APPLICATION OF LITHIUM/HALIDE EXCHANGE REACTIONS TO THE SYNTHESIS OF COMPLEX POLYMER ARCHITECTURES: INVESTIGATION OF THEIR SELF-ASSEMBLING PROPERTIES AT THE AIR/WATER INTERFACE

By

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To my parents and my brother—thanks for everything.
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An entire set of hydrocarbon-soluble polycarbanionic initiators and macroinitiators was synthesized by using a simple halogen-lithium exchange reaction (Gilman’s reaction) carried out on multibromo molecule and macromolecule precursors. Using these multicarbanionic (macro)initiators an entire set of complex polymer architectures has been synthesized by anionic polymerization using a divergent method.

This strategy was first applied to the preparation of simple polymer architectures such as poly(styrene-\(b\)-butadiene-\(b\)-styrene) triblock copolymers with excellent mechanical properties, obtained using a new hydrocarbon soluble dicarbanionic organolithium initiator containing a side C\(_{15}\)-alkyl chain.

The same exchange reaction has been successfully applied to generate tri- and tetracarbanionic species from tris- and tetrakis-bromoaryl compounds. The use of a \(\sigma/\mu\) ligand was instrumental in obtaining polycarbanionic initiators soluble in apolar medium, and the subsequent preparation of various well-defined three and four-armed polystyrene and polybutadiene stars synthesized by the “core-first” method. The efficiency of the latter was even exploited to synthesize poly(butadiene-\(b\)-ethylene oxide) (PB-\(b\)-PEO)\(_n\) amphiphilic star block
copolymers and poly(styrene-b-butadiene-b-methyl methacrylate) \( (P(S-b-B-b-M)_n) \) star block terpolymers \( n = 3 \) or \( 4 \).

The potential of PB-\( b \)-PEO star block copolymer to self-assemble at the air/water interface was exploited to synthesize a two-dimensional polymeric nanomaterial consisting of a continuously cross-linked polybutadiene two-dimensional network with poly(ethylene oxide) domains of controlled sizes trapped within the network. To reach that goal, novel \((PB(Si(OEt)_3)-b-PEO)_3\) star block copolymers were designed by hydrosilylation of the pendant double bonds of \((PB-b-PEO)_3\) star block copolymer precursors with triethoxysilane. Self-condensation of the triethoxysilane groups under acidic conditions led to a successful cross-linking of the polybutadiene blocks directly at the air/water interface without any additives or reagents.

Finally, the Gilman reaction was extended on \( \omega,\omega' \)-dibromo chain-end polymers after the introduction of a branching agent whose halogen atoms are carried by separate aryl rings to afford hydrocarbon-soluble polycarbanionic macroinitiators. This provided an efficient synthetic route to the asymmetric and “miktoarm” star (co)polymers based on the combination of different polymers such as polystyrene, polybutadiene, and polyisoprene. By the reiteration of this sequence of reactions (branching and halogen-lithium exchange reactions) starting from a tetrafunctional initiator, dendrimer-like PS and PB up to the seventh and third generations, respectively, could be successfully synthesized.
APPLICATION DE REACTIONS D’ECHANGE HALOGENE/LITHIUM A LA SYNTHESE DE POLYMERES A ARCHITECTURES COMPLEXES. ETUDE DE L’AUTO-ASSEMBLAGE A L’INTERFACE AIR/EAU

par

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Une nouvelle famille d’amorceurs et de macroamorceurs pluricarbanioniques solubles en solvant apolaire a été synthétisée par une réaction d’échange halogène-lithium (réaction de Gilman) effectuée sur des composés halogénés (macro)moléculaire. L’utilisation de ces espèces pluricarbanioniques comme (macro)amorceurs a permis la synthèse de différentes architectures polymères complexes par polymérisation anionique par voie divergente.

Cette stratégie a tout d’abord été appliquée à la préparation d’architectures polymères simples telles que des copolymères triblocs poly(styrène-b-butadiène-b-styrène), aux propriétés mécaniques intéressantes, obtenus à l’aide d’un amorceur dicarbanionique soluble en milieu apolaire et ce sans additif grâce à l’ajout d’une chaîne alkyle de 15 carbones sur la structure de l’amorceur.

Cette même réaction d’échange halogène-lithium a été appliquée à la préparation d’espèces tri- et tétracarbanioniques à partir de composés tri- et tétrabromoaryl. Dans ce cas, l’utilisation de ligand σ/µ a néanmoins été nécessaire pour l’obtention d’amorceurs multicarbanioniques solubles en milieu apolaire et la préparation de polystyrène et de polybutadiène en étoile à trois et quatre branches synthétisées par la méthode « core-first ».
L’efficacité de ces espèces pluricarbanioniques a aussi été exploitée pour la synthèse de copolymères diblocs amphiphiles en étoile poly(butadiène-b-oxyde d’éthylène) et de copolymères triblocs en étoile poly(styrène-b-butadiène-b-méthacrylate de méthyle) à trois et quatre branches.

L’intérêt potentiel d’architectures polymères tels que les copolymères amphiphiles en étoile poly(butadiène-b-oxyde d’éthylène) à l’interface air/eau a pu être démontré à travers la synthèse de nanomatériaux polymères bidimensionnels basés sur un réseau en deux dimensions de polybutadiène réticulé possédant des domaines de poly(oxyde d’éthylène) de tailles contrôlées piégés au sein du réseau. Pour atteindre cet objectif, les blocs de polybutadiène ont d’abord été fonctionnalisés par des groupements triethoxysilane après hydrosilylation des doubles liaisons pendantes du copolymère en étoile poly(butadiène-b-oxyde d’éthylène). La condensation des groupements pendants triethoxysilane sous conditions acides a ainsi permis la réticulation des blocs polybutadiène directement à l’interface air/eau.

L’utilisation de la réaction de Gilman a finalement été étendue à la préparation de macromamorceurs pluricarbanioniques solubles en milieu apolaire à partir de chaînes polymères possédant un groupement dibromé en extrémité de chaîne, après l’introduction d’un agent de branchement dont les atomes d’halogènes sont portés par deux noyaux aromatiques différents. Cette méthode a permis l’élaboration de (co)polymères en étoile asymétriques et « miktoarms » constitués de polystyrène et polydiènes. La répétition de cette séquence de réactions (branchement et réaction d’échange halogène-lithium) en partant d’un amorceur tétrafonctionnel a ainsi amené à la synthèse de dendrimères de polystyrène de septième génération et de polybutadiène de troisième génération.
CHAPTER 1
POLYLITHIATED SPECIES: APPLICATION TO POLYMER SYNTHESIS

1.1 Introduction

For many years it was thought by organic chemists that it was impossible to prepare polylithium organic compounds defined as organic compounds containing two or more lithium on the same or adjacent carbons. It was widely believed that having two lithiums on the same or adjacent carbon atoms would lead to a destabilization and lithium hydride elimination. This misconception was changed in the early 1970s by work of West\(^1\) and Lagow.\(^2\) Actually, there are four distinct methods to quantitatively convert a multifunctional compound to polylithiated species.

1.2 By Reaction with Lithium

The reaction with lithium metal or vapor on different categories of molecules such as alkanes, alkenes, aromatics, or also alkyl and aryl halide was the first synthetic method discovered for the preparation of polylithium organic compounds. The use of lithium metal, notably used for the synthesis of butyllithium, was first reported in the early 1950s by West \textit{et al.}\(^1,3,4\) with the conversion of 1,5-dichloropentane to 1,5-dilithio compound. This strategy was later developed by the Lagow group\(^5-13\) with the reaction at high temperature of lithium vapor with halogenated organic compounds as a general synthesis for polylithium compounds.

However, extremely low yield reactions with a mixture of compounds avoid any purification or characterization of the pure product. This very low yield is explained first by \(\alpha\)-lithium-halide elimination occurring from molecules having a halide and a lithium on the same or adjacent carbons producing carbenes and lithium halides. Furthermore, the reaction of lithium on the halide compound is in competition with a secondary reaction of intermolecular coupling reaction between the lithiated species and the alkyl halide reagent (Wurtz coupling)\(^14\) (Figure 1-
1) which has no serious consequence for a monofunctional initiator, but not for the case of pluricarbanionic compounds.

### 1.3 By Reaction of Alkyllithium on Multifunctional Unsaturated Molecules

The most recent method is based on the reaction of alkyllithium on the unsaturations of a multifunctional agent. This strategy was first applied for the synthesis of dilithiated compounds by reaction of butyllithium on difunctional unsaturated reagents such as divinylbenzene (DVB) derivatives,\(^{15,16}\) or double diphényléthylène (DDPE) derivatives.\(^{17-19}\) The latter dilithiated species were actually used, as shown below (Chapter 2), for the preparation of poly(styrene-\(b\)-butadiène-\(b\)-styrene) (SBS) triblock copolymers. By using this strategy, only one group was successful in the preparation of pluricarbanionic species of functionality higher than 2. Indeed, Quirk and Tsai\(^{20}\) synthesized tricarbanionic species, soluble in apolar solvents by reaction of 3 moles of sec-butyllithium with 1,3,5-tris(1-phenylethenyl)benzene (tri-DPE) as presented in Figure 1-2. This hydrocarbon-soluble initiator was found to be efficient for the anionic polymerization of styrene, but only when THF was also added in the reaction mixture ([THF]/[Li] = 20). The addition of THF as a polar additive modified the aggregation rate of the pluricarbanionic species and gave by the same way a quantitative initiation.

The same initiator was also used to produce three-arm polybutadiene stars.\(^{21}\) Even though a complete monomer consumption was observed, the size exclusion chromatography (SEC) analysis showed a bimodal distribution. This behavior was attributed to the strong aggregation effects of the trifunctional initiator in a non polar solvent. The problem was overcome when \(s\)-BuOLi was added in the reaction mixture in a ratio \([s\text{-BuOLi}]/[Li] = 2\). \(s\)-BuOLi was shown to be capable of disrupting the initiator association without affecting appreciably the microstructure of the polybutadiene chains.
The limitations of the method include the extreme care that should be exercised over the stoichiometry of the reaction between s-BuLi and tri-DPE to avoid the presence of a second population of linear polymers or the formation of initiators of lower functionality and the fact that a minimum arm molecular weight of around $6.10^3$ g.mol$^{-1}$ is required for the growth of the polymer chains on the three carbanionic sites at the same time.

By the same manner, the Möller group$^{22}$ employed polylithiated carbosilane dendrimers, as multifunctional initiator (Figure 1-3). The dendrimers had 16 or 32 allyl groups at their periphery. A hydrosilylation route was performed to react half of these terminal allyl groups with didecylmethylsilane (Figure 1-3). The remaining allyl groups were lithiated by the addition of s-BuLi, to produce the multifunctional initiators. These initiators carrying theoretically 8 or 16 carbanionic sites were soluble in polar solvents (THF) and were subsequently used for the polymerization of styrene, ethylene oxide, and hexamethylcyclotrisiloxane (D$_3$). The polymer stars obtained demonstrated a monomodal molecular weight distribution. However, molecular weight characterization data were not provided in this study and the number of branches for these stars was not determined, thus leaving uncertain the formation of the desired structures.

Parallel to these pluricarbanionic species of precise functionality, many research groups worked on the synthesis of multifunctional initiators most certainly less well-defined, but allowing the access to star polymers with a very high number of branches. First demonstrated by Eschwey et al.$^{23,24}$ and later developed by Rempp and colleagues$^{25,26}$ DVB was polymerized by butyllithium or naphtalene lithium in benzene at high dilution to obtain a stable microgel suspension. These heterogeneous microgel nodules, which were described as “living” microgel nodules covered by living anionic sites (for example, by using a ratio of [DVB]/[BuLi]=2, a microgel with a molecular weight of $M_n = 1.9 \times 10^3$ g.mol$^{-1}$ and a polydispersity of 16.8 could be
obtained)\textsuperscript{24} (Figure 1-4), were subsequently used as multifunctional initiators to polymerize styrene, isoprene, or butadiene. However, it should be noted a relatively bad control over the star functionality since it is impossible to predict the number of branches using this method.

A slight variation was adopted by Okay and Funke\textsuperscript{27,28}. The polymerization of DVB was initiated by living poly(\textit{tert}-butylstyryl)lithium chains having low molecular weights in order to avoid the solubility problems arising from the strong association of the carbon-lithium functions in the nonpolar solvent. By using this strategy, Rempp and colleagues\textsuperscript{26} synthesized poly(\textit{tert}-butyl acrylate) (PtBuA) and poly(ethylene oxide) (PEO) stars. The synthesis was performed in THF to minimize the strong association effects, using naphtalene lithium or cumyl potassium to polymerize DVB for the PtBuA or PEO star synthesis, respectively. DVB polymerization was initiated by electron-transfer instead of by addition. The polymerization of \textit{t}BuA was carried out at –55 °C in the presence of LiCl after the active centers have been reacted with a suitable amount of 1,1-diphenylethylene (DPE) to reduce their nucleophilicity. It was found that the mole ratio \([\text{DVB}]/[\text{Li}^+]\) should vary between 1.5 and 2.5 to afford a stable microgel suspension. The molecular characteristics of the final products and the calculated molecular weight of the branches determined by SEC and light scattering (LS) revealed the existence of multimodal molecular weight distribution with large numbers of arms, ranging from 22 to 1300 and from 5 to 219 for the PtBuA or PEO stars, respectively.

1.4 By Lithium-Halogen Exchange Reaction

The third method based on the exchange reaction between a halide and a metal described by Gilman \textit{et al.}\textsuperscript{29} is one of the most used methods for the preparation of aryllithium species. It consists in the reaction of an aryl halide, such as bromobenzene, with an alkyllithium, typically butyllithium (Figure 1-5).\textsuperscript{29,30} This equilibrated reaction is strongly displaced to the most stable lithiated compound and was described as quantitative under certain conditions. The Wurtz
coupling reaction (Figure 1-1), non negligible in the case of alkyl bromides, does not happen in the case of aryl bromides due to the low nucleophilicity of phenyllithium toward the bromide compounds.\textsuperscript{14}

Thus, Lagow and colleagues\textsuperscript{31,32} used this halogen-lithium exchange reaction notably for the synthesis of hexalithiobenzene from the hexachlorobenzene, but with a relatively low yield (53%).

By the same manner, some other groups took advantage of this halogen-lithium exchange reaction for molecule functionalization. Kleij \textit{et al.}\textsuperscript{33} developed a useful synthetic procedure for the incorporation of the potentially multidentate monoanionic ligands \textit{via} the para-position on the periphery of carbosilane dendrimers. Dendritic carbosilanes functionalized with (N)CNPh-Br end groups could be selectively lithiated in presence of \textit{t}-BuLi in Et\textsubscript{2}O to give their multilithiated aminoaryl derivatives with stable C-Li bonds which were used to introduce various metals such as Pt \textit{via} lithiation/transmetalation sequences.

Jayaraman and Nithyanandhan\textsuperscript{34} proposed also another example of dendrimer functionalization through an efficient halogen-lithium exchange reaction. Poly(alkyl aryl ether) dendrimers were functionalized with bromophenyl groups at their periphery so as to have 3, 6, 12, and 24 groups in the zero, first, second, and third generation dendrimers, respectively. The bromophenyl functionalized dendrimers were converted quantitatively to their polyolithiated derivatives by reaction with \textit{n}-BuLi in benzene. Although the polyolithiated dendrimers precipitated as a white solid, they were reacted either with D\textsubscript{2}O or with CO\textsubscript{2}, so as to afford the corresponding deuterated and carboxylic acid functionalized dendrimers, respectively. The carboxylic acid functionalized dendrimers were modified further to methyl esters during their characterization.
The Saà group\textsuperscript{35} proposed the generation of polylithiated derivatives of salicylic and
oligosalicylic acids soluble in THF by means of the halogen-metal exchange reaction from
bromo-substituted salicylic and oligosalicylic acids, including some with base-sensitive chiral
centers avoiding the need to use protecting groups. These polylithiated species were notably used
for the introduction of specific functions (-SMe, -CH(OH)C\textsubscript{6}H\textsubscript{5}, or –C(=O)OEt) under these
conditions.

More recently, a two-step synthetic procedure towards coil-rod-coil triblock copolymers
was developed by Tsitsilianis \textit{et al.}\textsuperscript{36} In the first step, \(\alpha,\omega\)-oligophenylenes (rod part) were
modified by halogen-lithium exchange reaction to anionic bifunctional initiators soluble in THF
(Figure 1-6). In the second step, flexible chains were grown from both ends of the rod part by an
anionic polymerization procedure leading to polystyrene-rod-poly styrene and/or poly(2-vinyl
pyridine)-rod-poly(2-vinyl pyridine) triblock copolymers.

It should be noticed that the yield of the halogen-lithium exchange reaction depends on
different experimental parameters such as the concentration in bromide compound, the nature of
the solvent, the temperature and the nature of the alkyllithium agent used.\textsuperscript{37-41} Although \(n\)-BuLi
was the most used until now, Tsitsilianis \textit{et al.}\textsuperscript{36} demonstrated that the reaction is quantitative in
presence of \(s\)-BuLi for the aryl bromide compounds. \(t\)-BuLi is rather used for the iode/lithium
exchange reaction.\textsuperscript{42} The concentration of the bromo precursor \([\text{Ar-Br}]=5.3.10^{-2} \text{ mol.L}^{-1}\) was
found by Trepka and Sonnenfeld\textsuperscript{40} to be the most appropriate for a good conversion to
phenyllithium species (> 95\%). The exchange reaction could be done either in apolar\textsuperscript{40} or polar
solvents,\textsuperscript{29} the most appropriate being the one in which the polylithiated compound is soluble.
However, in the case of polar solvents the reaction should be done between –40 and –100 °C
because of the low stability of the lithiated species in polar solvents such as THF or dimethyl
ether. Indeed, lithiated compounds could react with ether functions to form by cleavage reaction alkene and lithium alkoxide. In the case of apolar solvents such as cyclohexane or benzene, the reaction could be done at room temperature with no limitation in term of temperature.

1.5 By Reaction with a Base

The last method was less used with only a few cases proposed. This method consists in removing an acidic proton by metalation or with the help of a base. For example, Fujimoto et al. were successful in preparing a soluble pluricarbanionic initiator in a mixture of THF/diglyme by reaction of 1,3,5-tris-(α-methoxybenzyl)benzene and a mixture of sodium/potassium. However, this trifunctional initiator was not able to quantitatively initiate the polymerization of α-methylstyrene leading to a mixture of linear chains, dimer species, and star polymers. Hogen-Esch and colleagues also proposed the synthesis of a trifunctional initiator by metalation of 1,3,5-tris[2-(2’-pyridyl)ethyl]benzene in presence of α,ω-dipotassio-α-methylstyrene. Used as initiator for the polymerization of 2-vinylpyridine and 4-vinylpyridine in THF, the latter compound leads to polymer samples with large molecular weight distribution and residual initiator. Studies of the reaction of bases on trimethylbenzene have shown the formation of a mixture of mono-, di-, and trilithiated species under these conditions. Although the use of a Lochmann base by Gordon et al. allowed the formation of pure tricarbanionic species by trimetalation of 1,3-cycloheptadiene in pentane, no interest was found in this polylithiated species as initiator for the polymerization.

1.6 Conclusion

The reasons that are generally held responsible for polylithiation to be impractical—especially when the halogens to be substituted happened to be on the same carbon or on adjacent carbons—are two-fold. α-Lithium-halide eliminations and intermolecular couplings between the
lithiated reagent and the halide-substituted species are two important competing reactions that have long prevented polylithiation reactions from being practically considered. Another reason for the little attention given to multiple metal-halide exchanges is because polylithiated compounds exhibit limited solubility in most organic solvents, forming rather insoluble aggregates of little utility. Added to the previous complications, different requirements have to be fulfilled by a multifunctional initiator in order to produce polymers with uniform arms, low molecular weight distribution, and controllable molecular weights. All the initiation sites must be equally reactive and have the same rate of initiation. Furthermore, the initiation rate must be higher than the propagation rate.

For instance, in polymer chemistry polylithiation has never been contemplated for the reasons mentioned above; had it been mastered and the experimental conditions worked out polylithiation would be a viable and straightforward route to prepare multicarbanionic initiators for the subsequent synthesis of star-shaped polymers. So far the only possibility of generating such multicarbanionic initiators was lithiation by addition to multivinyl compounds, but the very small number of reports on this strategy of synthesis indicates that it is not that convenient a route. It indeed requires the prior synthesis of multivinyl compounds that would not homopolymerize upon addition of organolithium reagents. These constraints explain why the only initiator of precise functionality (higher than 2) ever synthesized by this method is the tricarbanionic compound of Quirk and Tsai\textsuperscript{20} who obtained it upon addition of $\text{sec}$-butyllithium onto a molecule containing three 1,1-diphenylethylene-type unsaturations (Figure 1-2).
\[ \text{R-Li} + \text{R'}-\text{X} \rightarrow \text{R-R'} + \text{LiX} \]

\(X: \text{Halide atom}\)
\(\text{R and R': Alkyl groups}\)

Figure 1-1. Wurtz coupling reaction.

Figure 1-2. Synthesis of a tricarbanionic initiator.

Figure 1-3. Synthesis of polylithiated carbosilane dendrimers.
Figures 1-4. Synthesis of pluricarbanionic species from DVB.

\[ s-\text{BuLi} + \text{Ar-Br} \rightarrow \text{Ar-Li}^+ + \text{Br}^- \]

Figures 1-5. Halogen-lithium exchange reaction.

CHAPTER 2
A NOVEL ADDITIVE-FREE DICARBANIONIC INITIATOR FOR THE SYNTHESIS OF POLY(STYRENE-\textit{b}-DIENE-\textit{b}-STYRENE) TRIBLOCK COPOLYMERS IN NON-POLAR MEDIUM

2.1 Introduction

Living anionic polymerization is certainly the most reliable and versatile technique for the synthesis of block copolymers. Under appropriate conditions anionic polymerization indeed proceeds in absence of transfer and termination reactions for a large number of monomers. For this reason, it occupies a key position in the industrial production of block copolymers, the most emblematic being SBS triblock copolymers comprising a low T\textsubscript{g} polybutadiene block flanked by two glassy polystyrene end blocks. Such triblocks are industrially obtained by sequential polymerization of styrene and butadiene initiated by butyllithium (BuLi), followed by the deactivation of growing living carbanionic chains by a difunctional electrophilic reagent. Although applied for the last forty years this method is very sensitive to the stoichiometry of the final dichain coupling, and therefore fails to deliver diblock-free pure triblock copolymers. The presence of diblock contaminants in the final sample is detrimental to excellent stress-strain properties—23% decrease in tensile strength due just 5% of diblocks—and prejudicial to its ultimate in commercial applications. The use of a dicarbanionic initiator that could trigger polymerization in two directions and afford SBS triblocks by a two-step sequential monomer addition therefore appeared as the only viable alternative. However, one major difficulty met in the latter case is the limited solubility of dicarbanionic initiators in apolar solvents, media that are required for the preparation of a polybutadiene (PB) central block with a high content in 1,4-PB units and elastomers with optimal properties (high tensile strength and elongation at break). Although a number of patents and papers have reported on the synthesis of various organolithium diinitiators in non-polar solvents, none of them could be practically used to prepare well-defined SBS triblock copolymers with a large content in 1,4 linkages and equal amounts of cis- and trans-
unsaturations. Whether obtained by reaction of BuLi with appropriate diolefinic species in 2:1 ratio (m-diisopropenylbenzene,16,54-72 double diphenylethylene-type molecules17,18,73-82 or more complicated precursors19,83,84) or by generation of ion-radical species which then couple (electron-transfer from lithium to α-substituted vinyl monomers),52,85-103 all these organolithium diinitiators indeed require the presence of active polar additives—often in small proportions—to efficiently initiate polymerization, modifying the stereochemistry of the polydiene block and increasing its content in 1,2 unsaturations. A dicarbanionic initiator that would be entirely soluble in apolar medium in absence of any additives or ligands and yet reactive enough is thus still in great demand.

2.2 Literature Overview on Symmetric ABA Triblock Copolymers

Linear triblock copolymers consisting of two chemically different monomers of the symmetric type contain three blocks of A and B monomers arranged in a way that the first and the third block have the same chemical nature and molecular weight, whereas the middle block differs in chemical nature. There are three possible procedures to synthesize block copolymers of this type.

2.2.1 Sequential Monomer Addition

The preparation of block copolymers by sequential addition of monomers using living anionic polymerization and a monofunctional initiator is the most direct method for preparing well-defined block copolymers. In this reaction scheme (Figure 2-1), the first monomer is polymerized by an alkyllithium initiator followed by the polymerization of the second one. After complete consumption of the second monomer, an equal amount of the first monomer is added to the reaction mixture resulting in an ABA triblock copolymer (Figure 2-1).

This approach involves three monomer additions, and, therefore, the probability of partial termination of growing chains during the second or the third reaction step increases, due to impurities present in the monomers used. This can result in the presence of undesirable
homopolymer A and/or diblock AB in the final product. Furthermore, small differences in the quantity of monomer A used in the first and third step may result in the synthesis of a triblock, which is not perfectly symmetric. Another point that must be considered is the ability of monomer B to initiate polymerization of monomer A. If this criterion is not fulfilled, ill-defined products will be obtained. This critical aspect can be illustrated by considering the preparation of SBS triblock copolymers. Indeed, the rate of the crossover reaction of polybutadienyllithium to styrene monomer to form polystyryllithium chain end is slow compared to the rate of styrene propagation (order of reaction rate constants is \( k_{SB} > k_{SS} > k_{BB} > k_{BS} \)).\textsuperscript{104} Because of the slow rate of styrene initiation relative to propagation, a broad molecular weight distribution would be expected for the final polystyrene block segments. To obtain polystyrene end blocks with narrow molecular weight distributions, a Lewis base such as an ether or amine is often added before styrene monomer addition in this third stage of the triblock copolymer synthesis.\textsuperscript{50,53,105-108} Sometimes even monomer A may not be able to initiate polymerization of monomer B appropriately. A typical example is the preparation of PI-PS-PI triblock copolymers.\textsuperscript{109} Initiation of styrene by PILi can be successful if a small amount of THF is used before the addition of styrene,\textsuperscript{109} but one should have in mind that the presence of THF will alter the microstructure of the third PI block. It is obvious that the outlined method cannot be used in the present example if high 1,4-microstructure of the PI blocks is desired. However, it can be applied in the case where the 1,4-microstructure is not essential. In this case THF can be added from the beginning of the polymerization and both end PI blocks will have the same microstructure.

### 2.2.2 Coupling of Living AB Chains

Another general method for the of ABA triblock copolymers involves first the synthesis by a two-step sequential monomer addition sequence of a living AB diblock copolymer, having the same composition but half the molecular weight of the final triblock
copolymers. Then an appropriate coupling agent, i.e. a compound having two functional groups able to react with the active anions forming covalent bonds, is used to connect two AB chains producing the desired symmetric triblock copolymer (Figure 2-2). This two-step method with coupling offers many advantages over the three-step sequential monomer addition method. From a practical point of view, the polymerization time is reduced to one-half that required for the three-step synthesis of a triblock copolymer with the same molecular weight and composition. One problem avoided in the two-step process is that the final crossover step from polybutadienyllithium or polyisoprenyllithium to styrene is eliminated. The elimination of the third monomer addition step also decreases the possibility of termination by impurities in a third monomer addition. However, caution should be exercised in the stoichiometry of the coupling reaction. In practice, it is difficult to control the stoichiometry of the coupling reaction and many two-step syntheses yield triblock copolymers with significant amounts of uncoupled diblock contaminants. Indeed, excess of living anions is usually used to ensure complete reaction of both groups of the coupling agent. In general, the presence of diblock material affects the triblock copolymer morphology, which has a detrimental effect on physical properties of triblock copolymers (ultimate tensile strength and elongation at break). This makes necessary an additional fractionation step in order to separate the ABA triblock copolymers from excess AB diblock copolymers. Finally, the coupling reaction may be completed in days. Obviously, this synthetic route is more time consuming than the sequential addition method.

PS-PI (or PB)-PS triblock copolymers have been synthesized by the coupling method by Morton and co-workers (Scheme 2-2). A PS-PD diblock is formed first where the length of the polydiene (PI or PB) block is half of that in the final triblock copolymer. Then the living diblocks are coupled using (CH₃)₂SiCl₂ as the coupling agent. A small excess of the living diblock is used in order to ensure complete coupling. Solvent/nonsolvent fractionation
of the crude product is performed in order to isolate the pure triblock copolymers. These triblocks have found applications as thermoplastic elastomers in everyday life. PD-PS-PD symmetric triblock copolymers can also be made in the same way. \((\text{CH}_3)_2\text{SiCl}_2\) can also be used as a coupling agent for PS (or PD)-polysiloxane living diblocks in order to produce triblocks with a siloxane central block.\(^{113,114}\) When the outer blocks are PB with high 1,4-microstructure, PE-PDMS-PE triblocks with semicrystalline outer and elastomeric inner blocks are obtained by hydrogenation of the parent PB-PDMS-PB materials.\(^{114}\)

Another advantage of the two-step process is that it is more versatile with respect to the chemical composition of the center block. With the two-step method, the center block can be a more reactive monomer that would not be capable of reinitiating polymerization of styrene because of the increased stability of the chain end (Figure 2-3).

For example, bis(bromomethyl)benzene has been used as a coupling agent in cases where living (meth)acrylate (M) and vinylpyridine (2VP) anions were involved.\(^{115}\) Due to the greater reactivity of the C-Br bond, this agent is efficient for coupling less reactive anions at lower temperatures (Figure 2-3). Well-defined symmetric triblock copolymers with pyridine or (meth)acrylate central blocks can be prepared in both cases. Varshney et al.\(^{116}\) used terephthaloyl chloride as the coupling agent for the synthesis of ABA symmetric triblock copolymers with PS, P2VP, or polydiene of high 1,4 microstructure end blocks, and poly(tert-butyl acrylate) middle blocks. The PrBuA blocks could be converted to other types of acrylic blocks by transesterification reactions, leading to a larger variety of ABA triblock copolymers.

**2.2.3 Use of a Difunctional Initiator**

One of the most versatile methods for the synthesis of symmetric ABA triblock copolymers is the use of a difunctional initiator, i.e., an organometallic compound having two anionic sites able to initiate polymerization, in a two-step sequential monomer addition
sequence. The middle B block is formed first followed by the polymerization of A monomer. A number of difunctional initiators soluble in polar and/or nonpolar solvents have been reported in the literature.\textsuperscript{15-19} The points that deserve attention are:

i) The quality of the difunctional initiator used, which is essentially its ability to form pure difunctional polymer. This depends on the precise chemical structure of the initiator and sometimes the solvent medium as well as the chemical nature of the monomer used. Not all known difunctional initiators behave in the desired manner in all solvents commonly used for anionic polymerization and towards any available monomer. If the initiator/solvent/monomer system cannot generate pure difunctional polymers, it is obvious that the final product will be a mixture of homopolymer, diblock, and triblock copolymer.

ii) The purity of the monomers must be high in order to avoid deactivation of one or both initiators’ active sites or lead to premature termination of growing chains, which will result in a mixture containing the desired triblock and other undesired impurities that are difficult to be eliminated by fractionation or other separation methods.

In our case, we will be especially interested in the hydrocarbon-soluble dilithium initiators required for the two-step synthesis of polystyrene-\textit{b}-polybutadiene-\textit{b}-polystyrene triblock copolymers. Indeed, a hydrocarbon-soluble dilithium initiator ensures that the polydiene center block will have a high 1,4-microstructure and a correspondingly low glass transition temperature.

\subsection{Divinylbenzene derivatives}

Adduct of divinylbenzene (DVB) derivatives with \textit{s}-BuLi were the first examples of difunctional initiators studied since the early 1970’s.\textsuperscript{54,58,59} Different studies on DVB demonstrated first that the two unsaturations of the meta isomeric compound were equally reactive to BuLi, in opposition to the conjugated unsaturations of the para compound (1,4-DVB). However, a mixture of soluble mono- and dilithiated and oligomeric species, with
functionality higher than two due to possible polymerization of DVB, was obtained which did not guarantee a good control of the diene polymerization. Another dilithium initiator claimed by Rempp and colleagues was a bis-adduct of BuLi onto \( m \)-Diisopropenylbenzene (\( m \)-DIB), which was an efficient bifunctional initiator in apolar solvent that affords a good control over the molar mass and narrow molar mass distribution even in the presence of a mixture of multiadduct, diadduct and unreacted sec-BuLi. Foss et al. and Cameron et al. have also used \( m \)-DIB as a difunctional precursor, but had to add a \( \sigma \)-complexing polar agent such as triethylamine (Et\(_3\)N) to avoid precipitation of the initiator. However, even in the presence of Et\(_3\)N a mixture of species was still observed after the reaction between \( m \)-DIB and sec-BuLi. We have to wait the work of Yu et al. who also revisited these experiments and demonstrated that the use of precursors such as \( 1,3 \)-diisopropenylbenzene with twice the amount of sec-BuLi in non-polar medium such as cyclohexane did not result in a soluble well-defined truly bifunctional initiator; they found that the reaction of tert-BuLi—instead of sec-BuLi—and \( 1,3 \)-DIB in the presence of 1 equivalent of Et\(_3\)N at \(-20^\circ\)C can lead to a well-defined difunctional initiator, i.e. 1,3-bis(1-lithio-1,3,3’-trimethylbutyl)benzene (DiLi) (Figure 2-4).

Some other \( \sigma \)-complexing polar agents such as diethyl ether, tert-butyl methyl ether, N,N,N’,N’-tetramethylethlenediamine (TMEDA) and THF were found to be efficient polar additives, but leading to a high 1,2-microstructure of the PB block. The same group finally demonstrated that the combination of the initiator seeding technique and weakly polar additives such as tert-BuOLi and anisole was necessary to prevent the presence of residual initiator and achieve equal reactivity of both ends active centers so as to obtain SBS and MBM triblock copolymers with high content of 1,4-PB units. \( \pi \)-Complexing agents such as 1,2,4,5-tetramethylbenzene (durene) or tetraphenylethylene (TPhE) were also proposed which
did not interact so strongly as σ-complexing agents with the Li⁺ cation to bring about the dissociation of the organolithium aggregates.⁶⁹,⁷⁰,⁷²

2.2.3.2 Diphenylethylene-type molecules

Other researchers concentrated their efforts on the reaction of double Diphenylethylene-type (DDPE) molecules with stoichiometric amount of sec-BuLi in non-polar solvents. Broske et al.⁷⁶,⁷⁸ observed at 60°C after 2 hours in cyclohexane in presence of a small excess of sec-BuLi the formation of a soluble well-defined difunctional initiator with a negligible quantity of oligomers. It was demonstrated that this difunctional initiator was efficient in the case of the butadiene polymerization, but only at low monomer conversion. Later, Quirk and Ma⁷⁹ reported that the dilithium initiator based on 1,3-di(1-phenylethenyl)benzene (PEB), although soluble in hydrocarbon solvents such as cyclohexane and benzene, led to bimodal molar mass distribution for molar masses lower than 50,000 and 150,000 g.mol⁻¹ in the cases of PS and PB, respectively. This is only after the addition of sec-butoxylithium (sec-BuOLi) as an additive that PB samples were obtained with a narrow molar mass distribution and a high content of 1,4-PB units (Figure 2-5).⁷⁹

More recently, Tung and Lo,¹⁷,¹⁸,⁸⁰-⁸² who first proposed the idea of using DDPE as precursors, developed dilithium initiators based on different derivatives of DDPE (Figure 2-6), which were soluble in benzene, cyclohexane and/or toluene depending on the structure of the DDPE derivative. Although the addition reactions of these latter precursors with sec-BuLi were found to be clean and rapid, the resulting dilithium initiators were insoluble forming fine suspensions, which would coagulate into hard particles after several hours. The fine suspensions were effective in initiating butadiene or isoprene polymerization, but only after solubilizing the dilithium initiators by using additives such as N,N,N’,N”-,N”-pentamethyldiethylenetriamine (PMDETA) and lithium alkoxides or by reaction with a
fractional amount of diene first and then with the rest of the monomer, also called seeding technique.

Finally, more complicated precursors such as \(\alpha,\omega\)-bis(phenylvinylidenyl)alkanes\(^{19,83,84}\) and \(\alpha,\omega\)-bis(isopropenylphenyl)alkanes\(^{19,83,84}\) or some other listed below (Figure 2-6) were developed and found to be effective for the polymerization of styrene or diene, but difficult to synthesize.

2.2.3.3 Use of alkali metals

Another way of making diinitiators consists in the reaction of alkali metals with \(\alpha\)-substituted vinyl monomers.\(^{88,89,91-101}\) For example, this reaction is useful for the preparation of homogeneous difunctional initiators from \(\alpha\)-methylstyrene in polar solvents such as THF. Because of the low ceiling temperature of \(\alpha\)-methylstyrene, dimers or tetramers can be formed depending on the alkali metal system, temperature, and concentration. SBS triblock copolymers were synthesized using a dicarbanionic initiator formed by the reaction of lithium metal and \(\alpha\)-methylstyrene (Figure 2-7).\(^{89}\) However, the presence of THF needed for the formation of the dicarbanionic initiator resulted in SBS triblock copolymers with poor mechanical properties.

Many aromatic hydrocarbons such as naphtalene can also react with alkali metals by reversible electron transfer in polar aprotic solvents such as THF to form stable solutions of the corresponding radical anions (Figure 2-8).\(^{47,48,102,103}\) PEO-PI-PEO symmetric triblock copolymers were synthesized using sodium or potassium naphthalene as the difunctional initiator.\(^{103}\) Isoprene was polymerized first followed by addition of EO (Scheme 2-8). The copolymers had a variety of block compositions and total molecular weights. Their molecular weight distributions were narrow and monomodal. Since Na or K naphthalenide is soluble only in polar solvents (e.g., THF), the microstructure of PI obtained was mostly 3,4. Thus, these initiators are of limited utility for the preparation of elastomeric block copolymers.
because they are prepared and utilized in polar solvents such as THF that result in polydiene with high vinyl microstructures and relatively high Tg values.

2.3 Results and Discussion

We reported in chapter 3 the preparation of tri- and tetrafunctional polylithium organic compounds by lithium-halogen exchange and their use as initiators for the synthesis of polystyrene (PS) and polybutadiene star polymers and SBM triblock star copolymers (Chapter 3). This method rests on the metallation of poly(arylhalide)s whose halogens are carried by separate aryl rings. However, the polylithiated species formed are soluble only in the presence of σ/µ-coordinating ligands. We propose here a new dicarbanionic initiator that is totally soluble in apolar media in absence of any additive, and is efficient enough to generate well-defined telechelic PB and SBS triblock copolymers with a high content in 1,4-PB units.

For this purpose, 3-pentadecyl phenol, obtained from cashew nut shell—a renewable resource material and by-product of agro industry—served as a precursor for the dibromo compound \textit{viz}, 1-bromo-4-(4′-bromophenoxy)-2-pentadecyl benzene; the latter was subsequently dilithiated and eventually used for difunctional initiation. In this chemistry advantage is taken of the saturated 15-carbon side chain to obtain a soluble dilithiated initiator.

The dibromo compound 1 was synthesized by a two-step synthetic procedure (Figure 2-9). In the first step, 1-pentadecyl-3-phenoxy benzene was prepared by reaction of potassium 3-pentadecyl phenolate (product of the deprotonation of 3-pentadecyl phenol) and bromobenzene. In the second step, the dibromoprecursor 1 was obtained in excellent yields (84 %) after bromination in para position of 1-pentadecyl-3-phenoxy benzene (Figure 2-9). The structure of the dibromo compound 1 was confirmed by \textit{H and }\textit{C NMR spectroscopy and mass spectrometry (Figures 2-10 and 2-11).
Next, 1 was treated with stoichiometric amounts of sec-butyl lithium (s-BuLi) in cyclohexane to generate 1' and 2-bromobutane (Figure 2-12). Among the different alkyl lithium reagents sec-butyl lithium was found to be the most efficient for the bromide/lithium exchange reaction (quantitative reaction with no side reactions such as coupling and elimination). tert-Butyllithium is more suitable for the iodine/lithium exchange reaction. To avoid any chance of deactivation of the growing carbanionic chains of PS or PB by 2-bromobutane during polymerization (Figure 2-13), another equivalent of s-BuLi was added prior to monomer addition to give 3,4-dimethylhexane (2) as previously demonstrated (Figure 2-12).

Indeed, the different possible secondary reactions that could happen during the halogen-lithium exchange reaction were previously studied. It was first demonstrated by gas chromatography analysis that aryllithium species are not nucleophilic enough to react with 2-bromobutane without the presence of polar additives such as tetramethylethylenediamine (TMEDA). Even in presence of TMEDA, this reaction is slow since only 10% of 2-bromobutane is consumed after 90 minutes of reaction (Figure 2-13). Some other previous studies have also shown that benzene when used as solvent can react with s-BuLi in presence of TMEDA to give the corresponding phenyllithium species (Figure 2-13). The latter are able to initiate the monomer polymerization to generate a multimodal distribution.

The diadduct product 1' resulting from the reaction of 1 with s-BuLi took in cyclohexane a yellow color at the concentration of [Li+] = 5.3x10^{-2} M and a gelly aspect unlike the insoluble precipitate formed from the reaction of 4,4'-dibromobenzene with s-BuLi in the same solvent. The formation of such a physical gel instead of a solid precipitate is due to the presence of the C15 side alkyl tail which helped preventing the irreversible precipitation of the dilithiated species.
The halogen/lithium exchange reaction between 1 and s-BuLi was thoroughly investigated by $^1$H and $^{13}$C NMR spectroscopy and mass spectrometry (Figure 2-14). The structure of the dilithium diadduct $1'$ was first confirmed by $^1$H (good integration values) and $^{13}$C NMR spectroscopy analysis of the product isolated after methanol quenching of a solution of $1'$ in cyclohexane ($[Li^+] = 5.3 \times 10^{-2}$ M). Moreover, mass spectrometry analysis showed the total disappearance of the peak of the dibromo precursor 1 ($M = 538$ g/mol) in favor of $1'$ with a principal peak at $M = 381$ g/mol after methanolysis (Figure 2-15).

After checking the quantitative halogen/lithium exchange reaction at this concentration ($[Li^+] = 5.3 \times 10^{-2}$ M) and the truly difunctional initiator structure, styrene or butadiene were polymerized by addition of the corresponding monomer (Figure 2-16). After introduction of a few monomer units the dilithiated species appear totally soluble in cyclohexane even in absence of stirring and of any polar additives. On deactivation of the living carbanionic chains by ethylene oxide after complete monomer consumption $\alpha,\omega$-dihydroxy telechelic polymers were obtained from $1'$. Analysis by size exclusion chromatography (SEC) indicated the complete consumption of the initiator (Figure 2-17). No peak attributable to residual 1 could be detected in the low molar mass region, and the only trace seen was a narrow and monomodal peak corresponding to the expected linear polymer in the high molar mass region (Figure 2-17).

Such good control over the molar mass (good agreement between the experimental and theoretical values of molar masses) and narrow molar mass distribution ($M_w/M_n < 1.1$) reflects a rate of initiation by $1'$ comparable to that of propagation (Table 2-1). The structure of the difunctional polymer formed could be established first by $^1$H NMR analysis using $\alpha,\omega$-dihydroxy telechelic polybutadiene samples of low degrees of polymerization (Figure 2-18). From the ratio of the integration values due to the signal of the aromatic protons of the difunctional initiator ($\delta = 6.5-7.5$ ppm) to that of $\text{-CH}_2\text{-OH}$ chain ends ($\delta = 3.7$ ppm) the
actual functionality of the samples prepared could be determined: functionality values close to 2 were obtained for the polybutadiene telechelics. Furthermore, the microstructure of the polybutadiene samples determined by $^1$H and $^{13}$C NMR spectroscopy (Figures 2-18 and 2-19) demonstrated a high percentage of 1,4-PB units (86-91%) in agreement with the fact that the polymerization occurred in an apolar solvent without any additives. This proportion of 1,4-PB units was almost half constituted of 1,4-cis and 1,4-trans (Table 2-1 and Figure 2-19), which is generally the case for linear polybutadiene synthesized using butyllithium as initiator in apolar solvents.\textsuperscript{15}

After demonstrating the efficiency of this dicarbanionic initiator for the synthesis of polybutadiene telechelics with optimal elastomeric properties (high percentage of 1,4-PB units), SBS triblock copolymers were derived by sequential anionic polymerization of butadiene (B), and styrene (S) with $\mathbf{I'}$ as initiator (Figure 2-20).

The initiation of styrene by polybutadienyllithium being slow compared to the reverse situation, it was necessary to dilute further the reaction medium with fresh cyclohexane and some THF (Cyclohexane/THF: 100/1 in volume). Upon introduction of styrene, the color of the medium changed instantaneously from the characteristic yellow color of polybutadienyllithium carbanions to the orange color of polystyryllithium carbanions. By taking an aliquot before the introduction of styrene, the formation of the SBS samples could be easily followed by SEC (Figure 2-21).

The absolute molar masses of the SBS triblock copolymers were deduced by $^1$H NMR spectroscopy knowing that of their polybutadiene precursor determined by SEC (Table 2-2 and Figure 2-22). In all cases narrow molar mass distributions were observed either for the polybutadiene precursor or for the triblock copolymer structure with a complete consumption of the polybutadiene precursor during the polymerization of styrene as attested by SEC with the disappearance of the polybutadiene peak (Figure 2-21): this demonstrates that the growth
of either the polybutadiene middle block or the two polystyrene glassy end blocks occurred under living conditions. The mechanical properties, e.g., ultimate tensile strength and elongation at break, of the SBS triblock copolymers containing small polystyrene end blocks (%wt (PS) < 35%) were also studied to bring an other proof of the well-defined structure of these SBS triblock samples. As shown in Table 2-2, excellent mechanical properties are obtained with ultimate tensile strength higher than 30 MPa and elongation at break of 1000% (Runs 10 and 11, Table 2-2) which are in good agreement with the mechanical properties generally obtained by SBS copolymers.132-135

2.4 Conclusion

In summary, the halogen-lithium exchange reaction has been successfully applied to generate a new dicarbanionic initiator from a dibromoaryl compound. The presence of a C15 side alkyl tail in the dibromo precursor is essential to the solubility of the dilithiated initiator in apolar solvent. This is the first example of dilithiated species initiating efficiently anionic polymerization in absence of additive and affording well-defined polybutadiene telechelics with a high percentage of 1,4-PB units (91%).122,123 This initiator has proved to be very efficient in providing SBS triblock copolymers with excellent mechanical properties, e.g., ultimate tensile strength higher than 30 MPa and elongation at break of 1000%.122,123 A long-standing problem faced by the industry of styrenic thermoplastic elastomers for the last forty years could be worked out with the results disclosed in this contribution.
Figure 2-1. Synthesis of SBS triblock copolymer by sequential monomer addition.

Figure 2-2. Synthesis of SIS triblock copolymer by coupling of living chains on dichlorodimethylsilane.
Figure 2-3. Synthesis of P(S-\(b\)-tBA-\(b\)-S) triblock copolymer by coupling of living chains on bis(bromomethyl)benzene.

Figure 2-4. Synthesis of SBS triblock copolymer using 1,3-diisopropenylbenzene as precursor.

Figure 2-5. Synthesis of SBS triblock copolymer using 1,3-di(1-phenylethenyl)benzene as precursor.
Figure 2-6. Complex diolefinic precursors used for the synthesis of organolithium diinitiators (A\textsuperscript{19,83}, B\textsuperscript{16}, C\textsuperscript{84}, D\textsuperscript{117}, E-M\textsuperscript{17,82,118}, N\textsuperscript{119}, O\textsuperscript{120}).
Figure 2-7. Synthesis of SBS triblock copolymer from a dicarbanionic initiator formed by the reaction of lithium metal and α-methylstyrene.

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Figure 2-9. Synthesis of 1-bromo-4-(4’-bromophenoxy)-2-pentadecyl benzene (1).
Figure 2-10. $^1$H and $^{13}$C NMR spectra (CD$_2$Cl$_2$, 400 MHz) of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene (1).
Figure 2-11. Mass spectrum of 1-bromo-4-(4’-bromophenoxy)-2-pentadecyl benzene (1).

Figure 2-12. Synthesis of a dicarbanionic initiator by halogen-lithium exchange reaction using 1 as dibromo precursor.
Figure 2-13. Secondary reactions resulting from the halogen-lithium exchange reaction.
Figure 2-14. $^1$H and $^{13}$C NMR spectra (CD$_2$Cl$_2$, 400 MHz) of the addition product of 1 with sec-butyllithium obtained after methanolysis.
Figure 2-15. Mass spectrum of the addition product of $1$ with sec-butyllithium obtained after methanolysis.

\[
\begin{align*}
\text{Br-O-Br} & \quad \text{4 s-BuLi} \\
\text{C}_5\text{H}_{11} & \quad \text{Cyclohexane} \\
\text{R.T., } 30 \text{ min} & \quad \text{Li-O-Li} + 2
\end{align*}
\]

1) $1$, R.T., 24h

2) $1'$, R.T., 30 min

3) CH$_3$OH/HCl

Figure 2-16. Synthesis of $\alpha,\omega$-dihydroxy telechelic polybutadiene from $1'$. 

\[
\begin{align*}
\text{HO-} & \quad \text{OH}
\end{align*}
\]
Figure 2-17. SEC eluograms of (PS)$_2$ difunctional polystyrene and (PB)$_2$ difunctional polybutadiene: a) Protonated version of 1'; b) Linear polystyrene (Run 2, Table 2-1); and c) Linear polybutadiene (Run 7, Table 2-1).
Figure 2-18. $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of $\alpha$,$\omega$-dihydroxy terminated polybutadiene (Run 3, Table 2-1).

Figure 2-19. $^{13}$C NMR spectrum (CDCl$_3$, 400 MHz) of a $\alpha$,$\omega$-dihydroxy terminated polybutadiene (Run 6, Table 2-1).
Figure 2-20. Synthesis of SBS triblock copolymer from $1'$.

Figure 2-21. SEC eluograms monitoring the formation of a SBS triblock copolymer initiated in cyclohexane with $1'$ (Run 11, Table 2-2).
Figure 2-22. $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of a SBS triblock copolymer (Run 11, Table 2-2).

Table 2-1. Characterization of PS and PB samples synthesized from $\mathbf{1'}$ difunctional initiator.$^{[a]}$

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Polymer</th>
<th>$M_n$ $^{[b]}$</th>
<th>$M_n$/$M_n$ $^{[b]}$</th>
<th>$M_n$ (theo) $^{[c]}$</th>
<th>Yield (%)</th>
<th>Microstructure (%) $^{[d]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1,4-cis</td>
</tr>
<tr>
<td>1</td>
<td>PS$_2$</td>
<td>11400</td>
<td>1.15</td>
<td>12000</td>
<td>97</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>PS$_2$</td>
<td>43800</td>
<td>1.13</td>
<td>44000</td>
<td>98</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>PB$_2$</td>
<td>2100</td>
<td>1.2</td>
<td>2000</td>
<td>98</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>PB$_2$</td>
<td>6200</td>
<td>1.13</td>
<td>7000</td>
<td>98</td>
<td>39</td>
</tr>
<tr>
<td>5</td>
<td>PB$_2$</td>
<td>16600</td>
<td>1.07</td>
<td>17000</td>
<td>99</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>PB$_2$</td>
<td>43700</td>
<td>1.06</td>
<td>43000</td>
<td>98</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>PB$_2$</td>
<td>51900</td>
<td>1.08</td>
<td>52000</td>
<td>97</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>PB$_2$</td>
<td>67400</td>
<td>1.1</td>
<td>70000</td>
<td>98</td>
<td>41</td>
</tr>
</tbody>
</table>

[a] Butadiene polymerization was initiated in cyclohexane with $\mathbf{1'}$ ([Li$^+$] = 5.3*10$^{-2}$ M). [b] Determined by SEC in THF using a refractometric detector. A conversion factor of 0.55 was used for the calculation of the PB molar mass. [c] $M_n$ (theo) = $M_{\text{butadiene}}$ x ([Butadiene]/[-PhLi]) x 2. [d] Calculated by $^1$H and $^{13}$C NMR.
Table 2-2. Mechanical properties of SBS triblock copolymers initiated by \( \text{I'} \).\[a\]

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>PB(_2)</th>
<th>1,4-PB(_c) (%)</th>
<th>Ultimate tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M_n )[b]</td>
<td>( M_w / M_n )[b]</td>
<td>( M_n )[b]</td>
<td>( M_n )[c]</td>
</tr>
<tr>
<td>9</td>
<td>6200</td>
<td>1.13</td>
<td>20400</td>
<td>18300</td>
</tr>
<tr>
<td>10</td>
<td>43700</td>
<td>1.1</td>
<td>78300</td>
<td>60300</td>
</tr>
<tr>
<td>11</td>
<td>67400</td>
<td>1.1</td>
<td>110900</td>
<td>93500</td>
</tr>
</tbody>
</table>

\[a\] Butadiene polymerization was initiated in cyclohexane with \( \text{I'} \) ([Li\(^+\)] = 5.3*10\(^{-2}\) M). \[b\] Determined by SEC in THF using a refractometric detector. A conversion factor of 0.55 was used for the calculation of the PB molar mass. \[c\] Determined by \(^1\)H NMR from the molar mass of the polybutadiene block, assuming 100% efficiency in the initiation of the second block.
CHAPTER 3
TRI- AND TETRACARBANIONIC INITIATORS BY A LITHIUM/HALIDE EXCHANGE REACTION : APPLICATION TO STAR-POLYMER SYNTHESIS

3.1 Introduction

Star-branched polymers represent the most simple polymer branched structures. A star-branched polymer consists of several linear chains linked together at one end of each chain by a single branch or junction point,\textsuperscript{136-138} in opposition to graft, dendrimer-like, and hyperbranched polymers. Among these star-branched polymers, three categories of star polymers can be distinguished by the nature and the lengths of their branches:

- Asymmetric stars with branches of same nature (i.e., same polymer), but different length.\textsuperscript{139,140}
- “Mikto-arm” stars which are constituted of polymer branches of different nature connected to the same core.\textsuperscript{139}
- \((A)_n\) (homopolymer) or \((AB)_n\) (diblock branches) stars connecting branches of same nature and length.\textsuperscript{140,141}

We will be especially interested in this chapter by the \((A)_n\) and \((AB)_n\) star polymers.

Star polymers are produced through three general synthetic routes (Figure 3-1).\textsuperscript{141} The first also called “arm-first” method involves the synthesis of preformed arms followed by reaction with a multifunctional linking agent. The second route is a slight variation of the latter one, which sometimes is also termed the “in-out” method. This approach entails a coupling reaction of linear living chains with multifunctional agent such as divinyl compounds and a cross-over reaction to a second monomer to form star polymers. The third one is the “core-first” technique, which involves the use of a multifunctional initiator to initiate the polymerization of multiple branches of the star. Basically, the number of arms of the star polymer can be determined by the number of initiating sites. The latter approach is a major challenge since it requires the prior design of well-defined multifunctional initiator.
Furthermore, all the initiation sites must exhibit the same reactivity. However, anionic polymerization suffers from the lack of pluricarbanionic initiator exhibiting precise functionality and good solubility. In comparison to controlled radical\textsuperscript{142} and cationic\textsuperscript{143} polymerizations where various plurifunctional initiators were described, only a few pluricarbanionic initiators could be successfully developed in anionic polymerization\textsuperscript{20,22}.

3.2 Literature Overview on (A)\textsubscript{n} and (AB)\textsubscript{n} Star Polymer Synthesis

3.2.1 “Arm-first” Method

Two distinct strategies were used in this case. The first strategy involves the synthesis of living macroanionic chains and their subsequent reaction with a well-defined multifunctional electrophile, which acts as the linking agent (Figure 3-2).

In such a case, the polymer chains possess either active centers (*) at their chain ends or functions capable of reacting with the antagonist functions (F) of the coupling agent. The required conditions for obtaining well-defined star polymers (i.e. low molecular weight distribution) are the precise functionality (number of functions F) of the coupling agent and the selectivity of the reaction between active centers and the latter F functions.

In some other cases, it was needed to compensate for the lack of deactivating linking agent of precise and higher functionality by the copolymerization of the living macroanionic chains with a difunctional comonomer (divinyl, diepoxide, etc…). This second strategy was elaborated to access star polymers with a very high number of branches. The principle of the copolymerization of living chains with a difunctional comonomer is illustrated in Figure 3-3.

The grafting reactions on the pendant vinylic groups—which can be in competition with the intramolecular cyclization—has as a consequence on the formation of a cross-linked core possessing a certain number of branches and affording by the fact a star structure. However, it is difficult to avoid the presence of residual linear chains because of the low reactivity of the pendant sites (double bonds) towards active centers.
3.2.1.1 Use of multifunctional coupling agent

Several linking agents have been used for the synthesis of star polymers.\textsuperscript{15} The most important of those are chlorosilanes\textsuperscript{144} and chloromethyl or bromomethyl benzene derivatives.\textsuperscript{145,146}

**Chlorosilane compounds.** The use of tetrachlorosilane as electrophilic coupling agent for the synthesis of four-armed PS stars was described for the first time in 1962 by Morton \textit{et al.}\textsuperscript{144} Isomolecular polystyryllithium chains initiated by \textit{n}-butyllithium were added on this tetrafunctional linking agent in hydrocarbon solvent. However, this reaction is not complete even in the presence of large excess of living chains. The purification by a fractionation technique was needed in this case to separate the four-arm from the three-arm stars.

In 1965, Zelinski and Wofford\textsuperscript{147} also used the tri- and tetrachlorosilane derivatives for the synthesis of PB star polymers by deactivation of polybutadienyllithium chains. In opposition to the results obtained for the polystyryllithium chains, the reaction is quantitative and lead to the formation of well-defined PB stars. The molecular-weight data, the good correlation between the intrinsic viscosity and the molecular-weight, and the fractionation data allowed them to conclude to the complete stoichiometric coupling reaction between the polybutadienyllithium chains and this family of chlorosilane compounds.

Fetters and Morton\textsuperscript{148} demonstrated in their case that the stoichiometric reaction of the polyisoprenyllithium chains with tetrachlorosilane agent gives in majority three-arm stars.

From these previous results, it appears that the grafting reaction efficiency varies as follow:

\[
\text{polybutadienyllithium} > \text{polyisoprenyllithium} > \text{polystyryllithium}
\]

Since the observed evolution is in opposition to the evolution of the intrinsic reactivity of the living chains, it was concluded that only the steric hindrance generated as the coupling reaction proceeds influences the reaction efficiency. To remedy this problem and thus
increase the yield of the coupling reaction in the cases of polystyryllithium and polyisoprenyllithium chains, few butadiene units (average of five) were added before the reaction with the chlorosilane compound. By this way, Fetters and Morton\textsuperscript{148} were able to obtain in a quantitative manner four-arm PI star polymers using tetrachlorosilane as linking agent.

Another way consists in the use of compounds which have halogenated silyl groups separated by an alkyl chain. 1,2-bis(dichloromethylsilyl)- and 1,2-bis(trichlorosilyl)ethane allowed Roovers and Bywater\textsuperscript{149,150} to synthesize and study a series of four- and six-arm PS stars. The addition of few isoprene units to the polystyryllithium chains allowed a considerable decrease of the time needed for the quantitative obtention of four-arm stars and was essential for the preparation of six-arm stars. Hadjichristidis and Roovers\textsuperscript{151} used the same linking agents for the preparation of four- and six-arm PI star polymers.

The synthesis of coupling agents of functionality equal to 8, 12 and 18 was done by Hadjichristidis \textit{et al.}\textsuperscript{152,153} by adapting the synthetic strategy for the obtention of the desired functionality (Figure 3-4).

The efficiency of the coupling reactions between the latter polychlorosilane agents and polydienyllithium allowed the formation of well-defined star polymers with 8, 12, and 18 PI branches. It should be noted that the authors advocated the addition of butadiene units to increase the coupling reaction efficiency. By using this category of electrophilic agents, Toporowski and Roovers\textsuperscript{154} have obtained PS stars of 12 and 18 branches. In the latter case, some triethylamine was added to decrease the coupling reaction time; indeed this additive allowed the increase of the carbanionic species reactivity in hydrocarbon solvents.

These results confirmed that the reaction of chlorosilane derivatives with polymer chains possessing a butadienyllithium chain-end allowed the access to well-defined structures and this even if the coupling agent functionality increases.
To prepare star polymers of largely higher functionality, Roovers et al.\textsuperscript{155} had the idea to use as linking agent third- and fourth-generation dendrimers possessing at their periphery chlorosilane groups of same reactivity.\textsuperscript{156,157} The dendrimers were prepared starting with tetravinylsilane and using two reactions, the hydrosilylation of the vinylsilane groups with dichloromethylsilane and the nucleophilic replacement of silicon chloride by vinylmagnesium bromide, as shown in Figure 3-5.

PB stars of 32, 64 and 128 branches could be synthesized. However, it should be noted that the reaction for the preparation of 32- and 128-arm star polymers is very slow (8 weeks). These works generated the best results obtained in the area of the star polymer synthesis because of the very high number of branches and the good definition of these structures.

The use of methyltrichlorosilane and tetrachlorosilane has also been extended to some other polymers. Ressia et al.\textsuperscript{158} thus demonstrated that it was possible to obtain three- and four-arm polydimethylsiloxane (PDMS) stars by using these coupling agents. In this case, fractionation is needed to separate four-arm stars from three-arm stars. Mays and colleagues\textsuperscript{159} prepared three-arm poly(cyclohexadiene) stars by deactivation of the corresponding living chains on the methyltrichlorosilane.

In 1989, an original method capable of generating PB star polymers of several hundred branches was described by the Roovers group.\textsuperscript{160} The synthesis took place in two steps. First, the 18-arm PB stars containing a large majority of 1,2-PB units were hydrosilylated to be modified into chlorosilane functions. In a second instance, polybutadienyllithium chains were deactivated on these latter chlorosilane groups. By using this strategy star polymers with an average of 270 branches were prepared. The coupling reaction is very slow and this even in the presence of triethylamine as additive. It is also impossible to precisely control the exact number of branches obtained which depends on the yield of each of the two steps.
More recently, Quirk and colleagues\textsuperscript{161} proposed a new methodology derived from the chlorosilane chemistry for the synthesis of star polymers utilizing the reaction of living polymers with alkoxyethyl-functionalized polymers. After functionalization of a PS-\textit{b}-oligoPB polymeric organolithium compound with an excess of multifunctional chlorosilane linking agent (1,2-bis(dichloromethylsilyl)ethane) in benzene, the resulting polymeric chlorosilyl groups were converted to methoxysilyl groups with anhydrous methanol in the presence of triethylamine to minimize linking reactions. Finally, a four-arm star-branched polystyrene was prepared by treating methoxysilyl-functionalized PS-\textit{b}-oligoPB with excess of PS-\textit{b}-oligoPBLi living chains (Figure 3-6). However, fractionation is still needed to separate four-arm PS stars from the excess PS-\textit{b}-oligoPBLi.

**Halomethylbenzene compounds.** The halomethylbenzene compounds is another category of polyhalogenated agents which were used for star synthesis. Yen and Wenger\textsuperscript{162,163} have demonstrated that the coupling reaction between 1,2,4-trichloromethylbenzene and polystyryllithium species leads to a mixture of several populations, one corresponding to star polymers of functionality higher than 3. The same procedure was also applied by Allen and colleagues\textsuperscript{164,165} for the four-arm star polymer synthesis. For this purpose, the reaction was carried out in a mixture of THF/Benzene (50/50) at high temperature in the presence of 1,2,4,5-tetrachloromethylbenzene. In this case again, a mixture of polymers with functionality in the range of 2 to 4 and even higher was obtained; the percentage of species with a functionality higher than the targeted one was found around 40%.

From these previous studies, it was concluded that the low coupling reaction yield and the formation of polymer with functionality higher than the theoretical one is due to a secondary reaction. This latter is the halogen-lithium exchange reaction described below (Figure 3-7).
This parasitic reaction generates in the reaction medium on the one hand chloride-functionalized polystyrene chains and on the other hand a second carbanionic species (RMeCl_{X-1}). The latter species can then react on the halide function of the coupling agent (RCl_{X}) and thus lead to the formation of a coupling agent of higher functionality, polystyryllithium chains being capable of reacting again with this new linking agent. Altares et al.\textsuperscript{165} demonstrated that the coupling agent should be added on the polystyryllithium chains and not the reverse. Processing in this way, only 7\% of the final product was contaminated by star polymers of functionality higher than the expected one.

When carried out in dry THF, Bryce et al.\textsuperscript{166} deactivated polystyryllithium chains in 1,3,5-trichloromethylbenzene. Meunier and Van Leemput\textsuperscript{167} also used the same conditions in the case of 1,2,4,5-tetrachloromethylbenzene and hexakis[p-(chloromethyl)phenyl]benzene. In the latter cases, the star samples did not show any species of functionality higher than the targeted one. The use of THF allowed the elimination of the halogen-lithium exchange reaction. The same observation was reported by Yen who worked with potassium as counter-ion.\textsuperscript{163}

As described by Bryce et al.,\textsuperscript{166} the use of 1,3,5-tribromomethylbenzene does not allow the preparation of PS stars. They demonstrated that this reaction leads only to the formation of a difunctional polymer. However, the multifunctional bromobenzene compounds proved to be more efficient for some other polymers. Indeed, Pitsikalis et al.\textsuperscript{168} recently used tetrabromomethylbenzene for the preparation of poly(2-vinylpyridine) (PVP) and poly(methyl methacrylate) (PMMA) stars (Figure 3-8). The deactivation reaction of the corresponding living chains in THF at low temperature leads to the formation of four-arm stars. Other four- and six-arm stars were synthesized by Lazzari et al.\textsuperscript{169} who resorted to 1,2,4,5-tetrakis(bromomethylbenzene) and hexakis(bromomethyl)benzene as coupling agents (Figure 3-8).
This arm-first method was also applied by Müllen and colleagues\textsuperscript{170} for the synthesis of core-shell nanoparticles consisting of a shape-persistent polyphenylene dendrimer as the core and of different polymers PS, PI, PEO as mono- or double-shells. For example, monoshell systems were obtained by “grafting-onto” (arm-first) process attaching PEO chains to a second-generation polyphenylene dendrimer with an average of 12 chloromethyl functions. Well-defined PEO-functionalized polyphenylene dendrimers with molecular weights between $10^4$ and $10^6$ Da were prepared.

**Phosphonitrile chloride compounds.** Some other research groups turned towards another category of multifunctional electrophilic compounds. For example, Gervasi and Gosnell\textsuperscript{171} compared the coupling reaction efficiency of polystyryllithium chains with cyclic trimer phosphonitrile chloride in the first case and bis(trichlorosilyl)ethane in the second one. The first coupling agent allowed the formation of six-arm stars, whereas the second one gives at best four-arm stars. These results could be surprising when compared with that of Roovers \textit{et al.}\textsuperscript{172} However, the experimental conditions used by Gervasi and Gosnell\textsuperscript{171} are different since they did not add any additives and used a mixture of polar/apolar solvent which changes the reactivity of the polystyryllithium species.

**Multifunctional fluorinated coupling agent.** More recently, Bates and colleagues\textsuperscript{173} have investigated, a simple, unique method for star polymer synthesis. Living anionic polyisoprene (PILi) chains were terminated by addition of hexafluoropropylene oxide (HFPO). Through a series of fluoride ion (F\textsuperscript{−}) eliminations (creating carbonyl groups) and nucleophilic attacks by additional PILi chains, each molecule of HFPO coupled three chains, forming regular three-armed stars (PI\textsubscript{3}) (Figure 3-9). The authors claimed that this strategy eliminates the need for fractionation (in contrast to chlorosilane system) of the resultant polymer since unreacted homopolymer and two-chain coupling products are negligible under appropriate reaction conditions. However, complete coupling of PILi chains was never
observed using arm molecular weights higher than 5 kg/mol. Indeed, for larger molecular weights, uncoupled PI chains and two-chain coupling products were observed by SEC.

**Unsaturated multifunctional compounds. Allyloxy based compounds.** Herz and Strazielle\textsuperscript{174} were the first to employ allyloxy-based compounds, such as tri-(allyloxy)-2,4,6-s-triazine (TT), as deactivating agent. After checking the efficiency of this latter linking agent on the case of small organometallic molecules, this reaction was extended to polystyrylpotassium chains. This method allowed the formation of three-arm PS stars with narrow molecular weight distribution. However, the presence of small quantity of linear PS chains deactivated by impurities could not be completely avoided. By reaction of TT with the tetraphenyl diisobutane, the same authors\textsuperscript{175} obtained a tetrafunctional coupling agent which result in the formation of four-arm star polymers.

**Unsaturated multifunctional compounds. DDPE-type derivative.** 1,3,5-Tris(1-phenylethenyl)benzene was used by Quirk and Tsai\textsuperscript{20,176} as a linking agent for the synthesis of a three-arm PS star, as shown in Figure 3-10. SEC and light scattering (LS) results showed that the reaction is stoichiometric and complete leading to a well-defined star. Despite the fact that the arm molecular weight used was rather low ($M_n = 8.5 \times 10^3$ g/mol), it can be concluded that there is no steric limitation for the synthesis of three-arm PS stars using this coupling agent. Previous efforts to use methyltrichlorosilane as a linking agent for the synthesis of three-arm PS stars were not successful, due to incomplete coupling (steric hindrance effects).

**Unsaturated multifunctional compounds. Fullerene.** Soon after the discovery of fullerenes, efforts were made to use $C_{60}$ as a coupling agent for the preparation of star polymers. Samulski \textit{et al.}\textsuperscript{177} reported the reaction of living polystyryllithium chains with $C_{60}$, and later Ederlé and Mathis\textsuperscript{178} extended this work, providing mechanistic aspects on this reaction in different solvents. In a nonpolar solvent such as toluene, it was found that by using an excess of living PSLi chains over $C_{60}$ a six-arm star can be prepared by addition of the
carbanions onto the double bonds of fullerene. A similar behavior was observed when living polyisoprenyllithium was used for the coupling reaction. In polar solvents such as THF a different situation was observed. During the reaction of a living polystyrylpotassium with $C_{60}$ in THF, a two-electron transfer was initially observed followed by the addition of four chains, according to Figure 3-11.

However, in both types of solvents, the functionality of the product could be adjusted by changing the reactivity and/or the steric hindrance of the living chain end. Thus, when the living PS chains were end-capped with one unit of diphenylethylene (DPE), only the three-arm star was produced. The functionality could be also controlled by the stoichiometry of the reaction between the living polymers and $C_{60}$. However, it was impossible to selectively incorporate one or two chains per $C_{60}$ molecule.

3.2.1.2 Copolymerization with a divinyl compound

**Divinylbenzene.** The copolymerization between a difunctional monomer and living anionic polymer chains is also another way to get star polymers with a large number of branches. First considered by Milkovich, Rempp and colleagues described the synthesis of star polymers by anionic copolymerization of styrene and divinylbenzene (DVB). Thus, these star polymers are constituted of a cross-linked polydivinylbenzene core linked to several PS chains which ensure the star solubilization. However, by using this way, star polymers with large molecular weight distribution have been obtained. Moreover, the star polymer samples were spoiled by a non-negligible quantity of linear PS indicating that the reaction between living linear chains and double bonds was less probable as the polyDVB central core is growing. This process led also to the same results when applied to the PI star synthesis: a large molecular weight distribution and the presence of linear chains. In 1969, Worsfold were able to obtain a more homogeneous molecular weight distribution for the star polymers by using a pur para- or meta-DVB compound and benzene instead of THF.
However, it is still difficult to predict the number of branches linked to the polyDVB core. All the previous studies demonstrated that the number of branches is dependent on numerous parameters. Besides the ratio \( R = \frac{[\text{DVB}]}{[\text{Living chains}]} \), the length of the chain precursors, the nature of the solvent (THF or benzene), the stirring conditions, the purity and the composition of DVB, the temperature, and the chemical nature of the living chains (styrene, butadiene, or cyclohexadiene), could influence the copolymerization reaction and at the same time the star preparation.

In conclusion, DVB is certainly useful for the preparation of star polymers of different chemical nature and the coupling reactions are efficient for \( R \) values higher than 4. Even though this method allowed the formation of star polymers with a number of branches varying in a large range in function of the ratio \( R \), this is still impossible to obtain well-defined structures.

**Ethylene glycol dimethacrylate.** Ethylene glycol dimethacrylate (EGDM) was also used as comonomer for the plurifunctional cross-linked core synthesis, especially in the case of PMMA stars. Indeed, in this latter case, the use of DVB and chlorosilane compounds is unthinkable because of the low reactivity of the PMMALi living chains. The first example of EGDM use was proposed by Zilliox et al. who obtained PMMA star samples with large molecular weight distribution. More recently, the same EGDM comonomer allowed Efstratiadis et al. to prepare PMMA stars with a better structure definition, but only for arm molecular weight higher than 40 kg/mol. Below this value, intermolecular coupling reactions between different stars occurred giving samples with large molecular weight distributions.

Researchers from DuPont proposed, in their case, the synthesis of PMMA stars by group transfer polymerization (GTP) using PMMALi living chains and EGDM as comonomer at 85 °C. The same comonomer was employed by Helder and Müller for poly(\( t \)-butyl acrylate) (PrBuA) star synthesis.
However, as for the case of DVB, all the studies\textsuperscript{182,193,195} result in the same conclusions, that is namely the number of branches in the star polymers depends on:

- length of the living chains
- the ratio $\text{[EGDM]}_0/\text{[Living chains]}_0$
- reaction time of the living chains on the difunctional comonomer.

Moreover, the quantity of residual linear chains is decreasing with the polymer chain length and increasing with the reaction time and the ratio $\text{[EGDM]}_0/\text{[Living chains]}_0$.

For example, the reaction of isotactic PMMALi living chains, initiated by $t$-butylmagnesium bromide in the presence of 1,8-diazabicyclo[5.4.0]undec-7ene, with EGDM comonomer led to the formation of star polymers with a number of branches estimated between 20 and 30.\textsuperscript{197} In the case of syndiotactic PMMALi, Hatada \textit{et al.}\textsuperscript{197} advocated the use of butane-1,4-diol in place of EGDM to make easier the coupling reaction (obtention of star polymers with number of branches ranging from 50 to 120).

3.2.2 “Core-first” Method

In this second method a multifunctional organometallic compound, that is capable of simultaneously initiating the polymerization of several branches, is used in order to form a star polymer (Figure 3-12). There are several requirements that a multifunctional initiator has to fulfill in order to produce star polymers with uniform arms, low molecular weight distribution, and controllable molecular weights. All the initiation sites must be equally reactive and have the same rate of initiation. Furthermore, the initiation rate must be higher than the propagation rate. Only a few multifunctional initiators satisfy these requirements, and consequently, this method is not very successful. Complications often arise from the insolubility of these initiators, due to the strong aggregation effects. The steric hindrance effects, caused by the high segment density, causes excluded volume effects.
3.2.2.1 Multifunctional oxanionic initiators

These plurifunctional initiators possess hydroxyl functions which can, once deprotonated, initiate the polymerization of oxirane monomers in a more or less efficient way as shown by the different examples below.

The first example of PEO stars was reported in the literature by Gnanou et al.\textsuperscript{198} in 1988. In this paper, the authors propose three different methods to prepare PEO stars.

The first strategy results from the deprotonation of hydroxyl functions of trimethylolpropane. The successive metalation of the alcohol groups has as consequence the decrease of the precursor solubility. Indeed, once all the hydroxyl functions are deprotonated, the multioxanionic species are totally insoluble. However, the addition of ethylene oxide in the reaction medium leads to the formation of three-arm PEO stars.

The second one consists in the synthesis of a graft copolymer which can be considered as a star polymer, if the pendant chains are largely longer than the polymer backbone. For this purpose, potassium 2-alkoxide ethylstylene was first polymerized to build the backbone. In a second step, the alkoxide sites were used as initiators for the ethylene oxide polymerization. The average number of PEO side chains obtained is close to 25.

The last method proposed consists in the reaction of naphtalene potassium with a difunional monomer such as DVB to form a microgel nodule covered by living anionic sites which can be used as a multifunctional initiator. The ratio [DVB]/[K\textsuperscript{+}] should be kept lower than 3 in order to reduce the aggregation and to avoid a network formation.

PEO stars having 4, 8, and 16 arms were also prepared using hydroxyl-functionalized carbosilane dendrimers of several generations.\textsuperscript{199} For this purpose, the end groups of a chloride-functionalized carbosilane dendrimer were converted to hydroxyl groups and were activated using potassium naphthalene. The polymerization of ethylene oxide was initiated by these active sites. The results of these methods confirmed the preparation of well-defined star
polymers with narrow molecular weight distributions. However, the tedious preparation of the dendrimer core molecules is the only drawback of this method.

Hyperbranched polyglycerol and polyglycerol modified with short poly(propylene oxide) chains, activated with diphenylmethylpotassium (DPMK), were also employed as multifunctional initiators for the synthesis of PEO stars. Hyperbranched polyglycerol was found to be an unsuitable initiator due to the strong association effects caused by its highly polar groups. The incorporation of the poly(propylene oxide) chains (degree of polymerization, 23-52) was crucial for the synthesis of the PEO stars. Moderate to large molecular weight distributions were obtained ranging from 1.4 up to 2.2. The functionalities of these stars were calculated to vary between 26 and 55.

Second-generation polyphenylene dendrimers functionalized with exactly 16 hydroxymethyl groups prepared by the Müllen group were also used as multiinitiator for the living anionic polymerization of ethylene oxide to obtain well-defined core-shell nanoparticles.

3.2.2.2 Pluricarbanionic initiators

This category of multifunctional initiators, especially used for the polymerization of vinyl and diene monomers, was not really successful compared to the multifunctional initiators used in the other polymerization type such as radical controlled polymerization (ATRP, RAFT, NMP, etc...). The tedious synthesis of precursors of higher functionality and the low solubility of the pluricarbanionic species in different solvents are the main reasons of this lack of interest. Moreover, even when the latter were soluble, the results obtained after polymerization were in most cases disappointing.

The different examples of pluricarbanionic initiators reported in the literature were already discussed earlier (Chapter 1). The only convincing example is the synthesis of a tricarbanionic initiator proposed by Quirk and Tsai. This multifunctional initiator, was found
soluble in apolar solvents after reaction of 3 moles of sec-butyllithium with 1,3,5-tris(1-phenylethenyl)benzene (tri-DPE) as presented in Figure 1-2. The efficiency of the tricarbanionic species was demonstrated for the anionic polymerization of styrene and butadiene, but always in the presence of polar additives to avoid the formation of polylithiated species aggregates.\textsuperscript{20,21}

3.2.2.3 Polythiolates initiators

Nicol \textit{et al.}\textsuperscript{201} have first reported the synthesis of sulfur-containing star polymers by anionic polymerization of propylene sulfide initiated with multifunctional thiols in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) as the co-initiator. However, the lack of diversity in multifunctional thiol structures, which originates from oxidative coupling to form disulfides, reduces versatility in designing star poly(sulfide)s.

Endo and colleagues\textsuperscript{202} proposed in their case a novel trifunctional initiator synthesized by reaction of a five-membered cyclic dithiocarbonate with benzylamine or octadecylamine (Figure 3-13). The initiator system was constructed by addition of DBU, which leads to the thiolates/thiols equilibrium through rapid proton exchange. Anionic polymerization of propylene sulfide using trifunctional initiator/DBU system was carried out in dimethylformamide (DMF) at 0 °C and was quenched by 1-(chloromethyl)naphtalene, which has been to be effective for termination of thirane polymerization. The trifunctional initiator efficiently initiated the polymerization of propylene sulfide to afford the corresponding star-shaped polymers quantitatively with narrow molecular weight distribution.

3.2.3 “In-Out” Method

This method consists in resorting, in a first time, to the “core-first” method to generate carbanionic sites, which could in a second instance initiate the polymerization of the same or another monomer introduced in the reaction medium.\textsuperscript{27,187,191,203-207}
Zilliox et al.\textsuperscript{181} were the first to employ this strategy. Indeed, after the preparation of a stable polyDVB suspension by addition of PSLi chains on DVB, another styrene aliquot was added in the reaction medium. However, large molecular weight distributions were obtained for the different star samples and the control over the number of branches was not reliable.

In order to improve the control over the star structure by using this “In-Out” method, Quirk et al.\textsuperscript{208} replaced DVB by a diphenylethylene derivative and studied the coupling reaction of PSLi living chains with 1,3-bis(1-phenylethenyl)benzene (MDDPE) followed by the initiation of styrene polymerization by the carbanionic sites generated after the coupling step (Figure 3-14).

The coupling reaction of poly(styryllithium) of various molecular weights with MDDPE in benzene is a very efficient reaction when the stoichiometry of the reaction is carefully controlled (yield > 96%). Because of the lack of reactivity of poly(dienyllithium) chains in addition reactions with 1,1-diphenylethylene units, it is necessary to add a small amount of Lewis base such as THF for the formation of (PB)\textsubscript{2}-MDDPE targeted product. After addition of a second amount of monomer, calculated to obtain the same monomer unit number as for the initial branches, a four-arm PS star is obtained. Through their studies, they demonstrated that the addition of Lewis base such as THF and s-BuOLi is needed during the crossover reaction to prevent chain-end association behavior for these dilithium macroinitiators in hydrocarbon solvent. Moreover, a minimum arm lengths of 3x10\textsuperscript{3} g/mol (value determined by UV-Vis spectroscopy studies) is required for complete crossover reaction of diphenylalkyllithium sites with styrene monomer. By comparing the samples prepared with the ones obtained by coupling reaction with SiCl\textsubscript{4}, Quirk et al.\textsuperscript{208} could conclude to the four-arm structure of the star polymers synthesized by this “In-Out” method.
3.2.4 “In-In” Method

The basis of the two-step “In-In” method\textsuperscript{209,210} is as follows: star polymers with polyDVB cores, synthesized by the arm-first method, include many unreacted double bonds in their cores, and these double bonds can be attacked by the carbanions of some monomers such as styrene and dienes (Figure 3-15). Therefore, in the first step of this method, a star-shaped polymer with a polyDVB core is synthesized in the same way as an arm-first method. In the second step, a known amount of the star polymer synthesized in the previous step is dissolved in THF and added to living PS or polydiene chains. The carbanions located at the end of the living linear chains attack the double bonds of the cores of the star molecule and attach to them by reacting with these double bonds. However, for some monomers such as alkyl methacrylate, vinyl pyridine, and ethylene oxide, which have higher electrophilicity than styrene or divinylbenzene, the carbanions of these monomers cannot attack the double bonds of the cores of the star molecules.

3.3 Results and Discussion

3.3.1 Application of Halogen-Lithium Exchange Reaction to Star Polymer Synthesis

We have exploited here the possibilities offered by this halogen-lithium exchange reaction to prepare novel tri- and tetracarbanionic initiators for the synthesis of well-defined three- and four-arm star polymers obtained by the “core-first” method.\textsuperscript{121} This method rests on the metallation of poly(arylhalide)s whose halogens are carried by separate aryl rings. Unlike regular halogen-metal exchanges, the metallation in our case could be conducted at room temperature and in apolar medium for the polylithiated species formed, which were unexpectedly found soluble in the presence of $\sigma/\mu$-coordinating ligands; this remarkable feature could be further exploited for star synthesis.

To successfully demonstrate the viability/pertinence of our method, we have utilized a commercially available diaryl halide (1) and have also designed two poly(arylhalide)s carrying respectively three (2) and four (3) halides. The two poly(arylhalide)s of functionality
3 and 4 have been obtained using reported procedures (see Chapter 7: Experimental Part)\textsuperscript{211-213}. \textsuperscript{2} was derived from the reaction of 4-bromoacetophenone diethyl ketal with acetyl chloride using samarium trichloride as catalyst; as for \textsuperscript{3}, it was generated in excellent yields (> 90%) by Diels-Alder reaction between 2,3,4,5-tetrakis(p-bromophenyl)-cyclopentadienone and phenylacetylene, carbon monoxide being extruded in this process. The expected structures of the different multibromo compounds were demonstrated by \textsuperscript{1}H NMR spectra of \textsuperscript{2} and \textsuperscript{3} (see Chapter 7: Experimental Part).

Next \textsuperscript{1}, \textsuperscript{2} and \textsuperscript{3} were subjected to reaction with stoichiometric amounts of sec-butyllithium in benzene to generate \textsuperscript{1}', \textsuperscript{2}', \textsuperscript{3}', the corresponding di-, tri-, and tetracarbanionic initiators (Figure 3-16).

The formation of 2-bromobutane (\textsuperscript{4}) which accompanies these reactions was monitored by gas chromatography (GC) (see Chapter 7: Experimental Part). In the three cases the yields were quantitative as only 2-bromobutane and the corresponding protonated polyaryl compounds were found in the analyzed products. No coupling between 2-bromobutane and the pluricarbanionic species formed, \textsuperscript{1}', \textsuperscript{2}' or \textsuperscript{3}', was ever detected, indicating that in apolar medium no such side reactions occurred. However, the resulting polylithiated species were insoluble in benzene and therefore could not be used as such for initiation purpose, the monomers tried—styrene, butadiene, 1,1-diphenylethylene—failing to react with these aggregates. Various additives have thus been employed to solubilize these pluricarbanionic species. Even though tetramethylethylenediamine (TMEDA) was able to solubilize the di- and tetrалithiated initiators, out of the additives tried the ligand that proved the most efficient at solubilizing these carbanionic aggregates no matter their functionality was lithium 2-methoxyethoxide (\textsuperscript{5}) (Figure 3-17); this σ/µ-ligand was previously employed by Teyssié and colleagues\textsuperscript{214} to prevent lithium enolates from aggregating in apolar medium and by this means bring about livingness in the anionic polymerization of methacrylic monomers. A ratio
of [lithium 2-methoxyethoxide] to [-PhLi] equal to 4 was necessary to obtain fully soluble initiators in benzene (Figures 3-17 and 3-18). In these attempts at solubilizing $1'$, $2'$, $3'$, $5$ was prepared separately by reaction of sec-butyllithium with 2-methoxyethanol, but in the polymerization experiments conducted subsequently $5$ was simply generated in-situ by addition of sec-butyllithium prior to the lithium-halide exchange undergone by $1$, $2$, or $3$ (Figure 3-18).

Before triggering polymerization by monomer addition, we managed to neutralize $4$ that resulted from the lithium-halide exchange reaction; even though $4$ was inert enough not to react with $1'$, $2'$, and $3'$, the poly(aryllithium)s formed, it is sufficiently electrophilic to deactivate the growing carbanionic chains of polystyrene or polybutadiene. Indeed, in a separate experiment conducted under stoichiometric conditions and in benzene we observed the occurrence of such deactivation of polystyryllithium anions by $4$ in the presence of TMEDA, the disappearance of $4$ being complete in less than thirty minutes. To neutralize $4$ prior to monomer addition one equivalent of sec-butyllithium was added and the formation of 3,4-dimethylhexane ($6$) that resulted was monitored by GC (see Chapter 7: Experimental Part). The disappearance of $4$, and the concomitant formation of $6$ were monitored by gas chromatography (GC) with trace of undecane as internal standard. After checking that the neutralization of $4$ was complete, the polymerization of styrene or butadiene could be triggered upon addition of the corresponding monomers. Upon deactivation of the living carbanionic chains by ethylene oxide after complete monomer consumption, $\omega$-hydroxyl three- and four-armed polystyrene and polybutadiene stars could be isolated from $2'$, and $3'$ used as initiators (Figure 3-18). $\alpha,\omega$-dihydroxyl telechelic samples were obtained from $1'$.

Analysis by gas chromatography and size exclusion chromatography (SEC) indicated the complete consumption of initiators. No peak attributable to the presence of residual $1$, $2$, or $3$ could indeed be detected in the low molar mass region, the only trace seen being a
narrow and monomodal peak corresponding to the expected star or linear polymer in the high molar mass region (Figure 3-19).

Such a narrow molar mass distribution ($\frac{M_w}{M_n} < 1.1$) reflects a rate of initiation by $1'$, $2'$, or $3'$ comparable to that of propagation (Table 3-1). The structure of the polymer formed and specially the star character could be established first by $^1$H NMR analysis using polybutadiene samples of low degrees of polymerization (Figure 3-20). From the ratio of the integration values due to the signal of the aromatic core ($\delta = 6.8-7.3$ ppm) to that of $-\text{CH}_2$-$\text{OH}$ chain ends ($\delta = 3.7$ ppm) the actual functionality of the various samples prepared could be determined: functionality values close to 3 and 4 were respectively obtained for the three- and four-arm polybutadiene stars and close to 2 for the telechelics.

Characterization of both linear and star polystyrene and polybutadiene samples by SEC equipped with a light-scattering detector (SEC-LS) also showed an excellent agreement between experimental and expected values of molar masses.

Further evidence of the three- and four-arm star structure could also be obtained by comparing the intrinsic viscosity $[\eta]$ of our samples with that of linear polymers. Indeed, one classical means to probe star-like architectures and their actual functionality is to determine $g'$ which represents $[\eta]_{\text{star}}/[\eta]_{\text{linear}}$. As can be seen in Table 3-1, the $g'$ values calculated are close to the ones predicted by theoretical models. These results thus confirm that the structures initially targeted were actually obtained and validate the pertinence of our novel approach of star synthesis by anionic means.

After demonstrating the efficiency of these di-, tri- and tetracarbanionic initiators for the synthesis of polystyrene and polybutadiene telechelics and stars, $(ABC)_n$ (with $n = 2, 3$ or 4) linear and star block terpolymers were derived by sequential anionic polymerization of styrene (S), butadiene (B) and methyl methacrylate (M) using $1'$, $2'$ or $3'$ as initiators. These novel architectures—$\text{P(S-b-B-b-M)}_2$ pentablock from $1'$, $\text{P(S-b-B-b-M)}_3$ and $\text{P(S-b-B-b-M)}_4$
star block terpolymers from $2'$ and $3'$, respectively—were actually prepared by the same sequence of monomer addition as for the synthesis of P(S-b-B-b-M) linear block terpolymers (Figure 3-21).  

Since lithium 2-methoxyethoxide ($5$) was present as an additive to solubilize $1'$, $2'$ or $3'$ methyl methacrylate could be polymerized under living conditions—as disclosed by Teyssié and colleagues $^{214}$—from polybutadienyllithium anions. Prior to the addition of M polybutadienyllithium anions were end-capped with 1,1-diphenylethylen (DPE) to reduce the probability of side reactions on the ester group of M while initiating its polymerization. The reaction medium was also diluted with tert-butylbenzene and the temperature decreased to $-40^\circ$C to further prevent the above mentioned side reactions. Upon addition of M, the medium turned from red characteristic of diphenylethyllithium carbanions to colorless. An aliquot being sampled out before introduction of each type of monomer, the formation of these SBM-based architectures could be easily followed by SEC (Table 3-2 and Figures 3-22 and 3-23).

The absolute molar mass of the first PS block could be obtained by SEC-LS; as for PB and PM blocks their respective molar masses were deduced by $^1$H NMR spectroscopy knowing that of their precursor (Table 3-2, Figure 3-24). In all cases narrow molar mass distributions were observed for the three types of structures, attesting that the growth of the three blocks occurred under living conditions. In some instances, P(S-b-B-b-M)$_n$ star block terpolymers were contaminated with P(S-b-B)$_n$ precursors (less than 10%) but the latter could be easily removed by fractionation through silica column.

### 3.3.2 Synthesis of Amphiphilic Star Block Copolymers Based on Polybutadiene and Poly(ethylene oxide)

We present here the first synthesis of (PB-b-PEO)$_n$ ($n = 3$ or 4) amphiphilic star block copolymers based on a polybutadiene core and poly(ethylene oxide) corona by anionic polymerization.$^{219}$ The divergent or “core-first” method appears to be the best route to prepare such materials. The convergent method would require the synthesis first of PEO-b-PBl$^+$
linear living chains with a first block of PEO and a second block of PB, which is not known to date. The only attempt to synthesize PB-\textit{b}-PEO block copolymer with complex architecture was the work of Xu and Zubarev,\textsuperscript{220} who prepared 12-arm PB-\textit{b}-PEO heteroarm or miktoarm star copolymers by the coupling of V-shaped PB-\textit{b}-PEO chains to an aryl ester dendrimer core; these were certainly not star block copolymers containing PEO blocks at the corona and PB blocks at the core as in our case so that both bulk and solution properties would be different. Previously, we presented the synthesis of novel tri- and tetracarbanionic initiators based on a halogen-lithium exchange reaction and the example of well-defined three and four-arm polystyrene and polybutadiene stars obtained by the “core-first” method.\textsuperscript{121}

The preparation of (PB-\textit{b}-PEO)_n (n = 3 or 4) star block copolymers begins with the transformation of the hydroxyl end groups in the (PB-OH)_n (n = 3 or 4) star polymers (Figure 3-25). For this purpose, two star-shaped polybutadiene precursors were used as macroinitiators for the PEO polymerization (Table 3-3). The polybutadiene stars were first purified by freeze-drying in benzene or dioxane, and then reacted. A solution of diphenylmethylpotassium (DPMK) in THF of known concentration, was then added dropwise over a colorless solution of a known amount of (PB-OH)_n (n = 3 or 4) in anhydrous THF to titrate the hydroxyl end groups. At stoichiometry, a color change of the solution depending on the initiator concentrations is observed. The macroinitiator solutions are green, red or yellow for initiator concentrations of 1.5\times10^{-3}M, 6.25\times10^{-4}M or 3.15\times10^{-4}M, respectively. In addition, the amount of (PB-OH)_n (n = 3 or 4) macroinitiator, calculated from the molecular weight and the mass of polybutadiene stars introduced in the flask, was used to confirm that such titrations with DPMK were quantitative.

After titration, ethylene oxide was added to the (PB-O\textsuperscript{K}+)n (n = 3 or 4) macroinitiator solution as a liquid at \textdegree{\textminus}30 °C and the solution immediately became colorless. Then the reaction mixture was heated to 45 °C and the polymerizations were typically run for 3 days to
ensure complete conversion of ethylene oxide. Deactivation of the “living” chains was accomplished by the addition of acidic methanol (MeOH/HCl). Potassium chloride salts (KCl) precipitated upon termination were isolated from the hydroxyl-terminated star block copolymers by filtration. After concentration of the (PB-b-PEO)_n (n = 3 or 4) solution on the rotary evaporator, the block copolymers were precipitated in MeOH for the short PEO blocks and in ethylic ether for the long PEO blocks and finally dried under dynamic vacuum.

All the data for the (PB-b-PEO)_n (n = 3 or 4) star block copolymers are summarized in Table 3-3. The recovered polymers were weighed, and the high yields demonstrate that the conversion of ethylene oxide was near quantitative in all cases. Knowing the molar mass of the PB core estimated by SEC/LS, the actual molar masses of the star block copolymer has been determined by comparing the resonance signal at $\delta = 3.6$ ppm ($(OCH_2CH_2)_n$ (PEO block)) with that at $\delta = 4.8-6.0$ ppm (protons of the double bonds (PB block)) (Figure 3-26). A good agreement was found between the theoretical and experimental molar masses as shown in Table 3-3.

The apparent molar mass values and polydispersity indices for the (PB-b-PEO)_n (n = 3 or 4) block copolymers were measured by SEC in THF (Figure 3-27). A shift to high molar masses with the disappearance of the (PB-OH)_4 precursor peak (see (PB_{76}-b-PEO_{1725})_4), a good control over the PEO molar masses and the relatively narrow polydispersities ($M_w/M_n<1.32$) indicate that the block copolymers obtained are free of any PB-OH star precursors demonstrating that all hydroxyl groups of the (PB-OH)_4 star polymer were deprotonated during the deprotonation step and that the alkoxides formed initiated the polymerization of ethylene oxide. The broadening of the molar mass distribution after the EO polymerization merely results from the fact that some alkoxides have a tendency to form aggregates in equilibrium with unaggregated alkoxides.221
However, it can be seen that as the PEO molar mass per arm in \((PB_{76-b}-PEO_{444})_4\) and \((PB_{76-b}-PEO_{1725})_4\) increases molar mass distribution narrows with a symmetrical SEC trace for the \((PB_{76-b}-PEO_{1725})_4\) sample. In addition, we did not detect any amount of PEO linear homopolymer (which could result from a slight excess of DPMK in the reaction mixture) even in the case of the samples with longest PEO blocks \((PB_{76-b}-PEO_{444})_4\) and \((PB_{76-b}-PEO_{1725})_4\) : they were indeed precipitated in diethyl ether and the presence of linear PEO was never observed which would have been totally insoluble in diethyl ether as well. The same observations were made in the case of the three-arm star block copolymers.

The amphiphilic character of the \((PB-b-PEO)_4\) star block copolymers was first demonstrated by \(^1\)H NMR spectroscopy in CD\(_2\)Cl\(_2\) and CD\(_3\)OD (Figure 3-28). Figure 3-28A shows the resonance signals of both the hydrophobic and hydrophilic blocks in solution in CD\(_2\)Cl\(_2\), whereas Figure 3-28B shows that only the resonance signals corresponding to the PEO hydrophilic block are observed in CD\(_3\)OD solution. The latter observation is consistent with previous literature results that demonstrate CD\(_3\)OD is a good solvent for PEO blocks and a non-solvent for PB blocks and as a consequence the formation of amphiphilic micelles in CD\(_3\)OD with the PB core hidden by the PEO branches.\(^{222-224}\)

**3.4 Conclusion**

In summary, halogen-lithium exchange reactions have been successfully applied to generate di-, tri- and tetracarbanionic species from bis-, tris- and tetrabromoaryl compounds. The use of a \(\sigma/\mu\) ligand was instrumental in obtaining polycarbanionic initiators soluble in apolar medium and the subsequent preparation of various well-defined star-shaped (co)polymers. These are the first examples of three and four-armed polystyrene and polybutadiene stars obtained by the so-called “core-first” method using anionic polymerization.\(^{121}\) Analysis of the macromolecular architectures obtained by different means including SEC-LS, \(^1\)H NMR spectroscopy and viscometry all endorse the star character and a
functionality of 3 and 4 for the samples derived from 2' and 3', respectively. The efficiency of the latter was even exploited to synthesize (PB-\(b\)-PEO)\(_n\) amphiphilic star block copolymers\(^{219}\) and P(S-\(b\)-B-\(b\)-M)\(_n\) star block terpolymers (\(n = 3\) or 4).\(^{121}\)

The phase separation and morphologies that develop in such P(S-\(b\)-B-\(b\)-M)\(_n\) star block terpolymers could be investigated and compared with those reported for linear SBM copolymers.\(^{225}\) Moreover, the good definition of the (PB-\(b\)-PEO)\(_n\) amphiphilic star samples allowed us to study their behavior either in aqueous solution or at the air/water interface.

Figure 3-1. General strategies for star polymer synthesis.
Figure 3-2. Convergent method.

Figure 3-3. Reaction of polymer chains with a difunctional monomer.

Figure 3-4. Synthesis of a coupling agent with 18 chlorosilane functions.
Figure 3-6. Anionic synthesis of 4-arm star branched polystyrene using 1,2-bis(dichloromethylsilyl)ethane as functionalizing agent.

\[
\text{Excess of PS-}\text{–}\text{b-oligoPBLi} \xrightarrow{\text{Benzene}} \text{PS-}\{\text{B}\}_3 \quad \text{H}_3\text{C-}\text{Si-C}_2\text{H}_4-\text{Si-}\text{CH}_3 \\
\text{PS-}\{\text{B}\}_3 \quad \text{PS-}\{\text{B}\}_3 \quad \text{PS}
\]

Figure 3-7. Halogen-lithium exchange reaction.

\[
\text{Met} + \text{RCI}_x' \xrightarrow{} \text{MetCl}_x + \text{RCI}_x
\]

Figure 3-8. Synthesis of 4-arm star branched polymers using tetrabromomethylbenzene as linking agent.

\[
\text{PMMALi} + \text{PtBuMALi} + \text{P2VPLi}
\]

Figure 3-9. Synthesis of PI star polymer using HFPO as multifunctional coupling agent.

\[
\text{PI Li} \xrightarrow{1) \text{RT, 16h}} \text{CF}_3 \quad \text{OH} \\
\text{RT, 16h} \quad \text{2) MeOH}
\]
Figure 3-10. Use of 1,3,5-tris(1-phenylethenyl)benzene as coupling agent.

$$3 \text{ PS} \Theta \text{Li} + C_{60} \rightarrow \text{PS-PS} + C_{60} \Theta (K^\Theta)_2$$

Figure 3-11. Use of fullerene C$_{60}$ as linking agent for star polymer synthesis.

$$2 \text{ PS} \Theta K + C_{60} \xrightarrow{\text{THF, 25 °C}} 2 \text{ PS} + C_{60} \Theta (K^\Theta)_2 \xrightarrow{\text{THF, 25 °C}} \text{PS-PS} + C_{60} \Theta (K^\Theta)_2$$

Figure 3-12. Divergent method.

Specific functions depending on the polymerization type

Monomer

Functional groups
Figure 3-13. Synthesis of three-armed poly(propylene sulfide) star.

2 PS$^\ominus$Li$^\ominus$ + \[ \text{diaryl} \] \rightarrow \[ \text{diaryl-Li} \]

Figure 3-14. Synthesis of four-arm PS star by the “In-Out” method.
Figure 3-15. Application of the “In-In” method for star synthesis.

Figure 3-16. Synthesis of dilithiated (1'), trilithiated (2'), and tetralithiated (3') initiators.
Figure 3-17. Scheme of the tetracarbanionic initiator/lithium 2-methoxyethoxide σ-μ complex.

Figure 3-18. Synthesis of four-armed polystyrene stars.
Figure 3-19. SEC eluograms of (PS)$_4$ polystyrene and (PB)$_4$ polybutadiene stars: a) protonated version of $3'$; b) polystyrene star; c) polybutadiene star; and d) flow marker.
Figure 3-20. $^1$H NMR spectra (CD$_2$Cl$_2$; 400MHz) of (PB-OH)$_4$ ($M_{w,LS} = 1800$ g.mol$^{-1}$; $M_w/M_n = 1.1$) and (PB-OH)$_3$ ($M_{w,LS} = 2400$ g.mol$^{-1}$; $M_w/M_n = 1.1$) hydroxyl terminated star polymers.
Figure 3-21. Reaction scheme for the synthesis of SBM star block terpolymers.

Figure 3-22. SEC eluograms monitoring the formation of a P(S-b-B-b-M)2 pentablock copolymer.
Figure 3-23. SEC eluograms monitoring the formation of a P(S-b-B-b-M)\textsubscript{n} (n = 3 or 4) star block terpolymer: a) (PS)\textsubscript{n} polystyrene star; b) P(S-b-B)\textsubscript{n} star block copolymer; and c) P(S-b-B-b-M)\textsubscript{n} star block terpolymer.
Figure 3-24. $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of P(S-b-B-b-M)$_3$ star block terpolymer.
Figure 3-25. Synthesis of \((PB-b-PEO)_4\) star block copolymers.
Figure 3-26. $^1$H NMR spectra (CDCl$_3$; 400MHz) of a star copolymer (PB$_{76}$-$b$-PEO$_{444}$)$_4$ ($M_{n,\text{NMR}} = 94600\text{ g.mol}^{-1}$, $M_w/M_n = 1.22$).

Figure 3-27. SEC traces of the (PB-OH)$_4$ precursor ($M_{w,\text{LS}} = 16\ 400\text{ g.mol}^{-1}$; $M_w/M_n = 1.05$) and of the star copolymers (PB$_{76}$-$b$-PEO$_n$)$_4$ ($n = 57$, 137, 444, and 1725) in THF.
Figure 3-28. $^1$H NMR spectra (200MHz) of (PB$_{76}$$-b$-PEO$_{444}$)$_4$ in CD$_2$Cl$_2$ (A) and in CD$_3$OD (B).
Table 3-1. Characterization of PS and PB samples synthesized from $1'$, $2'$ and $3'$ initiators, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_w / \bar{M}_n$</th>
<th>$\bar{M}_n$ (theo)</th>
<th>$f$</th>
<th>$g'$</th>
<th>$g'(\text{theo})$</th>
<th>$Zimm$-Stockmayer$^{[f]}$</th>
<th>Berry$^{[g]}$</th>
<th>Grest$^{[h]}$</th>
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</thead>
<tbody>
<tr>
<td>PS2</td>
<td>11000</td>
<td>11200</td>
<td>1.12</td>
<td>12000</td>
<td>1.9</td>
<td>-</td>
<td>0.91</td>
<td>0.88</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80900</td>
<td>90800</td>
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<td>89000</td>
<td>3.0</td>
<td>0.805</td>
<td>0.83</td>
<td>0.79</td>
<td>0.79</td>
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<tr>
<td></td>
<td>96700</td>
<td>131000</td>
<td>1.13</td>
<td>128000</td>
<td>3.0</td>
<td>0.846</td>
<td>0.91</td>
<td>0.88</td>
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<td>39500</td>
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<td>84700</td>
<td>98600</td>
<td>1.08</td>
<td>120000</td>
<td>3.9</td>
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<td>0.83</td>
<td>0.79</td>
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<td>PS4</td>
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<td>32500</td>
<td>1.03</td>
<td>30000</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>9400</td>
<td>16400</td>
<td>1.05</td>
<td>172000</td>
<td>3.9</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td></td>
</tr>
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</table>

[a] Determined by SEC in THF using a multiangle laser light scattering detector. The $dn/dc$ value was taken equal to that of linear polystyrene ($dn/dc = 0.183cm^3/g$ in THF). [b] Derived from refractometric detector. [c] $\bar{M}_n$ (theo) = $M_{\text{styrene}} \times [(\text{Styrene})/(-\text{PhLi})] \times n$ ($n = 2, 3$ or $4$). [d] Average functionality of the samples as determined by $^1$H NMR. [e] Experimental values of: $g' = [\eta]_{\text{star}}/[\eta]_{\text{linear}}$. [f] $g'_{\text{R.W.}} = (2/f)^{1.5}[(0.396(f-1)+0.196)^{0.586}].^{215}$ [g] $g' = g'_{\text{R.W.}}^{0.5} = [(3f-2)/f^2]^{0.5}.^{216}$ [h] $g' = K'.F^\beta (K=2.37$ and $\beta=-0.789).^{217}$
Table 3-2. Characterization of P(S-b-B-M)\textsubscript{2} pentablock, P(S-b-B-M)\textsubscript{3} and P(S-b-B-M)\textsubscript{4} star block terpolymer samples.

<table>
<thead>
<tr>
<th></th>
<th>PS</th>
<th>P(S-b-B)</th>
<th>P(S-b-B-M)</th>
<th>Microstructure (%1,2-(B))\textsuperscript{[d]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_w)\textsuperscript{[a]}</td>
<td>30000</td>
<td>35000</td>
<td>41000</td>
<td>60</td>
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<tr>
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<td>1.09</td>
<td>1.1</td>
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<td></td>
</tr>
<tr>
<td>(M_n)\textsuperscript{[c]}</td>
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<td>5700</td>
<td>7500</td>
<td>75</td>
</tr>
<tr>
<td>(M_n/M_w/M_n)\textsuperscript{[b]}</td>
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<td>1.1</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>(M_n)\textsuperscript{[c]}</td>
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<td>12100</td>
<td>16100</td>
<td>70</td>
</tr>
<tr>
<td>(M_n/M_w/M_n)\textsuperscript{[b]}</td>
<td>1.05</td>
<td>1.1</td>
<td>1.2</td>
<td></td>
</tr>
</tbody>
</table>

\(\text{[a]}\) Determined by SEC in THF using a multiangle laser light scattering detector. The \(dn/dc\) values of PS was 0.183 cm\(^3\)/g in THF. \(\text{[b]}\) Derived from refractometric detector. \(\text{[c]}\) Determined by \(^1\text{H NMR}\) from the molar mass of the polystyrene block, assuming 100% efficiency in the initiation of the second and third blocks. \(\text{[d]}\) Calculated by \(^1\text{H NMR}\).
Table 3-3. Characteristics of hydroxyl functionalized (PB-OH)_n star polymers and (PB-b-PEO)_n (n = 3 or 4) amphiphilic star block copolymers.

<table>
<thead>
<tr>
<th>(PB-OH) star precursors</th>
<th>Amphiphilic (PB-b-PEO) star copolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stars</td>
</tr>
<tr>
<td>(PB-OH)_3</td>
<td>32500</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>58000</td>
</tr>
<tr>
<td>(PB-OH)_4</td>
<td>16400</td>
</tr>
<tr>
<td></td>
<td>29400</td>
</tr>
<tr>
<td></td>
<td>34500</td>
</tr>
</tbody>
</table>

\(^{a)}\) Determined by SEC in THF equipped with a multiangle light scattering detector. The \(dn/dc\) value was measured in THF (\(dn/dc = 0.094\) cm\(^3\)/g).

\(^{b)}\) Apparent molar masses determined by SEC in THF using a polystyrene calibration.

\(^{c)}\) \(M_{n,th} = M_{Butadiene} \times ([Butadiene]/[-PhLi]) \times n (n = 3 or 4).\)

\(^{d)}\) Estimated by \(^1\)H NMR analysis.

\(^{c)}\) \(M_{n,th} = M_{EO} \times ([EO]/[(PB-OH)_n] + M_{w,(PB-OH)_n}.\)
CHAPTER 4
TWO-DIMENSIONAL POLYMERIC NANOMATERIALS THROUGH CROSS-LINKING OF POLYBUTADIENE-\textit{B}-POLY(ETHYLENE OXIDE) MONOLAYERS AT THE AIR/WATER INTERFACE

4.1 Introduction and Literature Overview

The idea of stabilizing amphiphile self-assemblies by polymerization was introduced at least 30 years ago for monolayers and about 10 years later for bilayer vesicles\cite{226,227}. This emerging approach to bridging the nanoscale world of labile, interfacially driven self-assemblies with the meso-scale has resulted in several examples of massively cross-linked 3D structures\cite{228-232}. For example, Bates and colleagues\cite{228} were the first to succeed in retaining the cylindrical morphology formed by gigantic wormlike rubber micelles of polybutadiene-\textit{b}-poly(ethylene oxide) PB-\textit{b}-PEO diblock copolymers in water by chemical cross-linking of the PB cores through the pendant double bond of the 1,2-polybutadiene units (Figure 4-1) using water-soluble redox combination of potassium persulfate (K$_2$S$_2$O$_8$) and sodium metabisulfite (Na$_2$S$_2$O$_5$)-ferrous sulfate (FeSO$_4$.7H$_2$O) for the initiation of cross-linking. This type of free-radical initiator, used extensively in emulsion polymerizations\cite{233}, is ideally suited for generating a specified number of radicals in the aqueous phase that are subsequently captured by the nanoscopic micelles. In this work, the authors produced a relatively high concentration of radicals, one for every two PB double bonds, thereby ensuring a high degree of cross-linking without disruption of the cylindrical morphology. Although they have not determined the exact cross-link density for the chemically fixed micelles, experiments indicate that every block copolymer has been covalently bonded together within individual giant wormlike molecules. For example, extraction with chloroform, which efficiently removes unreacted block copolymers from aqueous solution, fails to recover any detectable PB-\textit{b}-PEO linear diblock copolymers from the cross-linked system.
The Bates group$^{232,234}$ also proposed the fabrication of massively cross-linked and property-tunable membranes by free-radical polymerization of self-assembled, block copolymer vesicles—polymersomes (Figure 4-2). They described a PB-\textit{b}-PEO diblock copolymer that has a hydrophilic weight fraction like that of lipids and forms robust fluid phase membranes in water. The polymersomes sustain free radical polymerization of the hydrophobic butadiene, thereby generating a semipermeable nano-shell. Cross-linked giant vesicles proved stable in chloroform and could also be dehydrated and re-hydrated without modifying the ~9 nm thick membrane core; the results imply defectfree membranes many microns-squared in area.

However, relatively few groups have shown interest in stabilization by cross-linking of two-dimensional (2D) copolymer self-assemblies formed at the air/water interface; most studies have involved interfacial polymerization of small molecules in Langmuir monolayers.$^{235-263}$

In the early 1970’s the group of Veyssié$^{235,237,240,241}$ was the first to demonstrate the formation of 2D cross-linked material by cross-linked polymerization of monolayers of dimethacrylates, and several other difunctional reactive amphiphiles under UV irradiation at a constant surface pressure at the air/water or oil/water interface. This idea was further followed by other groups. Regen and colleagues$^{238,239}$ introduced the concept of a 2D-network of molecular pores, i.e., “perforated monolayers” derived from calix\([n]\)arene-based amphiphiles. For this purpose, they employed a series of derived calix\([n]\)arene-based amphiphilic surfactants (mercurated calix\([n]\)arene,$^{238,239}$ thio-, amide-, thioamide- or imine-functionalized calix\([n]\)arene,$^{244-246}$ or unsaturated calix\([n]\)arene$^{245}$) to form stable monolayer at the air/water interface (Figure 4-3). By polymerization of the calix\([n]\)arene-based molecules either by introduction of a cross-linking agent such as malonic acid (Figure 4-3B) or via UV irradiation, they were able to synthesize porous and cohesive “perforated monolayers” (pore diameters in the
range 2-6 Å) that can function as molecular sieves for gas permeation selectivity (Figure 4-3A).\textsuperscript{245,246}

The Michl group\textsuperscript{252,259} proposed the preparation of 2D grids through 2D supramolecular chemistry. The general strategy consists in the linear coupling of arm-ends of star-shaped monomers forced to adhere to a surface (mercury surface in this case) with their arms parallel to the surface. After the polymerization of the star-shaped monomer (for example, the anionic lanthanum sandwich complex of tetapyridy1porphyrin, Figure 4-4b) by introduction of a coupling agent (p-xylene dibromide, Figure 4-4a) by diffusion from a solution contacting the surface, well-defined covalent 2D square- or hexagonal-grid polymers could be synthesized (Figure 4-4c and d).\textsuperscript{252,259,264} They also proposed the preparation of 2D grids through cation-bonded or hydrogen-bonded supramolecular chemistry.\textsuperscript{265-267}

Palacin and colleagues\textsuperscript{242,243,247} also designed supramolecular assemblies of amphiphilic porphyrins by molecular engineering through molecular recognition between oppositely charged monomers at the air/water interface. Two porphyrin monomers P\textsubscript{2} and P\textsubscript{3} bear four positive charges while the third porphyrin monomer P\textsubscript{1} bears four ionizable carboxylic functions (Figure 4-5): via an acid/base reaction between the functional groups of each macrocycle, spatially oriented flat-lying heterodimers P\textsubscript{1}-P\textsubscript{2} and P\textsubscript{1}-P\textsubscript{3} are spontaneously formed at the air/water interface.

Kloeppner and Duran\textsuperscript{254} were the first to demonstrate mechanical properties sufficient to allow the removal of free standing fibers from the water surface a 2D cross-linked 1,22-bis(2-aminophenyl)docosane (BAD) polyanilines. For this purpose, the oxidative polymerization of BAD at the air/aqueous interface was done in the presence of a strong chemical oxidant, ammonium peroxydisulfate, and an acid (sulfuric acid). The polymerization was monitored by observing the barrier movement needed to maintain a specific applied surface pressure, assuming
that the polymerization rate can be calculated from the change in the area of the surfactant at a constant surface pressure.

O’Brien and colleagues\textsuperscript{226} described three different approaches (thermal with AIBN, redox with potassium persulfate or sodium bisulfite, or photoirradiation polymerizations) to polymerize monomeric lipids in a two-dimensional assembly proceeding in a linear or cross-linking manner depending on the number of polymerizable groups (double bonds) per monomeric lipid. Lipids that contain a single reactive moiety in either of the hydrophobic tails or associated with the hydrophilic head group yield linear polymers. Polymerization of lipids with reactive groups in each hydrophobic tail generally yield cross-linked polymeric networks.

Teyssié and colleagues\textsuperscript{260,262} proposed the first spontaneous styrene sulfonate polymerization in Langmuir films following an anionic mechanism. Indeed, when a dioctadecyldimethylammonium bromide (DODA) monolayer is spread over styrene sulfonate (SSt) aqueous solution, this monomer was shown to undergo a spontaneous polymerization process. This process was followed by monitoring the surface pressure variations at constant molecular area and/or the molecular area variation at constant surface pressure versus time. The spontaneous polymerization characteristics depend upon the monomer concentration, the surface pressure, the subphase ionic strength and pH. The polymerization occurring at the interface with a probable anionic mechanism is inhibited by carbon dioxide, sodium bicarbonate and LiClO\textsubscript{4}.

Finally, Carino \textit{et al.}\textsuperscript{257,258,263} followed the 2D gelation during the polymerization of alkylalkoxysilane molecules under acidic conditions at the air/water interface by monitoring the mean molecular area decrease and the surface viscosity increase versus time as the monolayer was cross-linked. They also used brewster angle microscopy to show the complete coverage of the water surface by the cross-linked material at the end of the reaction (Figure 4-6).
Concerning the cross-linking between true amphiphilic copolymeric chains at the air/water interface, only one example based on a polymerizable lipopolymer was previously proposed by O’Brien and colleagues.\(^{268}\) The amphiphilic copolymer investigated had a linear hydrophilic backbone consisting of poly(ethylene imine-co-ethyl oxazoline) and containing 20\% of hydrophobic sorbyl side chains, making it capable of forming stable Langmuir monolayers (Figure 4-7). Network formation after photopolymerization of the sorbyl moiety upon UV light exposure was demonstrated by monitoring the surface dynamic shear modulus (elasticity measurement). Unfortunately, they were not able to characterize the 2D morphologies obtained before and after the cross-linking reaction.

### 4.2 Interfacial Behavior of (PB-\(b\)-PEO)\(_n\) (\(n = 3\) or 4) Star Block Copolymers at the Air/Water Interface

Amphiphilic block copolymers containing both hydrophilic and hydrophobic segments form an important class of materials due to their wide variety of potential applications as polysoaps, polymeric surfactants, solution modifiers, emulsifiers, wetting agents, foam stabilizers and drug carriers.\(^{269-271}\) In most of the above areas, controlling the size as well as the surface properties of block copolymer assemblies is a major issue. In this chapter, we investigate star copolymers containing poly(butadiene) (PB) blocks.

The amphiphilic character of block copolymers has also been widely exploited for the preparation of monolayers at the air/water interface. These monolayers are somewhat different from classical low molecular weight amphiphiles in that the copolymer is constituted of hydrophilic and hydrophobic blocks of considerable molecular weight. The hydrophilic block by itself would be soluble in water, but the hydrophobic block acts as a buoy, anchors the polymer chains at the interface, and thus prevents the hydrophilic part from dispersing into the bulk water subphase. Numerous studies published on the field of monolayers at the air/water interface during
the past years demonstrate the utility in using the nonelectrolyte poly(ethylene oxide) (PEO) water soluble block due in particular to its properties and its biocompatibility and subsequent potential for applications in drug-delivery and other fields. Among copolymers investigated at the air/water interface, polystyrene-block-poly(ethylene oxide) (PS-b-PEO) block copolymers certainly form the most commonly studied systems.272-290

Although PS is a convenient choice due to its inexpensive price, monomer availability, and facile synthesis, polybutadiene-b-poly(ethylene oxide) (PB-b-PEO) is the primary amphiphilic diblock copolymer studied to provide control over spherical rodlike and vesicular architectures in bulk or aqueous solutions.228,234,291,292 Furthermore polybutadiene offers the possibility to stabilize block copolymer assemblies by cross-linking through the pendant double bond of the 1,2-polybutadiene units.

However, in spite of the significant interest showed for PB-b-PEO copolymers, few groups have studied the behavior of such amphiphilic copolymers at the air/water interface.293-295 Among these, only Discher and colleagues293 were able to show characteristic morphological organization of this amphiphile at the air/water interface through AFM images, and were the only ones who attempted crosslinking stabilization. Moreover, the behavior of any PB-b-PEO diblock copolymer with architecture more complex than linear chains, whether in bulk, in solution, or at the interface has not yet been investigated.

The structure of the AB diblock copolymers either in the bulk state or in solution is most certainly influenced by the volume fraction of each block and by the segment-segment interaction parameter $\chi$, but the molecular architecture, the conformational asymmetry and the compositional fluctuations all also have an effect on structure.296 Systematic investigation of the influence of all these factors on the organization of AB diblock copolymers in a star architecture necessitates the
preparation of monodispersed materials with well-defined molecular weights, block volume fractions and architecture.297

4.2.1 Surface Pressure-Area Isotherms

Surface property characterization of the four different (PB-\(b\)-PEO)\(_4\) star block copolymers started with isotherm measurements. Figure 4-8 shows the surface pressure-area (\(\pi\)-A) isotherms (25°C) on compression with a log scale on the x-axis for convenient visualization. The isotherm of each copolymer was reproducible and independent of spreading solution concentration. Together, the isotherms revealed several characteristics. First, all the monolayers were compressible up to surface pressures beyond 30 mN.m\(^{-1}\). Second, all of the isotherms are characterized by the three distinct regions illustrated in the cartoons of Figure 4-8: at high molecular areas the so-called “pancake” region (I), a pseudoplateau (II), and the brush region (III) at low surface areas. The dotted lines in Figure 4-9 also shows the extrapolation used to estimate the three corresponding parameters \(A_{\text{pancake}}\), \(A_o\), and \(\Delta A\). Third, the pressure of the pseudoplateau region was very similar for all samples, while its width varied systematically. In fact at the highest PEO composition, the pseudoplateau represents more than a 50-fold compression. Fourth, the copolymers (constituted from the same PB core and different PEO chain lengths) occupied similar areas in the high pressure brush region, independent of the PEO chain length.

Considering the affinity of PEO for the air/water interface and the hydrophobicity of PB, we suppose that the expanded surface film at large molecular areas (I) corresponds to a film dominated by the behavior of PEO at the surface. Quantitative comparison of \(A_{\text{pancake}}\), the area occupied by the pancake-like PEO domains when adsorbed at the air/water interface, supports this interpretation. A fit of the data revealed a linear dependence of \(A_{\text{pancake}}\) with the number of
EO units ($y = 1.399x + 113.09; R^2 = 0.989$) indicating that the “pancake” region area was largely dependent on the PEO block length (Figure 4-10).

Second, as the monolayer is compressed, a pseudoplateau is observed at a pressure of about 10 mN.m$^{-1}$, which is a signature of adsorbed EO monomer units at the air-water interface.\cite{298,299} The length of the PEO block clearly influences the length of the pseudoplateau ($\Delta A$) as seen in Figure 4-11. In fact, a fit of $\Delta A$ with the number of EO units gives the very good linear dependence ($y = 0.6136x - 6.0107; R^2 = 0.999$) shown by Figure 4-11. The magnitude of the slope, $61 \text{ Å}^2/$EO repeat unit, is reasonable for EO units lying flat at the interface. The observed linearity and small intercept implies that the change in area between $A_{\text{pancake}}$ and $A_0$ can be interpreted by PEO segments being successively submerged into the water subphase during compression at approximately 10 mN/m along the pseudoplateau. This is also in qualitative agreement with previous studies on analogous PS-$b$-PEO star block copolymers at the air/water interface.\cite{282,283}

Upon further compression, a second large pressure increase is observed up to values of 32 mN.m$^{-1}$, a trend also observed in the case of PB-$b$-PEO linear block copolymers.\cite{293,294} In this regime of high density, a brush conformation is expected. The latter is supported by the theoretical area $A_0$ that a compact film would occupy at zero pressure. Table 4-1 reveals that the occupied surface area $A_0$ is effectively the same for all the four samples ($A_0$/molecule = 32 ± 4 nm$^2$). The low area per butadiene repeat unit is a strong indication that the PB units have been compressed into a 3D structure rather than lying flat at the air/water interface. This result also confirms that only the PB segments have an effect on the brush region since the copolymers synthesized all possess the same PB core size.
4.2.2 Film Relaxation

By hysteresis experiments, we then investigated the ability of these four arm (PB-\textit{b}-PEO)$_4$ stars to relax to the same area as that occupied in their original uncompressed state. We examined the effects of pressure variation, compression/expansion cycles and the PEO block length on the degree of hysteresis and these results are shown in Figure 4-12.

**Pressure variation.** As shown in Figure 4-12A, at low pressures ($\Pi < 8$ mNm$^{-1}$), only minimal hysteresis was observed on compression and expansion, indicating that the surface films were capable of expanding at the same rate as they were compressed independent of the PEO block length. Thus, the star copolymers are elastic and highly surface active in the low pressure region I.

For pressures in the range of 10 mN.m$^{-1}$ a dramatic increase in hysteresis was observed with increasing pressure as shown in Figure 4-12B and C. This trend is consistent with the interpretation that a higher surface pressure ($\Pi \geq 10$ mN.m$^{-1}$) is necessary to start to submerge the higher molecular weight PEO branches into the water subphase. The observed compression/expansion curves also indicate that the surface film now relaxes at a slower rate than the compression.

**Compression/expansion cycles.** Hysteresis also changed with repeated compression/expansion cycles. At lower pressures ($\Pi < 8$ mN.m$^{-1}$), the hysteresis remained relatively minor and independent of the number of compression-expansion cycles applied. In contrast, at higher pressures, the degree of hysteresis, the width of the pseudoplateau, and the pancake limiting area systematically changed. The large initial hysteresis in Figure 4-12B-left may indicate reorganization of the high molecular weight PEO arms between the first and second compression. Subsequent creep to smaller surface areas indicate that with each cycle, slightly
more PEO is submerged into the water subphase and does not resurface over the time of the experiment. However, we observed at higher pressures (Π > 10 mN.m⁻¹) that for samples consisting of very long PEO chains ((PB_{76-b}-PEO_{1725})₄; Figure 4-12C-left), the compression curve of one cycle does not match the expansion curve of the previous cycle, but match the compression curve of the previous cycle, unlike short PEO sample. In this last case, it could be supposed that because of the very long PEO blocks, it is very difficult to submerge all EO units into the water subphase and some could resurface at the air/water interface upon expansion.

4.2.3 AFM Characterization of the Transferred Monolayers

Atomic Force Microscopy was used to study the morphology of surface films at the air/water interface after transfer to a solid surface. To this end, Langmuir-Blodgett films of two different samples (PB_{76-b}-PEO_{1725})₄ and (PB_{76-b}-PEO_{57})₄ were transferred to mica substrates over a range of pressures. Table 4-2 and Figure 4-13 shows that for applied surface pressures below 9 mN/m, positive transfer ratio values of approximately 1.0 were observed indicating “ideal” transfer with no change in macroscopic film dimensions. Whereas surface pressures above 8 mN/m lead to transfer ratios of approximately 2.0, or significant densification of the surface film upon transfer. In all cases LB transfers were characterized by a linear instantaneous transfer ratio indicating that the monolayer was transferred uniformly over the entire mica substrate.

Due to the hydrophilic nature of the mica, we assume PEO transfers as the bottom layer, represented in the scanned images as the continuous dark phase, whereas PB occupies the top portion of the film corresponding to the white higher elevation microdomains shown in Figure 4-14.
Effect of surface pressure. First, an effect of the surface pressure can be seen (Figure 4-14) in the “pancake” region for the sample with the longest PEO blocks. At lower pressures ($\Pi = 2 \text{ mN.m}^{-1}$) the PB microdomains are not homogeneous in size. However, when increasing pressure from $\Pi = 2 \text{ mN.m}^{-1}$ to $8 \text{ mN.m}^{-1}$ the PB microdomains are more organized, of larger size and less numerous for a same area. These observations were confirmed by the quantitative analysis of the AFM scans shown in Table 4-3. In comparing AFM scans (Figure 4-14A - D), first a gradual increase in the diameter of PB domains (from 61 to 132 nm), their height (from 2 to 5 nm), and in the number of molecules per PB domain (from 4 to 186), and second a decrease in the number of PB domains (from 445 to 18) and in the PB coverage (from 32% to 6%) with the surface pressure increasing were observed (Table 4-3).

The above trend is also observed in the molecules/domain vs. pressure curve of Figure 4-15, which shows more molecules continually aggregating (dramatic increase above pressure $\Pi = 4 \text{ mN/m}$) to form larger circular 2D micelles. This data is a strong indication that the surface micelles formed on spreading the PB-$b$-PEO stars are fluid and dynamic at the air/water interface in sharp contrast to PS-$b$-PEO systems where vitrification of PS leads to frozen surface micelles.

The AFM data also show that during compression, the distance between the PB microdomains increases from an average distance of 70 nm at $\Pi = 2\text{mN.m}^{-1}$ to 540 nm at $\Pi = 8\text{mN.m}^{-1}$. The estimated theoretical length of one extended PEO branch (1725 EO units and assuming 3.19 Å per EO unit) is about 550 nm, which is very close to the average distance between two PB microdomains at $\Pi = 8 \text{ mN.m}^{-1}$ (540 nm) illustrated in Figure 4-16.

At higher pressures ($\Pi > 8 \text{ mN.m}^{-1}$), a second type of morphology is observed (Figure 4-14E - H). This change in morphology is mirrored by a significant increase of the transfer ratio (T.R.) illustrated in Figure 4-13. The sudden jump in T.R. from $\approx 1.0$ to $2.0$ implies significant
densification of the film upon transfer in the pseudoplateau region ($\Pi \geq 8 \text{ mN.m}^{-1}$). The AFM data show that at $\Pi = 9 \text{ mN/m}$, PB microdomains are spaced much more closely compare to $\Pi = 8 \text{ mN/m}$ and then form elongated stripes, or chains, at $\Pi = 10 \text{ mN/m}$. The onset of the chain morphology correlates with the onset of significant hysteresis (Figure 4-12C) observed with the PEO$_{1725}$ blocks. Moreover, neither the chain morphology (Figure 4-14I and J) nor the same hysteresis (Figure 4-12C) is observed for the shorter PEO$_{57}$ material, indicating a PEO length influence chaining aggregation.

The observed results led to the model shown in Figure 4-16 for the (PB$_{76}$-b-PEO$_{1725}$)$_4$ block copolymer. At low pressure, microdomains of polydisperse size, some 2 nm vertical thickness, and few polymer chains per domain are observed. The relatively low density of PEO chains allows these domains to be closely spaced and the PEO chains to be in a relatively compact conformation. Upon compression the PB domains clearly flow and coalesce to form progressively larger surface micelles of more monodisperse size and higher and higher PEO chain densities that should lead to an overall extension of the PEO segments. We suppose that reduction in the line tension between the PB and PEO rich phases helps drive the aggregation. This process also increases the vertical thickness and significantly increases the lateral spacing between domains. At higher surface pressure ($\Pi > 8 \text{ mN.m}^{-1}$), and perhaps also associated with compaction during LB transfer, we suppose the PB microdomains start to chain as illustrated in Figure 4-16C. During chaining we hypothesize that the long PEO chains are further extended in a direction perpendicular to the chain axis and this hinders spherical aggregation and favors aggregate through points of contact at opposite ends of the elongated domain. Similar surface morphology has also been observed in the case of PB-b-PEO linear block copolymers. At
higher applied surface pressures, we suppose that the remaining PEO chains are hydrated and larger aggregates are formed, quickly leading to thicker films.

In contrast, we suppose that the short PEO branches of the (PB_{76-b}-PEO_{57})_4 material are much more easily submerged into the water subphase at higher pressure, and micelle chaining is hindered.

4.3 Cross-linking of Polybutadiene-b-Poly(ethylene oxide) Monolayers at the Air/Water Interface

We are interested in crosslinking monolayers of block copolymers to achieve porosity at the submicron scale. Here, a 2D polymeric nanomaterial consisting of a continuously cross-linked polybutadiene material with poly(ethylene oxide) domains of controlled size trapped within the PB network is illustrated. The strategy opens up the possibility to retain a specific morphology at the mesoscopic scale defined by a given surface pressure (\(\pi\)). Such porous polymer thin films have potential applications in the preparation of membranes which will show large differences in permeability to water, methanol, and other polar compounds depending on the effective PEO “pore” size.

With this in mind, we investigated two different methods for forming 2D cross-linked monolayers with a (PB-b-PEO)_3 amphiphilic star block copolymer material based on a polybutadiene core and a poly(ethylene oxide) corona. In the first method, cross-linking of the PB hydrophobic block was achieved by using AIBN as a radical initiator under UV light directly at the air/water interface. The second method was based on the self-condensation of the triethoxysilane-functionalized polybutadiene blocks of the (PB(Si(OEt)_3)-b-PEO)_3 star block copolymer under acidic conditions. The latter route is extremely general and should be applicable to functionalization and coupling via other silanes and metal alkoxides. In both cases, the surface properties of the cross-linked materials were characterized by surface pressure measurements
such as surface pressure-mean molecular area (MMA: interfacial area occupied by one polymer molecule) isotherms at different reaction times and isobar experiments (MMA evolution versus time for a given $\pi$) at different subphase pH values. The monolayer morphologies obtained at different surface pressures were studied by atomic force microscopy (AFM) imaging the Langmuir-Blodgett (LB) films obtained before and after cross-linking.

### 4.3.1 Interfacial Behavior of (PB-*b*-PEO)$_3$ Star Block Copolymers

We first investigated the surface properties of monolayers of a new set of (PB-*b*-PEO)$_3$ amphiphilic three-arm star block copolymers at the air/water interface. A divergent anionic polymerization method yielded copolymers with well-defined architecture, molecular weights, and block volume fractions (Chapter 3). Different samples of well-defined (PB-*b*-PEO)$_3$ amphiphilic star block copolymers exhibiting narrow molecular weight distributions were prepared with poly(ethylene oxide) coronas over a broad range of volume fractions (Table 4-4). Isotherm experiments at the air/water interface showed three characteristic regions: a “pancake” region (I) at high mean molecular areas where $\pi$ slowly increases as the monolayer is compressed, a pseudoplateau at a pressure of ca 10 mN/m (II) that corresponds to the dissolution of the PEO chains and finally a compact brush region (III) at low surface areas affected only by the PB segments (Figure 4-17). A fit of the pseudoplateau data revealed a linear dependence of $\Delta A$ with the number of EO units ($y = 12.351x - 0.4889; R^2 = 0.99$) indicating that the “pseudoplateau” region area was largely dependent on the PEO block length (Figure 4-18). The extrapolated curve falls almost perfectly through the origin with a x-axis intercept corresponding to less than 1 EO unit, indicating a strong phase separation between blocks compared with slight intermixing observed with PS-PEO systems. Our data indicate that along the pseudoplateau, a
monomer of EO occupies 12.4 Å², which is in good agreement with the value found for PS-PEO systems.\textsuperscript{282,283}

The monolayers were also transferred as Langmuir-Blodgett films on mica at various surface pressures and analyzed by Atomic Force Microscopy (AFM) (Figure 4-21A), showing different morphologies from analogous (PS-\textit{b}-PEO) star copolymers.\textsuperscript{282,283}

4.3.2 Reaction of the Polybutadiene Block at the Air/Water Interface in the Presence of AIBN

Initially, photocleavage of AIBN under UV light was attempted to crosslink the hydrophobic PB blocks of the (PB-\textit{b}-PEO)\textsubscript{3} copolymer monolayers directly at the air/water interface. For this purpose, 100 µL of a solution of (PB\textsubscript{200-\textit{b}}-PEO\textsubscript{76})\textsubscript{3} star block copolymer in chloroform at a concentration of \( C = 1 \text{ mg/mL} \) and 100 µL of a solution of AIBN in chloroform at a concentration of \( C = 0.2 \text{ mg/mL} \) were successively deposited on the water surface. The monolayer was then compressed up to the desired surface pressure (20 mN/m) and the radical polymerization reaction of the 1,2-PB double bonds initiated by the photo-induced dimethylcyano radicals was carried out for 24 hours. At the end of the reaction, the surface properties of the reacted material were investigated through isotherm and AFM studies. As shown in Figure 4-19, a shift towards the low mean molecular area region was observed after reacting the polybutadiene blocks. Furthermore, the progression of the reaction was followed by IR analysis of an aliquot of the material removed directly from the water surface (Figure 4-20). The disappearance of the peaks at 3100 cm\textsuperscript{-1} and 1600 cm\textsuperscript{-1} corresponding to the 1,2-PB double bonds (=CH\textsubscript{2} anti-symmetric stretch and alkenyl –HC=CH\textsubscript{2} stretch, respectively) confirmed significant consumption of the pendant double bonds.

AFM characterization of the morphologies obtained before and after the reaction confirmed the previous observations. Figure 4-21 shows images of monolayers transferred to
mica substrates at $\pi = 20$ mN/m at different reaction times. The images reveal submicron-sized white circular domains that enlarge with reaction time, but remain separated. Due to the hydrophilic nature of mica, we assume PEO transfers as the bottom layer, represented in the images as the continuous dark phase, whereas PB occupies the top portion of the film corresponding to the white higher elevation domains shown in Figure 4-21A. We suppose that the bright domains correspond to crosslinked PB regions. The fraction of the surface occupied by the bright domains increases with the reaction time until large portions of the surface is covered with cross-linked and hydrophobic PB after 24 hours. However, the picture scanned at 40 $\mu$m (Figure 4-21E) reveals that the bright domains remain isolated from each other and do not interconnect across the film. The formation of these domains is consistent with a chain polymerization occurring precisely at the spots of a radical initiation, which are also the nucleation spots. The continuous PEO phase indicates that while some areas might have reacted, this strategy failed to afford homogeneously cross-linked PB covering the entire surface.

4.3.3 Cross-linking with Hydrosilylated Polybutadiene Blocks at the Air/Water Interface

4.3.3.1 Application on polybutadiene homopolymer

To successfully demonstrate the viability of our method, we utilized linear polybutadiene which is commercially available because of its world wild application as a commodity rubber (Figure 4-22). Unsaturated polymers, especially diene polymers, are ideal for selective chemical modification because of the technological importance associated with the parent materials. A particularly interesting reaction involves the hydrosilylation of diene polymers to obtain silane-modified rubber materials. Many papers and patents have appeared on the hydrosilylation of polymers. In most cases, the hydrosilylated polydienes were used for the synthesis of macromolecular complex architectures such as arborescent graft polybutadienes, multigraft copolymers of polybutadiene and polystyrene, or side-loop polybutadiene.
We apply here the hydrosilylation reaction on the double bonds of polybutadiene chain polymers. Triethoxysilane was used as the hydrosilylating agent in stoichiometric amount with the total molar amount of double bonds in the polybutadiene chain (1,2- and 1,4-units), and platinum(0)-divinyltetramethyldisiloxane complex (Karstedt catalyst) was used as the catalyst (Figure 4-22). The reaction was heated up under argon for 24 hours at 80 °C in dry toluene (water free environment). After workup, the hydrosilylated copolymer was analyzed by $^1$H NMR and FTIR spectroscopy (Figures 4-23, 4-24, and 4-25).

The $^1$H NMR spectrum of the polybutadiene starting material was used to determine the distribution of 1,2- and 1,4-units. The two protons of the pendant vinyl carbon in the 1,2-units (\(=\text{CH}_2\)) and the other hydrogens in the double bonds (\(-\text{CH}=\text{CH}-\) and \(-\text{CH}==\text{CH}_2\)) having chemical shifts of 4.9 ppm and 5.4 ppm, respectively, the polybutadiene turned out to be composed of 89 mole % of 1,2-PB units (Figure 4-23). The $^1$H NMR spectrum of the hydrosilylated polybutadiene revealed a strong decrease in the intensity of the signal corresponding to the \(-\text{CH}=\text{CH}_2\) (\(\delta = 4.9\) ppm) protons of the pendant double bonds. Furthermore, the appearance of intense peaks at \(\delta = 1.2\) ppm and \(\delta = 3.8\) ppm corresponding respectively to the \(-\text{Si}–\text{OCH}_2\text{CH}_3\) methyl protons and \(-\text{Si}–\text{OCH}_2\text{CH}_3\) methylene protons indicated a high degree of conversion. However, some pendant double bonds remained unreacted after hydrosilylation (Figure 4-24). Based on the integration values of the signals at \(\delta = 4.9\) ppm and \(\delta = 5.4\) ppm, a conversion of 75 % of the 1,2-PB pendant double bonds was found, knowing that triethoxysilane reacts predominantly with the 1,2-PB units as previously demonstrated.\(^{312}\)

This result was confirmed by IR spectroscopy as shown in Figure 4-25, where the absorbance peaks at 3100 cm\(^{-1}\) and 1640 cm\(^{-1}\) characteristic of \(-\text{CH}=\text{CH}_2\) double bonds (\(=\text{CH}_2\) anti-symmetric stretch and alkenyl \(-\text{HC}=\text{CH}_2\) stretch, respectively) strongly decreased in
intensity after hydrosilylation. However, there are still unreacted pendant double bonds remaining after reaction indicating less than 100% conversion.

After characterization of the PB_{68-co-PB(Si(OEt)_3)_{136}} triethoxysilane-functionalized polybutadiene, its cross-linking at the air/water interface by self-condensation of the triethoxysilane pendant groups was studied.

Alkylalkoxysilanes have been widely used as reactive amphiphilic molecules at the air/water interface.\textsuperscript{257,258,263,316-327} Our group has for instance investigated some of the fundamental aspects of the chemical cross-linking of octadecyltrimethoxysilane (OTMS) and octadecyltrithoxysilane (OTES) molecules under acidic conditions at the air/water interface.\textsuperscript{257,258,263,327}

The mechanism of this 2D-acid-catalyzed cross-linking involves two different steps (Figure 4-26): first, the hydrolysis of the ethoxy groups with the elimination of three ethanol molecules to give the corresponding silanols, followed by condensation between the silanols leading to the formation of a 2D-network.

The air/water interfacial cross-linking of the chemically modified PB(Si(OEt)_3) polybutadiene was first studied by recording isotherms after different reaction times (subphase pH = 3.0 and $\pi = 0$ mN/m) (Figure 4-27) with a barrier compression speed (100 mm/min) to prevent additional cross-linking during monolayer compression. For comparison, the blue curve illustrates the same polymer spread and rapidly compressed at pH = 3.0 before any significant reaction could occur (Figure 4-27). As the reaction time is increased, the isotherms shift towards the low mean molecular area region (loss of ethanol and water molecules during hydrolysis and condensation, respectively). For reaction times longer than 10 hours, the isotherms essentially overlapped which indicates completion of the cross-linking.
As shown in Figure 4-28 the monolayer static elastic modulus $\varepsilon_s$ calculated from the expression (1): \[ (1) \]

$$
\varepsilon_s = -\text{MMA} \times \frac{d\pi}{d\text{MMA}}
$$

significantly increases versus reaction time, indicating that the material becomes more and more rigid as the extent of cross-linking is increased.

From these isotherms, the interfacial area occupied by one silane repeat unit before reaction and its decrease during cross-linking were estimated ($\pi = 5 \text{ mN/m}, \text{pH} = 3.0$) and compared with the values previously reported for OTES under similar experimental conditions. The MMA for the hydrosilylated polybutadiene decreases from $6300 \text{ Å}^2$ (46 $\text{Å}^2$/silane repeat unit) down to $3520 \text{ Å}^2$ (26 $\text{Å}^2$/silane repeat unit), which corresponds to a decrease of approximately $\Delta A = 20 \text{ Å}^2$/silane repeat unit. These values are in very good agreement with the ones reported for OTES (46 $\text{Å}^2$/molecule before cross-linking, 24 $\text{Å}^2$/molecule after cross-linking, and $\Delta A = 22 \text{ Å}^2$/molecule), and they clearly indicate that the extent of sol-gel cross-linking is not reduced when starting from true polymeric chains compared to alkylalkoxysilane molecules.

The pH influence on the cross-linking reaction kinetics was shown by carrying out isobar experiments at $\pi = 10 \text{ mN/m}$ and for different subphase pH values (Figure 4-29). As expected, the MMA decreases faster for lower pH values. The isobar at pH = 7.0 shows a very slow creep over time which demonstrates that the reaction is likely insignificant under neutral pH conditions. For lower pH values (pH = 2.0 and 3.0), the curves overlap with the MMA leveling off after about 7 hours indicating completion of the cross-linking reaction. The kinetics were consistent with those reported for OTES and were slower compared to the results obtained for
OTMS\textsuperscript{257,258,263,327} which is related to the slower elimination of larger alkoxy substituents during the hydrolysis step.

Upon completion of the cross-linking reaction, the cross-linked material could be subsequently manually removed from the interface with a spatula after its compression to a final area of ca. $2 \times 15 \text{ cm}^2$ (Figure 4-30), leading to a film of approximately 50 monolayers thick. It was self-supporting and gel-like, and could be collected as elongated sheets, which in turn could be drawn into very long fibers at high elongation (Figure 4-30). As expected, it was insoluble in common organic solvents such as chloroform or THF, making molecular weight analysis by SEC impossible.

The evolution of the monolayer morphology during cross-linking was characterized by AFM imaging of the LB film after transfer onto mica substrates (Figure 4-31, $\pi = 10 \text{ mN/m}$). As a control experiment, it was first observed that under neutral pH conditions ($\text{pH} = 7.0$, no cross-linking) the hydrosilylated polybutadiene forms a smooth and featureless monolayer (Figure 4-31B) in opposition to the highly hydrophobic polybutadiene starting material which forms typical rubbery continuous aggregates above the water surface (Figure 4-31A). After its hydrosilylation, the polybutadiene becomes amphiphilic (hydrophobic backbone and hydrophilic triethoxysilane side groups) and consequently surface active with the triethoxysilane pendant groups solvated into the water subphase. This interfacial property of the hydrosilylated polybutadiene was also shown in the isotherms where stable monolayers could be formed for surface pressures as high as 40 mN/m before collapsing (Figure 4-27). After 20 minutes of reaction ($\approx 50\%$ extent of cross-linking according to the isobar at $\text{pH} = 3.0$ and $\pi = 10 \text{ mN/m}$), the cross-linked material becomes more hydrophobic and can be clearly observed in Figure 4-31C (bright areas) with an average height of 1 nm as determined by cross-section analysis (Figure 4-31E). The cross-linked
polybutadiene has irregular borders and doesn’t cover yet the entire mica surface. An AFM image obtained after completion of the cross-linking reaction is shown in Figure 4-31D (10 hours, pH = 3.0, \( \pi = 10 \) mN/m). Under these experimental conditions, most of the mica surface was covered with a smooth and cross-linked monolayer. Therefore, we deliberately found an area with a crack (that probably formed during film transfer) to clearly show the presence of the cross-linked monolayer (bright area) on top of the mica substrate with a thickness that stays constant around 1 nm during cross-linking (Figure 4-31F).

4.3.3.2 Application on \((\text{PB-}b\text{-PEO})_3\) star block copolymer

**Hydrosilylation of \((\text{PB-}b\text{-PEO})_3\) star block copolymers.** We also applied the hydrosilylation reaction on the polybutadiene segments of the \((\text{PB}_{200-b}\text{-PEO}_{326})_3\) star block copolymer. Triethoxysilane was used as the hydrosilylating agent in stoichiometric amount with the total molar amount of double bonds in the polybutadiene block (1,2 and 1,4 units), and platinum(0)-divinyltetramethyldisiloxane complex (Karstedt catalyst) was used as the catalyst (Figure 4-32). The reaction was heated up under argon for 24 hours at 80 °C in dry toluene (water free environment). After workup, the hydrosilylated copolymer was analyzed by \(^1\)H NMR and FTIR spectroscopy (Figures 4-33 and 4-34).

Figure 4-33 shows the \(^1\)H NMR spectra of the \((\text{PB-}b\text{-PEO})_3\) star block copolymer before and after triethoxysilane hydrosilylation. The \(^1\)H NMR spectrum of the \((\text{PB-}b\text{-PEO})_3\) starting material was used to determine the distribution of 1,2- and 1,4-units in the polybutadiene block. The two hydrogens of the pendant vinyl carbon in the 1,2-units (=CH\(_2\)) and the other hydrogens in the double bonds (-CH=CH- and –CH=CH\(_2\)) having chemical shifts of 4.9 ppm and 5.4 ppm, respectively, the PB block turned out to be composed of 75 mole % of 1,2-PB units. The \(^1\)H NMR spectrum of the \((\text{PB(Si(OEt)}_3)-b\text{-PEO})_3\) star block copolymer revealed a strong decrease in the intensity of the signal corresponding to the -CH=CH\(_2\) (\( \delta = 4.9 \) ppm) protons of the pendant
1,2-double bonds. Furthermore, the fact that the signal of the –Si–OCH₂CH₃ methyl protons increased in intensity (δ = 1.2 ppm) indicated that the reaction occurred with a high efficiency. However, as shown in Figure 4-32, some pendant double bonds remain after hydrosilylation. Based on the integration values of the signals at δ = 4.9 ppm (-CH=CH₂) and δ = 0.5 ppm (-CH₂-Si-), a conversion of 85% of the 1,2-PB pendant double bonds was found, knowing that triethoxysilane reacts predominantly with the 1,2-PB units as previously demonstrated.³¹² This result was confirmed by IR spectroscopy (Figure 4-34). The absorbance peak at 3100 cm⁻¹ originating from –CH=CH₂ double bonds (=CH₂ anti-symmetric stretch) disappears after hydrosilylation, but there are still remaining unreacted pendant double bonds as demonstrated by the signal at 1640 cm⁻¹ (alkenyl –HC=CH₂ stretch) indicating less than 100% conversion.

**Study of the cross-linking reaction at the air/water interface.** The air/water interfacial behavior of the chemically modified (PB(Si(OEt)₃)-b-PEO)₃ star block copolymer was first studied through isotherms at a subphase pH = 3.0 (Figure 4-35). Initially, the (PB(Si(OEt)₃)-b-PEO)₃ star block copolymer was spread on the water surface, and the cross-linking reaction (pH = 3.0) was carried out for 10 hours at very large surface areas where no surface pressure was observed, then isotherms were recorded as shown in the lower curve of Figure 4-35. For comparison, the top curve illustrates the same copolymer spread and rapidly compressed at pH = 3 before any significant reaction could occur. The isotherm of the non-silylated (PB-b-PEO)₃ starting material forms the central curve of Figure 4-35. It is first observed that the isotherm of the unreacted (PB(Si(OEt)₃)-b-PEO)₃ star block copolymer is shifted to higher mean molecular area region compared to the non-hydrosilylated starting material. The shift to larger areas is in good agreement with the molecular weight increase of the star block copolymer after hydrosilylation, with the hydrosilylated star block copolymer molecules occupying a larger
interfacial area. When the isotherm is carried out 10 hours after the monolayer formation at pH = 3.0 (complete cross-linking), a significant shift towards the low mean molecular area region was observed (loss of ethanol and water molecules during hydrolysis and condensation, respectively) indicating that the material is more compact. Another interesting feature is the lack of the pseudoplateau at 10 mN/m in the unreacted silylated material, and its reappearance upon crosslinking. This pseudoplateau corresponds to desorption of the poly(ethylene oxide) chains from the surface to the aqueous phase below. We suppose that disappearance of the plateau is due to increased mixing between the EO units and the significantly more hydrophilic silylated units, while the crosslinking reaction would appear to induce demixing. The above interpretation is corroborated by the length of the PEO pseudoplateau $\Delta A$, which after cross-linking was 12,500 Å$^2$ and compared well with that of the (PB-$b$-PEO)$_3$ starting material at 12,080 Å$^2$.

These above observations were confirmed by recording isotherms at pH = 3.0 after different reaction times (Figure 4-36A). Fresh monolayers were spread for each experiment and the barrier compression speed was set to 100 mm/min to prevent additional cross-linking during monolayer compression. As the reaction proceeds, the isotherms shift to the low mean molecular area region corresponding to a more compact cross-linked material with the PEO pseudoplateau becoming more and more pronounced. Before the cross-linking starts, both the hydrosilylated PB blocks and the PEO blocks are adsorbed at the interface with no PEO pseudoplateau. As the reaction proceeds, we suppose the area occupied by the hydrosilylated PB decreases whereas the fractional area occupied by the PEO stays the same. The reaction induces demixing of PEO chains which explains the more pronounced PEO pseudoplateau. This observation was also confirmed by plotting monolayer compressibility (K) versus mean molecular area for different reaction times (Figure 4-36B). The compressibility (K) was calculated from the expression (2):
where $A$ is the mean molecular area and $\Pi$ is the surface pressure. The development of the pseudoplateau can be observed with the increase of the compressibility peak corresponding to the PEO pseudoplateau transition ($\pi = 10 \text{ mN/m}$) that also shifts towards the low mean molecular area region.

The pH influence on the cross-linking reaction kinetics is shown by the isobar experiments carried out at $\pi = 5 \text{ mN/m}$ and for different subphase pH values (Figure 4-37). The low surface pressure was chosen to avoid the PEO phase transition. As expected, the MMA decreases faster for lower pH values. The isobar at pH = 7.0 shows slow creep over time which demonstrates that the reaction is likely insignificant at this pH. At lower pH values the mean molecular areas overlap and stay constant after about 7 hours indicating completion of the cross-linking reaction. As for the hydrosilylated PB, the cross-linking reaction kinetics were slower in the case of triethoxysilane compared to the results obtained by Carino et al.\textsuperscript{263} for octadecyltrimethoxysilane (OTMS), which is consistent with the slower elimination of larger alkoxy substituents.

Once the cross-linking reaction was complete, the cross-linked material could be removed from the interface with a spatula after its compression to a final area of ca. $2 \times 15 \text{ cm}^2$ (Figure 4-38), approximately 50 monolayers thick. Unlike the (PB-$b$-PEO)$_3$ star block copolymer, this material was self-supporting and gel-like and could be collected as elongated elastic sheets, which in turn could be drawn into very long fibers at high elongation (Figure 4-38). As expected, it was insoluble in common organic solvents such as chloroform and THF, making molecular weight analysis by SEC impossible. It should be noted that this behavior was in sharp contrast to
the films formed from AIBN, which could not be pulled from the surface as free standing films or fibers under any conditions attempted.

**Surface pressure influence on the morphology of the cross-linked material.** The LB film morphologies obtained after cross-linking at different surface pressures were characterized by AFM after monolayer transfer to mica substrates (Figure 4-39). It is assumed that the monolayer morphologies are not modified during LB film formation as indicated by the transfer ratio values close to unity (T.R. = (Area of the surface film transferred) / (Area of the mica substrate)). As a control experiment, it was first observed that at $\pi = 5$ mN/m and pH = 7.0 (no cross-linking reaction), a smooth featureless monolayer with no phase separation between the hydrosilylated PB blocks and the PEO blocks is obtained (Figure 4-39A). After the hydrosilylation reaction, the PB block becomes more hydrophilic because of the triethoxysilane pendant groups and therefore is adsorbed at the air/water interface just like the PEO block. This interfacial property of the hydrosilylated PB block was also demonstrated with hydrosilylated PB homopolymers that formed stable monolayers for surface pressures as high as 40 mN/m (Figure 4-27). Such behavior differs significantly from the PB block of the (PB-$b$-PEO)$_3$ star block copolymer which is much more hydrophobic and aggregates above the water surface. When LB transferred monolayers of the silylated block copolymer reacted under isobaric conditions for 10 hours at $\pi = 2$ mN/m and pH 3.0 were examined by AFM (Figure 4-39B) a clear phase separation between the cross-linked material (yellow areas) and the poly(ethylene oxide) chains (dark areas) could be observed with the average height of the cross-linked monolayer being about 2 nm. However it is only at surface pressures of about 6 mN/m and above that true PEO pores can be seen within the PB network (Figure 4-39D). As the surface pressure increases, the average
PEO pore size decreases (Figure 4-39D-G) to reach a morphology with very small PEO domains trapped within a 2D cross-linked PB network ($\pi = 9$ mN/m; Figure 4-39G). For higher surface pressures such as 15 mN/m (Figure 4-39H), the cross-linked material covers the entire surface with the PEO “pores” barely visible. This is in good agreement with the observation that PEO chains are pushed under the water surface at 10 mN/m.

The topography was further investigated by section analysis of the AFM images (Figures 4-40A and B). The height signal amplitude is significantly smaller for the image scanned for a surface pressure of 15 mN/m since the PEO pores are barely visible. The average sizes of the PEO pores obtained for different surface pressures were roughly determined from the analysis of the power spectral density (PSD) (Figures 4-40C and D) of the surface morphology measured by AFM. The maximum of the large peak in the PSDs corresponds to the average distance between nearest neighbor domains for non-porous material and the average size of the PEO pores for a porous material (Figure 4-40D). We observe that for a surface pressure of 5 mN/m, at which the cross-linked material is not “porous”, the approximate distance between two PB cross-linked domains is $\approx 180$ nm. This characteristic pore size decreases with surface pressure applied during the cross-linking reaction from $\approx 130$ nm for $\pi = 6$ mN/m until it reaches a value in the range $\approx 40$ nm for $\pi = 9$ mN/m (Figure 4-40C). The curves for surface pressures of 7 and 8 mN/m were not included for easier visualization, but the average PEO “pore” sizes for these surface pressure were found to be equal to 46 and 42 nm, respectively. For higher surface pressure such as 15 mN/m, no maximum is observed for the PSD curve. This is in agreement with the fact that no PEO “pores” can be seen at this surface pressure as shown by the AFM picture (Figure 4-39H). From these AFM images and the spectral power density study, it can be concluded that with hydrosilylated PB blocks, the cross-linking reaction is more homogeneous than with AIBN,
allowing the formation of a two-dimensional gel with controlled PEO “pore” size by simply changing the polymerization surface pressure. The silane chemistry proceeds by a step growth mechanism which will favour homogeneous coupling over the entire surface in contrast to the chain growth mechanism of AIBN which would favour nucleation spots.

An experiment to illustrate retention of the morphology after cross-linking was attempted. The (PB(Si(OEt)₃)-b-PEO)₃ monolayer was cross-linked at constant surface pressure π = 9 mN/m and pH = 3.0 (t = 10 hrs), and then the cross-linked monolayer was transferred (Figure 4-41). A second transfer of the same cross-linked material was performed after the expansion of the system to π = 2 mN/m. As shown by the images in Figure 4-41, the same morphology is observed before (π = 9 mN/m; pH = 3.0, t = 10h) and after expansion (π = 2 mN/m; pH = 3.0) with only a slight increase of the PEO pore size after monolayer expansion.

A final experiment was attempted to prove that for high surface pressures, the PEO chains are irreversibly displaced to the aqueous phase underneath the cross-linked PB network. After cross-linking the monolayer (t = 10 hrs, pH = 3.0) at 20 mN/m (surface pressure above PEO aqueous dissolution), the barriers were expanded and the isotherm of the resulting cross-linked monolayer was recorded as shown in Figure 4-42 (Blue curve). The PEO pseudoplateau is no longer present which indicates that the PEO chains were irreversibly positioned underneath the PB cross-linked network and could not readsorb at the interface during monolayer expansion. A control experiment was carried out by recording the isotherm of the monolayer cross-linked at 5 mN/m, that is below the surface pressure corresponding to the PEO blocks aqueous dissolution (Figure 4-42, red curve). As expected, the PEO pseudoplateau is still present (even after several hysteresis cycles), which confirms that it is possible for high surface pressures (π > 10 mN/m) to
freeze the “thicker” conformation (PEO sublayer underneath a PB network) of the cross-linked material.

### 4.4 Conclusion

The main objective of this study was to propose a new and general method to synthesize a novel two-dimensional polymeric nanomaterial consisting of a continuous cross-linked polybutadiene network containing poly(ethylene oxide) pores of controlled sizes. To reach that goal, novel \((PB(Si(OEt)_{3})-b-PEO)_{3}\) star block copolymers were synthesized by hydrosilylating the PB pendant double bonds of \((PB-b-PEO)_{3}\) star block copolymers with triethoxysilane. The hydrolysis and condensation of the triethoxysilane pendant groups of the \((PB(Si(OEt)_{3})-b-PEO)_{3}\) star block copolymer under acidic conditions allowed us to easily crosslink the polybutadiene block directly at the air/water interface without any additives or reagents. This demonstrated the improved efficiency of this method compared to the radical polymerization in the presence of AIBN to get a homogeneously cross-linked material with controlled and fixed morphologies. This strategy permits the control of the PEO pore size by simply adjusting the surface pressure during the cross-linking reaction as shown by AFM imaging of the LB films.

The characterization of these 2D amphiphilic cross-linked materials are currently under investigation (permeability, small angle scattering, and 2D viscometry) to understand the benefits provided by 2D self-assembly at the air/water interface over conventional solution self-adsorption and other processes. At stake is the possibility to use 2D self-organization as a means to construct materials with anisotropic structures, to reproducibly engineer such structures, and to target defined functions with these materials. In addition, such copolymer silanes monolayer could be easily transferred and grafted through covalent bonds to inorganic surfaces (glass support such as silicon wafer) for polymer/inorganic composite synthesis. Work is also in progress to introduce triethoxysilane groups, and other metal alkoxides on other polydiene block copolymers of more
complex architectures such as triblock copolymers with the aim toward the stabilization of other original 2D and 3D morphologies.

Figure 4-1. Direct visualization of the 1% unreacted (A) and 0.05% cross-linked (B) wormlike micelles of PB$_{45}$-b-PEO$_{55}$ diblock copolymer by cryotransmission electron microscopy. Sketches illustrate the local structure of pristine and cross-linked PB cores. Use of a lower concentration in (B) was necessitated by the gel-like character of the 1% cross-linked solution.

Figure 4-2. Formation and osmotic deflation of PB$_{46}$-b-PEO$_{26}$ diblock copolymer, vesicles either without (A, B) or with (C) cross-linking between the hydrophobic segments of butadiene.
Figure 4-3. (A) Representation of the concept of a two-dimensional network of molecular pores, i.e., “perforated monolayers”. (B) Stabilization of the resulting assembly via polymerization before and after transfer to a macroporous substrate.

Figure 4-4. A quasilinear coupler (a, \(\rho\)-xylylene dibromide), a cross-shaped monomer (b, lanthanum sandwich complex of tetrapyridylporphyrin), an idealized structure (c), and an STM image (d) of a square grid.
Figure 4-5. (a) Amphiphilic porphyrins P₁ and P₂. P₁: R = R₁ (M = H₂, Cu); P₂: R = R₂ (M = H₂, Cu, Fe). (b) Amphiphilic porphyrazine P₃ (M = Cu).

A)

1. Hydrolysis

\[ \text{Si} \left( \text{CH₃} \right)_{16} \text{OH} + \text{H}^+ \rightarrow \text{Si} \left( \text{CH₃} \right)_{16} \text{H} + \text{H₂O} \]

2. Condensation

\[ \text{Si} \left( \text{CH₃} \right)_{16} \text{OH} + \text{Si} \left( \text{CH₃} \right)_{16} \text{OH} \rightarrow \text{Si} \left( \text{CH₃} \right)_{16} \text{Si} \left( \text{CH₃} \right)_{16} + \text{H₂O} \]

B)

C)

Figure 4-6. (A) General reactions involved in the polymerization of alkoxy silanes; (B) Pressure-area isotherms obtained for pH = 3.5 at 25 °C after different reaction times; (C) Gelation of the OTMS monolayer as observed from Brewster angle micrographs.
Figure 4-7. Molecular structure of the lipopolymer polymerized by exposure to UV light.

Figure 4-8. Surface Pressure-Area per polymer molecule isotherms at 298K for (PB_{76-b}-PEO_n)_{4} star block copolymers (n = 57, 137, 444 and 1725).
Figure 4-9. Isotherm of (PB$_{76}$-$b$-PEO$_{444}$)$_4$ depicting how measurements of molecular area for the three principal regions are obtained.

Figure 4-10. Linear dependence of $A_p$ on the total number of ethylene oxide units.
Figure 4-11. Linear dependence of $\Delta A_{\text{pseudoplateau}}$ on the total number of ethylene oxide units.
Figure 4-12. Compression/expansion curves for two different samples of PB₃₆-b-PEO₄ star block copolymers ((PB₇₆-b-PEO₁₇₂₅)₄ and (PB₇₆-b-PEO₁₇₂₅)₄) at (A) 5 mN.m⁻¹, (B) 10mN.m⁻¹ and (C) 15mN.m⁻¹.
Figure 4-13. Evolution of transfer ratio with the surface pressure in the case of (PB_{76-b}-PEO_{1725})_4 star block copolymer sample.
Figure 4-14. AFM tapping mode amplitude images of the (PB$_{76}$-b-PEO$_{1725}$)$_4$ (A, B, C, D, E, F, G and H) and (PB$_{76}$-b-PEO$_{57}$)$_4$ (I and J) star block copolymers transferred to a mica plate support at various surface pressures. The films are scanned at a scan rate of 1Hz with a scale of 2 x 2 µm (A, B, C, D, E and I) and 5 x 5 µm (F, G, H and J).
Figure 4-15. Dependence of the number of molecules per domain on the surface pressure in the case of the (PB_{76}-b-PEO_{1725})_4 star block copolymer sample. The general trend shows that as pressure increases, more molecules aggregate (dramatic increase from Π = 4 mN/m) to form the observed circular PB microdomains.
Figure 4-16. Model proposed to explain the formation of a network of elongated stripes. (a) Long PEO branches staying at the water surface as globules create a weak separation between the PB microdomains. (b) As the surface pressure increases, the PEO blocks are pushed to the maximum hydration by a total extension of their chains on the surface of water. (c) Upon further compression, the PEO chains, too long to be totally submerge into the water subphase, shift to allow the PB microdomains to aggregate through only one point of contact to give elongated stripes.
Figure 4-17. Surface Pressure-Area per polymer molecule isotherms for \((PB_{200-b-PEO_n})_3\) star block copolymers \((n = 76, 326, 970,\) and \(2182)\).

Figure 4-18. Linear dependence of \(\Delta A_{\text{pseudoplateau}}\) on the total number of ethylene oxide units.
Figure 4-19. Surface Pressure-Area isotherms for \((PB_{200-b}-PEO_{76})_3\) star block copolymer before (—) and after (—) cross-linking in the presence of AIBN under UV light \((\pi = 20\, \text{mN/m})\).

Figure 4-20. IR spectra of \((PB_{200-b}-PEO_{76})_3\) before (—) and after (—) cross-linking in the presence of AIBN under UV light.
Figure 4-21. AFM topographic images of the (PB$_{200}$-$b$-PEO$_{76}$)$_3$ star block copolymer transferred to mica substrates ($\pi = 20$ mN/m) before (A) and after cross-linking (B, C, D, and E) at different reaction times. The films are scanned with a scale of 10 x 10 $\mu$m (A, B, C, and D) and 40 x 40 $\mu$m (E).
Figure 4-22. Hydrosilylation of the pendant double bonds of the PB homopolymer.

Figure 4-23. $^1$H NMR spectrum (CDCl$_3$ ; 300MHz) of the commercial linear polybutadiene.
Figure 4-24. $^1$H NMR spectrum (CDCl$_3$ ; 300MHz) of the hydrosilylated polybutadiene.

Figure 4-25. IR spectra of the polybutadiene before and after hydrosilylation.
Figure 4-26. Cross-linking reaction involving hydrolysis and condensation of the triethoxysilane groups of the polybutadiene backbone.

Figure 4-27. Surface pressure-Mean Molecular Area isotherms of the hydrosilylated polybutadiene carried out after different reaction times (subphase pH = 3.0).
Figure 4-28. Static elastic modulus-surface pressure curves of the hydrosilylated polybutadiene at different reaction times (subphase pH = 3.0).

Figure 4-29. Mean Molecular Area-Time isobars of the hydrosilylated polybutadiene for various subphase pH values ($\pi = 10$ mN/m).
Figure 4-30. (A and B) Removal of the cross-linked homopolymer from the Langmuir trough surface. The white material easily comes off the interface using a spatula. (C) Picture of the long cross-linked fiber dried under vacuum.

Figure 4-31. AFM topographic images of the LB films transferred onto mica substrates at $\pi = 10$ mN/m: the commercial polybutadiene (A) and the hydrosilylated polybutadiene at pH = 7.0 (B; t = 0 h) and 3.0 for different reaction times (C ; t = 20 min and D; t = 10 h). (E and F) Cross-section analysis of the images C and D. The images are 7 x 7 $\mu$m$^2$ (A) and 50 x 50 $\mu$m$^2$ (B, C, and D).
Figure 4-32. Hydrosilylation of the pendant double bonds of the (PB-b-PEO)$_3$ star block copolymer.
Figure 4-33. $^1$H NMR spectra (CDCl$_3$; 300MHz) of (PB$_{200}$-b-PEO$_{326}$)$_3$ star copolymer and the corresponding hydrosilylated (PB$_{78}$-co-PB(Si(OEt)$_3$)$_{122}$-b-PEO$_{326}$)$_3$ star block copolymer.
Figure 4-34. IR spectra of the (PB$_{200}$-b-PEO$_{326}$)$_3$ star block copolymer and the corresponding hydrosilylated (PB$_{78}$-co-PB(Si(OEt)$_3$)$_{122}$-b-PEO$_{326}$)$_3$ star block copolymer.

Figure 4-35. Surface Pressure-Area isotherms for (PB$_{200}$-b-PEO$_{326}$)$_3$ star block copolymer and the corresponding hydrosilylated (PB(Si(OEt)$_3$)-b-PEO)$_3$ star block copolymer before (pH = 3.0, t = 0h) and after (pH = 3.0, t = 10h) cross-linking.
Figure 4-36. Surface pressure-Area isotherms (A) and Compressibility-Area curves (B) for the hydrosilylated (PB(Si(OEt)₃)-b-PEO)₃ star block copolymer carried out at different reaction times (subphase pH = 3.0).
Figure 4-37. Isobars of the hydrosilylated \( \text{PB(} \text{Si(OEt)}_3 \text{-b-PEO)}_3 \) star block copolymer for various subphase pH values \( (\pi = 5 \text{ mN/m}) \).

Figure 4-38. Removal of the cross-linked \( \text{PB(} \text{Si(OEt)}_3 \text{-b-PEO)}_3 \) star copolymer from the Langmuir trough surface. The dark yellow material easily comes off the subphase using a spatula.
Figure 4-39. AFM topographic images of the (PB(Si(OEt)_3)-b-PEO)_3 star block copolymer LB films transferred to mica substrates at subphase pH = 7.0 (A; t = 0 h) and 3.0 for different surface pressures (B, C, D, E, F, G and H; t = 10 h). The films are scanned with a scale of 2 x 2 μm.
Figure 4-40. (A and B) AFM section analysis of the images of the (PB(Si(OEt)₃)-b-PEO)₃ star block copolymer LB films transferred to mica substrates at subphase pH 3.0 for different surface pressures (t = 10 h). The films are scanned with a scale of 2 x 2 µm. (C) PEO pore size-Surface pressure curve for the hydrosilylated (PB(Si(OEt)₃)-b-PEO)₃ star block copolymer after cross-linking at different surface pressures (subphase pH = 3.0). (D) PSD curves obtained from AFM images of (PB(Si(OEt)₃)-b-PEO)₃ star block copolymer LB films.

Figure 4-41. AFM topographic images of the (PB(Si(OEt)₃)-b-PEO)₃ star block copolymer LB films transferred to mica substrates at subphase pH = 3.0 (t = 10 h) before (π = 9 mN/m) and after (π = 2 mN/m) expansion of the monolayer.
Figure 4-42. Surface Pressure-Area isotherms for the hydrosilylated (PB(Si(OEt)3)-b-PEO)₃ star block copolymer cross-linked at subphase pH 3.0 (t = 10 hrs) for two different surface pressures (π = 5 and 20 mN/m).

Table 4-1. Measurements obtained from isotherm experiments of (PB-b-PEO)₄ amphiphilic star block copolymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A₀/molecule (nm²)</th>
<th>A₀/PB unit (nm²)</th>
<th>A₀/number of PB branches (nm²)</th>
<th>∆A pseudoplateau (nm²)</th>
<th>Aₚancake (nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PB₇₆-b-PEO₅₇)₄</td>
<td>29.6</td>
<td>0.097</td>
<td>7.4</td>
<td>35.23</td>
<td>109.77</td>
</tr>
<tr>
<td>(PB₇₆-b-PEO₁₃₇)₄</td>
<td>32.66</td>
<td>0.107</td>
<td>8.16</td>
<td>81.22</td>
<td>254.38</td>
</tr>
<tr>
<td>(PB₇₆-b-PEO₁₇₄₄)₄</td>
<td>37.2</td>
<td>0.122</td>
<td>9.3</td>
<td>254.33</td>
<td>904.87</td>
</tr>
<tr>
<td>(PB₇₆-b-PEO₁₇₂₅)₄</td>
<td>36.01</td>
<td>0.118</td>
<td>9</td>
<td>1055.07</td>
<td>2489.23</td>
</tr>
</tbody>
</table>
Table 4-2. Characteristics of LB film experiments.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Run</th>
<th>Surface pressure (mN/m)</th>
<th>Mean molecular area (MMA) (Å²)</th>
<th>Transfer ratio (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{PB}<em>{76\text{-}}\text{b-PEO}</em>{1725})_4)</td>
<td>A 2</td>
<td>217038</td>
<td>1.029</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B 4</td>
<td>173599</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C 6</td>
<td>146140</td>
<td>0.943</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D 8</td>
<td>119154</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E 9</td>
<td>96736</td>
<td>2.089</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F 10</td>
<td>10843</td>
<td>1.937</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G 11</td>
<td>3749</td>
<td>2.12</td>
<td></td>
</tr>
<tr>
<td>((\text{PB}<em>{76\text{-}}\text{b-PEO}</em>{57})_4)</td>
<td>H 15</td>
<td>1991</td>
<td>1.916</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F 20</td>
<td>1169</td>
<td>1.84</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) (Area of the surface film)/(Area of the pulled mica substrate).

Table 4-3. AFM characteristics of \((\text{PB}-\text{b-PEO})_4\) four-arm star copolymers.

<table>
<thead>
<tr>
<th>Run</th>
<th>Surface pressure (mN/m)</th>
<th>Average diameter of PB domains (nm) (± 7)</th>
<th>Vertical height (nm) (± 1)</th>
<th>Number of domains (± 50)</th>
<th>PB coverage area (^a) (%) (± 10)</th>
<th>Number of molecules per domain (^b) (± 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>61</td>
<td>2.234</td>
<td>445</td>
<td>32</td>
<td>4</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>67</td>
<td>3.413</td>
<td>170</td>
<td>15</td>
<td>14</td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>71</td>
<td>4.729</td>
<td>27</td>
<td>3</td>
<td>101</td>
</tr>
<tr>
<td>D</td>
<td>8</td>
<td>132</td>
<td>4.837</td>
<td>18</td>
<td>6</td>
<td>186</td>
</tr>
<tr>
<td>E</td>
<td>9</td>
<td>84</td>
<td>4.526</td>
<td>193</td>
<td>9</td>
<td>22</td>
</tr>
<tr>
<td>F</td>
<td>10</td>
<td>c(^c)</td>
<td>4.9</td>
<td>c(^c)</td>
<td>c(^c)</td>
<td>c(^c)</td>
</tr>
<tr>
<td>G</td>
<td>11</td>
<td>c(^c)</td>
<td>5.09</td>
<td>c(^c)</td>
<td>c(^c)</td>
<td>c(^c)</td>
</tr>
<tr>
<td>H</td>
<td>15</td>
<td>c(^c)</td>
<td>5.181</td>
<td>c(^c)</td>
<td>c(^c)</td>
<td>c(^c)</td>
</tr>
<tr>
<td>F</td>
<td>20</td>
<td>54</td>
<td>2.082</td>
<td>380</td>
<td>22</td>
<td>900</td>
</tr>
<tr>
<td>G</td>
<td>30</td>
<td>550</td>
<td>5.282</td>
<td>38</td>
<td>36</td>
<td>87836</td>
</tr>
</tbody>
</table>

\(^a\) Coverage area = \((\pi r^2)\)\((\text{Number of domains})/\text{Scan area}\). \(^b\) Molecules/domain = \(\text{Scan area}/[(\text{Number of domains})(\text{Mean molecular area})]\). \(^c\) At these surface pressures, films are in a multilayer regime.
Table 4-4. Data for (PB-\(b\)-PEO)\(_3\) and (PB(Si(OEt)\(_3\))-\(b\)-PEO)\(_3\) star block copolymers.

<table>
<thead>
<tr>
<th>Run</th>
<th>(M_n) (^a) (SEC)</th>
<th>(M_n) (^b) ((^1)H NMR)</th>
<th>(M_n) (^c) (theo)</th>
<th>(M_w/M_n) (^a)</th>
<th>1,2-PB (^b) (%)</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45900</td>
<td>42500</td>
<td>40500</td>
<td>1.2</td>
<td>75</td>
<td>(PB(<em>{200})-(b)-PEO(</em>{76}))(_3)</td>
</tr>
<tr>
<td>2</td>
<td>56000</td>
<td>75500</td>
<td>77500</td>
<td>1.15</td>
<td>75</td>
<td>(PB(<em>{200})-(b)-PEO(</em>{326}))(_3)</td>
</tr>
<tr>
<td>3</td>
<td>58000</td>
<td>160500</td>
<td>164500</td>
<td>1.2</td>
<td>75</td>
<td>(PB(<em>{200})-(b)-PEO(</em>{970}))(_3)</td>
</tr>
<tr>
<td>4</td>
<td>74000</td>
<td>320500</td>
<td>323000</td>
<td>1.2</td>
<td>75</td>
<td>(PB(<em>{200})-(b)-PEO(</em>{2182}))(_3)</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>135500</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>(PB(<em>{72})-(co)-PB(Si(OEt)(<em>3))(</em>{128})-(b)-PEO(</em>{326}))(_3)</td>
</tr>
</tbody>
</table>

\(^a\) Apparent molecular weights determined by SEC in THF using a polystyrene calibration.

\(^b\) Estimated by \(^1\)H NMR analysis.

\(^c\) \(M_{n,th} = M_{\text{Butadiene}} \times ([\text{Butadiene}] / [-\text{PhLi}]) \times 3 + M_{\text{EO}} \times ([\text{EO}] / [(\text{PB-OH})_3])\).
5.1 Introduction and Literature Overview

In the past five decades, a lot of efforts was put on the synthesis of more and more complex macromolecular structures, because of their unique and particular properties as well as their usefulness and potential, starting from the most simple one, star polymers, including asymmetric and “miktoarm” star polymers with only one junction point, until the synthesis of the most complex ones, such as regular dendrimers, comb-type, graft, dendritic macromolecules (dendrigrafts, comb-burst polymers, polymers with dendritic branching, and dendrimer-like polymers) and hyperbranched polymers.

The chemists are still trying to get easier strategies for the synthesis of such complex architectures. As it is well-known, the strategy usually used for the synthesis of AA’2 and AB2 three-arm asymmetric and miktoarm star polymers consists first in the introduction of a branching point at the linear chain end to obtain thus two geminal initiating or electrophilic sites for the growth of two new polymer chains (divergent method) or for the coupling reaction of two “living” chains (convergent method), respectively. This is also a model used for the preparation of dendrimer-like polymers: the reiteration of the aforementioned sequence of reactions allowed to derive dendrimer-like polymers of different generation.

5.1.1 Asymmetric and “Miktoarm” Star Polymers

Asymmetric stars are a special class of stars (see p. 56 for regular stars) that is characterized by an asymmetry factor compared to the classical symmetric structures previously described (Chapter 3). The following parameters have been considered as asymmetry factors (Figure 5-1):
• **Molecular Weight Asymmetry.** All the arms of the star are identical in chemical nature, but they have different molecular weights.

• **Functional Group Asymmetry.** The arms are of the same chemical nature and have the same molecular weight, but they have different end groups.

• **Topological Asymmetry.** The arms of the star are block copolymers that may have the same molecular weight and composition but differ with respect to the polymeric block that is covalently attached to the core of the star.

Another important class of stars is the miktoarm, or heteroarm star polymers. The term “miktoarm” or heteroarm star polymer refers to stars consisting of chemically different arms. In the past decade considerable effort has been made toward the synthesis of miktoarm stars, when it was realized that these structures can exhibit very interesting properties.\textsuperscript{336,352,353} The most common examples of miktoarm stars are the $\text{AB}_2$, $\text{AB}_3$, $\text{A}_2\text{B}_2$, $\text{A}_n\text{B}_n$ ($n > 2$) and $\text{ABC}$ types. Other less common structures, like the $\text{ABCD}$, $\text{AB}_5$, and $\text{AB}_2\text{C}_2$ are now also available.

In our case, we will be especially interested in $\text{AA}'_2$ and $\text{AB}_2$ three-arm asymmetric and miktoarm star polymers. There are two different methods to prepare such $\text{AA}'_2$ and $\text{AB}_2$ polymer structures by anionic polymerization: the chlorosilane method and the diphenylethylene derivative method.\textsuperscript{141} The chlorosilane method was initially reported by Fetters\textsuperscript{354} and was later developed by Hadjichristidis, Mays, and collaborators.\textsuperscript{139,336,353,355} Chlorosilanes are used as linking agents for the stepwise replacement of the chlorine atoms by the polymer chains (Figure 5-2). This method was first applied to the synthesis of asymmetric polystyrene (PS), polybutadiene (PB), and polyisoprene (PI) stars having two arms of equal molecular weights and a third one having molecular weight either half or twice that of the identical arms.\textsuperscript{354,356}

The procedure, given in Figure 5-2, involves the reaction of the living arm $\text{PS}_A\text{Li}$ with a 10-fold excess of methyltrichlorosilane for the preparation of the methyl dichlorosilane end-capped $\text{PS}_A$. This is the crucial step of the synthesis, keeping in mind that there is a possibility to
form the coupled byproduct, i.e., the two-arm star with only one remaining Si-Cl group. This is avoided by using a large excess of the linking agent, adding the linking agent solution to a dilute living polymer solution under vigorous stirring and performing the linking reaction at low temperatures (5 °C). Under these conditions, no coupled byproduct was observed.

After the removal of the silane excess, the two remaining Si-Cl bonds of the methyldichlorosilane end-capped PS_A arm were reacted with a small excess of living PS_B Li chains. The PS_B Li chains were end-capped with a few units of butadiene to facilitate the completion of the linking reaction.

The same strategy was also used for the preparation of miktoarm star copolymers. A near monodisperse miktoarm star copolymer of the AB_2 type was first reported by Mays, A being PS and B PI. The synthetic method adopted was similar to the one applied by Fetters for the synthesis of the asymmetric PS and PB stars. The living PS chains were reacted with an excess of methyltrichlorosilane to produce the monosubstituted macromolecular linking agent. The steric hindrance of the living polystyryllithium and the excess of the silane led to the absence of any coupled byproduct. The silane excess was removed and then a slight excess of the living PI chains was added to produce the miktoarm star PS(PI)_2. Excess PI was then removed by fractionation. This method was later extended by Mays, Fetters and Hadjichristidis to the synthesis of the AB_2 stars, where A and B were all possible combinations of PS, PI, PB and PDMS.

A different approach was adopted by Eisenberg and colleagues for the synthesis of P2VP-b-(PS)_2 miktoarm stars, where P2VP is poly(2-vinylpyridine). Methyldichlorosilane (CH_3SiCl_2H) was used as linking agent to produce the two-arm PS star. Living P2VP was reacted with allyl bromide to give an end-functionalized polymer carrying a terminal vinyl group. In the last step a hydrosilylation reaction of the Si-H group of the two-arm star with the end-double
bond of the P2VP chain produced the desired structure (Figure 5-3). Rather high molecular weight distributions \((M_w/M_n = 1.33\text{-}1.50)\) were obtained, probably due to incomplete hydrosilylation reaction. High molecular weight P2VP, end-capped with vinyl groups (macromonomer), were used to avoid the steric hindrance effects and facilitate the hydrosilylation reaction. Consequently, the method suffers limitations and cannot be used in general for the synthesis of miktoarm stars.

On the other hand, the diphenylethylene derivative method is based on the use of 1,1-diphenylethylene derivatives that are non-homopolymerizable monomers. A rich chemistry was developed, leading to the formation of several types of asymmetric stars. The groups of Quirk and Tung\(^{15,17,18,21,208,362}\) reacted living PS chains with either 1,3-bis(1-phenylethenyl) benzene (MDDPE), or 1,4-bis(1-phenylethenyl) benzene (PDDPE). It was shown that 2 mol of the living polymer reacts rapidly with the DPE derivatives to form the dilithium adduct in hydrocarbon solvents, whereas in THF monoaddition is reported. Moreover, PDDPE exhibited less tendency to form the corresponding diadduct in both hydrocarbon solution and in the presence of THF. Taking into account the above observations, a three-arm asymmetric PS star was successfully prepared (Figure 5-4).\(^{362}\)

The monoadduct product was reacted with a second polystyryllithium chain, having different molecular weight, to form the coupled product. The efficiency of this coupling reaction depends on the control of the stoichiometry between the reactants. Under optimum conditions the efficiency of the coupling reaction can be higher than 96%. Finally, the addition of styrene leads to the formation of three-arm asymmetric PS stars.\(^{362}\) The polymerization took place in the presence of THF to accelerate the crossover reaction. The SEC analysis showed the existence of a small quantity of the monoadduct product and the second arm of the PS homopolymer, due to incomplete linking reactions. The weak points of the method are the great care that should be
exercised over the stoichiometry of the reactions and the inability to isolate and consequently characterize the third arm. However, the method is valuable, since it provides the possibility to functionalize the third arm by reaction with a suitable electrophilic agent.

More recently Hirao and colleagues\textsuperscript{363-365} developed a general method employing DPE derivatives carrying protected chloromethyl groups. PS asymmetric stars of the types AA’\textsubscript{2}, AA’\textsubscript{2}A’’\textsubscript{2}, AA’\textsubscript{3}, AA’\textsubscript{4}, AA’A’’\textsubscript{2}, and AA’\textsubscript{4}A’’\textsubscript{4} were prepared by this method. The whole procedure is based on the reaction sequence shown in Figure 5-5. Living PS was reacted with 1,1-bis(3-methoxymethylphenyl) ethylene followed by transformation of the methoxymethyl groups to chloromethyl groups using BCl\textsubscript{3} in CH\textsubscript{2}Cl\textsubscript{2} at 0 °C for 10-30 min. Despite the difficult multistep procedure of this method, it was shown that polystyrenes with predictable molecular weights, narrow molecular weight distributions, and almost nearly quantitative degrees of functionalization could be synthesized. Small amounts (<5\%) of coupled PS byproducts can be produced during the transformation reaction, due to a Friedel-Crafts side reaction among the polymer chains. Following the same scheme, AB\textsubscript{2} miktoarm stars, where A is PS and B is PI or PrBuMA, were synthesized by Hirao and Hayashi.\textsuperscript{364} In the latter cases, a small amount (5\%) of the dimeric product was observed by SEC analysis. It was proposed that this byproduct is obtained by the Li-Cl exchange and/or electron transfer reactions.

5.1.2 Dendrimer-like Polymers

5.1.2.1 Introduction to dendrimers

The term “dendrimer” coming from the greek words “dendron” (trees) and “meros” (part) was introduced for the first time by Tomalia to describe the highly branched structure of the poly(amidoamine)s (PAMAM).\textsuperscript{366,367} Dendrimers are globular, size monodisperse macromolecules centred on a central focal point or plurifunctional core (N\textsubscript{c} functions) from
which branches of different generations emerge radially in the three directions of the space. The branches (repeat units) are connected between branching points of precise functionality \( N_b \), symmetrically distributed around the core, with the terminal reactive functions \( F \) (number of terminal functions = \( N_b \times (N_c)^G \) with \( G \), the number of generations) located at the periphery of the dendrimer (Figure 5-6a). Because of the high connectivity of their repeating units, which in turn shape them into globular structures, these highly branched macromolecules exhibit unique properties and have been extensively investigated for a wide range of applications, including catalysis,\(^{368-372}\) biological molecular recognition,\(^{373-375}\) where dendrimers can engage in host-guest interactions, energy and electron transfer,\(^{334,376,377}\) and surface modification.\(^{378}\)

It is well-documented, however, that a distinction should be made between “regular” dendrimers\(^{332,335,350,370,379-381}\) and hyperbranched polymers,\(^{331,348,349,351,382,383}\) although both exhibit similarities not only from a structural viewpoint (Figure 5-6a and b), but also regarding their overall properties in solution or in bulk. The former species are prepared in stepwise fashion by repeating a sequence of coupling/modification reactions and exhibit a perfectly defined architecture with a degree of branching equal to unity. In contrast, hyperbranched polymers are generally synthesized in a non-iterative one-pot polymerization procedure from \( AB_n \)-type monomers, where A and B are antagonist functional groups. Therefore these hyperbranched structures exhibit an irregular architecture (Figure 5-6b) with incompletely reacted branch points throughout the structure (much higher polydispersity compared to dendrimers and degree of branching generally ranging from 0.5 to 0.6).

Two complementary general approaches, the divergent and the convergent, have been used for the synthesis of dendrimers (Figure 5-7).\(^{332,384-386}\)

The divergent approach developed by Tomalia\(^ {366,367}\) and Newkome\(^ {387}\) in 1985 consists in the growths of branches which starts at the multifunctional core and proceeds radially outward
toward the dendrimer periphery. Successive generations have been prepared in a stepwise fashion by repeating a sequence of coupling/modification reactions.

The concept of repetitive growth with branching was first reported in 1978 by Vögtle and colleagues who developed an iterative “cascade” method for the synthesis of low molecular weight branched polyamines by repeating a two-step cycle: the Michael addition of acrylonitrile on amine functions, and then the reduction of the nitrile functions into amine functions (Figure 5-8). The low yield of the reduction step due to cyclization side-reactions and the difficulties met during the purification forced them to stop at the second-generation. Even though, these objects could not be considered as “true dendrimers”, this was the first attempt in synthesizing dendrimers. A decade and a half later, two research groups, the Mülhaupt (DSM) ones, significantly improved this approach developed by Vögtle leading to well-defined true poly(propylene imine) dendrimers. The route developed by the DSM group is particularly worth mentioning because it constitutes a viable commercial route to this family of aliphatic amine dendrimers.

However, the first paper published on the macromolecular synthesis of “true dendrimers” also called “starburst” polymers was reported by the Tomalia’s group (Dow Chemical Co.). Using chemistry and conditions less prone to cyclization side-reactions and therefore more suitable for repetitive growth, Tomalia et al. disclosed the synthesis and characterization of the first family of dendrimers in 1984-1985. The synthesis was initiated by Michael addition of a “core” molecule of ammonia to three molecules of methyl acrylate, followed by exhaustive amidation of the triester adduct using a large excess of ethylenediamine, a process that generates a molecule with six terminal amine groups (Figure 5-9). Iterative growth is then continued using alternating Michael addition and amidation steps with the appropriate excess of reagents. Optimization of this procedure enabled the synthesis of globular poly(amidoamine) (PAMAM)
dendrimers (up to tenth generation) on a commercial scale with molecular weights well above 25,000.

Shortly thereafter, in 1985, Newkome reported preliminary results toward another family of trisbranched poly(ether amide) hydrosoluble dendrimers, also called “arborols” because of the terminal hydroxyl functions at the periphery. This divergent approach involves a repetitive multi-step cycle: a Williamson etheration reaction on the multifunctional core, an introduction of $-C(CO_2Et)_3$ groups activated by tosylation and an amidation using tris(hydroxymethyl)aminomethane (Figure 5-10). The use of AB$_3$-type groups makes the growths of the dendrimer faster with a second-generation dendrimer carrying 27 hydroxyl-terminal functions (3$^3$).

Several other novel applications of the divergent approach have recently appeared, leading to silicon- (siloxane, silane, carbosilane, etc...) phosphorus-, boron-, or germanium-containing dendrimers, giant polyallyl dendrimers, and organometallic dendrimers. All these different works have shown that given an appropriate choice of coupling and activation steps, reagents, and reaction conditions, the divergent approach is ideally suited for the large-scale preparation of dendrimers as the quantity of dendrimer sample essentially doubles with each generation increment. The rapid increase in the number of reactive groups at the chain ends of the growing macromolecule is a significant feature of all the divergent approaches.

However, this leads to a number of potential problems as growth is pursued. Firstly, any incomplete reaction of these terminal groups would lead to imperfections or failure sequences in the next generation; the probability of this occurring increases as the growing macromolecule increases. Secondly, to prevent side reactions such as cyclizations or coupling of “starburst” molecules and to force reactions to completion, extremely large excess amounts of reagents are
required in latter stages of growth.\textsuperscript{423} These large excesses must be completely removed before continuing with the next-generation growth step in order to prevent the initiation of new growth centers.\textsuperscript{423}

In 1989-1990, Hawker and Fréchet introduced the “convergent” growth approach to dendrimers,\textsuperscript{424,425} the second general route to dendritic structures. The convergent growth, first demonstrated with poly(ether) dendrimers, starts at what will become the periphery of the molecule proceeding “inward” to afford building blocks (dendrons) that are subsequently coupled to a branching monomer through reaction of a single reactive group located at its “focal point” (Figure 5-7). The strategy developed by Fréchet and co-workers for the poly(benzyl ether) synthesis is based on two repetitive steps (Figure 5-11): the Williamson coupling reaction of the benzylic bromide on the phenolic groups of the 3,5-dihydroxybenzyl alcohol used as the monomer and then a bromination step of the focal benzylic alcohol function in presence of CBr$_4$ affording brominated dendron. Subsequent repetitions of the Williamson coupling and bromination steps, and purification after each steps, enabled the production of the sixth generation dendrons with molecular weight distribution close to 1 and good control over molecular weights.

This convergent strategy allows both for a drastic reduction in the amount of reagents used and for intermediate purification at each step of growth. More importantly, the convergent growth allows unparalleled control over functionality at specified locations of the growing macromolecule, and it provides access to numerous novel architectures through the attachment of dendrons to other molecules.\textsuperscript{425-427} This has led to different dendrimers based on aryl ether\textsuperscript{425,427,428}, aryl alkene\textsuperscript{429-434}, aryl alkyne\textsuperscript{435-439}, phenylene\textsuperscript{426,440-442}, alkyl ester\textsuperscript{443-445}, alkyl ether\textsuperscript{446,447}, or other type\textsuperscript{332} of repeating units, and to innovative dendritic architectures such as dendrimers with chemically varied layers or encapsulated functional entities,\textsuperscript{448,449} dendrimers
with differentiated “surface” functionalities, linear-\(b\)-dendron hybrid dendritic macromolecules consisting of a linear polymer block with either one or two dendrimers chain ends, metalloporphyrin dendrimers, or also dendritic fullerenes.

5.1.2.2 Dendrimers with “true” macromolecular generations or dendrimer-like polymers

This is only 10 years that the “dendrimer-like star polymers”, term coined by Hedrick, have first appeared with the preparation of third generation dendrimer-like poly(ethylene oxide) (PEO) by Gnanou and Six in 1995 in a report where they showed that polymeric chains could be connected between branching points regularly distributed within a dendritic structure. These architectures exhibit a similar structure to the well-known “regular” dendrimers (a central core, a precise number of branching points, and outer terminal functions) but carry true polymeric chains (in opposition to the regular dendrimers) connected by branching points regularly distributed within the dendritic structure (in opposition to the hyperbranched polymers) (Figure 5-6c and d). Therefore, the arborescent architecture of these dendrimer-like polymers give to these radially, topologically layered and isomolecular branched architecture a better solubility and a lower viscosity compared to the linear homologues.

More recently the improvement of such a synthesis, relying on the reiteration of two same steps that are the anionic polymerization of ethylene oxide from multifunctional alkoxides and the chemical modification of the chain ends in order to introduce the branching points and two new initiating sites for each branches for the next generation, allowed Gnanou and colleagues to prepare a dendrimer-like poly(ethylene oxide) up to the eighth generation with a molar mass of 900 000 g.mol\(^{-1}\) and 384 external hydroxyl functions (Figure 5-12).

The same group adopted a similar approach to engineer PS\(_n\)-b-PEO\(_{2n}\) and PEO\(_n\)-b-PS\(_{2n}\) dendrimer-like amphiphilic copolymers by combining atom transfer radical polymerization (ATRP) of styrene and anionic ring-opening polymerization (AROP) of ethylene
oxide. The general approach for introducing branching points at the PEO or PS termini consists in transforming the end-groups of these polymers into twice as many functions that can subsequently serve to initiate the polymerization of either the same or another monomer by ATRP or AROP (Figure 5-13). The switch from ATRP of styrene to AROP of ethylene oxide, and *vice versa* were achieved by chemical modification of brominated PS chain ends to generate twice the number of hydroxyl groups for the anionic polymerization of EO, and by selective functionalization of oxanionic sites of PEO into twice the number of 2-bromoisobutyrate groups for the ATRP polymerization of styrene, respectively.462,463

More recently, Gnanou and co-workers were successful in synthesizing \((\text{PS}_n-b-\text{PS}_2n-b-\text{PS}_{4n})\) dendrimer-like polystyrene of third generation464 and \((\text{PS}_n-b-\text{PAA}_{2n})\) polystyrene-\(b\)-poly(acrylic acid) dendrimer-like copolymers465 based on calixarene cores by using exclusively ATRP in combination with chain end modifications. Calixarene-based cores were used as initiators for ATRP of styrene yielding star polymers containing precisely 4, 6, or 8 arms. The latter were modified in a two-step sequence of two chain end modifications to introduce the branching points and at the same time multiply by a factor of 2 the number of initiating sites for the next generation so as to generate PS stars carrying 8, 12, or 16 terminal bromoisobutyrate groups, respectively (Figure 5-14). These precursors served as multifunctional macroinitiators for the formation of the second generation of dendrimer-like PS. Reiteration of the aforementioned sequence of reactions allowed to derive dendrimer-like polystyrene of third generation that were constituted of 16, 24, or 32 outer arms, respectively. The latter dendrimer-like PS demonstrated similar viscosity behavior with the “regular” dendrimers.464

Using a variation of this divergent “grafting from” approach, the Hedrick group347,466-468 derived an entire array of dendrimer-like polyesters and related copolymers by successive grafting of polylactones and polylactides obtained by ring-opening polymerization and
polymethacrylic blocks by ATRP. A hexahydroxyl-functional core 2,2-bis(hydroxymethyl) propionic acid derivative was used as an initiator for the stannous-2-ethylhexanoate-catalyzed “living” ring opening polymerization (ROP) of ε-caprolactone, L-lactide, and racemic L,D-lactide producing a hydroxyl terminated six arm star polymer with controlled molecular weight and narrow polydispersities (PDI < 1.1) (Figure 5-15). Branching junctions at the chain ends were introduced with benzylidene-protected 2,2-bis(hydroxymethyl) propionic acid. Subsequent generations were then polymerized, after deprotection, from these star-shaped macroinitiators (Figure 5-15). Successive chain end capping and initiation produced three generations of polymers with molecular weights in excess of 130,000 g/mol and narrow polydispersities (<1.20).468

The capping of the six-arm star chain ends with dendrons containing activated bromide moieties could also produce “macro-initiators” for atom transfer radical polymerization (ATRP). Methyl methacrylate was thus polymerized from these “macro-initiators” in the presence of an organometallic promoter to produce the requisite dendrimer-like star polymers.466

Not fundamentally different either was the synthetic scheme followed by Percec et al.469,470 for the synthesis of dendrimer-like polymethacrylates of third generation. Starting from a trifunctional initiator for the copper-catalyzed living radical polymerization of methyl methacrylate, they developed multipurpose compounds-named TERMINI-acting as chain terminators as well as reinitiators and served to introduce branching points (Figure 5-16). After demasking, the TERMINI repeat unit enables the quantitative reinitiation, in the presence or absence of a catalyst, of the same or a different living polymerization, thus becoming a branching point (Figure 5-17). The demonstration of this concept was made by using a combination of
metal-catalyzed living radical polymerization (LRP) and as TERMINI, to elaborate dendritic macromolecules based on methyl methacrylate (MMA).469

In contrast, Hadjichristidis and Chalarì471 followed a convergent approach to assemble their dendrimer-like copolymers of styrene (S) and isoprene (I), the central core being built in this case in the last instance. Such dendritic copolymers were obtained via anionic polymerization using a dual-functionality compound as a branching agent and trichloromethylsilane or tetrachlorosilane as deactivators to build the central core. First, the succession of three different steps: the selective reaction of a living chain with the chlorosilane group of 4-(chlorodimethylsilyl)styrene (a dual-functionality compound) to produce a macromonomer, the addition of a second living chain (same or different) to the double bond of the macromonomer, and the polymerization of isoprene initiated by the anionic sites, allowed the synthesis of off-center “living” graft polymer (Figure 5-18). Finally, the reaction of the produced off-center living species with trichloromethylsilane or tetrachlorosilane leads to the synthesis of second-generation dendritic macromolecules (S₂I)₃, (SI′I)₃, (I′I′I)₃, and (I′₂I)₄.

More recently, the same group472 adopted a similar approach to engineer a series of well-defined second (G-2) and third (G-3) generation dendritic polybutadienes (PB) synthesized by the coupling of the living G-2 and G-3 dendrons with methyltrichlorosilane, using anionic polymerization high-vacuum techniques (Figure 5-19). The synthetic approach of the living G-2 and G-3 dendrons involves the repetition of (a) the synthesis of an in-chain double-bond PB by selective replacement of the two chlorines of 4-(dichloromethylsilyl)-diphenylethylene (DCMSDPE), a linking reagent with dual functionality, with PB by titration with PBLi (or living G-2 dendrons), (b) the addition of s-BuLi to the double bond, and finally (c) polymerization of butadiene from the newly created anionic site (Figure 5-19).
Quirk and co-workers\textsuperscript{473} synthesized a series of three end-branched, star-branched polystyrenes with 6, 9, and 13 end branches by the linking reactions between three-arm polystyrene star precursors end-functionalized with different chlorosilane linking agents and an excess of polystyrene-\textit{b}-\textit{b}-(oligobutadienyl)lithium (PS-\textit{b}-B\textsuperscript{+}Li\textsuperscript{+}). By using this coupling reaction between three-arm trichlorosilane end-functionalized polystyrene stars and an excess of (PS-\textit{b}-B\textsuperscript{+}Li\textsuperscript{+}) living chains, they were able to obtain a second-generation dendritic architecture (Figure 5-20).\textsuperscript{473}

Very recently, the Hirao group\textsuperscript{474,475} also proposed a convergent approach involving coupling reactions of living anionic poly(methyl methacrylate)s (PMMA) and functionalization of chain ends to derive dendrimer-like polymethacrylate-based systems up to seventh generation. This two-step sequence of reaction involves a coupling reaction of \textit{R}-functionalized living PMMA with two \textit{tert}-butyldimethyloxymethylphenyl (SMP) groups with benzyl bromide (BnBr) chain-end-functionalized PMMA and a transformation reaction of the introduced SMP groups into BnBr functionalities. The dendrimer-like star-branched PMMAs up to the seventh generation have been successfully synthesized by repeating these two reactions seven times (Figure 5-21).\textsuperscript{475}

5.2 Results and Discussion

5.2.1 Synthesis of Asymmetric and Miktoarm Star Polymers

We previously described the synthesis of a new category of tri- and tetracarbanionic initiators by the halogen-lithium exchange reaction between a tri- or tetrabromocompound and \textit{sec}-butyllithium (Chapter 3).\textsuperscript{121} These multicarbanionic initiators were first used for the anionic polymerization of styrene and butadiene to result in well-defined tri- and tetraarmed polystyrene and polybutadiene stars exhibiting monomodal and narrow molar mass distribution.\textsuperscript{121} These
pluricarbonionic initiators were also employed to obtain (PB-b-PEO)$_n$ amphiphilic diblock	extsuperscript{219} and P(S-b-B-b-MMA)$_n$ (n = 3 or 4) triblock star copolymers.	extsuperscript{121} The same halogen-lithium exchange reaction was applied here, but in this case a $\omega,\omega'$-dibromo end-functionalized chain polymer was used instead of small multibromo molecules.

5.2.1.1 Introduction of the branching point at the chain end of a linear polymer

The first objective of this work was the introduction of a dibromo end group, whose halogen atoms are carried by separate aryl rings. We tried in a first attempt the reaction of polystyryllithium living chains with 4,4'-dibromodiphenylethylene. Unfortunately, as demonstrated by size exclusion chromatography (SEC) analysis after methanol quenching (Figure 5-22), three different populations could be observed corresponding for the first peak (1) in the low molar mass region to the PS chain functionalized by the dibromo compound and for the two other peaks (2 and 3) in the high molar mass region to the PS after the coupling reaction on either one or two bromide positions (Figure 5-22). That demonstrated that the polystyryllithium living chain end is too nucleophilic to react only on the insaturation and thus to obtain pure $\omega,\omega'$-dibromo end-functionalized chain polymer.

The reactivity of the living chain ends of the polystyrene chains was thus reduced by replacing the alkyllithium chain ends by less reactive potassium alkoxide living chain ends. For this purpose, we used hydroxyl-terminated commercial linear PEO and hydroxyl-terminated linear PS or PB synthesized using sec-butyllithium as initiator in cyclohexane and an excess of ethylene oxide to deactivate the living chain ends. The latter were well-characterized by $^1$H NMR spectroscopy demonstrating a quantitative functionalization. The hydroxyl functions of these linear polymer chains were first deprotonated in the presence of a stoichiometric amount of diphenylmethylpotassium (DPMK) in THF to give potassium alkoxide living chain ends and then
a solution of an excess of 4,4'-dibromodiphenylethylene (4 equivalents per hydroxyl group) in THF was added to the mixture (Figure 5-23). The SEC analysis of the polymer after methanol quenching demonstrated this time the presence of only one peak with a small shift to the high molar mass region after the functionalization by the dibromo compound (Figure 5-24).

Indeed, the $^1$H NMR spectra of the PEO-(PhBr)$_2$, PS-(PhBr)$_2$ and PB-(PhBr)$_2$ samples of low molecular weight showed the total disappearance of the signal at $\delta = 5.4$ ppm corresponding to the unsaturation of the dibromo compound and exhibit signals at $\delta = 6.9$-8.0 ppm assignable to the aromatic protons $-\text{CH}_2-\text{CH}(\text{PhBr})_2$ at the chain end and at $\delta = 4.2$ ppm (in the case of PEO) or $\delta = 3.7$ ppm (in the case of PS or PB) corresponding to the protons carried by the primary terminal carbon groups $-\text{CH}_2-\text{CH}(\text{PhBr})_2$ (Figures 5-25 and 5-26). Specifically, the experimental functionality values calculated by the ratios of resonance signals at $\delta = 3.3$ or 0.9 ppm (methyl protons of the initiator $-\text{CH}_3$ in the cases of PEO or PS and PB, respectively) with those at $\delta = 6.9$-8.0 ppm assignable to the aromatic protons at the chain end are always close to 1.

The same experimental functionality close to 1 was obtained by the ratios of resonance signals at $\delta = 3.6$ ppm (($\text{OCH}_2\text{CH}$)$_n$ methylene protons of the PEO chains) or at $\delta = 4.9$-5.8 ppm (protons of the double bonds of the PB chains) with those at $\delta = 6.9$-8.0 ppm assignable to the aromatic protons at the chain end.

As well-known, following the reactivity scale of the nucleophilic conjugated base, it should be impossible for an alkoxide group, which is not nucleophilic enough, to react with an unsaturation. However, these results demonstrate that in the case of the 4,4'-dibromodiphenylethylene the potassium alkoxide living chain end is able to react with the unsaturation. Furthermore, the reaction of living end-functionalized PEO with diphenylethylene was tried. In this case, no addition on the diphenylethylene unsaturation was observed by $^1$H
NMR spectroscopy. This demonstrates the influence of the halogen atoms carried by the aryl rings, which have an electron withdrawing and thus an activation unsaturation. Therefore, the unsaturation is reactive enough to react with a potassium alkoxide living chain end. All these proofs attest to the synthesis of pure well-defined $\omega,\omega'$-dibromo end-functionalized PEO, PS and PB chains, which can be now used for the synthesis of polylithium macroinitiators by the halogen-lithium exchange reaction.

5.2.1.2 Preparation of pluricarbanionic macroinitiators for star polymer synthesis

These different $\omega,\omega'$-dibromo end-functionalized PS and PB chains were treated with stoichiometric amounts of sec-butyllithium in benzene or cyclohexane to generate the corresponding dilithiated species in presence of 2-bromobutane (Figure 5-23). These polylithiated species were found to be totally soluble in apolar solvents such as cyclohexane or benzene. To neutralize the 2-bromobutane, which could deactivate the living polymer chains, and prior to monomer addition some equivalents of sec-butyllithium were added giving the formation of 3,4-dimethylhexane (Figure 5-23). The polymerization of different monomer such as styrene, butadiene or isoprene were performed using different polylithiated macroinitiators such as PS-(Ph-Li$^+$)$_2$, or PB-(Ph-Li$^+$)$_2$ in cyclohexane or benzene at room temperature without any additives. These different asymmetric or miktoarm star samples were analyzed by SEC, size exclusion chromatography with a light scattering detector (SEC/LS), and $^1$H NMR spectroscopy. Table 5-1 gives the data pertaining to these asymmetric and miktoarm star (co)polymers obtained from polylithium macroinitiators. Samples of narrow molar mass distribution ($1.01 < M_w/M_n < 1.15$) were obtained. The complete disappearance of the peak of the PS-(PhBr)$_2$ and PB-(PhBr)$_2$ precursors on the chromatograms meant that all precursor chains participated in the polymerization (Figures 5-27, 5-28 and 5-29).
The absolute molecular weight values drawn from SEC/LS were found to be higher than those obtained by SEC, especially in the case of asymmetric three-arm PS stars, and agreed well with the theoretical molecular weight, attesting that two polymer arms of well-controlled size could be grown from each linear chains and thus a compact architecture is obtained (Table 5-1).

The structures of the polymers formed and especially the star character could also be established by $^1$H NMR analysis on asymmetric and miktoarm star samples with low degrees of polymerization (Figure 5-30 and Table 5-1). From the ratio of the integration values of the signal of the methyl protons $-\text{CH}_3$ of the initiator at $\delta = 0.9$ ppm to that of the methylene protons of the $-\text{CH}_2\text{OH}$ chain ends ($\delta = 3.6$ ppm), the actual functionality of various samples prepared could be determined: functionalities close to 2 for the two arms grown from the branching point of the asymmetric and miktoarm star (co)polymers (Figure 5-30 and Table 5-1). Indeed, the hydroxyl end groups of the different samples of asymmetric and miktoarm star polymers were titrated in THF by a solution of DPMK of known concentration ([DPMK] = 0.521 mol.L$^{-1}$). The results of these titrations demonstrated functionalities close to 2 for all the stars (Table 5-1).

5.2.2 Synthesis of Dendrimer-Like Polystyrene and Polybutadiene

The same procedure as in the case of the preparation of the asymmetric and miktoarm star polymers was followed here for the synthesis of dendrimer-like polymers, but in this case a multifunctional initiator was used instead of a monofunctional one.

5.2.2.1 Synthesis of star-shaped (G-1) polystyrene and polybutadiene precursors

The first step of the procedure is the synthesis of the tetracarbanionic initiator based on the halogen-lithium exchange reaction. As previously described (Chapter 3), a tetrabromocompound is treated with stoichiometric amounts of sec-butyllithium in benzene to generate the corresponding tetraalkyllithium agent (Figure 5-31). The resulting polylithiated
species being insoluble in benzene, tetramethylethylene diamine (TMEDA) (ratio of [TMEDA]/[Li] = 2) was utilized to solubilize the polyalkyllithium species due to the complex formed between the lithiated species and the ligand. These complexes give stable species and enough steric bulk to prevent aggregation of the polylithiated initiators. As shown previously, minor amounts of the side product 2-bromobutane, which could deactivate “living” carbanionic sites, were neutralized by a small excess of sec-butyllithium yielding 3,4-dimethylhexane as an inert byproduct. The anionic polymerization of styrene and butadiene were carried out in benzene at room temperature using the solubilized tetralithiated initiator at a concentration of $5.3 \times 10^{-2}$ M. After complete conversion of the monomer, end capping was accomplished by adding a large excess of ethylene oxide.

The characteristics of these star samples are listed in Tables 5-2 and 5-3. The characterization of all the samples by size exclusion chromatography (SEC) showed the disappearance of the peak at low molecular weight region, implying total consumption of the tetrafunctional initiator by styrene and butadiene polymerization (Figure 5-32). The actual molecular weight of the hydroxyl chain end polystyrene and polybutadiene stars determined by SEC/LS were found to be in good agreement with the calculated values and their distributions were narrow ($M_w/M_n < 1.1$). The tetrafunctionality of the resulting polystyrene and polybutadiene stars were then demonstrated by $^1$H NMR spectroscopy analysis of star samples with low degrees of polymerization for each arm (Figure 5-33).

Specifically, the experimental functionality values calculated by the ratios of resonance signals at $\delta = 6.8-8.0$ ppm (aromatic protons of the tetrafunctional initiators) with those at $\delta = 3.6$ ppm ($\text{-CH}_2\text{-OH}$ chain end protons) are always close to 4 for the four-armed stars. Further
evidence for the four-arm star structure was obtained by comparing the intrinsic viscosity \[\eta]\ of our samples with that of linear polymers, as previously demonstrated.\textsuperscript{121}

5.2.2.2 Introduction of the branching points at each arm end

The next step in the synthesis of these dendrimer-like polymers was the introduction of a branching point and thus two geminal aryl bromide groups at each chain end of the stars. The same procedure as in the case of the preparation of asymmetric and miktoarm star polymers was followed. The hydroxyl functions at the chain ends of the polystyrene and polybutadiene stars were deprotonated in presence of a stoichiometric amount of DPMK in THF and then a solution of 4,4’-dibromodiphenylethylene in THF was added. After the deactivation of the living chain ends by methanol addition, the resulting functionalized star polymers were analyzed by SEC and \textsuperscript{1}H NMR spectroscopy (Figures 5-32 and 5-34). First, it can be observed by SEC, as in the case of linear chain polymers, a small shift of the peak to the high molar mass region and the absence of secondary peaks in the high molar mass region attesting that no coupling reactions occurred on the bromide positions. The good functionalization of the chain ends of each arm of the PB\textsubscript{4}(PhBr)\textsubscript{8} star polymers was established by \textsuperscript{1}H NMR analysis on polybutadiene samples with low degrees of polymerization (Figure 5-34). Indeed, the \textsuperscript{1}H NMR spectrum exhibit signals at \(\delta = 6.9-8.0\ \text{ppm}\) assignable to the aromatic protons –CH\textsubscript{2}—CH(PhBr)\textsubscript{2} at the chain end and \(\delta = 3.7\ \text{ppm}\) and \(\delta = 3.5\ \text{ppm}\) corresponding to the protons carried by the primary terminal carbon groups –CH\textsubscript{2}—CH(PhBr)\textsubscript{2} and –CH\textsubscript{2}–O–CH\textsubscript{2}—CH(PhBr)\textsubscript{2}, respectively (Figure 5-34). The experimental functionality was determined by the comparison of the integration values of the signals of the aromatic protons of the polyphenylene core and the dibromo end groups (\(\delta = 6.5-8.0\ \text{ppm};\ 54\text{H}\)) with that of the signals of the protons carried by the primary terminal carbon groups –CH\textsubscript{2}—CH(PhBr)\textsubscript{2} (\(\delta = 3.7\ \text{ppm};\ 8\text{H}\)) and –CH\textsubscript{2}–O–CH\textsubscript{2}—CH(PhBr)\textsubscript{2} (\(\delta = 3.5\ \text{ppm};\ 8\text{H}\)).
The ratio of 6.7 found between the intensities of the signals appearing at $\delta = 6.5-8.0$ ppm and the one at $\delta = 3.7$ ppm indicated that functionalization occurred quantitatively (Figure 5-34).

5.2.2.3 Preparation of pluricarbanionic initiators for second generation (G-2) dendrimer-like polystyrene and polybutadiene synthesis

PS$_4$(PhBr)$_8$ and PB$_4$(PhBr)$_8$ o$_2$o'-dibromo end-functionalized polystyrene and polybutadiene stars were treated with stoichiometric amounts of sec-butyllithium in benzene to generate the corresponding polylithiated species PS$_4$(Ph’Li$^+$)$_8$ and PB$_4$(Ph’Li$^+$)$_8$ in presence of 3,4-dimethylhexane after neutralization of 2-bromobutane. The addition of TMEDA (ratio of [TMEDA]/[Li] = 2) was necessary to solubilize the latter polylithiated species in benzene. The polymerizations of styrene and butadiene were performed in benzene at room temperature using the polylithiated species PS$_4$(Ph’Li$^+$)$_8$ and PB$_4$(Ph’Li$^+$)$_8$, respectively (Figure 5-31). After deactivation of the living chain ends by addition of an excess of ethylene oxide, the dendrimer-like polystyrene and polybutadiene obtained were analyzed by SEC and $^1$H NMR spectroscopy (Figures 5-35, 5-36, and 5-37). First, the complete disappearance of the peaks of the PS$_4$(PhBr)$_8$ and PB$_4$(PhBr)$_8$ precursors on the chromatograms of the PS$_4$PS$_8$(OH)$_8$ and PB$_4$PB$_8$(OH)$_8$ (Figures 5-35 and 5-36), respectively, showed that all precursor chains participated in the polymerization. Unfortunately, two other small populations were observed in the high molar mass region either in the case of hydroxyl-terminated dendrimer-like PS or PB which could be due to the strong aggregation of the end groups in THF (Figure 5-35).

To break this strong aggregation of the terminal end groups at the periphery of the dendrimer-like polymers, the different samples were characterized by high temperature size exclusion chromatography (SEC/HT) in dichlorobenzene at 130 °C equipped with a viscometer detector giving the absolute molar mass. In this case, no population corresponding to these aggregates and only one peak with a monomodal and narrow molar mass distribution (1.01<
were observed (Figures 5-36 and Tables 5-2 and 5-3). Indeed, the molar mass values determined from SEC/HT agreed well with the calculated values attesting that two PS or PB arms of well-controlled size could be grown from each of these branching points.

As to the characterization by \(^1\)H NMR spectroscopy of the second generation PB\(_4\)PB\(_8\)(OH)\(_8\) dendrimer-like polybutadiene (Figure 5-37), it clearly revealed the presence of four signals: the signals of the aromatic protons of the polyphenylene core (22H) and the branching points at \(\delta = 6.5-8.0\) ppm (32H at the branching points), the signals of the methylene protons carried by the branching points and at the chain ends \(-CH_2-CH-(\text{PhCH}_2)_2-\) at \(\delta = 3.7\) ppm (8H), \(-CH_2-O-CH_2-CH-(\text{PhCH}_2)_2-\) and \(-CH_2-OH\) at \(\delta = 3.4\) ppm (24H), and \(-CH_2-CH-(\text{PhCH}_2)_2-\) at \(\delta = 2.8\) ppm (4H). The ratios of 6.8, 2.2 and 13.8 found between the intensities of the signal appearing at \(\delta = 6.5-8.0\) ppm (54H) and the ones at \(\delta = 3.7\) ppm (8H), at \(\delta = 3.4\) ppm (24H) and at \(\delta = 2.8\) ppm (4H), respectively, indicated that initiation occurred with perfect efficiency (Figure 5-37). Indeed, the titration of the hydroxyl end groups at the periphery of the PS and PB dendrimer-like polymers in THF by a solution of DPMK of known concentration ([DPMK] = 0.521 mol.L\(^{-1}\)) demonstrated either in the case of PS or PB dendrimer-like polymers functionalities close to 8 (Tables 5-2 and 5-3). The good definition of these PS\(_4\)PS\(_8\)(OH)\(_8\) and PB\(_4\)PB\(_8\)(OH)\(_8\) second generation dendrimer-like polymers prompted us to prepare dendritic polymers of higher generation.

**5.2.2.4 Third-generation (G-3) dendrimer-like polystyrene and polybutadiene**

This methodology based on the iterative divergent approach as described above was repeated here (i.e., chain end modification and polymerization of styrene or butadiene) for the synthesis of dendritic polymers of higher generation. Similar to the cases of G-1 and G-2, the hydroxyl end groups at the periphery of the PS\(_4\)PS\(_8\)(OH)\(_8\) and PB\(_4\)PB\(_8\)(OH)\(_8\) dendrimer-like
polymers were deprotonated by reaction with stoichiometric amounts of DPMK and a solution of an excess of 4,4’-dibromodiphenylethylene was added (4 equivalents per –OH group). After deactivation of the living chain ends by addition of methanol, the resulting PS₄PS₈(PhBr)₁₆ and PB₄PB₈(PhBr)₁₆ dendrimer-like polymers were characterized by SEC, SEC/HT and ¹H NMR spectroscopy. As previously shown, no secondary coupling reactions on the bromide positions were observed. Indeed, the ¹H NMR analysis of the chain ends of the PB₄PB₈(PhBr)₁₆ dendrimer-like polybutadiene clearly indicates four distinct signals corresponding respectively to the aromatic protons of the polyphenylene core, of the aryl rings of the branching points and of the chain ends ($\delta = 6.8-8.0$ ppm; 118H), and to the methylene protons carried by the branching points and the chain ends $-\text{CH}_2\text{CH}-(\text{PhCH}_2)_2-$ at $\delta = 3.7$ ppm (24H), $-\text{CH}_2\text{OCH}_2\text{CH}-(\text{PhCH}_2)_2-$ at $\delta = 3.4$ ppm (24H), and $-\text{CH}_2\text{CH}-(\text{PhCH}_2)_2-$ at $\delta = 2.8$ ppm (12H) (Figure 5-38). In addition, the experimental -PhBr functionality, determined from the ratios of the integration values of the different signals at $\delta = 6.8-8.0$ ppm, $\delta = 3.7$ ppm, $\delta = 3.4$ ppm, and $\delta = 2.8$ ppm were found to correspond to the expected value of 16 groups per dendrimer-like polymer.

Next, the resulting PS₄PS₈(PhBr)₁₆ and PB₄PB₈(PhBr)₁₆ dendrimer-like polymers were treated with stoichiometric amounts of sec-butyllithium in benzene to generate the corresponding polylithiated species PS₄PS₈(PhLi⁺)₁₆ and PB₄PB₈(PhLi⁺)₁₆. At this stage of 16 carbanionic sites per polymer, a physical gel was formed due to the stronger aggregation of the polylithiated species in benzene. After the addition of some equivalents of TMEDA (2 equivalents per -PhLi), the polylithiated species were totally soluble in benzene and the monomer was polymerized. The living chain ends were deactivated by addition of an excess of ethylene oxide and the resulting dendritic polystyrene and polybutadiene were characterized by SEC, SEC/HT and ¹H NMR
spectroscopy. As shown in Figures 5-36, the SEC/HT profiles of the PS$_4$PS$_8$PS$_{16}$(OH)$_{16}$ and PB$_4$PB$_8$PB$_{16}$(OH)$_{16}$ third-generation dendrimer-like polymers exhibit only one sharp monomodal and narrow peak ($1.05<M_w/M_n<1.08$), corresponding to the dendritic polystyrene and polybutadiene, respectively, with in each case the total disappearance of the second generation macroinitiator. As in the case of the second generation sample, the hydroxyl end groups at the periphery of the PS$_4$PS$_8$PS$_{16}$(OH)$_{16}$ and PB$_4$PB$_8$PB$_{16}$(OH)$_{16}$ dendrimer-like polymers were titrated in THF by a solution of DPMK of known concentration ([DPMK] = 0.521 mol.L$^{-1}$) and demonstrated either in the case of PS or PB dendrimer-like polymers functionalities close to 16 indicating that initiation occurred as expected (Tables 5-2 and 5-3).

5.2.2.5 From the fourth- (G-4) to the seventh-generation (G-7) dendrimer-like polystyrene synthesis

The same iterative divergent approach as in the case of the synthesis of the third generation dendrimer-like polymers was applied here for the preparation of fourth- (G-4), fifth- (G-5), sixth- (G-6), and seventh-generation (G-7) dendrimer-like polystyrenes. Successively, the hydroxyl end groups at the periphery of different generation (G-4, G-5 and G-6) dendrimer-like polystyrenes were deprotonated by a solution of DPMK, functionalized after reaction with 4,4’-dibromodiphenylethylene, and finally these ω,ω’-dibromo end-functionalized dendrimer-like polystyrenes were used after reaction with s-BuLi as pluricarbanionic macroinitiators for the polymerization of styrene in presence of TMEDA as additive. After deactivation of the living polystyryllithium chain ends by an excess of ethylene oxide and degassed methanol, successively, all the dendritic polystyrene samples of different generation (G-4, G-5, G-6 and G-7) were characterized by SEC and SEC/HT (Figures 5-35 and 5-36). As in the previous cases, the same peaks corresponding to the aggregates were observed in the high molar mass region by SEC. However, the latter were not observed at high temperature as shown in the SEC/HT
chromatograms for the fourth- (G-4), fifth- (G-5), sixth- (G-6), and seventh-generation (G-7) dendrimer-like polystyrenes (Figure 5-36). As can be seen in Figure 5-36, the SEC/HT peak of each generation of PS is monomodal and narrow and moves to the high molar mass region with the total disappearance of the precursor as the iteration proceeds. Indeed, the experimental degree of -OH functionality was determined by titration of hydroxyl end groups by reaction with a solution of DPMK of known concentration ([DPMK] = 0.521 mol.L⁻¹). As may be seen in Tables 5-2 and 5-3, the results demonstrate experimental functionalities which are very close to the expected values. From the fourth-generation, this last method of titration of hydroxyl end groups has been found to be more efficient than ¹H NMR spectroscopy, because of the intensity of the resonance signals of the end groups which is too weak compared to the signal of the aromatic protons of the styrene repeat units. Thus, by the reiteration of the two reaction sequence (i.e., styrene polymerization and branching reaction) of this divergent approach a seventh-generation dendrimer-like PS (G-7) was synthesized with an absolute molar mass $M_n$ of 1,920x10³ g.mol⁻¹ and consisted of 256 OH end groups and 508 PS segments.

5.2.2.6 Viscosity behavior of dendrimer-like polystyrenes

In the literature, several papers deal with the viscometric behavior of star polymers, hyperbranched polymers,³⁵¹ dendrigrafts,³¹³,³³⁸,³⁴¹,⁴⁷⁶,⁴⁷⁷ and regular dendrimers.³⁹⁰,⁴²²,⁴⁷⁸ However Gnanou and colleagues⁴⁶⁴ were the first to demonstrate in the case of third-generation dendrimer-like polystyrenes synthesized by atom transfer radical polymerization, that dendrimer-like polymers show a behavior in solution similar to the regular dendrimers. In opposition to the hyperbranched polymers, whose intrinsic viscosity remains independent of the molar mass, the trace of log[$\eta$] with the generation or the molecular weight of the dendrimer-like PS showed an evolution where [$\eta$] first increases as a function of molecular weight/generation, passes through a
maximum to eventually decrease (bell-shaped curve) as in the case of regular dendrimers.\textsuperscript{351,390,422,478} In fact, it is well-known that molecular weight in regular dendrimers increase exponentially with \( g \) according to \( 2^{g-1} \) and their hydrodynamic volume grows with \( g^3 \); \([\eta]\) varying proportionally to \( g^3/2^{g-1} \), it passes therefore through a maximum with increasing \( g \).

For a better comparison with the results that was previously obtained by Gnanou and co-workers,\textsuperscript{464} the intrinsic viscosities of our dendrimer-like PS were determined at 35 °C using toluene as a solvent. First, from the experimental \([\eta]_{\text{dendritic}}\) (measured at 35 °C in toluene) and the \([\eta]_{\text{linear}}\) values (calculated from equation (1) for linear PS of same molecular weight under the same conditions), the \( g' \) ratio \( [\eta]_{\text{dendritic}}/[\eta]_{\text{linear}} \) (listed in Table 5-2) was determined. The intrinsic viscosity was found to be lower than the one corresponding to linear PS (until 30 times lower than the one of linear PS) and the \( g' \) parameter decreased with the generation attesting that the dendritic structure became more and more compact with increasing the number of generation and branched segments.

\[
[\eta] = 1.23 \times 10^{-2} M_n^{0.71} \tag{1}
\]

As shown by the relation between \([\eta]\)—which is also inversely proportional to the hydrodynamic density—and the hydrodynamic volume (\( V_H \))

\[
[\eta] = 2.5 N_a V_H/M = (10\pi/3)N_a R_H^3/M \tag{2}
\]

where \( R_H \) is the hydrodynamic radius and \( N_a \) the Avogadro number, such a constant \([\eta]\) in the particular case of arborescent polymers merely reflects the fact that both \( V_H \) of the sample and its mass (\( M \)) vary approximately in the same proportion upon increasing the number of generations. To determine how vary hydrodynamic volumes as a function of \( g \), we resorted to expression (3) given below, using \([\eta]\) and \( M \) determined experimentally.
As shown in Figure 5-39, $R_H$ increases nearly linearly with $g$ for the polystyrene dendrimer-like polymers with $g \leq 5$, indicating that $V_H$ thus grows in $g^3$ like regular dendrimers. However, $R_H$ becomes constant from the sixth generation. Above this critical generation ($g \geq 6$), the dendrimer-like structures seem to be too compact to distinguish the $R_H$ values obtained for the sixth and seventh-generation dendrimer-like polystyrenes.

From the trace of log $[\eta]_{dendritic}$ with the number of generation, we could see that $[\eta]$ reaches a maximum corresponding to the third-generation dendrimer-like PS and start to decrease gradually until the seventh generation (Figure 5-40). The evolution of log $[\eta]_{dendritic}$ as a function of log $M_n$ was also plotted (Figure 5-41). The same trend as the one observed for log $[\eta]_{dendritic}$ vs number of generation plot is seen here, indicating that $[\eta]$ is not independent of the molar mass for dendrimer-like PS in opposition to the hyperbranched polymers.

5.3 Conclusion

This methodology based on chain end modification, and involving the original reaction of a potassium alkoxide living chain end on the insaturation of 4,4'-dibromodiphenylethylene affords $\omega,\omega'$-dibromo chain polymers whose halogen atoms are carried by separate aryl rings. Using halogen-lithium exchange reaction the corresponding polylithiated species could be prepared, providing an efficient synthetic route to the asymmetric and “miktoarm” star (co)polymers based on the combination of different polymers such as polystyrene, polybutadiene, and polyisoprene. By the reiteration of this sequence of reactions, dendrimer-like PS and PB up to the seventh and third generations, respectively, could be successfully synthesized. The preparation of dendrimer-like PS of higher generation led us to confirm that this family of
macromolecular architecture has a viscosity behavior similar to that of the regular dendrimers with $[\eta]$ passing therefore through a maximum with increasing the number of generation.

This halogen-lithium exchange reaction previously applied by us on multifunctional halogenated polyphenylene molecules for the synthesis of pluricarbanionic initiators, demonstrated here his efficiency and utility for the preparation of polylithiated macroinitiators. This latter observation lets us hope that the same halogen-lithium exchange reaction can be carried out on linear chain polymers carrying pendant aryl bromide groups for the synthesis of more complex macromolecular architecture such as brush-type (co)polymers.

Figure 5-1. Representative structures of asymmetric and “miktoarm” star polymers.
**Figure 5-2.** Synthesis of three-arm asymmetric PS star using chlorosilane as linking agent.

\[
\text{PS}_A^- \text{Li}^+ + (\text{CH}_3\text{SiCl}_3) \text{(excess)} \rightarrow \text{PS}_A^-\text{Si(Ch3)Cl}_2 + \text{LiCl} + (\text{CH}_3\text{SiCl}_3)
\]

\[
\text{PS}_A^-\text{Si(Ch3)Cl}_2 + \text{PS}_B^- \text{Li}^+ \text{(excess)} \rightarrow \text{PS}_A^-\text{Si(Ch3)(PS}_B)_2
\]

**Figure 5-3.** Synthesis of (PS)\(_2\)-b-P2VP miktoarm star copolymer by combination of linking and hydrosilylation reactions.

\[
\text{PS}^- \text{Li}^+ + (\text{CH}_3\text{SiCl}_2\text{H}) \text{(excess)} \rightarrow \text{PS-Si-PS}
\]

(I)

\[
\text{P2VP}^- \text{Li}^+ + \text{Br} \rightarrow \text{P2VP-Br}
\]

(II)

(I) + (II) \(\xrightarrow{\text{Pt}}\) (PS)\(_2\)(P2VP)

**Figure 5-4.** Synthesis of asymmetric PS star using DDPE derivative as coupling agent.

\[
\text{PS}_A\text{Li} + \begin{array}{c}
\text{PS}_A\text{H}_2\text{C} \\
\text{1. Benzene} \\
\text{2. CH}_3\text{OH}
\end{array} \rightarrow \text{PS}_A\text{H}_2\text{C} \\
\begin{array}{c}
\text{PS}_A\text{H}_2\text{C} \text{Li}^- \\
\text{PS}_B\text{Li}
\end{array} \xrightarrow{\text{1. Styrene} \quad \text{2. CH}_3\text{OH}} \text{PS}_A\text{H}_2\text{C} \text{PS}_C \text{CH}_2\text{PS}_B
Figure 5-5. Use of DPE derivative as branching agent.
Figure 5-6. Representation of different tree-like macromolecular structures: (a) “regular” dendrimers; (b) hyperbranched polymer; (c) dendrigraft or arborescent polymer; and (d) dendrimer-like (star) polymer.
Figure 5-7. Representation of dendrimer growth by the divergent and convergent methods.

Figure 5-8. Synthetic route developed by Vögtle for the synthesis of branched polyamides.
Figure 5-9. Synthetic route for the preparation of PAMAM dendrimers by the divergent method.
Figure 5-10. Synthesis of poly(ether amide) dendrimers.
Figure 5-11. Synthesis of poly(benzyl ether) dendrimers by the convergent method.
Figure 5-12. Synthetic strategy toward dendrimer-like PEO.

- i) DPMK, DMSO
- ii) NaOH/H2O2, TBAB/THF, allyl chloride (50 °C)
- iii) NMO:OsO4
Figure 5-13. Synthesis of dendrimer-like copolymers PS$_3$-$b$-PEO$_6$. 

[Diagram of synthetic process involving reactants and products, showing the conversion of monomers to the desired copolymer structure.]
Figure 5-14. Synthesis of a second-generation dendrimer-like PS by ATRP.

Second-generation PS$_8$PS$_{16}$Br$_{16}$
Figure 5-15. Synthesis of a third-generation dendrimer-like poly(L-lactide).
Figure 5-16. Functionalization of PMMA star chain ends by a TERMINI compound.
Figure 5-17. Divergent iterative synthetic strategy elaborated for synthesis of dendritic PMMA by a combination of LRP and TERMINI.
Figure 5-18. Synthesis of a second-generation dendritic P(S₂I₃) copolymer.

Figure 5-19. General reaction scheme for the synthesis of third-generation dendritic PB.
Figure 5-20. Synthesis of second-generation dendrimer-like PS by coupling reaction of living chains on chlorosilane star chain ends.
Figure 5-21. Synthesis of second-generation dendrimer-like star-branched PMMA.

Figure 5-22. SEC trace (RI detector) of polystyryllithium living chains after reaction with 4,4’-dibromodiphenylethylene. Conditions: [4,4’-dibromodiphenylethylene]/[PSLi+] = 4, at R.T. in cyclohexane.
Figure 5-23. Synthesis of asymmetric and “miktoarm” star (co)polymers.
Figure 5-24. SEC traces (RI detector) of PS(Br)$_2$ aryl bromide-terminated polystyrene (Run 2, Table 5-1) and its precursor PS-OH hydroxyl-terminated polystyrene (Run 1, Table 5-1). Conditions: [4,4’-dibromodiphenylethylene]/[PSO$^{+}$K$^-$/] = 4, at R.T. in THF.
Figure 5-25. $^1$H NMR spectra (CD$_2$Cl$_2$; 400 MHz) of PEO(Br)$_2$ aryl bromide-terminated poly(ethylene oxide) (Run 4, Table 5-1) and its precursor PEO-OH hydroxyl-terminated poly(ethylene oxide) (Run 3, Table 5-1).
Figure 5-26. $^1$H NMR spectra (CD$_2$Cl$_2$; 400 MHz) of PB(Br)$_2$ aryl bromide-terminated polybutadiene (Run 6, Table 5-) and its precursor PB-OH hydroxyl-terminated polybutadiene (Run 5, Table 5-1).
Figure 5-27. SEC traces (RI detector) of asymmetric star polystyrenes PS-\(b\)-PS\(_2\) (Runs 7 (A), 8 (B) and 9 (C), Table 5-1) and its precursor PS-(Br)\(_2\) (Run 2, Table 5-1). Conditions: [Li\(^+\)] = 5\(\times\)10\(^{-3}\) mol.L\(^{-1}\), at R.T. in benzene.

Figure 5-28. SEC traces (RI detector) of asymmetric star polymer PB-\(b\)-PB\(_2\) (Run 10 (B), Table 5-1) and “miktoarm” star copolymer PB-\(b\)-PS\(_2\) (Run 13 (C), Table 5-1) and its precursor PB-(Br)\(_2\) (Run 6 (A), Table 5-1). Conditions: [Li\(^+\)] = 5\(\times\)10\(^{-3}\) mol.L\(^{-1}\), at R.T. in benzene.
Figure 5-29. SEC traces (RI detector) of “miktoarm” star copolymers PS-$b$-PB$_2$ (Run 11 (C), Table 5-1), PS-$b$-PI$_2$ (Run 12 (C), Table 5-1), and its precursor PS-(Br)$_2$ (Run 2 (A), Table 5-1). Conditions: [Li$^+$] = 5x10$^{-3}$ mol.L$^{-1}$, at R.T. in benzene.
Figure 5-30. $^1$H NMR spectrum (CD$_2$Cl$_2$; 400 MHz) of an asymmetric star polybutadiene PB-$b$-PB$_2$(OH)$_2$ (Run 10, Table 5-1).
Figure 5-31. Synthesis of third-generation dendrimer-like polystyrene.
Figure 5-32. SEC traces (RI detector) of PS₄(Br)₈ and PB₄(Br)₈ aryl bromide-terminated polystyrene and polybutadiene stars (Runs 2 and 28, Tables 5-2 and 5-3) and its precursors (PS-OH)₄ and (PB-OH)₄ hydroxyl-terminated polystyrene and polybutadiene stars (Runs 1 and 27, Tables 5-2 and 5-3) and the tetrabromoinitiator.
Figure 5-33. $^1$H NMR spectrum (CD$_2$Cl$_2$; 400 MHz) of (PB-OH)$_4$ hydroxyl-terminated polybutadiene star (Run 27, Table 5-3).

Figure 5-34. $^1$H NMR spectra (CD$_2$Cl$_2$; 400 MHz) of PB$_4$(Br)$_8$ aryl bromide-terminated polybutadiene star (Run 28, Table 5-3).
Figure 5-35. SEC traces (RI detector) of dendrimer-like polystyrenes (Runs 14, 16, 18, 20, 22, 24, and 26, Table 5-2). Conditions: [TMEDA]/[-PhLi] = 2, at R.T., in benzene.
Figure 5-36. SEC/HT traces (RI detector) of (A) dendrimer-like polystyrenes (Runs 14, 16, 18, 20, 22, 24, and 26, Table 5-2) and (B) dendrimer-like polybutadienes (Runs 27, 29, and 31, Table 5-3). Conditions: [TMEDA]/[-PhLi] = 2, at R.T., in benzene.
Figure 5-37. $^1$H NMR spectrum (CD$_2$Cl$_2$; 400 MHz) of a hydroxyl-terminated dendrimer-like polybutadiene PB$_4$-b-PB$_8$(OH)$_8$ (Run 29, Table 5-3).
Figure 5-38. $^1$H NMR spectrum (CD$_2$Cl$_2$; 400 MHz) of a aryl bromide-terminated dendrimer-like polybutadiene PB$_4$-$b$-PB$_8$(Br)$_{16}$ (Run 30, Table 5-3).
Figure 5-39. Evolution of the hydrodynamic radius ($R_H$) as a function of the number of generation (G) for dendrimer-like polystyrenes prepared using tetrafunctional (Runs 14, 16, 18, 20, 22, 24, and 26, Table 5-2).

Figure 5-40. Evolution of Log[$\eta$] as a function of the number of generation (G) for dendrimer-like polystyrenes prepared using tetrafunctional (Runs 14, 16, 18, 20, 22, 24, and 26, Table 5-2).
Figure 5-41. Evolution of Log[η] as a function of Log $M_n$ for dendrimer-like polystyrenes prepared from tetrafunctional (Runs 14, 16, 18, 20, 22, 24, and 26, Table 5-2).
Table 5-1. Characteristics of asymmetric and “miktoarm” star (co)polymers.

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<th>Type</th>
<th>$M_n \times 10^{-3}$ (g.mol$^{-1}$)</th>
<th>$M_w \text{SEC/LS} \times 10^{-3}$ (g.mol$^{-1}$)</th>
<th>$M_w/M_n$</th>
<th>Functionality$^a$</th>
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<td></td>
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<td>$^1$H NMR</td>
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<tr>
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<td>-</td>
</tr>
<tr>
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<td>51.0</td>
<td>47.0</td>
<td>51.8</td>
<td>52.2</td>
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$^a$ Estimated by $^1$H NMR spectroscopy. $^b$ Estimated by titration of the hydroxyl end groups by DPMK ([DPMK] = 0.521 mol.L$^{-1}$).
Table 5-2. Characteristics and solution properties of dendrimer-like polystyrenes.

<table>
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<th>Run</th>
<th>Type</th>
<th>( M_n \times 10^{-3} \text{(g.mol}^{-1}) )</th>
<th>( M_w/M_n )</th>
<th>Functionality(^a)</th>
<th>([\eta]) (dL/g)</th>
<th>( g^b )</th>
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<td></td>
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<td>( \text{SEC} )</td>
<td>( \text{SEC/HT} )</td>
<td>( \text{theor} )</td>
<td>( \text{OH} )</td>
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<td>1920.2</td>
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\(^a\) Estimated by \(^1\)H NMR spectroscopy. \(^b\) \( g^\prime = [\eta]_{\text{dendr}}/[\eta]_{\text{linear}} \); \( ([\eta] = 1.23 \times 10^{-2} \ M_n^{0.71}) \). \(^c\) Estimated by titration of the hydroxyl end groups by DPMK \(([\text{DPMK}] = 0.521 \text{ mol.L}^{-1})\).
Table 5-3. Characteristics and solution properties of dendrimer-like polybutadienes.

<table>
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<th>Type</th>
<th>( M_n \times 10^{-3} ) (g.mol(^{-1}))</th>
<th>( M_w/M_n )</th>
<th>Functionality(^a)</th>
<th>[(\eta]) (dL/g)</th>
<th>( g^b )</th>
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<td>( M_w ) theor</td>
<td>OH</td>
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<td>1.05</td>
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\( a \) Estimated by \(^1\)H NMR spectroscopy. \( b \) \( g^a = [\eta]_{\text{dendr}}/[\eta]_{\text{linear}} \); \( [\eta] = 1.23 \times 10^{-2} M_n^{0.71} \). \( c \) Estimated by titration of the hydroxyl end groups by DPMK (\([\text{DPMK}] = 0.521 \text{ mol.L}^{-1}\)).
CHAPTER 6
CONCLUSION AND PERSPECTIVES

We have seen (Chapter 1) that in polymer chemistry polylithiation has never been really contemplated, the main reasons held responsible for polylithiation to be impractical being the secondary reactions occurring during the preparation of the polylithiated species and their limited solubility in most organic solvents, forming rather insoluble aggregates of little utility.

We proposed here an entire set of hydrocarbon-soluble polycarbanionic initiators and macroinitiators synthesized by using a simple halogen-lithium exchange reaction (Gilman’s reaction) carried out on multibromo molecule and macromolecule precursors. Using these multicarbanionic (macro)initiators an entire set of complex polymer architectures have been synthesized by anionic polymerization using a divergent method.

This strategy was first applied on multihalide molecules for the preparation of polymer architectures such as SBS triblock copolymers with excellent mechanical properties, obtained from a new hydrocarbon soluble (additive-free) dicarbanionic organolithium initiator containing a side C_{15}-alkyl chain, or \((\text{PS})_n,(\text{PB})_n, \text{P(B-b-EO)}_n, \text{and P(S-b-B-b-M)}_n \) \((n = 3 \text{ or } 4)\) star \((\text{co})\)polymers obtained from tri- and tetracarbanionic initiators.

In a second instance, the Gilman reaction was extended on \(\omega,\omega’\)-dibromo chain-end polymers after the introduction of a branching agent whose halogen atoms are carried by separate aryl rings to afford hydrocarbon-soluble polycarbanionic macroinitiators. This provided an efficient synthetic route to the asymmetric and “miktoarm” star \((\text{co})\)polymers based on the combination of different polymers such as polystyrene, polybutadiene, and polyisoprene. By the reiteration of this sequence of reactions (branching and halogen-lithium exchange reactions)
starting from a tetrafunctional initiator, dendrimer-like PS and PB up to the seventh and third generations, respectively, could be successfully synthesized.

After demonstrating that a long side alkyl chain helps to solubilization of polylithiated species, a new tetrafunctional initiator (Figure 6-1) containing long side alkyl chains, and thus soluble in apolar solvents without any additives can be contemplated. Therefore, polydiene star (co)polymers with a high percentage of 1,4-microstructure polybutadiene could be synthesized.

Moreover, all the previous results obtained let us hope that the same halogen-lithium exchange reaction can be applied to linear chain polymers containing pendant aryl bromide groups for the synthesis of more complex macromolecular architecture such as brush (co)polymers (Figure 6-2).

We have also demonstrated that (PB-b-PEO)$_4$ star block copolymer could be used for the synthesis of two-dimensional polymeric nanomaterials consisting of a continuously cross-linked polybutadiene two-dimensional network with poly(ethylene oxide) domains of controlled sizes trapped within the PB network. To reach that goal, novel (PB(Si(OEt)$_3$)-b-PEO)$_3$ star block copolymers were designed by hydrosilylation of the pendant double bonds of (PB-b-PEO)$_3$ star block copolymer precursors with triethoxysilane. Self-condensation of the triethoxysilane pendant groups under acidic conditions led to a successful cross-linking of the polybutadiene blocks directly at the air/water interface without any additives or reagents.

The characterization of these 2D amphiphilic cross-linked materials should be investigated (permeability, small angle scattering, and 2D viscometry) to understand the benefits provided by 2D self-assembly at the air/water interface over conventional solution self-assembly and other processes. In addition, such copolymer silanes monolayer could be easily transferred and grafted through covalent bonds to inorganic surfaces (glass support such as silicon wafer) for
polymer/inorganic composite synthesis. It could be also interesting to introduce triethoxysilane groups, and other metal alkoxides on other polydiene block copolymers of more complex architectures such as P(S-b-B-b-EO) triblock copolymers with the aim of stabilizing other original 2D and 3D morphologies.

Figure 6-1. Conceivable tetracarbanionic initiator.

Figure 6-2. Synthetic strategy proposed for brush polymer preparation.
CONCLUSION ET PERSPECTIVES

Dand le premier chapitre, nous avons insisté sur le fait que les espèces plurilithiées ont été très peu utilisées dans le domaine de la chimie des polymères. La présence de réactions secondaires durant la préparation de ces espèces plurilithiées et leur solubilité limitée dans la plupart des solvants organiques, formant plutôt des agrégats insolubles peu utiles, en sont les raisons principales.

Nous avons montré dans cette étude qu’il était possible de préparer toute une nouvelle famille d’amorceurs et macroamorceurs pluricarbanioniques soluble en solvant apolaire en utilisant une réaction simple d’échange halogène-lithium (réaction de Gilman) à partir de précurseurs halogénés moléculaires et macromoléculaires. L’utilisation de ces (macro)amorceurs multicarbanioniques a permis la synthèse de toute une panoplie d’architectures macromoléculaires complexes par polymérisation anionique par voie divergente.

Cette stratégie a tout d’abord été appliquée à des molécules multihalogénées pour la synthèse d’architectures polymères tels que des copolymères triblocs SBS à haute performance mécanique, obtenus à partir d’un amorceur dicarbanionique soluble en solvant apolaire sans additif, ou des (co)polymères en étoile à base de différents monomères (styrène, butadiène, oxyde d’éthylène et méthacrylate de méthyle) à partir d’amorceurs tri- et tétracarbanioniques solubles en milieu apolaire.

Dans un deuxième temps, la réaction de Gilman a été étendue à des chaînes polymères divalentes (ω,ω’-dibromées) après introduction d’un agent de branchement composé de deux noyaux aromatiques halogénés amenant ainsi à des macroamorceurs pluricarbanioniques soluble en milieu apolaire. L’utilisation de ces derniers a permis la synthèse de (co)polymères en étoile.
assymétriques et « miktoarm », issus de différents monomères tels le styrène, le butadiène ou l’isoprène. La répétition de cette même séquence de réactions (introduction d’un agent de branchement et réaction d’échange halogène-lithium) à partir d’un amorceur tétracarbanionique a aussi amené à la préparation de dendrimères de polystyrène et polybutadiène de septième et troisième générations, respectivement.

Après avoir fait la démonstration de l’influence d’une longue chaîne alkyle sur la solubilité des espèces plurilithiées, nous pouvons tout à fait envisager la préparation d’un nouvel amorceur tétracarbanionique possédant de longues chaînes alkyles en position α (Figure 5-42), permettant ainsi leur solubilisation en milieu apolaire sans ajout d’additif. Cette stratégie permettrait alors la préparation de copolymères en étoile à base de polydiènes à haut taux d’unités 1,4.

D’autre part, les différents résultats préalablement obtenus nous laissent espérer l’application de la même réaction d’échange halogène-lithium sur des chaînes polymères possédant un groupement aromatique halogéné sur chaque unité monomère permettant ainsi la synthèse possible d’architectures plus complexes tels que des (co)polymères en peigne (Figure 5-43).

Nous avons pu aussi démontrer au cours du Chapitre 4 l’intérêt des copolymères à blocs en étoile (PB-b-PEO)₄ dans le cadre de la synthèse de nanomatériaux polymères bidimensionnels à base d’un réseau bidimensionnel de polybutadiène réticulé constitué de domaines de poly(oxyde d’éthylène) de tailles contrôlés au sein du réseau. Pour atteindre cet objectif, un copolymère à blocs en étoile silylé (PB(Si(OEt)₃)-b-PEO)₃ a été préparé par hydrosilylation des doubles liaisons pendantes du précurseur étoilé (PB-b-PEO)₃ en présence de triéthoxysilane. La condensation des groupements pendants triéthoxysilane sous conditions acides a ainsi amené à la
réticulation des blocs de polybutadiène directement à l’interface air/eau sans ajout d’additifs ou réactifs.

Il serait maintenant intéressant d’étudier plus en profondeur ce matériau amphiphile réticulé en deux dimensions à travers des techniques de caractérisation telles que la perméabilité, la diffusion aux petits angles et la viscosimétrie bidimensionnelle pour ainsi mieux comprendre l’intérêt de l’auto-assemblage en deux dimensions. D’autre part, il est tout à fait envisageable de transférer et greffer à travers des liaisons covalentes de telles monocouches de copolymères silylés sur des supports inorganiques (silicon wafer) pour la préparation de matériaux composites. Enfin, il serait intéressant d’appliquer la même stratégie à d’autres copolymères à base de diènes tels que les copolymères triblocs P(S-b-B-b-EO) avec pour objectif la rétention de nouvelles morphologies bi- et tridimensionnelles.

Figure 6-1. Amorceur tétracarbanionique envisageable.
Figure 6-2. Stratégie de synthèse proposée pour la synthèse de polymères en peignes.
CHAPTER 7
EXPERIMENTAL PART

7.1 Purification of Reactants

The living anionic polymerization process requires, for their good unfolding, high purity experimental conditions. For this purpose, all the polymerizations were run in glassware sets equipped with teflon faucets and flame-dried under vacumm. All the chemicals needed for the polymerization (solvents, monomers, additives) were beforehand purified, dried, and then distilled under vacumm just before use. The different purification procedures for the solvents, additives, and monomers are described in details below.

7.1.1 Solvents

Benzene (99%, J.T Baker), tert-butylbenzene (99%, Aldrich), toluene (99%, J.T Baker), and cyclohexane (99%, J.T Baker) for polymerizations were dried and distilled twice over CaH$_2$ and polystyryllithium, successively. THF (99%, J.T Baker) was purified by distillation over CaH$_2$ and then from a purple Na/benzophenone solution.

7.1.2 Initiators

All the multibromo precursors used for the pluricarbanionic initiators synthesis were beforehand purified by lyophilization in benzene overnight.

7.1.3 Additives

Tetramethylethylenediamine (TMEDA) (Aldrich, 99%) was sodium-dried and distilled, whereas 2-methoxy ethanol (Aldrich, 99%) was magnesium-dried and distilled.

7.1.4 Reactants for Halogen-Lithium Exchange and Deprotonation Reactions

Solutions of sec-Butyllithium (s-BuLi) (Aldrich) were used for halogen-lithium exchange reaction after double titration.$^{479}$ For the titration of s-BuLi, the following procedure was applied: a 25 mL round-bottom flask fitted with a septum and containing a magnetic stirring bar was
evacuated and flushed with argon or nitrogen. Approximately 300 mg (1.56 mmol) of N-pivaloyl-o-toluidine was charged into the flask. Anhydrous THF (10 mL) was added, and a white sheet of paper was placed behind the flask. s-BuLi solution was then added dropwise until the change in the color of the solution from colorless to yellow. Triplicate analyses were performed in all cases.

The diphenylmethylpotassium (DPMK) solution, used for hydroxyl-deprotonation, was prepared and titrated as described in the following procedures.462

**Synthesis of diphenylmethylpotassium (DPMK).** In a flame-dried 250 mL round-bottom flask, pieces of potassium (4.1 g, 0.105 mol) were introduced followed by the addition of dry THF (60 mL). Naphthalene (6.72 g, 5.25x10^{-2} mol) was added, turning the solution dark green (due to the dissolution of potassium). The remaining THF (115 mL) was added along with diphenylmethane (17.6 mL, 0.105 mol). All of these additions were performed under dry and inert conditions. The resulting solution was stirred for one week and then used as such for the anionic polymerization of ethylene oxide.

**Determination of the concentration of DPMK.** A flame-dried 100 mL round bottom flask was charged with dry DMSO (10 mL) followed by a few grains (end of spatula) of triphenylmethane. More DPMK was then added until the solution just turned red-orange. Acetanilide (~0.2 g, 1.48x10^{-3} mol) was added, instantly turning the solution a clear light yellow. The resulting solution was titrated with DPMK from a buret. Upon further addition of acetanilide, the titration was repeated. Each addition and titration was carried out under dry and inert conditions with the average concentration of DPMK determined be 5.162x10^{-4} mol/mL.
7.1.5 Monomers

Styrene (S) (Aldrich, 99%) was dried and distilled under vacuum twice over CaH₂ and dibutyl magnesium successively. Butadiene (B) (Aldrich, 99%) was stirred over s-BuLi at –30°C for 2 h and distilled prior to use. Ethylene oxide (EO) (Fluka, 99.8%) was stirred over sodium for 3 h at –40 °C and then distilled before use. Methyl methacrylate (MMA) (Aldrich, 99%) was purified and distilled under vacuum twice over CaH₂ and triethyl aluminium successively.

7.1.6 Terminating and Functionalization Agent

Diphenylethylene (Aldrich, 99%) used for the polybutadiene chain-end functionalization was purified and distilled twice over CaH₂ and s-BuLi successively.

Triethoxysilane (hydrosilylation agent) (Aldrich, 99%) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (3 wt% solution in xylene) (Karstedt catalyst) (Aldrich, 99%), used for the hydrosilylation of the pendant polybutadiene double bonds, were employed as received.

7.2 Preparation of Multibromo Precursors for Pluricarbanionic Initiator Synthesis

7.2.1 Synthesis of Dibromoprecursor for High Performance SBS Triblock Copolymers

Synthesis of 1-pentadecyl-3-phenoxy benzene. Into a two-neck round-bottom flask fitted with a Dean and Stark apparatus equipped with a reflux condenser were placed 100 g (0.33 mol) of 3-pentadecyl phenol, 22.06 g (0.39 mol) potassium hydroxide, 300 mL of N,N-dimethylacetamide and 150 mL of toluene. The reaction mixture was refluxed for 7 h with continuous removal of by-product water. After completion of the reaction, the solvent was distilled off and the obtained potassium salt of 3-pentadecyl phenol was dried under reduced pressure. To a round bottom flask containing 111 g (0.32 mol) potassium salt of 3-pentadecyl phenol were added 50.88 g (0.32 mol) of bromobenzene, 2.22 g Cu powder (2 wt % of potassium
salt of 3-pentadecyl phenol) and 150 mL of N,N-dimethylacetamide. The reaction mixture was heated at 150°C for 8 h. The obtained dark colored reaction mixture was poured into 500 mL of water and copper salts were removed by filtration. The filtrate was extracted with ethyl acetate (3 x 400 mL). The ethyl acetate solution was washed with water, followed by brine solution and again with water and dried over sodium sulfate. Solvent evaporation yielded crude 1-pentadecyl-3-phenoxy benzene. Pure 1-pentadecyl-3-phenoxy benzene was obtained by silica gel (60-120 mesh) column chromatography (pet ether). Yield: 70 g (57 %). $^1$H NMR (CD$_2$Cl$_2$), δ (ppm): 8.0-6.5 (m, 9H, ArH), 2.6 (m, 2H, -CH$_2$-Ar), 1.7-1.0 (b, 26H, -CH$_2$-CH$_3$), 0.8 (m, 3H, -CH$_3$).

**Synthesis of 1-bromo-(4-bromophenoxy)-2-pentadecyl benzene.** Into a three-neck round-bottom flask equipped with a magnetic stirring bar, a reflux condenser, a dropping funnel and a thermometer were placed 25 g (0.066 mol) 1-pentadecyl-3-phenoxy benzene and 150 mL dichloromethane. To the reaction mixture was added dropwise 22.08 g (0.14 mol) of bromine at a temperature between -5 to 0 °C over a period of 15 minutes while the reaction mixture was protected from light. After completion of bromine addition, the reaction mixture was stirred at the same temperature for 1 h and then refluxed overnight. The excess bromine and hydrobromic acid were neutralized with aqueous 10% NH$_3$ (100 mL). The organic layer separated was washed with water, followed by brine solution and again with water. The dichloromethane solution was dried over sodium sulfate, filtered and the solvent was removed on a rotary evaporator. The crude product was purified by silica gel (60-120 mesh) column chromatography to obtain pure 1-bromo-(4-bromophenoxy)-2-pentadecyl benzene. Yield: 30 g (84%). $^1$H NMR (CD$_2$Cl$_2$), δ (ppm): 8.0-6.5 (m, 7H, ArH), 2.6 (m, 2H, -CH$_2$-Ar), 1.7-1.0 (b, 26H, -CH$_2$-CH$_3$), 0.8 (m, 3H, -CH$_3$).
7.2.2 Synthesis of Tribromo Precursor

Synthesis of 1,3,5-tris(4-bromophenyl)benzene.\textsuperscript{211} To a solution of SmCl\textsubscript{3} (0.5 mmol), 4-bromoacetophenone diethyl ketal (10 mmol) and pentane (15 mL), acetyl chloride (12 mmol) was dropped under nitrogen atmosphere. After stirring for a proper time at room temperature, the reaction was quenched by a mixture of benzene (20 mL) and H\textsubscript{2}O (10 mL). The organic layer was separated and washed with the saturated aqueous solution of Na\textsubscript{2}CO\textsubscript{3} and brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. Concentrated and recrystallized from n-hexane/dichloromethane, a needle crystal was obtained (Yield = 60\%). Melting point: 280.5-282.0 °C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}), \(\delta\) (ppm): 7.8-7.5 (m, 15H, ArH). Anal. calc. for C\textsubscript{24}H\textsubscript{15}Br\textsubscript{3} (%): C, 53.08; H, 2.78; Br, 44.14. Found: C, 52.59; H, 2.55; Br, 43.67.

7.2.3 Synthesis of Tetrabromo Precursor

Synthesis of 1,3-bis(p-bromophenyl)-2-propane.\textsuperscript{212,213} Into a three-neck round-bottom flask equipped with a distillation column, a mixture of 5 g (0.023 mol) of p-bromophenylacetic acid and 1 g (0.024 mol) of magnesium oxide is heated up to 240 °C under vacuum during 5 hours to remove water formed during the condensation reaction. By heating up to 340 °C under vacuum in a second instance, the targeted ketone is extracted by distillation. The crude product is purified by recrystallization in ethanol (Yield = 60\%). Melting point: 120-122 °C. \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}), \(\delta\) (ppm): 7.5-6.9 (m, 8H, ArH), 3.7 (m, 4H, -CH\textsubscript{2}-C(=O)-).

Synthesis of 2,3,4,5-tetrakis(p-bromophenyl)-cyclopentadienone.\textsuperscript{212,213,480,481} Into a 500 mL three-neck round-bottom flask equipped with a reflux condenser, 13 g (0.035 mol) of compound A and 13 g (0.035 mol) of dibromobenzylc were dissolved in 250 mL of warm ethanol and 100 mL of thiophene. Once the solution is refluxing (90 °C), a solution of 2 g of potassium hydroxyde in 20 mL of ethanol is slowly added through the condenser. After 15
minutes refluxing, the reaction medium is dipped into an ice bath at 0 °C. The crude dark violet product is recovered by filtration and then washed three times with 10 mL of ethanol (Yield = 70 %). $^1$H NMR (CD$_2$Cl$_2$), δ (ppm): 7.1 (d, 8H, ArH), 6.8 (d, 8H, ArH). Anal. calc. for C$_{29}$H$_{16}$Br$_4$O (%): C, 49.75; H, 2.3; Br, 45.66; O, 2.29. Found : C, 49.65; H, 2.4; Br, 45.55; O, 2.4.

**Synthesis of (1,2,3,4-tetrabromophenyl)-5-phenyl)benzene.**$^{213}$ Into a three-neck round-bottom flask equipped with a reflux condenser, 11 g (1.57x10$^{-2}$ mol) of compound B, 0.89 g (8.72x10$^{-3}$ mol) of phenylacetylene, and 4.2 g (2.3x10$^{-2}$ mol) of benzophenone are dissolved in 100 mL of o-dichlorobenzene. The reaction was carried out under reflux during three days. During this time, the solution loses his violet color for a yellow color due to the carbon dioxide emission. Once the reaction medium is cooled down to room temperature, 100 mL of methanol were added to precipitate the tetrabromo compound. Recovered by filtration, the crude product was then washed with methanol (Yield = 90%). $^1$H NMR (CD$_2$Cl$_2$), δ (ppm): 7.1-6.5 (m, 22H, ArH). Anal. calc. for (1,2,3,4-tetrabromophenyl)-5-phenyl)benzene (%): C, 55.85; H, 2.86; Br, 41.26; Found : C, 55.75; H, 3.06; Br, 41.19.

**7.3 Preparation of a Branching Agent for Dendrimer-Like Synthesis**

**Synthesis of 4,4'-dibromodiphenylethylene.** In a flamed and vacuum dried three-neck flask equipped with a condenser and an additional funnel, 5 g (1.47x10$^{-2}$ mol) of dibromobenzophenone was dissolved in 40 mL of dry THF. 13 mL (1.82x10$^{-2}$ mol) of methylmagnesium bromide solution (1.4 M in toluene/THF (75:25)) were added dropwise to the colorless solution. After the addition, the reaction medium became gray and the reaction was stirred at 80 °C overnight. At the end of the reaction, the yellow reaction mixture obtained was concentrated on a rotary evaporator to give 4.9 g of yellow cristals corresponding to the intermediate 4,4'-dibromodiphenylethanol (Yield = 98 %). By dehydration of 4.9 g of 4,4'
dibromodiphenylethanol warmed up to 180 °C, 4.65 g of a brown solid corresponding to the 4,4’-dibromodiphenylethylene (Yield = 95 %). 1H NMR (CD₂Cl₂), δ (ppm): 4,4’-dibromodiphenylethanol: 7.5-6.7 (m, 8H, aromatic), 2.3 (s, 1H, –C(CH₃)—OH), 1.8 (s, 3H, –C(CH₃)—OH). 4,4’-dibromodiphenylethylene: 7.5-6.7 (m, 8H, aromatic), 5.4 (s, 2H, CH₂=C(PhBr)₂).

7.4 Polymerization and Functionalization

7.4.1 Synthesis of High Performance Poly(styrene-b-diene-b-styrene) Triblock Copolymers

**Polystyrene and polybutadiene telechelics preparation.** In a flask, 145 mg (2.69x10⁻⁴ mol) of 1-bromo-(4-bromophenoxy)-2-pentadecyl benzene were freeze-dried. 5 mL of cyclohexane were added to make a precursor solution concentration of 5.3x10⁻² mol.L⁻¹. 0.83 mL (1.08x10⁻³ mol) of sec-butyllithium at a concentration of 1.3 M were added to the solution. After 20 minutes of reaction, the monomer was added dropwise. After the total consumption of the monomer, an excess of ethylene oxide was added. The polymerization was deactivated by degassed methanol. The linear polymer was precipitated using methanol. Dihydroxy-terminated linear polybutadiene: Mₙ (SEC in THF) = 6,200 g/mol; Mₘ/Mₙ = 1.13. 1H NMR (CD₂Cl₂), δ (ppm): 8.0-6.9 (m, 7H, aromatic resonances from the difunctional initiator), 5.4 (m, 3H, —CH₂=CH—CH₂— and CH₂=CH—CH—), 4.9 (s, 2H, CH₂=CH—CH—), 3.6 (s, 4H, –CH₂—OH), 2.0 (b, 5H, —CH₂=CH—CH—CH₂— and CH₂=CH—CH—), 1.2 (b, 2H, CH₂=CH—CH(R)—CH—), 0.9 (b, 3H, –CH₃).

**Synthesis of SBS triblock copolymer.** In a flask, 75 mg (1.39x10⁻⁴ mol) of 1-bromo-(4-bromophenoxy)-2-pentadecyl benzene were freeze-dried. 3 mL of cyclohexane to obtain a precursor solution at the concentration of 5.3x10⁻² mol.L⁻¹ were introduced. 0.43 mL (5.56x10⁻⁴ mol) of sec-butyllithium at the concentration of 1.3 M was added to the solution. After 20
minutes of reaction, butadiene was added dropwise at 5 °C. After 24 hours of polymerization, the reaction medium was diluted with a solution of cyclohexane/THF (100/1 in volume). Then styrene was added and the color of the medium changed instantaneously from the characteristic yellow color of polybutadienyllithium carbanions to the orange color of polystyryllithium carbanions. The polymerization is let 12 hours at room temperature. Finally, the polymerization is deactivated by degassed methanol. The triblock copolymer was precipitated in methanol. SBS triblock copolymer: $M_n$ ($^1$H NMR in CDCl$_3$) = 93,500 g/mol; $M_w$/$M_n$ = 1.2. $^1$H NMR (CDCl$_3$), δ (ppm): 8.0-6.9 (m, 7H and 5H, aromatic resonances from the difunctional initiator and the styrene units), 5.4 (m, 3H, —CH$_2$—CH=CH—CH$_2$— and CH$_2$=CH—CH—), 4.9 (s, 2H, CH$_2$=CH—CH—), 2.0 (b, 6H, —CH$_2$—CH=CH—CH—, CH$_2$=CH—CH—, and Ar—CH(R)—CH$_2$—), 1.2 (b, 4H, CH$_2$=CH—CH(R)—CH$_2$— and Ar—CH(R)—CH$_2$—), 0.9 (b, 3H, —CH$_3$).

7.4.2 Synthesis of Asymmetric and Miktoarm Star (Co)polymers

Synthesis of PS-OH and PB-OH hydroxyl-functionalized polymers. In a flamed and vacuum dried three-neck flask, 1.55 mL (1.98x10$^{-3}$ mol; [s-BuLi]$_0$ = 1.28 mol.L$^{-1}$) were added on 30 mL of cyclohexane. 3.7 g of styrene was added and the color of the medium turned instantaneously to the orange color of polystyryllithium carbanions. The polymerization was allowed to proceed during 2 hours at room temperature and then end-capping was accomplished by addition of a large excess of ethylene oxide. The reaction was deactivated by degassed acidic methanol (3 mL of concentrated HCl in 50 mL of methanol). $^1$H NMR (CD$_2$Cl$_2$), δ (ppm): PS-OH ($M_n$ (SEC in THF) = 2,400 g/mol; $M_w$/$M_n$ = 1.04): 7.6-6.7 (m, 5H, aromatic), 3.6 (s, 2H, —CH$_2$—OH), 1.3-2.5 (m, 3H, Ar—CH(R)—CH$_2$— and Ar—CH(R)—CH$_2$—), 0.7-1.1 (m, 3H, —CH$_3$ of initiator). PB-OH ($M_n$ (SEC in THF) = 3,100 g/mol; $M_w$/$M_n$ = 1.03): 5.4 (m, 3H, —
Synthesis of ω,ω’-dibromo end-functionalized polymers. In a flame and dried three-neck flask, 1 g (3.22x10⁻⁴ mol) of PB-OH hydroxyl-terminated polybutadiene sample was freeze-dried. The hydroxyl-terminated polybutadiene was first solubilized in 40 mL of THF, followed by the addition of 0.62 mL (3.22x10⁻⁴ mol) of DPMK at a concentration of 0.521 mol.L⁻¹. After the titration of the hydroxyl end groups, the reaction medium became orange and then an excess of 436 mg (1.29x10⁻³ mol) of freeze-dried 4,4’-dibromodiphenylethylene in solution in dry THF were added to the mixture. The instantaneous reaction of potassium alkoxide living chain ends on 4,4’-dibromodiphenylethylene give a purple violet solution. The reaction was deactivated by addition of degassed methanol and concentrated on a rotary evaporator. The polymer was finally precipitated using methanol to give 0.71 g of a crude product (71 %). ¹H NMR (CD₂Cl₂), δ (ppm): PS-(PhBr)₂ (Mₙ (SEC in THF) = 2,800 g/mol; Mₘ/Mₙ = 1.06): 7.8-6.2 (m, 5H and 8H, aromatic resonances from styrene units and chain end functions), 3.7 (s, 2H, –O–CH₂–CH(PhBr)₂), 3.4 (s, 2H, –CH₂–O–CH₂–), 2.8 (m, 1H, –O–CH₂–CH(PhBr)₂), 1.3-2.5 (m, 3H, Ar–CH(R)–CH₂– and Ar–CH(R)–CH₂–), 0.7-1.1 (m, 3H, –CH₃ of initiator). PB-(PhBr)₂ (Mₙ (SEC in THF) = 3,500 g/mol; Mₘ/Mₙ = 1.04): 7.8-6.7 (m, 8H, aromatic), 5.4 (m, 3H, –CH₂–CH=CH–CH₂– and CH₂=CH–CH–), 4.9 (s, 2H, CH₂=CH–CH–), 3.7 (s, 2H, –O–CH₂–CH(PhBr)₂), 3.4 (s, 2H, –CH₂–O–CH₂–), 2.8 (m, 1H, –O–CH₂–CH(PhBr)₂), 2.0 (b, 5H, –CH₂–CH=CH–CH₂– and CH₂=CH–CH–), 1.2 (b, 2H, CH₂=CH–CH(R)–CH₂–), 0.7-1.1 (m, 3H, –CH₃ of initiator).
Synthesis of asymmetric and miktoarm star polymers. In a flamed and vacuum dried three-neck flask, 150 mg \((4.83 \times 10^{-5} \text{ mol})\) of PB-(PhBr)\(_2\) aryl bromide-terminated precursor were freeze-dried. The aryl bromide-terminated precursor was dissolved in 10 mL of dried benzene, and then 0.15 mL \((1.93 \times 10^{-4} \text{ mol})\) of sec-butyllithium at a concentration of 1.3 M were added. sec-Butyllithium was let to react with the aryl bromide end groups for 4 h to ensure the complete lithium-halogen exchange reaction. A red-colored solution characteristic of the aryl lithiated species was obtained at the end of the reaction. The monomer was added on the soluble polyliothiated species and the polymerization was allowed to proceed during 2 hours for styrene and 24 hours for butadiene and isoprene. The end-capping of the living chain ends was accomplished by addition of an excess of ethylene oxide. The reaction was deactivated by degassed acidic methanol \((3 \text{ mL of concentrated HCl in 50 mL of methanol})\). The reaction mixture was concentrated on a rotary evaporator. The LiCl inorganic salts were removed by extraction of a dichloromethane solution of the star polymer with distilled water. The polymer solution was dried over sodium sulfate and concentrated. The star polymer was finally precipitated using methanol. \(^1\)H NMR \((\text{CD}_2\text{Cl}_2), \delta \text{ (ppm)}\): PB-\(b\)-PB\(_2\)(OH)\(_2\) \((M_w \text{ (SEC/LS in THF)} = 18,000 \text{ g/mol}; M_w/M_n = 1.04): 7.8-6.2 \text{ (m, 8H, aromatic)}, 5.4 \text{ (m, 3H, —CH_2—CH=CH—CH_2— and CH_2=CH—CH—)}, 4.9 \text{ (s, 2H, CH_2=CH—CH—)}, 3.7 \text{ (s, 2H, —O—CH_2—CH(PhR)_2)}, 3.4 \text{ (s, 10H, —CH_2—O—CH_2—, —CH_2—OH and —CH(Ph—CH_2—CH=CH—CH_2—)_2)}, 2.8 \text{ (m, 1H, —O—CH_2—CH(PhR)_2)}, 2.0 \text{ (b, 5H, —CH_2—CH=CH—CH_2— and CH_2=CH—CH—)}, 1.2 \text{ (b, 2H, CH_2=CH—CH(R)—CH—)}, 0.7-1.1 \text{ (m, 3H, —CH_3 of initiator)}. 

7.4.3 Synthesis of Star (Co)polymers

Synthesis of \((\text{PS-OH})_n\) and \((\text{PB-OH})_n\) \((n = 3 \text{ or } 4)\) hydroxyl-functionalized star-shaped polystyrene and polybutadiene, G-1. In a flamed and vacuum dried three-neck flask,
50.1 mg (6.47×10⁻⁵ mol) of tetrabromoinitiator were freeze-dried. 12.2 mL of benzene were added to make a precursor solution concentration of 5.3×10⁻² mol.L⁻¹, followed by 0.122 mL (1.55×10⁻³ mol) of 2-methoxy ethanol. 1.6 mL (2.07×10⁻³ mol) of sec-butyllithium at a concentration of 1.3 M were added to the solution. After 20 minutes of reaction, butadiene was added. The polymerization was allowed to proceed during 24 hours and then end-capping was accomplished by addition of a large excess of ethylene oxide. The reaction was deactivated by degassed acidic methanol (3 mL of concentrated HCl in 50 mL of methanol). The reaction mixture was concentrated on a rotary evaporator. The LiCl inorganic salts were removed by extraction of a dichloromethane solution of the star polymer with distilled water. The polymer solution was dried over sodium sulfate and concentrated. The star polymer was finally precipitated using methanol to give 1.04 g of a crude product (98 %). \( M_w \) (SEC/LS in THF) = 16,400 g/mol; \( M_w/M_n = 1.05 \). \(^1\)H NMR (CD₂Cl₂), δ (ppm): 7.6-6.7 (m, 22H, aromatic resonances from tetrafunctional initiator), 5.4 (m, 3H, \(-\text{CH}_2\text{-CH}=\text{CH}-\text{CH}_2-\) and \(\text{CH}_2=\text{CH}-\text{CH}-\)), 4.9 (s, 2H, \(\text{CH}_2=\text{CH}-\text{CH}-\)), 3.6 (s, 6H and 8H for the three- and four-armed star, \(-\text{CH}_2-\text{OH}\)), 2.0 (b, 5H, \(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\) and \(\text{CH}_2=\text{CH}-\text{CH}-\)), 1.2 (b, 2H, \(\text{CH}_2=\text{CH}-\text{CH}(R)-\text{CH}_2-\)).

**P(styrene-\(b\)-butadiene-\(b\)-methyl methacrylate) star block terpolymer.** In a flamed and vacuum dried three-neck flask, 50.1 mg (6.47×10⁻⁵ mol) of tetrabromoinitiator were freeze-dried. 12.2 mL of benzene to obtain a precursor solution at the concentration of 5.3×10⁻² mol.L⁻¹ and 0.122 mL (1.55×10⁻³ mol) of 2-methoxy ethanol were introduced. 1.6 mL (2.07×10⁻³ mol) of sec-butyllithium at the concentration of 1.3 M were introduced. After 20 minutes of reaction, styrene is added dropwise. After 2 hours of polymerization, butadiene was added at 5 °C and the polymerization is let 24 hours at room temperature. Then an excess of diphenylethylene was
introduced to react with the polybutadienyllithium chain ends during 1 hour at 0°C. The reaction medium was diluted in 200 mL of tert-butylbenzene. Finally, methyl methacrylate was added dropwise at –40°C. After 1 hour, the polymerization was deactivated by degassed methanol. The star block terpolymer was precipitated in methanol and purified by fractionation through a silica gel column. P(SBM)_4: \(M_n (^{1}H \text{NMR in CDCl}_3) = 16,100 \text{ g/mol}; M_w/M_n = 1.2\). \(^{1}H \text{NMR (CDCl}_3), \delta (\text{ppm}): 8.0-6.5 (\text{m, 22H and 5H, aromatic resonances from the tetrafunctional initiator and the styrene units}), 5.4 (\text{m, 3H, } \text{—CH}_2—\text{CH}=\text{CH—CH}_2— \text{ and CH}_2—\text{CH—CH—}), 4.9 (\text{s, 2H, CH}_2=\text{CH—CH—}), 3.5 (\text{s, 3H, CH}_3—\text{O—C}(=\text{O})—), 2.0 (\text{b, 7H, } \text{—CH}_2—\text{CH—CH—CH}_2—, CH_2=\text{CH—CH—}, \text{Ar—CH(R)—CH}_2—, \text{CH}_3—\text{O—C}(=\text{O})—\text{CH(R)—CH}_2—, \text{Ar—CH(R)—CH}_2—, \text{and CH}_3—\text{O—C}(=\text{O})—\text{CH(R)—CH}_2—).

7.4.4 Synthesis of Dendrimer-Like Polymers

Synthesis of PS_4-(PhBr)_8 and PB_4-(PhBr)_8 \(\omega,\omega’\)-dibromo end-functionalized star-shaped polystyrene and polybutadiene, G-1-Br. The PS_4-(PhBr)_8 and PB_4-(PhBr)_8 \(\omega,\omega’\)-dibromo end-functionalized polystyrene and polybutadiene stars were synthesized according to the same procedure previously described for the preparation of PS-(PhBr)_2 and PB-(PhBr)_2 aryl bromide end-functionalized chain polymers. \(^{1}H \text{NMR (CD}_2\text{Cl}_2), \delta (\text{ppm}): \text{PS}_4-(\text{PhBr})_8 (\text{SEC/HT in dichlorobenzene}) = 8,200 \text{ g/mol}; M_w/M_n = 1.1): 7.8-6.2 (\text{m, 5H and 32H, aromatic resonances from styrene units and chain end functions}), 3.7 (\text{s, 8H, } –\text{O—CH}_2—\text{CH(PhBr)_2}), 3.4 (\text{s, 8H, } –\text{CH}_2—\text{O—CH}_2—), 2.8 (\text{m, 4H, } –\text{O—CH}_2—\text{CH(PhBr)_2}), 1.3-2.5 (\text{m, 3H, } \text{Ar—CH(R)—CH}_2— \text{ and Ar—CH(R)—CH}_2—). \text{PB}_4-(\text{PhBr})_8 (\text{SEC/HT in dichlorobenzene}) = 15,200 \text{ g/mol}; M_w/M_n = 1.03): 7.8-6.6 (\text{m, 22H and 32H, aromatic resonances from tetrafunctional initiator and chain end groups}), 5.4 (\text{m, 3H, } –\text{CH}_2—\text{CH=CH—CH}_2— \text{ and CH}_2=\text{CH—CH—}), 4.9 (\text{s, 2H, CH}_2=\text{CH—CH—}), 3.7 (\text{s, 8H, } –\text{O—CH}_2—\text{CH(PhBr)_2}), 3.4 (\text{s, 8H, } –\text{CH}_2—\text{O—CH}_2—), 2.8 (\text{m, 4H,
–O–CH₂–CΗ(PhBr)₂), 2.0 (b, 5H, —CH₂—CH=CH—CH₂— and CH₂=CH—CΗ—), 1.2 (b, 2H, CH₂=CH—CH(R)—CΗ₂—).

Synthesis of PS₄-b-PS₈(OH)₈ and PB₄-b-PB₈(OH)₈ hydroxyl-functionalized second-generation dendrimer-like polystyrene and polybutadiene, G-2. In a flame and vacuum-dried three-neck flask, 160.0 mg (1.95x10⁻⁵ mol) of PS₄-(PhBr)₈ aryl bromide-terminated precursor were freeze-dried. The PS₄-(PhBr)₈ aryl bromide end-functionalized precursor was dissolved in 10 mL of dry benzene, and then 0.24 mL (3.12x10⁻⁴ mol) of sec-butyllithium at a concentration of 1.3 M were added. sec-Butyllithium was let to react with the aryl bromide end groups for 4 hours to ensure the complete lithium-halogen exchange reaction. A red-colored solution characteristic of the aryl lithiated species was obtained at the end of the reaction. At the end of the halogen-lithium exchange reaction, 0.05 mL (2.28x10⁻³ mol) of TMEDA were added to the reaction medium. After the solubilization of the polylithiated macroinitiator, the monomer was added. The polymerization was allowed to proceed during 2 hours for styrene and 24 hours for butadiene and then end-capping was accomplished by addition of a large excess of ethylene oxide. The reaction was deactivated by degassed acidic methanol. The reaction mixture was concentrated on a rotary evaporator. The LiCl inorganic salts were removed by extraction of a dichloromethane polymer solution with distilled water. The polymer solution was dried over sodium sulfate and concentrated. The dendrimer-like polymer was finally precipitated using methanol. \(^1\)H NMR (CD₂Cl₂), δ (ppm): PS₄-b-PS₈(OH)₈ (\(M_n\) (SEC/HT in dichlorobenzene) = 57,000 g/mol; \(M_w/M_n = 1.07\)): 7.8-6.2 (m, 5H and 32H, aromatic resonances from styrene units and chain end functions), 3.7 (s, 8H, –O–CH₂–CΗ(PhR)₂), 3.4 (s, 32H, –CH₂–O–CH₂— and –CH₂—OH), 2.8 (m, 4H, –O–CH₂–CΗ(PhR)₂), 1.3-2.5 (m, 3H, Ar—CH(R)—CΗ₂— and Ar—CH(R)—CΗ₂—). PB₄-b-PB₈(OH)₈ (\(M_n\) (SEC/HT in dichlorobenzene) = 38,600 g/mol; \(M_w/M_n = \))
1.05): 7.8-6.6 (m, 22H and 32H, aromatic resonances from tetrafunctional initiator and chain end groups), 5.4 (m, 3H, —CH₂—CH=CH—CH₂— and CH₂=CH—CH—), 4.9 (s, 2H, CH₂=CH—CH—), 3.7 (s, 8H, —O—CH₂—CH(PhR)₂), 3.4 (s, 24H, —CH₂—O—CH₂— and —CH₂—OH), 2.8 (m, 4H, —O—CH₂—CH(PhR)₂), 2.0 (b, 5H, —CH₂—CH=CH—CH₂— and CH₂=CH—CH—), 1.2 (b, 2H, CH₂=CH—CH(R)—CH₂—).

7.5 Two-Dimensional Cross-linking at the Air/Water Interface

7.5.1 Radical Cross-linking

Preparation of cross-linked (PB-b-PEO)₃ star block copolymer monolayer with AIBN. 100 µL (C = 1 mg/mL) of a chloroform solution of (PB₂₀₀-b-PEO₇₆)₃ star block copolymer and 100 µL (C = 0.2 mg/mL) of a chloroform solution of AIBN were spread dropwise with a gastight Hamilton syringe on the Millipore water subphase. The chloroform was then allowed to evaporate for 15 min to ensure no residual solvent remained. The subphase temperature was maintained at 25 °C with water circulating under the trough. The monolayer was then compressed up to a surface pressure of 20 mN/m with barrier compression speed of 5 mm.min⁻¹, and the cross-linking reaction was carried out under UV light for 24 hours at 25 °C. For photocross-linking, the Langmuir films were exposed to the radiation of a 80 W/cm medium pressure mercury lamp, in the presence of air, at a passing speed of 50 m/min. At the end of the reaction, the isotherm of the cross-linked monolayer was recorded after barrier expansion. The cross-linked monolayer was removed from the water surface for FTIR study and transferred on a mica substrate for AFM characterization.

7.5.2 Cross-linking by Self-condensation of Triethoxysilane Groups

Hydrosilylation of polybutadiene homopolymer. In a flamed and vacuum dried three-neck flask equipped with a magnetic stirrer, a reflux condenser, a dry argon inlet and a heating
mantle, 142 mg (1.28x10^{-5} mol) of linear polybutadiene were freeze-dried and then dissolved in 20 mL of dried toluene. 0.573 mL (3.133x10^{-3} mol) of triethoxysilane and 0.1 mL of the catalyst platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (3 wt% solution in xylene) were added, and the reaction was carried out under argon for 24 hours at 80 °C. At the end of the reaction, the solvent and the nonreacted triethoxysilane were removed by evaporation under vacuum and small samples were taken for NMR, and Langmuir trough studies. The product was stored under dry argon (Crude product: $M_n$ ($^1$H NMR in CDCl$_3$) = 33,500 g/mol; m = 135 mg).

$^1$H NMR ($\delta$ ppm; CDCl$_3$): 5.4 (m, 3H, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$ and $\text{CH}_2=\text{CH}-\text{CH}-$), 4.9 (s, 2H, $\text{CH}_2=\text{CH}-\text{CH}-$), 3.8 (s, 6H, $-\text{CH}_2-\text{Si(OCH}_2\text{CH}_3)_3$), 2.0 (b, 5H, $-\text{CH}_2=\text{CH}-\text{CH}_2-$ and $\text{CH}_2=\text{CH}-=\text{CH}_2-$), 1.5-0.9 (b, 11H, $-\text{CH}_2-\text{Si(OCH}_2\text{CH}_3)_3$, and $\text{CH}_2=\text{CH}-\text{CH}(\text{R})-\text{CH}_2-$), and 0.3-0.8 (s, 2H, $-\text{CH}_2-\text{Si(OEt)}_3$).

**Preparation of crosslinked polybutadiene monolayers under acidic conditions.** 100 $\mu$L (C = 1mg/mL) of a chloroform solution of PB(Si(OEt)$_3$) hydrosilylated polybutadiene were spread dropwise with a gastight Hamilton syringe on the Millipore water subphase at pH = 3.0. The monolayer was immediately compressed and hold at the desired surface pressure. The cross-linking reaction was carried out for 10 hours at 25 °C to ensure a complete reaction and the crosslinked monolayers were subsequently transferred onto mica substrate for further AFM characterization. After cross-linking at 15 mN/m material initially formed could be with a spatula after compressing the monolayer to a final area of ca 2 x 15 cm$^2$, and was dried in a dessicator for further FTIR study and solubility experiments.

**Hydrosilylation of the (PB$_{200}$-$b$-PEO$_{326}$)$_3$ star block copolymer.** In a flamed and vacuum dried three-neck flask equipped with a magnetic stirrer, a reflux condenser, a dry argon inlet and a heating mantle, 164 mg (2.17x10^{-6} mol) of (PB$_{200}$-$b$-PEO$_{326}$)$_3$ star block copolymer
were freeze-dried and dissolved in 15 mL of dry toluene. 0.285 mL (1.562x10^{-3} mol) of triethoxysilane and 0.1 mL of the catalyst platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (3 wt% solution in xylene) were added, and the reaction was carried out under argon for 24 hours at 80 °C. At the end of the reaction, the solvent and the unreacted triethoxysilane were removed by evaporation under vacuum and small samples were taken for NMR, FTIR and Langmuir trough studies. The product was stored under argon (Crude product: $M_n$ ($^1$H NMR) = 135,500 g/mol; m = 160 mg). $^1$H NMR ($\delta_{ppm}$; CDCl$_3$): 5.4 (m, 3H, $-\text{CH}_2-\text{CH}=\text{CH-CH}_2-$ and $\text{CH}_2=\text{CH-CH}_2-$), 4.9 (s, 2H, $\text{CH}_2=\text{CH-CH}_2-$), 3.8 (s, 6H, $-\text{CH}_2-\text{Si(OC}_2\text{H}_5\text{CH}_3)_3$), 3.6 (s, 4H, $-\text{CH}_2-\text{CH}_2-\text{O-}$), 2.0 (b, 5H, $-\text{CH}_2-\text{CH}=\text{CH-CH}_2-$ and $\text{CH}_2=\text{CH-CH}_2-$), 1.5-0.9 (b, 11H, $-\text{CH}_2-\text{Si(OCH}_2\text{CH}_3)_3$, and $\text{CH}_2=\text{CH-CH(R)-CH}_2-$), and 0.3-0.8 (s, 2H, $-\text{CH}_2-\text{Si(OEt)}_3$).

**Preparation of cross-linked (PB(Si(OEt)$_3$)-b-PEO)$_3$ star block copolymer monolayers under acidic conditions.** 100 µL (C = 1mg/mL) of a chloroform solution of (PB(Si(OEt)$_3$)-b-PEO)$_3$ star block copolymer were spread dropwise with a gastight Hamilton syringe on the Millipore water subphase at pH = 3.0. The monolayer was immediately compressed and hold at the desired surface pressure with barrier compression speed of 100 mm.min$^{-1}$. The cross-linking reaction was carried out for 10 hours at 25 °C to ensure completion of the reaction and the cross-linked monolayers were subsequently transferred onto mica substrates for further AFM characterization. After cross-linking at 15 mN/m, the resulting material could be removed with a spatula from the interface after compressing the monolayer to a final area of ca 2 x 15 cm$^2$, and was dried in a dessicator for further solubility studies.
7.6 Characterization Techniques

7.6.1 Elemental Analysis

The elemental analysis were carried out by Service Central d’Analyse of Vernaison (69-France).

7.6.2 Gas Chromatography

The chromatography set used is a Varian 350 equipped with a flame ionization detector (FID).

Column characteristics:

Length : 15 m, internal diameter : 0.539 mm, non polar phase : dimethylsiloxane, film thickness : 1.5 \( \mu \)m, maximum temperature : 320 °C, and vector gas : He.

Analysis conditions:

Initial temperature : 35 °C during 2 minutes, final temperature : 240 °C (increase of 10 °C/min), \( T_{\text{injector}} = 250 \) °C, \( T_{\text{detector}} = 300 \) °C.

For the determination of the yield of the halogen/lithium exchange reaction in the case of the pluricarbanionic initiators, the external standard method was preferred. The process is based on the comparison of two chromatograms. For this purpose, a first reference solution of the compound studied was prepared at a precise concentration \( C_{\text{ref}} \). A precise volume \( V \) of this latter solution is injected and the area \( A_{\text{ref}} \) of the peak corresponding to the compound studied. Then, a same volume \( V \) of the sample containing the compound to titrate (concentration \( C_{\text{sample}} \)). In this case, \( A_{\text{sample}} \) is the area of the corresponding peak. Because of the equal volume injected, the areas \( A_{\text{ref}} \) and \( A_{\text{sample}} \) are proportional, the area of each peak depending on the mass injected and the corresponding concentration (\( m_{i} = C_{i}V \)).
For a precise adjustment of the apparatus, a linear relation exists for each peak between the area of the peak and the amount of the corresponding compound in the sample injected. This is valid for a range of concentrations depending on the type of detector used. This is expressed by the following relation:

\[ M_i = K_i A_i \]

where \( M_i \) is the mass of a compound \( i \) injected in the column, \( K_i \) is the absolute response coefficient of compound \( i \), and \( A_i \) is the area of the elution peak corresponding to the compound \( i \). This last expression applied on the chromatogram gives the following expression:

\[ C_{\text{ref}} = K A_{\text{ref}} \text{ and } C_{\text{sample}} = K A_{\text{sample}} \text{ where } (C_{\text{sample}})_t = C_{\text{ref}} (A_{\text{sample}}/A_{\text{ref}})_t. \]

For the kinetic studies, the internal standard method was used. This method is based on the use of the relative response coefficient of each compound to be titrated compared to the one of an extra-compound introduced as a reference. This allowed to avoid the uncertainty due to the injected volumes.

To select the internal standard it is necessary to get its elution peak well-defined (good resolution) compared to the other peaks present on the chromatogram. Its retention time should be close to the one(s) of the compound(s) to be titrated. Its concentration should be higher or at least close to the ones of the other compounds to get a linear response from the detector. Finally, the internal standard should be inert towards the other compounds of the sample.

During the kinetic studies the following relation was used to determine the consumption of the product studied:

\[ \% = \left[ (A_{\text{product}}/A_{\text{ref}})_t / (A_{\text{product}}/A_{\text{ref}})_{t=0} \right] \times 100 \]

7.6.3 Size Exclusion Chromatography (SEC)

Apparent molar masses were determined with a size exclusion chromatography (SEC) equipped with four TSK-gel columns (7.8 x 30 cm, 5 \( \mu \)m, G 2000, 3000, 4000 and 5000 HR with
pore sizes of 250, 1,500, 10,000 and 100,000 Å, respectively) and THF as the mobile phase (1 mL/min). This instrument was equipped with a refractive index (RI) (Varian RI-4) and UV-vis (Varian 2550 variable λ) detectors. The SEC was calibrated using linear polystyrene samples.

Absolute molar masses of the different star polymers were calculated using a multiangle laser light scattering (Photometer laser DAWV-F) detector (Wyatt Technology) connected to an SEC line (abbreviated SEC/LS). The dn/dc values for the different stars were measured in THF at 25°C with a laser source operating at 633 nm (dn/dc = 0.183 cm³/g for the four-arm regular and asymmetric polystyrene stars, 0.094 and 0.109 cm³/g for the four-arm regular and asymmetric polybutadiene stars, respectively, and 0.105, 0.108, and 0.135 cm³/g for the (PS)-b-(PB)₂, (PS)-b-(PI)₂, and (PB)-b-(PS)₂ miktoarm star copolymers, respectively).

Absolute molar masses of the dendrimer-like polymer samples were determined with a high temperature size exclusion chromatography (abbreviated SEC/HT in the following) using a Waters 2000 CV SEC instrument, equipped with one column of HT 2 styragel and two columns of HT 6E styragel and an online viscometric and refractive index detector, at 150 °C in dichlorobenzene as solvent at a flow rate of 0.7 mL/min.

7.6.4 Nuclear Magnetic Resonance (NMR) Spectroscopy

1H NMR spectra were recorded on a Bruker AC400© and AC300© spectrometer using CDCl₃, CD₂Cl₂ and CD₃OD as deuterated solvents. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane (TMS) and referenced to residual solvent.

To determine the 1,2- or 1,4-microstructures, the titration of two distinct peaks is used. The first one at 5.4 ppm corresponds to the protons α and α’ and the second one at 4.9 ppm to the protons β as shown in the following scheme.
Based on the previous informations, we can write:

\[
\frac{2x}{(2y + x)} = \frac{I(4.9)}{I(5.4)}
\]

\[x + y = 100\]

where \(x\) is the percentage of 1,2-structures, \(y\) is the one of 1,4-structures, and \(I(4.9)\) and \(I(5.4)\) are the integration values corresponding to the peaks at 4.9 and 5.4 ppm.

### 7.6.5 Mass Spectrometry

Mass determination was carried out using an AutoSpec mass spectrometer arranged in an EBE geometry (Micromass, Manchester, UK). The instrument was operated at 8kV accelerating voltage in positive mode. The caesium gun was set to 35 keV energy and 1 mL of sample was mixed in the tip of the probe with a nitrobenzylalcohol matrix.

### 7.6.6 Viscometry

Viscometric measurements were performed in toluene at 35 °C using an Ubbelohde viscometer (CT 52 Schott). The diameter of the capillar is 0.46 mm and the volume of the parent solution is 15 mL (concentration : 250 mg in 15 mL). The capillar is dipped in a water bath at 35 °C. Samples were filtered through glass filters (200 µm) before measurements.

From the flow time measured between two photodiodes for each polymer solution, \([\eta]\) value was determined by the traces of the two following straight lines:
\[ \eta_{\text{spe}}/C = f(C) \text{ and } \ln \eta_{\text{rel}}/C = f(C) \text{ where } \eta_{\text{rel}} = \eta/\eta_0 \text{ and } \eta_{\text{spe}} = (\eta-\eta_0)/\eta_0 \]

The intersection of the two straight lines, at zero concentration, gives the intrinsic viscosity of the polymer.

7.6.7 Infra-Red Spectroscopy

IR absorbance spectra were recorded on a Bruker/Vector 22 FT/IR spectrometer. The dry (co)polymers were solubilized in chloroform, and the solutions were subsequently spread dropwise onto KBr pellets and allowed to dry in a desiccator.

7.6.8 Mechanical Properties Analysis

Samples were tested on an Instron Universal Testing machine (model 4466) in a controlled environment room at 23 ± 2 °C and 50 % of relative humidity. A 500 N static load cell with self-aligning grips and stainless steel faces (Instron Corporation) was used. The tensile measurements were performed with a cross-head speed of 10 mm/min and an initial grip separation of 35 mm. Tensile properties (tensile strength and elongation at break) were calculated with Series IX Automated Materials Testing System software (Instron Corporation). The films had a thickness of approximately 0.75 mm, a width of 4 mm, and a gauge length of 40 mm (the mean thickness of each sample was performed with a Fowler micrometer). Five samples from the same film were tested for each copolymer.

7.6.9 Langmuir Films

Surface film characterization was accomplished using a Teflon Langmuir trough (Width = 150 mm and Length = 679 mm) system (KSV Ltd., Finland) equipped with two moving barriers and a Wilhelmy plate for measuring surface pressure. Between runs, the trough was cleaned with ethanol and rinsed several times with Millipore filtered water of ~ 18 MΩ.cm resistivity. The subphase temperature was maintained at 25 °C through water circulating under
the trough. Samples were typically prepared by dissolving \( \sim 1 \) mg of copolymer in 1 mL of chloroform and spread dropwise with a gastight Hamilton syringe on the Millipore water subphase. For the surface property studies of the \((\text{PB}-b\text{-PEO})_3\) star block copolymers, the chloroform was allowed to evaporate for 30 min to ensure no residual solvent remained and the isotherm and hysteresis experiments were run with barrier movement of 5 mm.min\(^{-1}\). The compression/expansion cycles for the hysteresis experiments were repeated five times after a delay of thirty minutes during which the monolayer was allowed to relax at \( \pi = 0 \) mN.m\(^{-1}\). Isotherm and hysteresis experiments were performed at least three times to verify reproducibility. The data resulting from the isotherms \((A_0, \Delta A, \text{and } A_{\text{pancake}})\) were plotted vs. the number of EO units and fitted by a linear curve.

In the case of the \((\text{PB}(\text{Si(OEt})_3-b\text{-PEO})_3\) star block copolymers, the isotherms were recorded after different reaction times during cross-linking for various subphase pH values with a barrier compression speed of 100 mm.min\(^{-1}\). The isobar experiments were carried out at a surface pressure of 5 or 10 mN/m for different subphase pH values.

### 7.6.10 Atomic Force Microscopy

Surface films of the linear homopolymers and star (co)polymers were transferred onto freshly cleaved mica at various pressures. The desired surface pressure was attained by a continuous compression of 0.5 mN.m\(^{-1}\) at rates of 10 mm.min\(^{-1}\). Once the film had equilibrated at a constant \( \pi \) for at least 15 minutes, the mica was then pulled at a rate of 1mm.min\(^{-1}\). The transferred film was dried in a dessicator for 24 hours and subsequently scanned in tapping mode with a Nanoscope III AFM (Digital Instruments, Inc. Santa Barbara, CA) using silicon probes (Nanosensor dimensions: \( T = 3.8-4.5 \) µm, \( W = 27.6-29.2 \) µm, \( L = 131 \) µm). Using Digital
Instruments software, the images were processed with a second order flattening routine while size, height and number of domains were measured through section analysis.

![Chemical structure](image1)

**Figure 7-1.** Synthesis of 1-pentadecyl-3-phenoxy benzene.

![Chemical structure](image2)

**Figure 7-2.** Synthesis of 1,3,5-tris(4-bromophenyl)benzene.

![Chemical structure](image3)

**Figure 7-3.** Synthesis of 1,3-bis(p-bromophenyl)-2-propane.

![Chemical structure](image4)

**Figure 7-4.** Synthesis of 2,3,4,5-tetrakis(p-bromophenyl)-cyclopentadienone.
Figure 7-5. Synthesis of (1,2,3,4-tetrabromophenyl)-5-phenyl)benzene.
LIST OF REFERENCES


(20) Quirk, R. P.; Tsai, Y. Macromolecules **1998**, *31*, 8016.


(23) Eschwey, H.; Burchard, W. Polymer 1975, 16, 180.


(49) Shell Chemical Co.: Kratons, Cariflex TR. Belg. Pat. 671460, 1966.


(60) Cameron, G.; Buchan, G. M. Polymer 1979, 20, 1129.


(146) Mayer, R. *Polymer* 1974, 15, 137.


BIOGRAPHICAL SKETCH

Rachid Matmour was born in Bordeaux, France, in 1978. After a brief stay in Bordeaux, he grew up in Périgueux (Dordogne, France). Rachid received his B.S. in chemistry in 2000 and his M.S. in polymer chemistry in 2002 from the University of Science and Technology of Bordeaux 1, France. Also in 2002, he started a joint Ph.D. program working in both Dr. Yves Gnanou’s group at the Laboratoire de Chimie des Polymères Organiques (LCPO) in the University of Bordeaux 1, and Dr. Randolph S. Duran’s group in the Center for Macromolecular Science and Engineering at the University of Florida. With Dr. Yves Gnanou, he worked on the synthesis of complex polymer architectures (block copolymers, star polymers, and dendrimer-like polymers) by living anionic polymerization and controlled radical polymerization. With Dr. Randolph S. Duran, he studied the surface active properties of amphiphilic star block copolymers and their application for the synthesis of two-dimensional polymeric nanomaterials at the air/water interface.