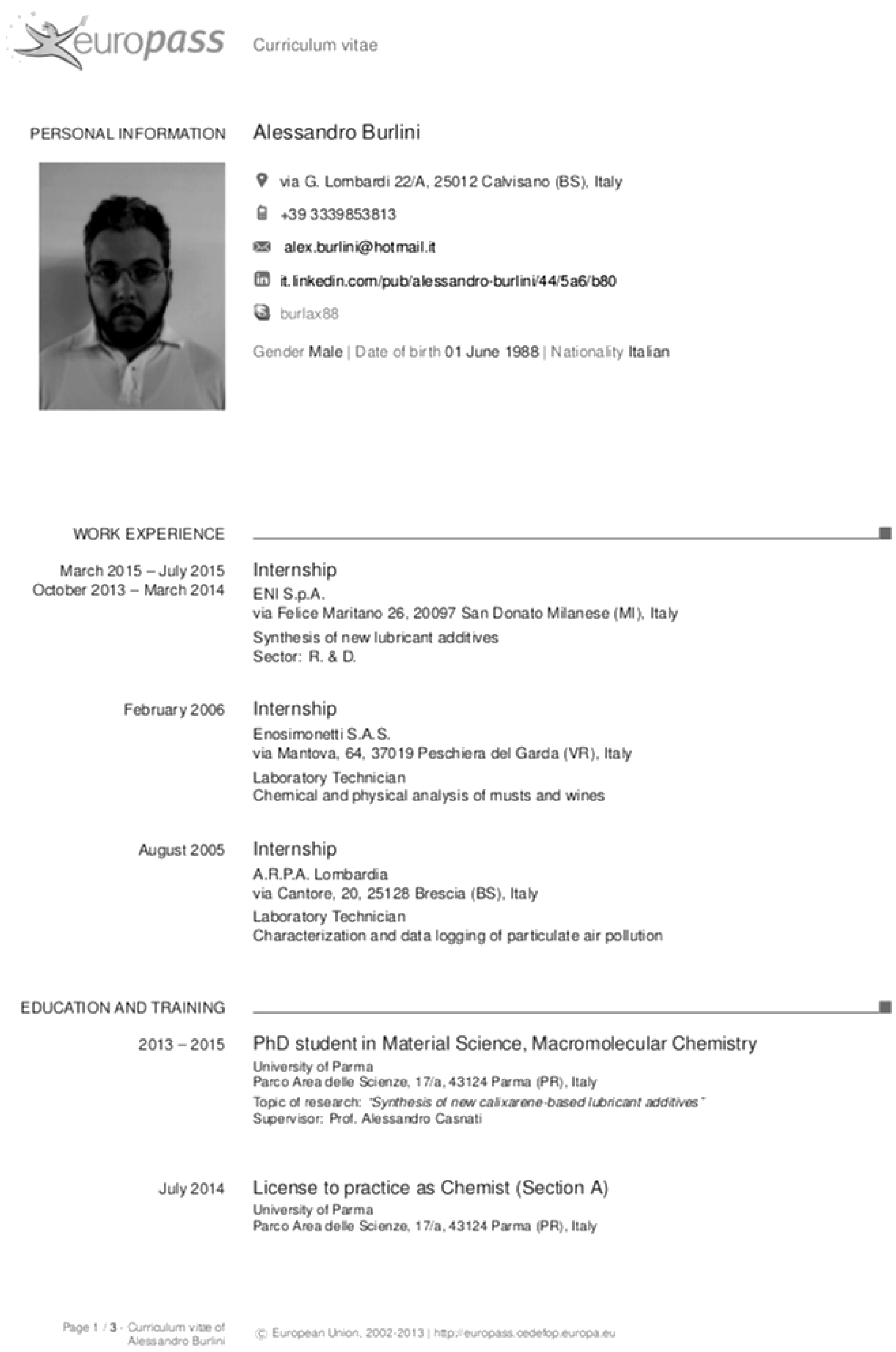
An example of this “material approach” has been carried out by polymer chemists who usually treats the polymeric materials referring to their single monomer units. In fact, normally some properties of these materials are strongly due to the related properties of their monomers. In this way, different concepts could be discussed such as “functionalization degree”, which represents the average number of functions per monomer unit. Following this approach (unless otherwise specified), the information discussed in this thesis was always correlated to the monomer unit.

Bibliography

[1] C. D. Gutsche and R. Muthukrishnan, *The Journal of Organic Chemistry*, 1978, **43**, 4905 – 4906.

[2] G. P. Moss, P. A. S. Smith and D. Tavernier, *Pure and Applied Chemistry*, 1995, **67**, 1307 – 1375.

[3] C. Patterson, *Walker, The Ring Index*, 1960.



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PERSONAL INFORMATION

Alessandro Burlini

via G. Lombardi 22/A, 25012 Calvisano (BS), Italy

+39 3339853813

alex.burlini@hotmail.it

it.linkedin.com/pub/alessandro-burlini/44/5a6/b80

burlax88

Gender **Male** | Date of birth **01 June 1988** | Nationality **Italian**

WORK EXPERIENCE

March 2015 – July 2015
October 2013 – March 2014

Internship
ENI S.p.A.
via Felice Maritano 26, 20097 San Donato Milanese (MI), Italy
Synthesis of new lubricant additives
Sector: R. & D.

February 2006

Internship
Enosimonetti S.A.S.
via Mantova, 64, 37019 Peschiera del Garda (VR), Italy
Laboratory Technician
Chemical and physical analysis of musts and wines

August 2005

Internship
A.R.P.A. Lombardia
via Cantore, 20, 25128 Brescia (BS), Italy
Laboratory Technician
Characterization and data logging of particulate air pollution

EDUCATION AND TRAINING

2013 – 2015

PhD student in Material Science, Macromolecular Chemistry
University of Parma
Parco Area delle Scienze, 17/a, 43124 Parma (PR), Italy
Topic of research: *"Synthesis of new calixarene-based lubricant additives"*
Supervisor: Prof. Alessandro Casnati

July 2014

License to practice as Chemist (Section A)
University of Parma
Parco Area delle Scienze, 17/a, 43124 Parma (PR), Italy

2010 – 2012

Master's Degree in Chemistry

University of Padua
via Marzolo, 1, 35122 Padova (PD), Italy

Degree thesis: *"Functionalization of carbon nanotubes with thienyl groups for photovoltaic applications"*
Supervisor: Prof. Enzo Menna

2007 – 2010

Bachelor's Degree in Chemistry

University of Padua
via Marzolo, 1, 35122 Padova (PD), Italy

Degree thesis: *"Catalysts for the photocatalytic splitting of water, state of the art and research perspectives"*
Supervisor: Prof. Marcella Bonchio

2002 – 2007

High-school diploma in Environmental technician

ITIS Ferraris; via del Pontiere, 40, 37122 Verona (VR), Italy (3 years)
ITIS Cerebotani; via Galilei, 1, 25017 Lonato (BS), Italy (2 years)

PERSONAL SKILLS

Mother tongue(s) Italian

Other language(s)

	UNDERSTANDING		SPEAKING		WRITING
	Listening	Reading	Spoken interaction	Spoken production	
English	B1	B2	B1	B2	B2

Levels: A1/A2: Basic user - B1/B2: Independent user - C1/C2: Proficient user
Common European Framework of Reference (CEF) level

Communication and social skills

- Organizational skills, determination, self-motivated
- Participation in research project working within both academic and industrial team
- Social skills acquired organizing community activities as volunteer

Organisational / managerial skills

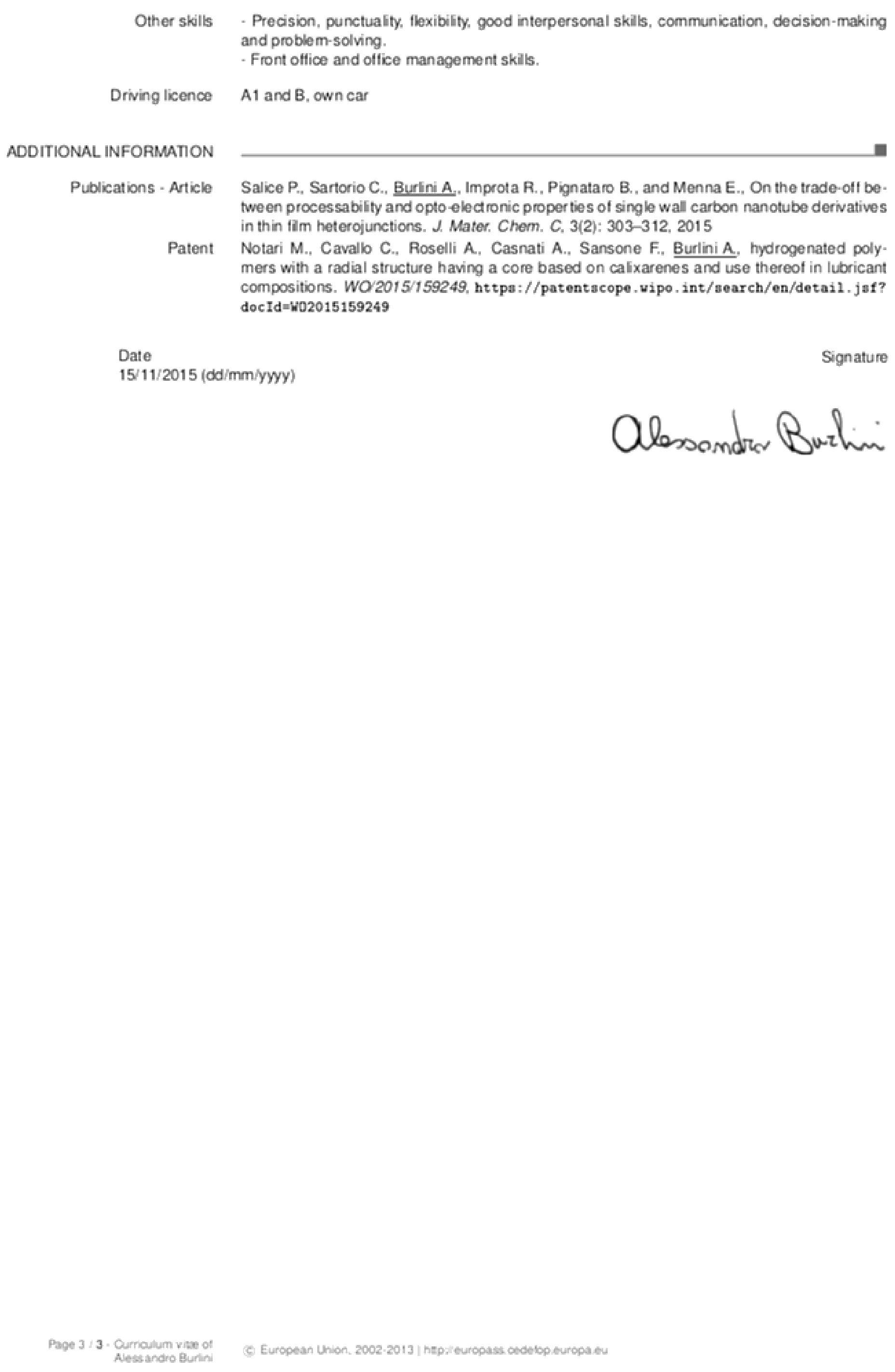
- Self-management and teamwork capability under stressed within working environment

Job-related skills

Technical skills and competences:
- Spectroscopic techniques (NMR, FT-IR, ATR, Raman, UV-Vis-NIR, 1D and 2D NMR Bruker).
- Chromatographic techniques (TLC, gravimetric column, GC, HPLC).
- Mass techniques (ESI-MS).
- Calorimetric and thermal analysis (Moisture balance, TGA, DSC).
- Dispersion of nano- and microparticles: use of ultrasonic lab devices (Misonix Sonicator 3000).
- Gravimetric separation devices (Centrifuge MR23i Jouan).
- Determination of aggregates size and shape in dispersion (DLS, SAXS).
- Lubricant additives: characterization by viscometer, turbidimeter, potentiometric and colorimetric titration TAN, TBN and DBN.
- Synthesis of new lubricant additives: use of the calorimeter Mettler Toledo RC1 as reactor.
- Use of the microwave reactor for organic synthesis.
- Implementation and use of continuous flow reactors for the functionalization of carbon-based nanomaterials, especially SWNT and DWNT.

Computer skills

- Advanced command of Microsoft Windows and Microsoft Windows tools.
- Good command of software Open Source based on Kernel Linux (Debian, Ubuntu, Mint ed Opensuse) used in working environment and private sector.
- Good command of LaTeX suite (layout program for scientific reports).
- Good command of Bash linux (shell scripting).
- Advanced command of OpenOffice tools acquired in working environment.
- Good command of main chemical and data processing softwares, especially MestreNova® (proprietary), ACD/SpecManager® (freeware), Origin® 8.5 (proprietary), Qtiplot (freeware), ChemBioDraw® Ultra 12.0 (proprietary) e ACD/ChemSketch® (freeware).



Other skills	- Precision, punctuality, flexibility, good interpersonal skills, communication, decision-making and problem-solving. - Front office and office management skills.
Driving licence	A1 and B, own car

ADDITIONAL INFORMATION

Publications - Article	Salice P., Sartorio C., Burlini A., Improta R., Pignataro B., and Menna E., On the trade-off between processability and opto-electronic properties of single wall carbon nanotube derivatives in thin film heterojunctions. *J. Mater. Chem. C*, 3(2): 303–312, 2015
Patent	Notari M., Cavallo C., Roselli A., Casnati A., Sansone F., Burlini A., hydrogenated polymers with a radial structure having a core based on calixarenes and use thereof in lubricant compositions. *WO/2015/159249*, `https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2015159249`

Date
15/11/2015 (dd/mm/yyyy)

Signature

Alessandro Burlini