

Polymers with Complex Architecture by Living Anionic Polymerization

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I. Introduction

Immediately after the discovery of the living character¹ of anionic polymerization,² polymer chemists started synthesizing well-defined linear homopolymers and diblock copolymers with low molecular

weight and compositional polydispersity. Later star homopolymers and block copolymers, the simplest complex architectures, were prepared. Polymer physical chemists and physicists started studying the solution³ and the bulk properties of these materials.⁴ The results obtained forced the polymer theoreticians either to refine existing theories⁵ or to create new ones.⁶ Over the past few years, polymeric materials having more complex architectures have been synthesized. The methods leading to the following complex architectures will be presented in this review:

(1) star polymers and mainly asymmetric and miktoarm stars; (2) comb and α,ω -branched polymers; (3) cyclic polymers and combinations of cyclic polymers with linear chains; and (4) hyperbranched polymers.

Emphasis has been placed on chemistry leading to well-defined and well-characterized polymeric materials. Complex architectures obtained by combination of anionic polymerization with other polymerization methods are not the subject of this review.

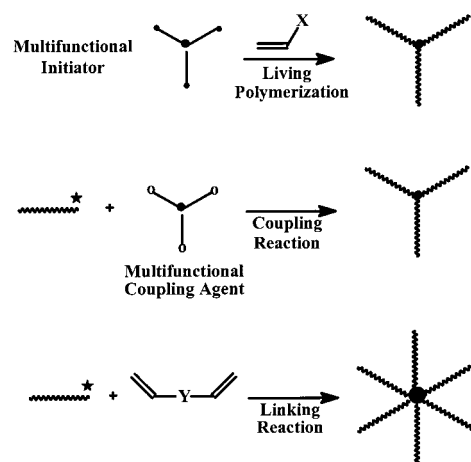
II. Star Polymers

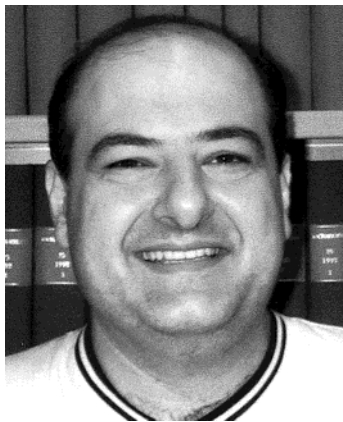
Star polymers are branched polymers consisting of several linear chains linked to a central core. The synthesis of star polymers has been the subject of numerous studies since the discovery of living anionic polymerization.^{7–10}

A. General Methods for the Synthesis of Star Polymers

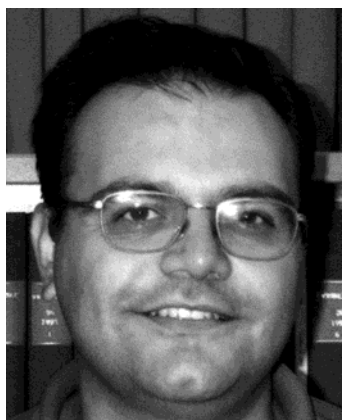
Three general synthetic methods have been developed, as outlined in Scheme 1:

Scheme 1





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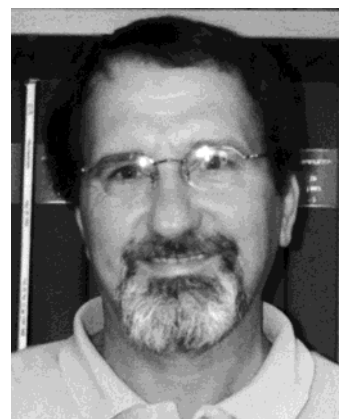


Stergios Pispas received his B.Sc. and Ph.D. from the University of Athens, Greece, in 1989 and 1994, respectively. He did postdoctoral research at the University of Alabama at Birmingham, with Prof. J. W. Mays (1994–1995). He has been a Research Associate at the University of Athens since 1997 and a Visiting Researcher at the National Hellenic Research Foundation of Greece since 2001. He has enjoyed being a Visiting Scientist at the following facilities: Foundation for Research and Technology, Greece (November 1990); University of Alabama at Birmingham (August–September 1992 and September–October 1993); Max Plank Institute for Polymer Science, Germany (February 1994); University of Massachusetts at Amherst (July–September 1995); IBM Almaden Research Center (October 1995); Foundation for Research and Technology, Greece (July 1998); and Institut de Chimie des Surfaces et Interfaces-CNRS, France (November 2000). In 1995, he received the American Institute of Chemists Foundation Award for Distinguished Postdoctoral Research. He has published 48 papers in refereed scientific journals and made 33 announcements at international scientific conferences.

Use of Multifunctional Initiators. In this method, multifunctional organometallic compounds that are capable of simultaneously initiating the polymerization of several branches are used in order to form a star polymer. 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



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Nikos Hadjichristidis received his B.Sc. from the University of Athens, Greece, in 1966, his Ph.D. from the University of Liège, Belgium, in 1971, and his D.Sc. from the University of Athens, Greece in 1978. He did postdoctoral research at the University of Liège with Professor V. Desreux (1971–1972) and National Research Council of Canada with Dr. J. Roovers (1972–1973). His career at the University of Athens has included being Lecturer (1973), Assistant Professor (1982), Associate Professor (1985), Full Professor (1988), Director of Industrial Chemistry Laboratory (since 1994), and Chairman of the Chemistry Department (1991–1995 and since 1999). His travels include the following: Visiting Scientist, University of Liège (Summers 1974, 1975); Visiting Research Officer, NRC of Canada (Summer 1976); Visiting Scientist, University of Akron, at Dr. L. Fetters' Laboratory (Summers 1977 through 1982); Distinguished Visiting Scientist, NRC of Canada (1983); Visiting Professor, Exxon Research and Engineering Co., NJ (since 1984, every year for 1–2 months). His further accomplishments include being President of the European Polymer Federation (1995–1996), a member of the National Advisory Research Council (since 1994), President of the State Highest Chemical Board (since 1995), and Director of the Institute of "Organic and Pharmaceutical Chemistry" of the National Hellenic Research Foundation (2000–2001). He has received the Academy of Athens Award for Chemistry (1989), the Empirikion Award for Sciences (1994), and the Greek Chemists Association Award (2000). He has published more than 220 papers in refereed scientific journals.

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.

Use of Multifunctional Linking Agents. This method involves the synthesis of living macroanionic chains and their subsequent reaction with a multifunctional electrophile, which acts as the linking agent. It is the most efficient way to synthesize well-defined star polymers, because there can be absolute control in all the synthetic steps. The functionality of the linking agent determines the number of the branches of the star polymer, provided that the linking reaction is quantitative. The living arms can be isolated and characterized independently along with the final star product. Consequently, the functionality of the star can be measured directly and with accuracy. Disadvantages of the method can be considered the sometimes long time required for the linking reaction and the need to perform fractionation in order to obtain the pure star polymer, since in almost all cases a small excess of the living arm is used in order to ensure complete linking.

Use of Difunctional Monomers. In this method a living polymer precursor is used as initiator for the polymerization of a small amount of a suitable difunctional monomer, such as divinylbenzene (DVB) or ethyleneglycol dimethacrylate (EGDM).^{3,11,12} Microgel nodules of tightly cross-linked polymer are formed upon the polymerization. These nodules serve as the branch point from which the arms emanate. The functionality of the stars prepared by this method can be determined by molecular weight measurements on the arms and the star product, but it is very difficult to predict and control the number of arms. The number of branches incorporated in the star structure is influenced by many parameters. The most important is the molar ratio of the difunctional monomer over the living polymer. The functionality of the star increases by increasing this ratio. Other parameters that influence the number of branches are the chemical nature (polystyrene, polydiene etc.), the concentration and the molecular weight of the living polymer chain, the temperature and the time of the reaction, the rate of stirring, the composition of the isomers in the case of DVB (ratio of *m*, *o*, and *p* isomers), etc. Another disadvantage of this procedure is that the final products are characterized by a distribution in the number of the arms incorporated into the star structure. Consequently, the number of the arms determined experimentally by molecular weight measurements is an average value. It is obvious that although this method is technologically very important and can be applied on an industrial scale, it is less suitable for the preparation of well-defined stars.

Recent advances in all three methodologies developed for the synthesis of star polymers will be presented in the following sections.

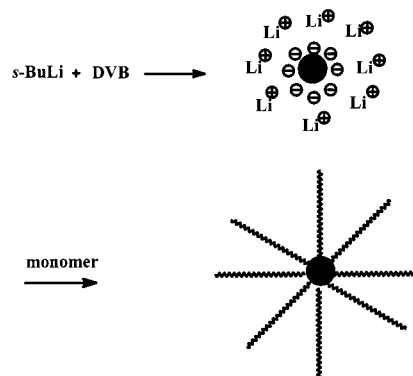
1. Multifunctional Initiators.

The use of DVB as a multifunctional initiator was initially demonstrated by Burchard et al.^{13,14} and was later developed by Rempp and his collaborators.^{15,16} DVB was polymerized by butyllithium in benzene at

high dilution to obtain a stable microgel suspension. These microgels, which were covered by living anionic sites, were subsequently used as multifunctional initiators to polymerize styrene, isoprene, or butadiene. A slight variation was adopted by Funke.^{17,18} The polymerization of DVB was initiated by living poly(*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.

Rempp et al. synthesized poly(*tert*-butyl acrylate)¹⁶ (PtBuA) and poly(ethylene oxide)¹⁹ (PEO) stars, according to Scheme 2.

Scheme 2

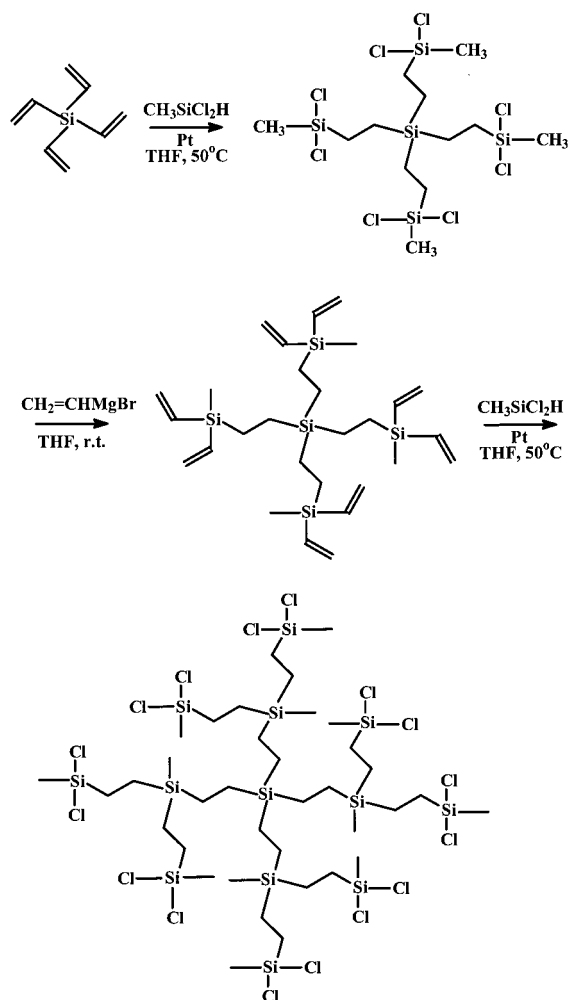


The synthesis of the PtBuA stars was performed in the polar solvent tetrahydrofuran (THF) to minimize the strong association effects, using naphthalene lithium to polymerize the DVB. DVB polymerization was initiated by electron-transfer instead of by addition. The polymerization of the tBuA was carried out at $-55\text{ }^{\circ}\text{C}$ in the presence of LiCl and 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 [DVB]:[Li⁺] should vary between 1.5 and 2.5 to obtain a stable microgel suspension. The molecular weight of the branch cannot be measured directly but can be calculated from the ratio of the monomer consumed during the polymerization over the total Li concentration. The products were characterized by size exclusion chromatography (SEC) and light scattering (LS). The results showed the existence of broad molecular weight distributions and even multimodal peaks. The formation of a rather small amount of aggregates was obtained in most cases. It was removed by filtration or centrifugation. The molecular characteristics of the final products and the calculated molecular weight of the branches revealed the existence of large numbers of arms, ranging from 22 to 1300.

For the synthesis of the PEO stars, potassium naphthalene was used to generate the multifunctional initiator. The molar ratio [DVB]:[K⁺] was less than 3 in all cases. The functionalities of the stars, as determined by LS measurements, were also rather large, ranging from 5 to 219.

Alternatively, PEO stars were synthesized using cumylpotassium to polymerize DVB and thus prepare the polyfunctional initiator.²⁰ The products exhibited

Scheme 3



a large distribution of functionalities and molecular weights.

The polyfunctional initiator method provides the possibility to prepare end-functionalized stars by deactivating the living branches by suitable electrophilic terminating agents. Polystyrene (PS) and PEO stars having end hydroxyl groups were prepared by this method.^{15,19}

Another approach was proposed by Lutz et al.^{21,22} *m*-Diisopropenylbenzene (DIB) was polymerized anionically under such conditions that the second double bond remained unaffected. Linear polymers having molecular weights between 3000 and 10 000 and pendent double bonds were prepared. The remaining double bonds were reacted with cumylpotassium to create active sites along the PDIB chain. The polymerization of ethylene oxide was initiated from these active sites to produce PEO stars.

PEO stars having 4, 8, and 16 arms were prepared using hydroxy-functionalized carbosilane dendrimers of several generations.²³ 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 Scheme 3. The end groups were converted to hydroxy groups and were activated using potassium naphthalene. The polymerization of

ethylene oxide was initiated by these active sites. The final products had narrow molecular weight distributions and were characterized by SEC, viscometry, NMR spectroscopy, static light scattering (SLS), and dynamic light scattering (DLS). The results of these methods confirmed the preparation of well-defined star polymers. The tedious preparation of the dendrimer core molecules is the only drawback of this method.

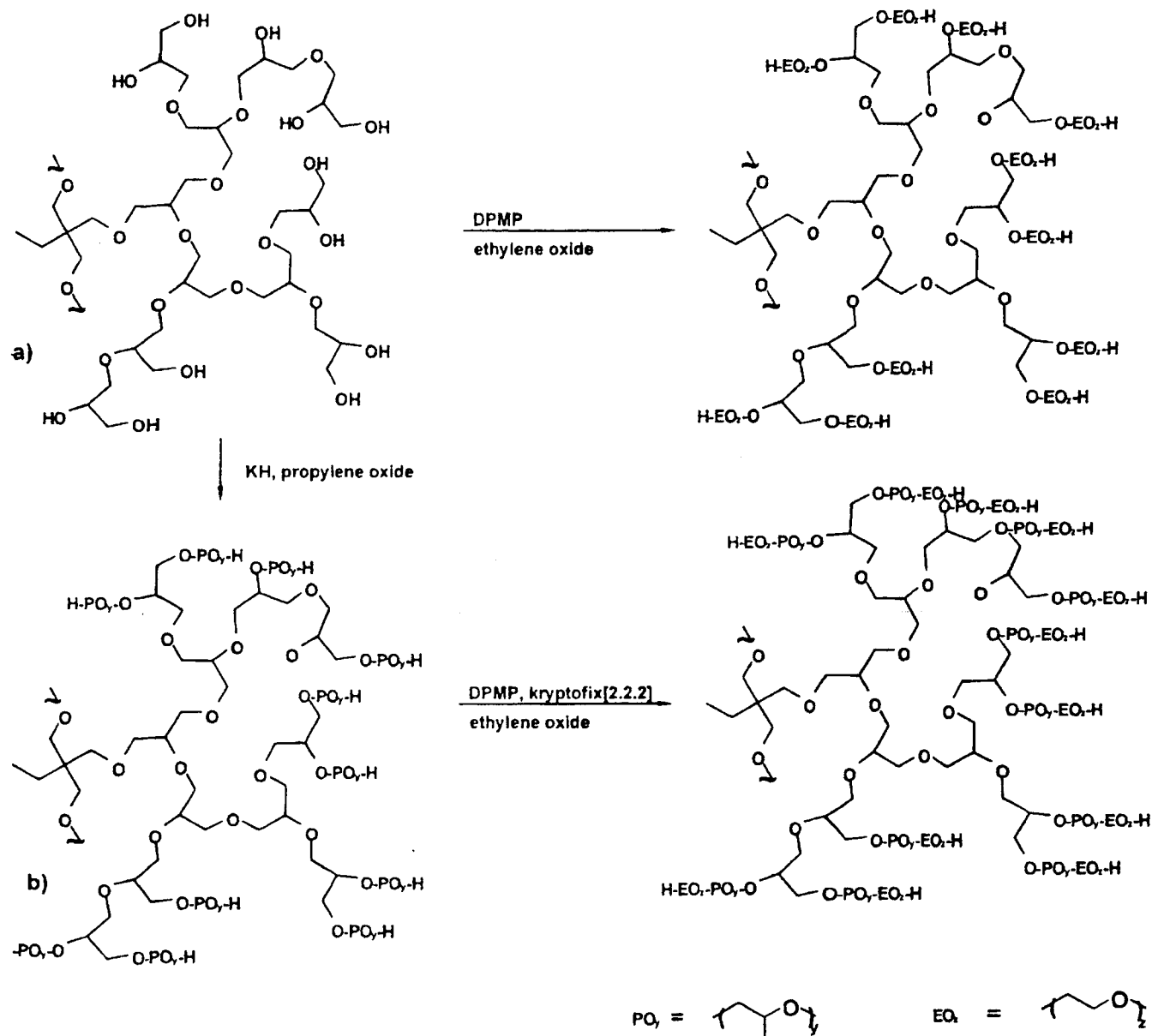
Hyperbranched polyglycerol and polyglycerol modified with short poly(propylene oxide) chains, activated with diphenylmethylpotassium (DPMP), were employed as multifunctional initiators for the synthesis of PEO stars,²⁴ as depicted in Scheme 4. Hyperbranched polyglycerol was found to be an unsuitable 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. These products were characterized by SEC coupled to a multiangle laser light scattering detector, as well as by NMR spectroscopy and differential scanning calorimetry. 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.

A novel hydrocarbon-soluble trifunctional initiator was proposed by Quirk et al.²⁵ It was prepared by the reaction of 3 mol of *sec*-butyllithium (*s*-BuLi) with 1,3,5-tris(1-phenylethenyl)benzene (tri-DPE), as presented in Scheme 5. This initiator was found to be efficient for the polymerization of styrene only when THF was also added in the reaction mixture ([THF]:[*s*-BuLi] = 20). The polymerization reaction was monitored by UV-vis spectroscopy. 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 and the fact that a minimum arm molecular weight around 6×10^3 is required for a successful synthesis. For arm molecular weights lower than this limit, incomplete initiation was observed. If these requirements are fulfilled, well-defined three-arm polystyrene stars can be prepared.

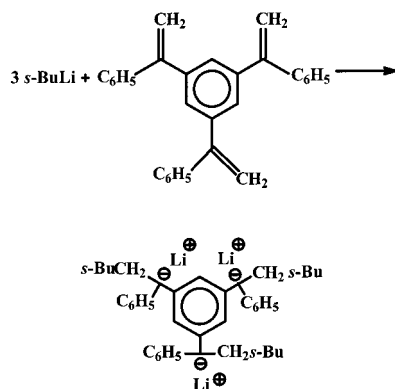
The same initiator was also used to produce a three-arm PBd star.²⁶ Complete monomer consumption was observed, but SEC analysis showed a bimodal distribution. This behavior was attributed to the strong association effects of the trifunctional initiator in a nonpolar solvent. The problem was overcome when *s*-BuOLi was added in the reaction mixture in a ratio [*s*-BuLi]:[*s*-BuOLi] = 2. *s*-BuOLi was shown to be capable of disrupting the initiator association without affecting appreciably the microstructure of the PBd chains. Therefore, a well-defined star polymer with low molecular weight distribution was obtained.

Polyolithiated carbosilane dendrimers were also employed as multifunctional initiators for the polymerization of styrene, ethylene oxide, and hexamethylcyclotrisiloxane (D₃),²⁷ according to Scheme 6. The dendrimers had 16 or 32 allyl groups at their periphery. A hydrosilylation route was performed to

Scheme 4



Scheme 5



react half of these terminal allyl groups with di-decylmethylsilane. 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 hydrocarbon solvents and were subsequently used

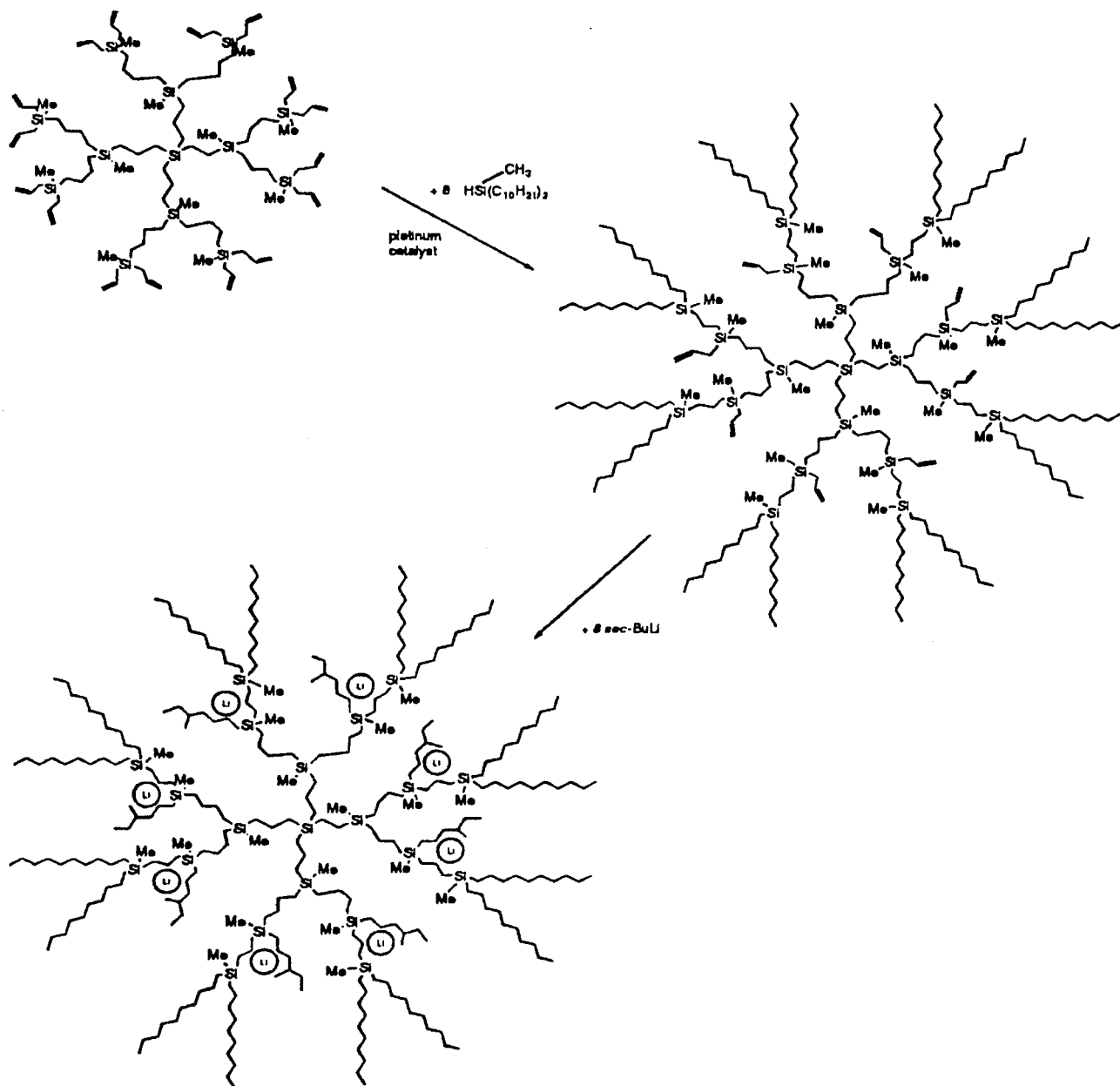
for the polymerization of St, EO, and D₃ under suitable conditions. SEC analysis showed the existence of monomodal peaks. However, molecular characterization data were not provided in this study and the number of branches for these stars was not determined, thus leaving uncertain the formation of the desired structures.

2. Multifunctional Linking Agents

The most general and useful method for the synthesis of star polymers by anionic polymerization is the linking reaction of the living polymers with a suitable electrophilic reagent. Several linking agents have been used for the synthesis of star polymers.⁷ The most important of those are the chlorosilanes²⁸ and the chloromethyl or bromomethyl benzene derivatives.^{29,30}

The linking reactions of living polymers with the chlorosilanes proceed without any side reactions. However, the efficiency of the linking reaction de-

Scheme 6



depends on the steric requirements of the linking agent and the living macromolecular chain end. The linking efficiency can be improved by separating the Si–Cl groups by spacers, such as methylene groups, and/or by end-capping the living chains with a few units of butadiene in order to reduce the steric hindrance and facilitate the linking reaction. Under these conditions, well-defined stars have been prepared with functionalities ranging from 3 up to 18.^{31–37} Recent advances in the synthesis of pure carbosilane dendrimers led to the preparation of linking agents with functionalities as high as 128.³⁸ These dendrimers were successfully used for the synthesis of PBd stars having 32, 64, and 128 branches.^{39,40} The products were characterized by SEC, membrane osmometry (MO), vapor pressure osmometry (VPO), and LS, and their dilute solution properties were extensively studied in the framework of several theoretical models. Low molecular weight distribution polymers having functionalities close to the

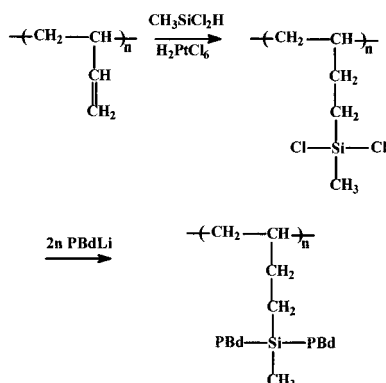
theoretical value were obtained in all cases. However, extended periods of time were needed for complete linking reactions, and fractionation was required to eliminate excess arm (purposely added) and low molecular weight impurities.

The validity of the chlorosilane linking agents for the synthesis of star polymers was reevaluated recently using NMR⁴¹ and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS)⁴² techniques. Polyisoprene (PI) and polybutadiene (PBd) stars having low arm molecular weights ($M \sim 10^3$) and functionalities ranging between 3 and 64 were prepared. It was observed that for stars having 16 or less arms, the structural quality with respect to the polydispersity and the functionality agrees very well with the theoretical values. For stars having theoretically 32 and 64 arms, the average functionalities of the chlorosilane linking agent was found to be 31 and 60, respectively, whereas the number of arms of the

stars were 29 and 54, respectively. Both the linking agents and the star products had narrow molecular weight distributions. These results clearly demonstrate the steric requirements of this linking reaction.

This method was extended to the synthesis of PBd stars having more than 200 arms.⁴³ Low molecular weight linear and star poly(1,2-butadiene) with 18 arms was extensively hydrosilylated with methylchlorosilane and used as linking agents to prepare multiarm PBd stars, as shown in Scheme 7. The

Scheme 7

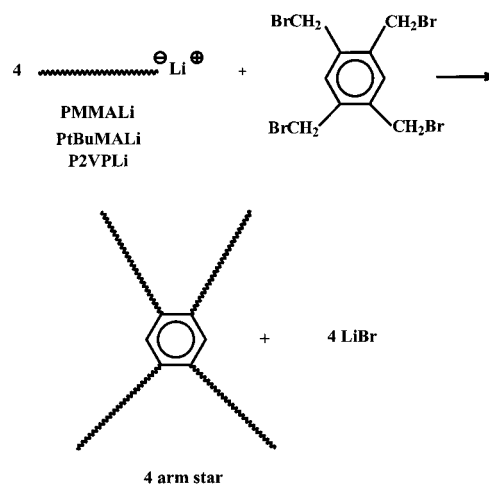


synthesis is similar to the one used for the preparation of graft polymers, but the low backbone molecular weight makes them behave as starlike structures. Star polymers having 270 and 200 arms were finally prepared from the linear and the 18-arm star poly(1,2-butadiene), respectively. These products are characterized by a distribution in the number of arms, due to the lack of absolute control over the hydrosilylation reaction. However, this arm number distribution was rather low, as was found by SEC-LALLS measurements.

Another important class of linking agents are the chloromethyl and bromomethyl benzene derivatives.^{29,30} The major drawbacks are that the use of these compounds is accompanied by side reactions such as lithium-halogen exchange, and linking agents with functionalities only up to 6 have been used.⁷ Nevertheless, these compounds are valuable for the synthesis of poly(meth)acrylates and poly(2-vinylpyridine) (P2VP) stars, since they can be used efficiently at $-78\text{ }^{\circ}\text{C}$, where the polymerization of these polar monomers takes place. The chlorosilanes cannot be used because the linking reaction either does not proceed at these low temperatures or leads to unstable products.

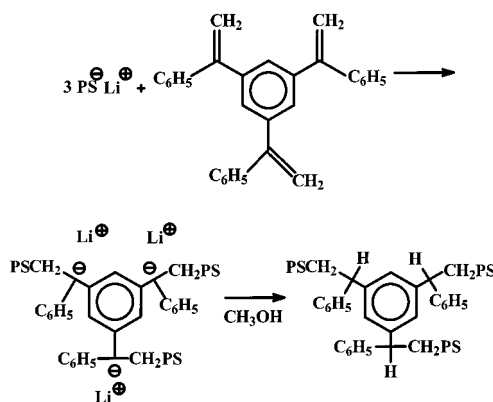
Hogen-Esch and Toreki reported the synthesis of three-arm P2VP stars using 1,3,5-tri(chloromethyl)benzene.⁴⁴ Only SEC and viscometry data were provided in this study. Mays et al. extended this work with the synthesis of four-arm stars having poly(*tert*-butyl methacrylate) (PtBuMA), poly(methyl methacrylate) (PMMA), and P2VP branches⁴⁵ (Scheme 8). 1,2,4,5-Tetra(bromomethyl)benzene was used as the linking agent. Combined characterization results by SEC and MO revealed the formation of well-defined star polymers. The use of bromo derivatives and the low temperatures under which the linking was conducted prevented the formation of byproducts.

Scheme 8

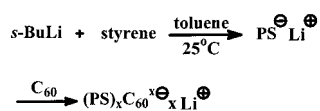


1,3,5-Tris(1-phenylethenyl)benzene was used by Quirk and Tsai as a linking agent for the synthesis of a three-arm PS star,²⁵ as shown in Scheme 9. SEC, MO, and LS results showed that a well-defined star was prepared by this procedure. Despite the fact that the arm molecular weight used was rather low ($M_n = 8.5 \times 10^3$), 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).²⁸

Scheme 9

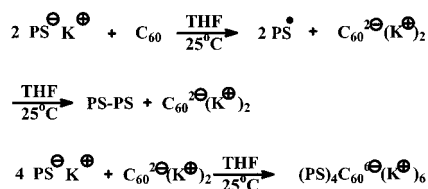


Soon after the discovery of fullerenes, efforts were made to use C_{60} as a coupling agent for the preparation of star polymers. Samulski et al.⁴⁶ reported the reaction of living polystyryllithium with C_{60} , and later Ederle and Mathis extended this work, providing mechanistic aspects on this reaction in different solvents.⁴⁷ In the nonpolar solvent toluene, it was found that by using an excess of living PSLi chains over the C_{60} a six-arm star can be prepared by addition of the carbanions onto the double bonds of the fullerene (Scheme 10). A similar behavior was observed when living polyisoprenyllithium was used for the coupling reaction. However, when the living PS chains were end-capped with one unit of DPE, only the three-arm star was produced, showing that the functionality of the product can be adjusted by

Scheme 10

changing the steric hindrance of the living chain end. The functionality could be also controlled by the stoichiometry of the reaction between the living polymers and the C₆₀. However, it was impossible to selectively incorporate one or two chains per C₆₀ molecule.

In polar solvents, such as THF a different situation was observed. During the reaction of a living polystyrylpotassium with C₆₀ in THF, a two-electron transfer was initially observed followed by the addition of four chains, according to Scheme 11. When the living PS chain was end-capped with 2-vinylpyridyl or 1,1-diphenylethyl groups, the number of the linked chains was reduced to 3 and 0, respectively, showing that both the reactivity and the bulkiness of the end group play an important role in this reaction.

Scheme 11**3. Use of Difunctional Monomers**

Several star polymers have been prepared by reacting living polymers with DVB. The method has been applied in the past for the synthesis of PS^{48,49} and polydiene⁵⁰ stars. Rather narrow molecular weight distribution PS stars were obtained when the [DVB]:[PSLi] ratio was varied from 5.5 to 30 and the corresponding functionality was between 13 and 39. Similar behavior was obtained for polydiene stars when the [DVB]:[PDLi] ratio was from 5 to 6.5 and the functionality of the star was varied between 9 and 13. In other cases, broad distributions were observed, caused by the large distribution of the functionalities of the stars prepared by this method.

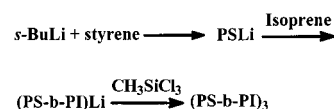
More recently, PMMA stars were prepared by reacting living PMMA chains with ethylene glycol dimethacrylate (EGDM).⁵¹ The polymers were characterized by SEC, LS, and viscometry. It was found that well-defined polymers can be prepared when the arm molecular weight was rather high (e.g. $M_w = 40\,000$). It seems that this high molecular weight is necessary to prevent intercore and gelation reactions from taking place.

EGDM was also reacted with isotactic living PMMA chains obtained using *tert*-butylmagnesium bromide as initiator in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene.⁵² A star polymer with a number of arms estimated between 20 and 30 was synthesized. SEC connected with LS and viscometry detectors was used to characterize the sample. Similar reaction using syndiotactic living PMMA chains, obtained with the initiator system *t*-BuLi/R₃Al, failed to give star

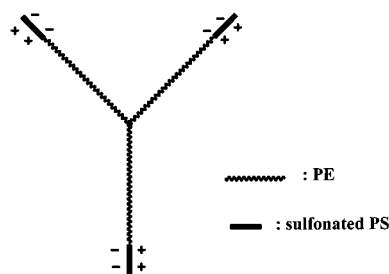
polymers. However, when EGDM was replaced by the butane-1,4-diol dimethacrylate, a PMMA star was obtained having 50–120 arms.

B. Star-Block Copolymers

Star-block copolymers are star polymers in which each arm is a diblock (or a triblock) copolymer. They can be prepared by all the methods reported earlier. The best way involves the linking reaction of a living diblock copolymer, prepared by sequential anionic polymerization of the two monomers, with a suitable linking agent. Using this method and chlorosilane linking agents, Fetters and collaborators synthesized star-block copolymers (PS-*b*-PI)_{*n*}, where *n* = 4, 8, 12, 18.^{53,54} An example is given in Scheme 12. Well-defined structures of low polydispersities were obtained.

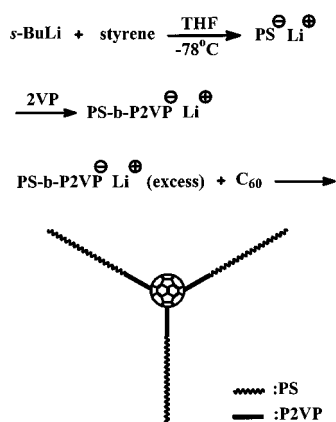
Scheme 12

Using the same method Storey et al. prepared ionic star-block copolymers.^{55,56} Styrene was oligomerized followed by the polymerization of butadiene. The living diblock copolymer was subsequently linked with methyltrichlorosilane to provide a three-arm star-block copolymer of styrene and butadiene. Hydrogenation of the diene blocks and sulfonation of the styrene blocks produced the desired ionic star-block structure having ionic outer blocks and hydrophobic inner blocks, as depicted in Scheme 13.

Scheme 13

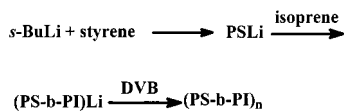
C₆₀ was also employed for the synthesis of star-block copolymers.⁴⁷ Living PS-*b*-P2VP diblocks, having short P2VP chains, were prepared by sequential anionic polymerization in THF. These living diblocks were reacted with a suspension of C₆₀ in THF, leading to the formation of a three-arm star-block copolymer (Scheme 14). The corresponding reaction with the living PS homopolymer results in the formation of a four-arm star. The lower reactivity of the 2VP anion seems responsible for this behavior. The SEC analysis showed that the product had a broad molecular weight distribution, indicating that a mixture of stars with different functionalities was obtained.

DVB was used to prepare a multifunctional initiator from which the polymerization of styrene was initiated, followed by the polymerization of ethylene oxide. Quite broad polydispersities were reported for these star-block copolymers, due to the random

Scheme 14

distribution of core sizes and functionalities.⁵⁷ Lithium naphthalene in the presence of lithium chloride was employed to form the multifunctional DVB cores. These cores initiated the polymerization of styrene at -40°C to produce the living PS stars. The living arms were end-capped with DPE to reduce their nucleophilicity and then were used to initiate the polymerization of *t*BuA at -55°C . Finally, methanol was added to deactivate the living diblock branches.¹⁶ The functionality of the stars was reported to range from 190 to 320. The molecular weight distributions were broad and sometimes multimodal. (PS-*b*-P2VP)_{*n*} star block copolymers, having P2VP interior blocks, were also prepared by the same method.⁵⁸

Living PS-*b*-PI diblock anions were reacted with a small amount of DVB in benzene to form star-block copolymers⁵⁹ (Scheme 15). The molar ratio of DVB

Scheme 15

to diblock anions ranged from 3.6 to 15.4, resulting in star functionalities ranging from 15.6 to 91.5. Narrow molecular weight distributions were obtained except in one case, where the distribution was bimodal.

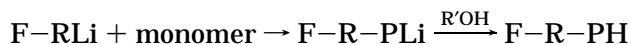
Star-block copolymers were also prepared by Teyssié et al.⁶⁰ from the reaction of living diblock copolymers with EGDM. (PS-*b*-PtBuA)_{*n*} and (PMMA-*b*-PtBuA)_{*n*} were synthesized by this method. The polydispersity of the stars was rather narrow but slightly increased compared to the parent diblocks, meaning that a distribution of functionalities existed in the final products. Only SEC was used to characterize the polymers.

C. Functionalized Stars

The introduction of functional groups at the end(s) or along the polymer chain can produce new materials that can be used as models to study and manipulate fundamental phenomena in polymer science, such as association, adsorption, chain dynamics, and block copolymer morphology.^{61–65} The synthesis of end-functionalized polymers remains a challenging problem in polymer chemistry. Among the different

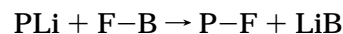
methods developed for the introduction of end-functional groups, anionic polymerization has been found to be a most valuable tool, since it proceeds without chain termination or chain transfer reactions.⁶⁶ There are two primary approaches to incorporate functional end groups:

Use of Functionalized Initiators.⁶⁷ This method can be described by the following reactions:



where F is the functional group and P the polymer chain. This procedure ensures complete functionalization, provided that the functional initiator produces narrow molecular weight distribution polymers with predictable molecular weights. The functional group should have low Lewis base character in order to maintain a low vinyl content in the polydiene. Another important parameter is that the functionalized initiator should be soluble in hydrocarbon solvents, in order to produce polydienes with low vinyl contents.

Use of Functionalized Terminating Agents.^{66,68} The living polymer is terminated with a functionalized electrophilic reagent, according to the reaction:



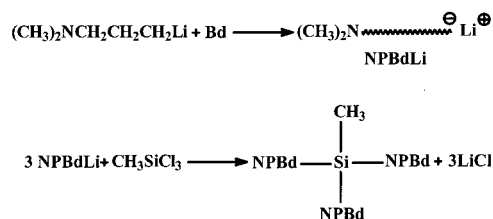
Care should be taken in the choice of the suitable terminating agent, since this reaction can be subject to several side reactions, leading to incomplete functionalization.

The synthesis of functional polymers is not always a straightforward procedure, because of the competition or antagonism of functional groups with the active living ends. Therefore, several protective groups have been used to mask reactive functionality.⁶⁸

These methods have also been employed for the synthesis of functionalized star polymers. Recent applications will be presented in the following sections.

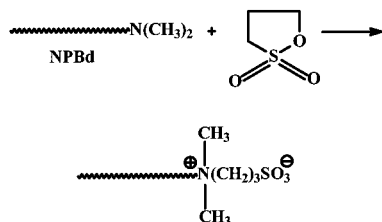
1. Functionalized Initiators

The polymerization of a monomer with a functionalized initiator followed by the reaction of the living chains with a suitable linking agent results in the formation of well-defined star polymers. Fetters et al.⁶⁹ prepared 3- and 12-arm star polyisoprenes (3N-PI and 12N-PI), end-functionalized with dimethylamine end groups, by reacting living PI chains, produced with 3-dimethylaminopropyl lithium (DMAPLi) and the appropriate chlorosilane linking agent. The same initiator was later employed for the synthesis of three-arm PBd stars (3N-PBd)⁷⁰ according to Scheme 16. The initiator is soluble in benzene and

Scheme 16

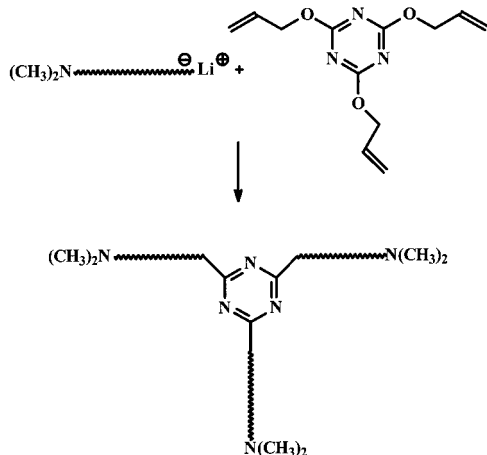
produces polydienes with low vinyl contents. It is also an efficient initiator for the polymerization of dienes, meaning that the rate of initiation is faster than the rate of propagation and the initiator is totally consumed during the initiation step.⁷¹ Polydienes with predictable molecular weights and narrow molecular weight distributions were prepared using this initiator. SEC, MO, and LS results showed that well-defined structures were obtained. The dimethylamine end groups were later transformed to sulfobetaine groups by reaction with 1,3-cyclopropane sultone (Scheme 17).

Scheme 17



DMAPLi was also used by Burchard to synthesize three-arm PS stars (3N-PS) having dimethylamine end groups.⁷² In this case 1,3,5-triallyloxy-2,4,6-triazine was the linking agent, as shown in Scheme 18.

Scheme 18

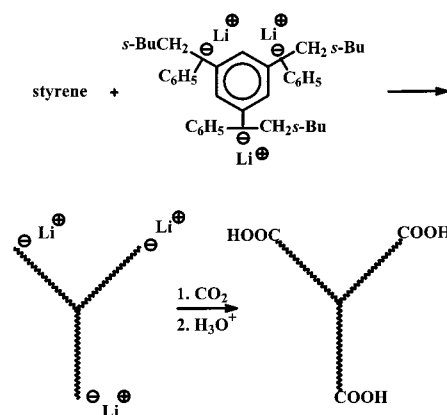


An acetal-protected lithium initiator was used to polymerize styrene followed by linking with 1,3,5-triallyloxy-2,4,6-triazine to produce three-arm star polystyrenes.⁷³ The protective acetal group was cleaved by weak acidic treatment in THF to give star polymers with terminal OH groups. These functional groups were coupled with toluene-2,4-diisocyanate to give randomly cross-linked products. Unfortunately, few characterization data were provided in this study.

2. Functionalized Terminating Agents

This functionalization method can be applied for the synthesis of star polymers only when a multifunctional initiator is used. The living branches emanate from the core and therefore can be subjected to several terminating reactions with suitable electrophilic reagents.

Scheme 19

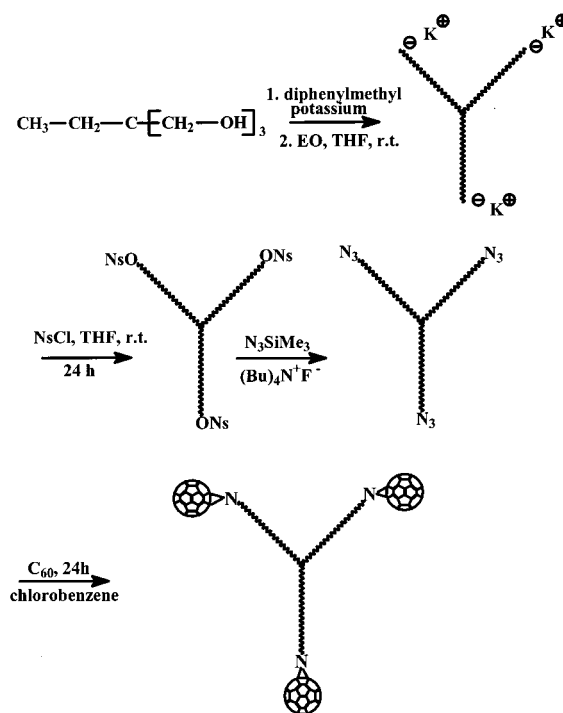


Multifunctional DVB initiators were used to polymerize styrene, and the living arms were subsequently reacted with ethylene oxide to produce PS chains with terminal hydroxyl groups.⁵⁷

The trifunctional initiator produced by the reaction of 3 mol of *s*-BuLi with 1,3,5-tris(1-phenylethenyl)benzene was also employed for the synthesis of an end-functionalized polystyrene star.²⁵ After the polymerization was completed, the living star polymer was carboxylated by the introduction of gaseous carbon dioxide (Scheme 19). End-group titration indicated that the star had 2.8 functional groups per molecule. However, SEC analysis revealed the existence of an appreciable amount of side high molecular weight products. The situation was not improved, even after end-capping the living branches with DPE units prior to the carboxylation reaction. It was shown that it is more successful to perform the carboxylation reaction with the freeze-dried living polymer solution. In this case the amount of byproducts was lower than 2%.

Three-arm PEO stars having terminal C_{60} groups⁷⁴ were prepared by the procedure given in Scheme 20.

Scheme 20



1,1,1-Tris(hydroxymethyl)propane treated with diphenylmethyl potassium (DPMP) was employed as a trifunctional initiator to produce a living three-arm PEO star. The living arms were reacted with 4-nitrobenzenesulfonyl chloride to transform the alkoxides to nosylate functionalities. The success of this procedure was evaluated by IR and NMR spectroscopies. The nosylated (Ns) PEO star was subjected to an azidation reaction using tetrabutylammonium fluoride and trimethylsilyl azide. The triazide PEO was then allowed to react with C₆₀ to produce the final functionalized star. IR, NMR, and SEC analysis revealed the formation of well-defined functionalized stars.

D. Asymmetric Stars

Asymmetric stars are a special class of stars that is characterized by an asymmetry factor compared to the classical symmetric structures described previously. The following parameters have been considered as asymmetry factors:

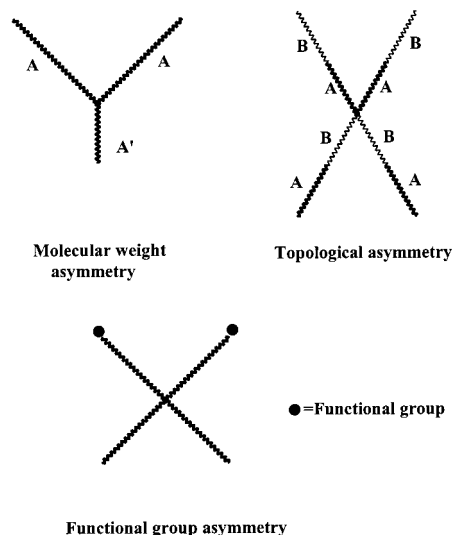
Molecular Weight Asymmetry. All the arms of the star are identical in chemical nature, but they have different molecular weights.

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.

These structures are schematically shown in Scheme 21. The synthesis of asymmetric stars can be accomplished by the same general methods reported for the symmetric stars but in such way that a controlled incorporation of the arms, differing in molecular weight, end functional groups, or topology is achieved. Efficient methods for the synthesis of asymmetric star polymers were developed only recently.

Scheme 21



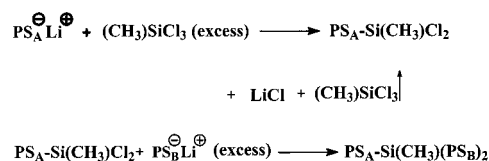
1. Molecular Weight Asymmetry

i. Chlorosilane Method. The chlorosilane method was initially reported by Fetters⁷⁵ and was later

developed by Hadjichristidis, Mays, and collaborators.^{88–91} Chlorosilanes are used as linking agents for the stepwise replacement of the chlorine atoms by the polymer chains. This procedure can be achieved taking into account the different reactivity of the living polymer ends toward the Si–Cl bond, as this is determined by the steric hindrance effects, the charge localization on the terminal carbon atom,⁷ and the excluded volume of the living chain that is affected by the reaction solvent. The reactivity of the living chain end decreases by charge delocalization and by increasing the steric hindrance. The latter can be affected by both structures, that of the living chain end and the chlorosilane linking agent. The steric hindrance concerning the living end increases in the order $\text{BdLi} < \text{IsLi} < \text{SLi} < \text{DPELi}$. The closer the Si–Cl groups in the linking agent, the more sterically hindered is the reaction with the living chains. For example, overall SiCl_4 is less reactive than $\text{Cl}_2\text{Si}-\text{CH}_2-\text{CH}_2-\text{SiCl}_2$. The reactivity is also influenced by other parameters such as the molecular weight of the living chain, the polarity of the solvent, where the reaction takes place, and the temperature. When all these factors are optimized, well-defined products are produced. However, the disadvantage of this method is that it is time-consuming and requires elaborate high-vacuum techniques to be performed.

The method was first applied to the synthesis of asymmetric PS stars having two arms of equal molecular weights (PS_B) and a third one (PS_A) having molecular weight either half or twice that of the identical arms.⁷⁵ The procedure, given in Scheme 22,

Scheme 22



involves the reaction of the living arm PS_ALi with a 10-fold excess of methyltrichlorosilane for the preparation of the methylchlorosilane end-capped 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 is observed.

After freeze-drying the end-capped PS_A branch, the excess silane was removed under high vacuum by heating the resulting porous material at 50 °C for at least 3 days. After the silane was removed the end-capped polymer was dissolved in benzene, which was introduced directly by distillation from the vacuum line.

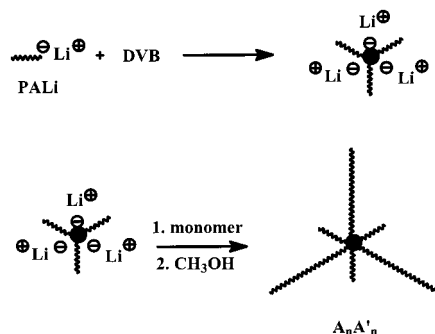
The two remaining Si–Cl bonds of the methylchlorosilane end-capped PS_A arm were then reacted with a small excess of living PS_BLi chains. The PS_BLi chains were end-capped with a few units of butadiene to facilitate the completion of the linking reaction.

The excess of the PS_B arm was removed by fractionation. Detailed characterization results by SEC, MO, and LS revealed that well-defined structures were obtained.

The method was also applied in the synthesis of asymmetric PBd^{75} and PI^{76} stars. When the molecular weight of the PI chain that was reacted with the excess silane was less than 5.5×10^3 , the formation of the coupled byproduct could not be avoided, due to the low steric hindrance of the living PI chain end. The byproduct was removed by fractionation. The stars were characterized by SEC, MO, and LS, showing that the desired structures having low polydispersities were efficiently prepared.

ii. Divinylbenzene Method. As already discussed, when appropriate living polymer chains react with a small amount of DVB, a star polymer is formed consisting of a highly cross-linked polydivinylbenzene core from which the arms emanate. This is actually a living star since the core carries anionic centers. The number of these active sites is theoretically equal to the number of the arms of the star. Subsequent addition of a new monomer results in the growth of new arms from the core and therefore the formation of an asymmetric star of the type $A_nA'_n$ can be achieved, if the molecular weight of the original chains is different than that obtained by the chains formed in the second step. This general procedure is depicted in Scheme 23.

Scheme 23



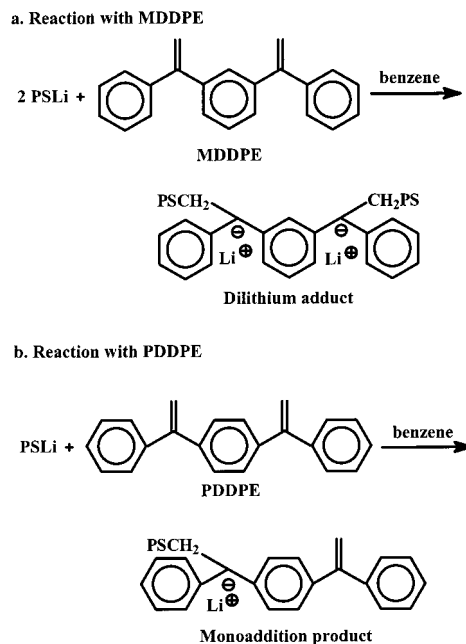
The drawbacks associated with this method have been already mentioned. Probably the most important is the architectural limitation, i.e., only asymmetric stars of the type $A_nA'_n$ can be prepared by this method. However, even these structures are not unambiguously characterized. A fraction of the living arms A is not incorporated in the star structure, probably due to steric hindrance effects. These living chains may act as initiators for the polymerization of the monomer that is added for the preparation of the asymmetric star. Another problem is that the active sites of the living A_n star are not equally accessible to the newly added A' monomers, due to steric hindrance effects. Furthermore, the rate of initiation is not the same for these active sites. For all these reasons, it is obvious that the final products are structurally ill-defined with a rather great dispersity of the n values and are characterized by broad molecular weight distributions. Nevertheless, this method is technically important, since it can be applied on an industrial scale and also provides the

possibility of preparing end-functionalized asymmetric stars after reaction of the growing living branches A' with suitable electrophilic compounds.

Using this method asymmetric stars of the type $(PS_A)_n(PS_B)_n$ were prepared.⁷⁷ Living PS chains were obtained by *s*-BuLi initiation and reacted with a small amount of DVB to give a living star polymer. The anionic sites of the star core were subsequently used to initiate the polymerization of a new quantity of styrene. This initiation step was accelerated by the addition of a small quantity of THF. It was revealed by SEC analysis that high molecular weight species were also present, probably due to the formation of linked stars. These structures can be obtained when living anionic branches of one star react with the residual double bonds of the DVB-linked core of another star.

iii. Diphenylethylene Derivative Method. The method is based on the use of 1,1-diphenylethylene derivatives that are nonhomopolymerizable monomers. Rich chemistry was developed, leading to the formation of several types of asymmetric stars. Quirk reacted living PS chains with either 1,3-bis(1-phenylethenyl)benzene, (MDDPE) or 1,4-bis(1-phenylethenyl)benzene (PDDPE), according to Scheme 24.

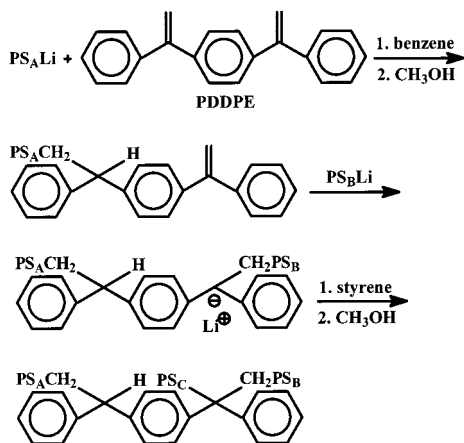
Scheme 24



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.^{7,26,78–80} This reaction was monitored by UV–visible spectroscopy. The analysis revealed that the stoichiometric addition of PSLi was quantitative. However, PDDPE exhibited less tendency to form the diadduct both in polar and nonpolar solvents. This behavior can be attributed to the better delocalization of the negative charge in the para than in the meta isomer. Mainly, low molecular weight polystyrenes have been used for these studies.

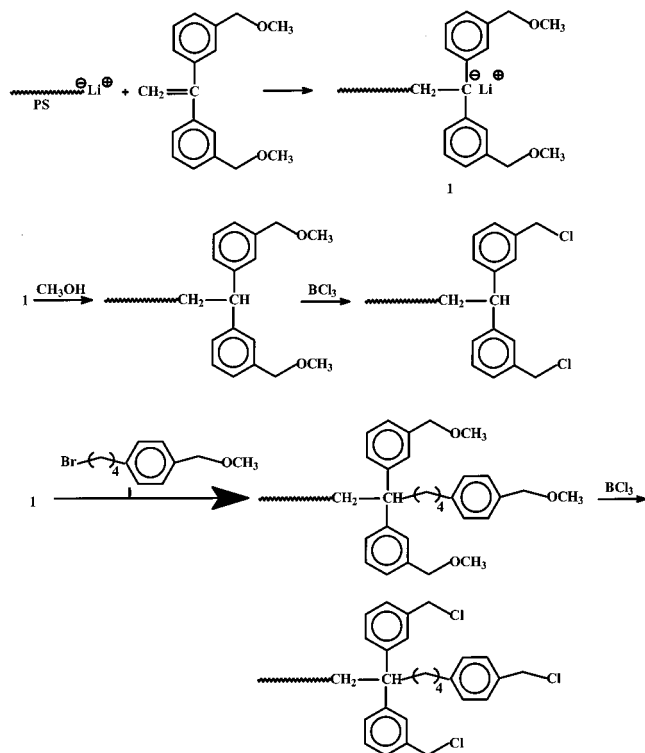
Taking into account the above observation, a three-arm asymmetric PS star was successfully prepared⁸¹

Scheme 25

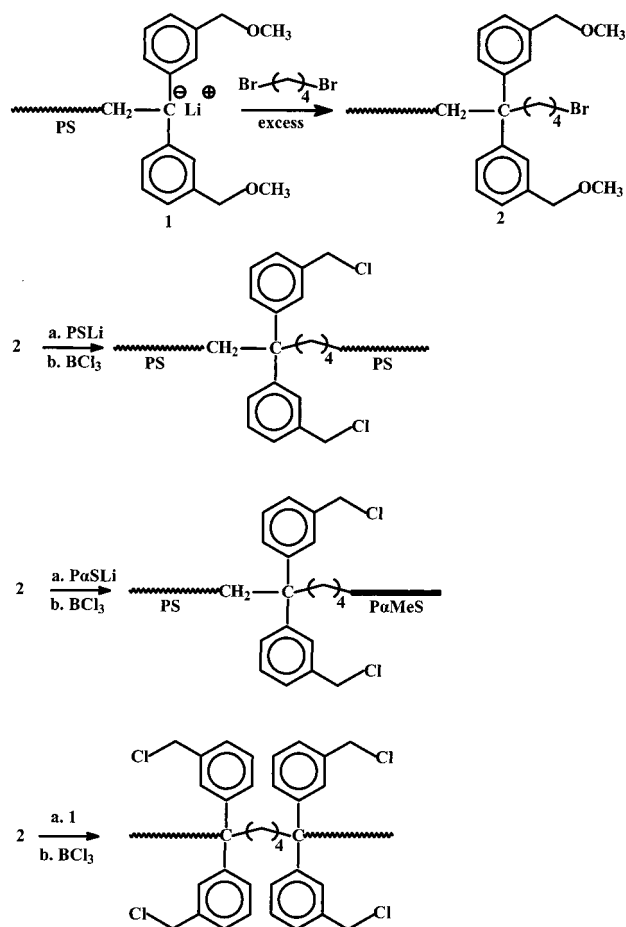


(Scheme 25). The monoadduct product was reacted with a second polystyryllithium chain, having different molecular weight, to form the coupled product. The efficiency of this coupling reaction depends on the control of the stoichiometry between the reactants. Under optimum conditions the efficiency of the coupling reaction can be higher than 96%. Finally, the addition of styrene leads to the formation of the product. 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 PS homopolymer product and the second arm of the monoadduct, 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.

Scheme 26



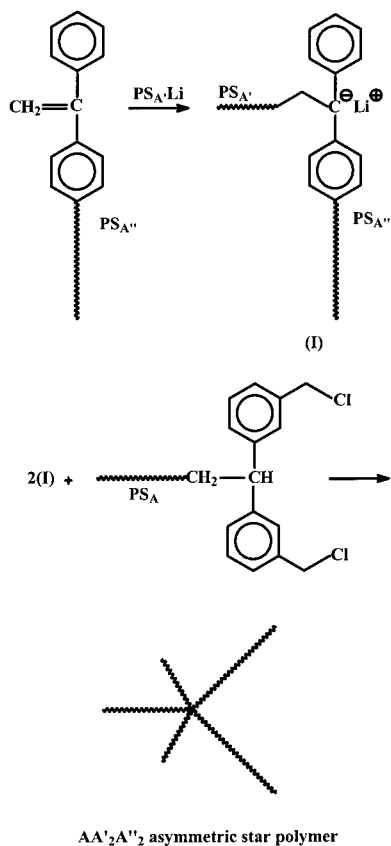
Scheme 27



More recently Hirao developed a general method employing DPE derivatives carrying protected chloromethyl groups.^{82–86} PS asymmetric stars of the types AA'₂, AA'₂A''₂, AA'₃, AA'₄, AA'A''₂, and AA'₄A''₄ were prepared by this method. The whole procedure is based on the reaction sequence shown in Scheme 26. Living PS was reacted with 1,1-bis(3-methoxymethylphenyl)ethylene followed by transformation of the methoxymethyl groups to chloromethyl groups using BCl₃ in CH₂Cl₂ at 0 °C for 10–30 min. Prior to the reaction with the BCl₃, the living end-functionalized PS is able to react with other compounds such as 1-(4'-bromobutyl)-4-methoxymethylbenzene as shown in Scheme 26. 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 can 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.

More complicated in-chain functionalized structures with two or four chloromethyl groups were prepared according to Scheme 27.⁸² The living end-functionalized PS with two methoxymethyl groups was reacted with a 10-fold excess of 1,4-dibromobutane to introduce a bromobutyl end group. The terminal bromobutyl group was subsequently coupled with living PS to afford a linear PS chain having two in-chain methoxymethylphenyl groups. These groups

Scheme 28

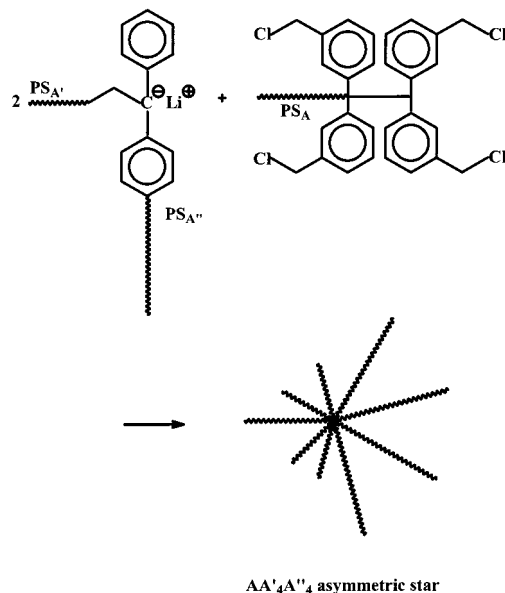


were transformed to chloromethyl groups. Alternatively, the terminal bromobutyl group can be reacted with another living end-functionalized PS with two methoxymethyl moieties, resulting in the synthesis of a linear PS chain having anywhere across the chain four functional chloromethyl groups, after performing the transformation reaction. If the four functions are required at the middle of the polymer chain, it is easier to couple a small excess of the living end-functionalized PS having two methoxymethyl moieties with 1,3-dibromobutane. Unreacted polymer from the coupling reactions was removed by HPLC fractionation.

These functionalized PS derivatives were used for the synthesis of complicated asymmetric star structures of the general type AA'₂, AA'₃, AA'₄, AA'A''₂, A₂A'₂, and AA'A''₄, where all the arms are polystyrenes having different molecular weights. The coupling reactions with living PS chains were not always complete, resulting in the formation of considerable amounts (up to 10%) of stars with lower functionalities. It was reported that side reactions such as Li-Cl exchange and single-electron transfer reactions take place to a certain extent. The formation of the byproducts was suppressed by end-capping the living PSLi chains with DPE. No steric hindrance problems were reported for these linking reactions. However, only low molecular weight arms were used for the synthesis of these asymmetric stars. It remains a question whether the use of high molecular weight arms will lead to the same success.

DPE-functionalized macromonomers were also used for linking reactions with living polymeric anions,

Scheme 29

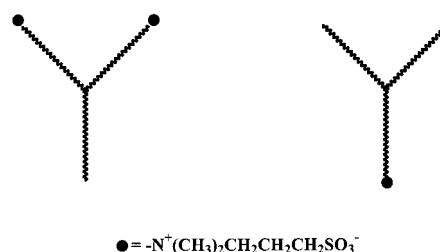


followed by the coupling with chloromethyl groups. Characteristic examples for the synthesis of AA'₂A''₂ and AA'₄A''₄ asymmetric star polymers are given in Schemes 28 and 29, respectively. Well-defined star polymers with rather low molecular weight branches were obtained with this method.

2. Functional Group Asymmetry

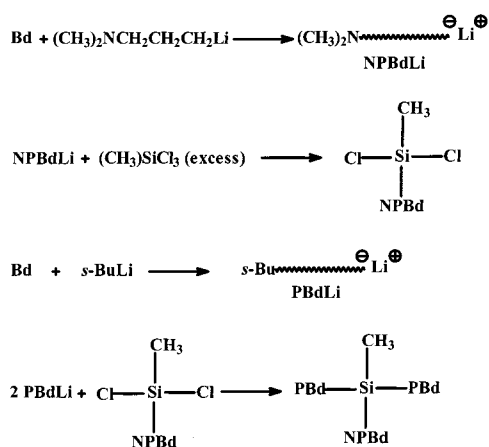
Several methods can be potentially used for the synthesis of functionalized symmetric stars. The chlorosilane method has been applied for the synthesis of three-arm PBd stars carrying one or two end-functional groups,⁷⁰ as shown in Scheme 30. The dimethylamino end groups were later transformed to sulfozwitterions by reaction with 1,3-propane sultone.

Scheme 30



The synthesis of three-arm stars with one end-standing dimethylamino group is given in Scheme 31. The functional initiator dimethylaminopropylolithium (DMAPLi) is used to polymerize butadiene. The living end-functionalized polymer is then reacted with a large excess of methyltrichlorosilane ($[\text{Si}-\text{Cl}]:[\text{C}-\text{Li}] = 100$) to produce the methyltrichlorosilane end-capped amine-functionalized PBd. The excess silane was removed on the vacuum line by continuous pumping for a few days, after the polymer was redissolved in benzene. Purified benzene was then introduced to dissolve the silane-capped arm. Finally, a slight excess of PBd living chains prepared by the nonfunctionalized initiator *s*-BuLi were reacted with

Scheme 31



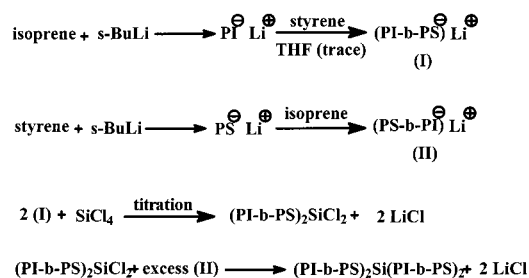
the macromolecular linking agent, giving the functionalized PBd star with one dimethylamine end group.

A similar procedure was followed for the synthesis of three-arm stars carrying two functional groups. The only difference is that the nonfunctionalized arm was prepared first and reacted with the excess methyltrichlorosilane followed, after the removal of the excess silane, with the addition of a small excess of the living functionalized arms. When the molecular weight of the living PBd arm was lower than 10 000, a considerable amount (10%) of coupling was observed during the reaction with the methyltrichlorosilane, due to the low steric hindrance of the living chain end. This amount was drastically suppressed when the arm was end-capped with a unit of DPE in the presence of THF to accelerate the crossover reaction. Well-defined products were obtained, as was evidenced by SEC, MO, and LS data.

3. Topological Asymmetry

A new star-block copolymer architecture, the inverse star-block copolymer, was recently reported.⁸⁷ These polymers are stars having four poly(styrene-*b*-isoprene) copolymers as arms. Two of these arms are connected to the star center by the polystyrene block, whereas the other two are connected through the polyisoprene block. The synthetic procedure is given in Scheme 32. The living diblocks (I) were prepared by anionic polymerization and sequential addition of monomers. A small quantity of THF was used to accelerate the initiation of the polymerization of styrene. The living diblock copolymer (I) was slowly added to a solution of SiCl_4 . The reaction was monitored by SEC on samples with-

Scheme 32



drawn from the reactor during the synthesis. The bulkiness of the living styryllithium chain end slows the incorporation of a third arm considerably. Only a minor quantity ($\sim 1\%$) of trimer was evidenced by SEC. The difunctional linking agent thus prepared was then reacted with a small excess of the living diblock copolymer (II) to produce the desired product. These living diblocks were end-capped with three or four units of butadiene to facilitate the linking reaction. Detailed characterization results by SEC, MO, LS, differential refractometry, and NMR spectroscopy revealed the formation of well-defined products.

E. Miktoarm Star Polymers

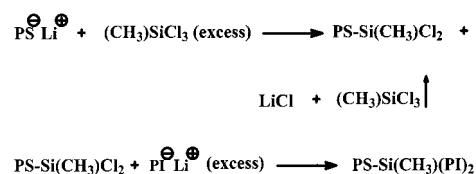
The term miktoarm (from the greek word $\mu\kappa\tau\acute{o}\varsigma$, meaning mixed), or heteroarm star polymers, refers to stars consisting of chemically different arms. In the past decade considerable effort has been made toward the synthesis of miktoarm stars, when it was realized that these structures exhibit very interesting properties.⁸⁸⁻⁹⁰ The synthesis of the miktoarm star polymers can be accomplished by methods similar to those reported for the synthesis of asymmetric stars. The chlorosilane, DVB, and DPE derivative methods have been successfully employed in this case. Furthermore, several other individual methods have appeared in the literature. The most common examples of miktoarm stars are the A_2B , A_3B , A_2B_2 , A_nB_n ($n > 2$) and ABC types. Other less common structures, like the ABCD, AB_5 , and AB_2C_2 are now also available.

1. Chlorosilane Method

i. A_2B Miktoarm Star Copolymers. A near monodisperse miktoarm star copolymer of the A_2B type was first reported by Mays,⁹¹ A being PI and B PS. The synthetic method adopted was similar to the one applied by Fetters for the synthesis of the asymmetric PS and PBd 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 excess silane was removed and then a slight excess of the living PI chains was added to produce the miktoarm star $\text{PS}(\text{PI})_2$. Excess PI was then removed by fractionation. The reaction sequence, given in Scheme 33 was monitored by SEC, and the molecular characterization of the arms and the final product was performed by MO.

This method was later extended by Iatrou and Hadjichristidis⁹² to the synthesis of the A_2B stars, where A and B were all possible combinations of PS, PI, and PBd. In this case a more sophisticated high-

Scheme 33

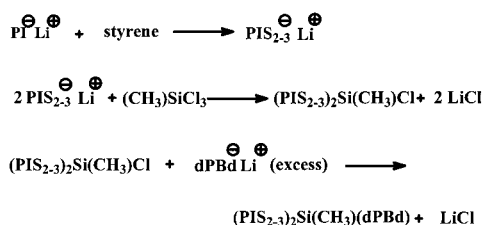


vacuum technique was employed to ensure the formation of products that are characterized by high degrees of chemical and compositional homogeneity. This was tested using several techniques such as SEC, MO, LS, differential refractometry, and NMR spectroscopy.

In a more recent study, a series of (d-PS)(PI)₂ stars, where d-PS is deuterated PS, was prepared by the same technique.⁹³ No difference was observed by using the deuterated arm compared to the PS(PI)₂ stars. A similar study concerning the synthesis of (d-PBd)-(PBd)₂ stars containing a deuterated PBd arm was also reported.⁹⁴ Both kinds of arms have almost the same molecular weight, and consequently, the only difference was that one of them was labeled with deuterium.

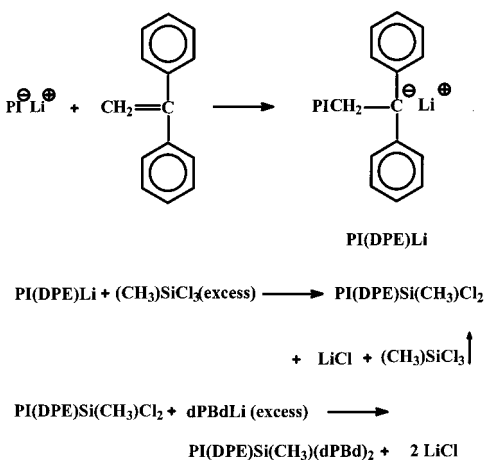
Miktoarm stars of the type (d-PBd)(PI)₂ and PI(d-PBd)₂ were synthesized according to the reaction Schemes 34 and 35, respectively.⁹⁵ A different ap-

Scheme 34



proach was adopted for the synthesis of the (d-PBd)-(PI)₂ star. Instead of incorporating the different arm first (d-PBd in this case), the two living PI chains were reacted with methyltrichlorosilane in a stoichiometric ratio of 2:1. To avoid the formation of the three-arm PI star, the living PI chains were end-capped with a few units of styrene to increase the steric hindrance of the living end. In the case of the PI(d-PBd)₂ star, the more common procedure was adopted. The living PI arm was reacted first with the linking agent. Due to the low molecular weight of the PI chain and the reduced steric hindrance of its living end, the polymer was end-capped with one unit of DPE. This method proved to be efficient to avoid the formation of coupled byproducts. Well-defined stars were obtained in both cases, as revealed by extensive molecular characterization results. In the final step

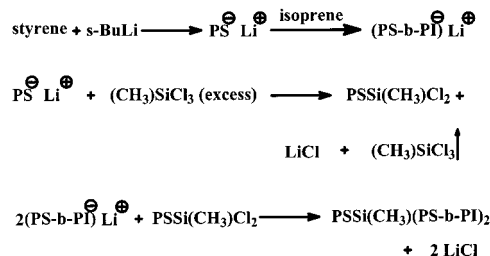
Scheme 35



the polymers were hydrogenated, transforming the PI branches to poly(ethylene-*alt*-propylene) and the d-PBd to partially deuterated polyethylene.

Miktoarm stars of the general type B(A-*b*-B)₂, where A is PI and B is PS, were prepared,⁹⁶ according to Scheme 36. The living PI arm was reacted with

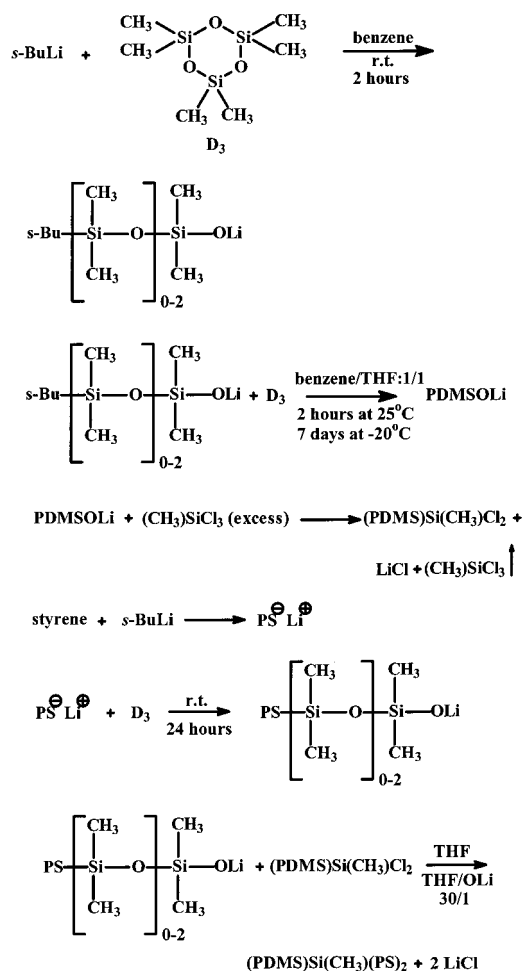
Scheme 36



an excess of the linking agent to give the dichloro end-capped macromolecular linking agent followed, after the removal of the excess silane, by the addition of the living diblock copolymer PS-*b*-PILi. The characterization data showed that polymers of high chemical and compositional homogeneity were formed.

Very recently the development of the controlled anionic polymerization of hexamethylcyclotrisiloxane (D₃) led to the synthesis of a PDMS(PS)₂ miktoarm star,⁹⁷ according to Scheme 37. A benzene:THF (50:50 v/v) solution of the living PDMS arm was added

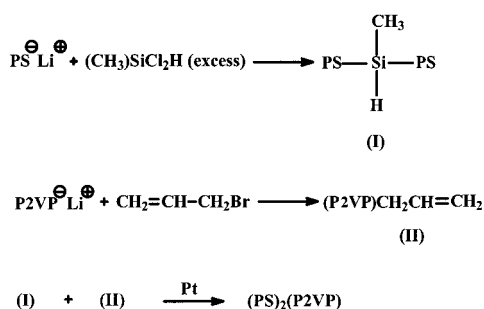
Scheme 37



slowly into a large excess of methyltrichlorosilane, leading to the formation of the monoadduct product. The macromolecular linking reagent thus formed was then reacted with living PS chains that were previously end-capped with D_3 . This capping reaction was necessary to avoid the backbiting side reactions of the very reactive PSLi anion to the PDMS arm and to facilitate the linking. THF was also added to accelerate the linking reaction.

A different approach was adopted by Eisenberg et al.⁹⁸ for the synthesis of P2VP(PS)₂ miktoarm stars, where P2VP is poly(2-vinylpyridine). Methylchlorosilane (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 (Scheme 38). Rather high molecular weight distribu-

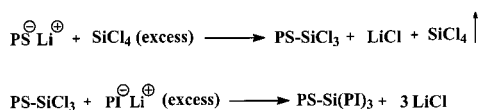
Scheme 38



tions ($M_w/M_n = 1.33-1.50$) 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.

ii. A₃B Miktoarm Star Copolymers. The method employed for the synthesis of the A₂B miktoarm stars can be expanded to the synthesis of A₃B structures using silicon tetrachloride ($SiCl_4$) instead of methyltrichlorosilane as the linking agent. Living PS chains were reacted with an excess of $SiCl_4$ to produce the trichlorosilane end-capped PS. After evaporation of the excess silane, the macromolecular linking agent was added to a solution containing a small excess of living PI chains to give the desired PSPI₃ star.⁹⁹ The reaction sequence, shown in Scheme 39, was monitored by SEC. Well-defined polymers with narrow molecular weight distribution were obtained.

Scheme 39



The same procedure was recently applied for the synthesis of four-arm PBd stars, where all the arms had the same molecular weight but one of them was

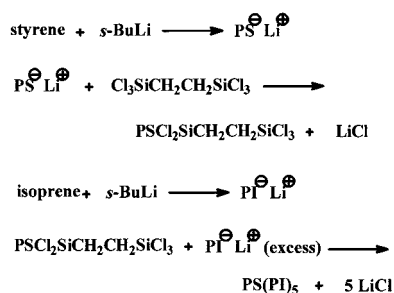
deuterated [(d-PBd)(PBd)₃].⁹⁴ The product was studied by SEC, MO, and LS.

As in the case of the B(A-*b*-B)₂ stars, the B(A-*b*-B)₃ structures were also prepared, A being PI and B being PS.⁹⁶ $SiCl_4$ was the linking agent in that case, and well-defined polymers were also obtained.

A different strategy was applied by Tsiang for the synthesis of (A-*b*-B)₃ stars, where A is PS and B is PBd.¹⁰⁰ The living chains B were reacted with the $SiCl_4$ in a molar ratio 3:1, followed by the addition of the living A-*b*-B chains. However, the control of the first step was rather limited, since not only the desired B₃SiCl but also the byproducts B₂SiCl₄ and B₄Si were formed. This behavior was observed due to the absence of steric hindrance of the living PBd chain end. It is obvious that this method is very demanding regarding the stoichiometric control of the reagents. It seems more appropriate in this case to incorporate the living A-*b*-B arm first and then to add the other three arms.

iii. A_nB (*n* > 3) Miktoarm Star Copolymers. The synthesis of PSPI₅ miktoarm stars¹⁰¹ was accomplished by the reaction sequence outlined in Scheme 40. Living PS was reacted with the hexafunc-

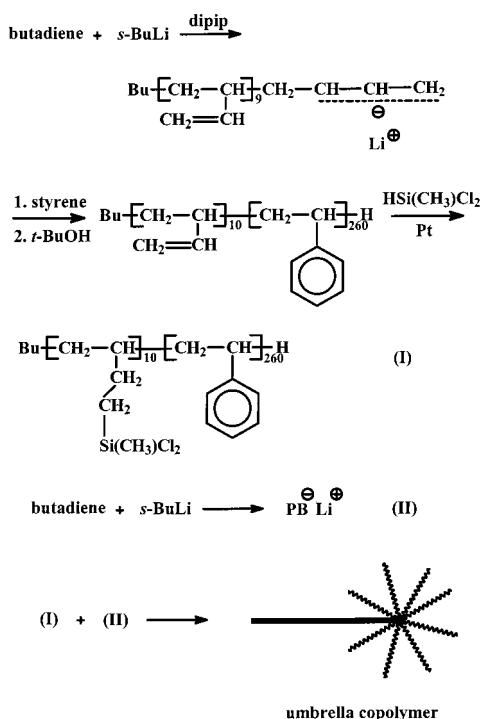
Scheme 40



tional chlorosilane 1,2-bis(trichlorosilyl)ethane in a ratio [C-Li]:[Si-Cl] = 1:6. Dropwise addition of the living polymer solution into the vigorously stirred solution of the linking agent was performed to link only one PS arm per chlorosilane molecule. However, even with these precautions the local excesses of the living polymer could not be completely avoided, leading to the formation of the coupled byproduct (~10% by SEC analysis). The macromolecular pentachlorosilane linking agent was then reacted with a small excess of the living PI chains to produce the final structure. Careful fractionation was performed to remove the excess PI and the (PS)₂(PI)₄ byproduct formed during the synthesis. The stoichiometric reaction between the living PS chains and the linking agent was chosen instead of an excess of the silane, since this high molecular weight chlorosilane is not volatile (mp ~26 °C) and its excess can only be removed by fractional precipitation, a process that is difficult to perform under vacuum. Despite these difficulties, narrow molecular weight distribution products characterized by compositional and chemical homogeneity were obtained.

More complicated structures of the general type AB_{*n*}, called umbrella copolymers, were synthesized by Roovers et al.^{102,103} using the procedure shown in Scheme 41. This name was given due to the relatively high molecular weight of the A compared to the B

Scheme 41

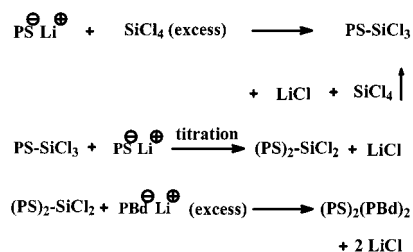


arms. Butadiene was oligomerized in the presence of dipiperidinoethane, followed by the polymerization of styrene. A block copolymer having a PS block and a short 1,2-PBd tail was thus prepared. The side double bonds of the 1,2-PBd units were hydrosilylated using $\text{HSi}(\text{CH}_3)_2\text{Cl}$ or $\text{HSi}(\text{CH}_3)\text{Cl}_2$ in the presence of a suitable platinum catalyst. Subsequent addition of living 1,4-PBdLi or P2VPK chains led to the formation of the umbrella stars. It is obvious that the number of the B branches is actually an average value and cannot be predicted by this method, since there is no absolute control over the hydrosilylation reaction and the short 1,2 PBd ends have a wider molecular weight distribution. However, this procedure offers the possibility to prepare complicated structures having interesting properties.

iv. A_nB_n ($n \geq 2$) Miktoarm Star Copolymers.

The most common type of polymers in this category is the A_2B_2 type of miktoarm star copolymers. The synthesis of the PS_2PBd_2 stars was accomplished by Iatrou and Hadjichristidis¹⁰⁴ using the reaction sequence outlined in Scheme 42. The living PS chains reacted with a large excess of SiCl_4 , which is the linking agent to produce the trichlorosilane end-capped PS. The excess silane was evaporated on the vacuum line as described earlier. The second living PS arm was incorporated to the macromolecular

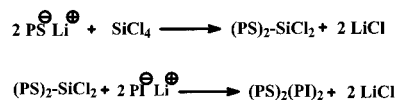
Scheme 42



linking agent PSSiCl_3 by a slow stoichiometric addition, called titration, to produce the dimer, PS_2SiCl_2 . This step was the most crucial of the synthesis and was monitored by SEC on samples withdrawn from the reactor. Finally, a small excess of living PBd chains was introduced to give the desired PS_2PBd_2 product. This method provides the best control over the steps of linking the various arms, but it is time-consuming and extreme care should be exercised, especially in the titration step.

PS_2PI_2 stars were prepared by Young et al.¹⁰⁵ using a different approach, shown in Scheme 43. Living PS

Scheme 43



chains were reacted with SiCl_4 in a molar ratio 2:1 for the formation of the two-arm product. The formation of the three-arm product is avoided by the increased steric hindrance of the living PS chain end. Subsequent addition of the living PI chains resulted in the formation of the desired miktoarm star. The control over the addition of the first two arms is not as absolute as in the previous method, but the procedure is faster and may lead to the formation of well-defined products.

The synthesis of the $(\text{PI})_2(\text{PBd})_2$ stars¹⁰⁶ was accomplished using the two different approaches presented above. The difficulty in this case is that both living PI and PBd chain ends are not sterically hindered, making the control of the incorporation of the first two arms more ambiguous. The problem was resolved by extending the living PI chains with a few units of styrene and then incorporating the PI chains in two consecutive steps (reaction with excess silane and then titration) and finally linking the two living PBd chains. A small quantity of THF was added to accelerate the capping reaction with styrene and ensure that all the PI chains are end-capped with styrene units. According to the second approach, the reactivity of the living PI chain ends was reduced by performing the linking stoichiometric reaction with the silane at -40°C for 3 days, followed by the addition of the living PBd arms at room temperature. Both approaches produced well-defined structures, as was evidenced by the extensive molecular weight characterization of the arms, the intermediate, and the final products.

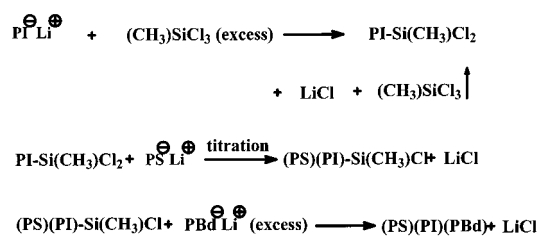
$(\text{PI})_2(\text{dPBd})_2$ stars were also prepared by the method developed by Iatrou and Hadjichristidis,⁹⁵ using deuterated butadiene. The final products were then hydrogenated, the PI arms being transformed to poly(ethylene-*alt*-propylene) and the dPBd arms to partially deuterated polyethylene.

The synthesis of the PS_8PI_8 miktoarm stars, also called Vergina star copolymers, was also reported.¹⁰⁷ A silane carrying eight Si-Cl₂ groups [$\text{Si}[\text{CH}_2\text{CH}_2\text{-Si}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2)_2]_4$] was used in this case as linking agent. The living PS chains were reacted with the linking agent in a molar ratio 8:1 for the synthesis of the eight-arm intermediate. The steric hindrance of the living PS chain ends prevents the

incorporation of more than one arm per SiCl₂ group, even if a 5% excess of PSLi is used. The characterization data of the purified PS₈(Si-Cl)₈ intermediate showed that the number of the PS arms was very close to the theoretical number. Subsequent addition of the living PI chains led to the formation of the PS₈PI₈ miktoarm star.

v. ABC Miktoarm Star Terpolymers. The synthesis of the (PS)(PI)(PBd) star terpolymer was accomplished by a method similar to the one developed for the synthesis of the PS₂PI₂ stars. Living PI chains reacted with a large excess of methyltrichlorosilane to produce the dichlorosilane end-capped polyisoprene. After the evaporation of the excess silane, the living PS arm was incorporated by a slow stoichiometric addition (titration). Samples were taken during the addition and were analyzed by SEC to monitor the progress of the reaction and determine the end point of the titration. When the formation of the intermediate product (PS)(PI)Si(CH₃)Cl was completed, a small excess of the living PBd chains was added to give the final product.¹⁰⁸ The reaction sequence is outlined in Scheme 44.

Scheme 44



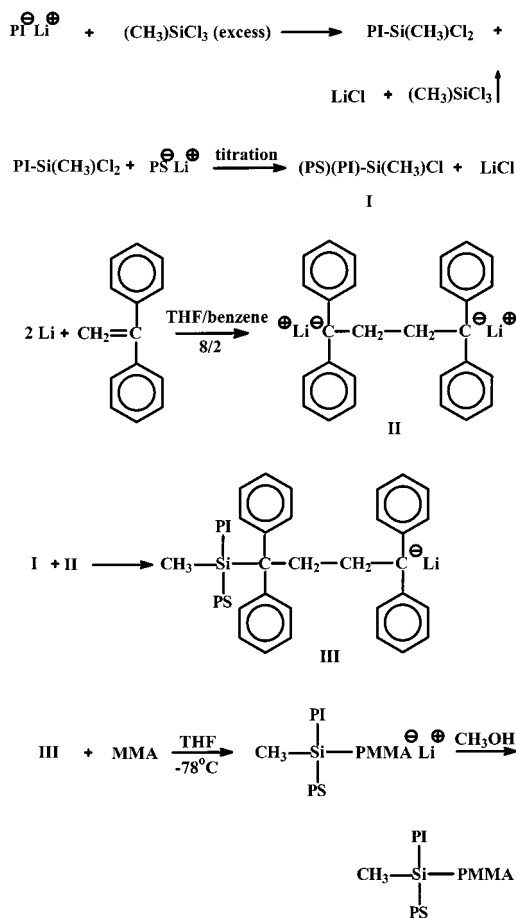
The order of linking of the various arms to the linking agent is crucial for the success of the synthesis. The less sterically hindered chain end, namely the PBdLi, has to be incorporated last, whereas the most sterically hindered, namely the PSLi, at the titration step. Extensive characterization data for the arms, the intermediate, and the final product confirmed that the ABC star was characterized by high structural and compositional homogeneity.

The same methodology was adopted for the synthesis of the (PS)(PI)(P2VP) miktoarm star terpolymer.¹⁰⁹ The monofunctional linking agent (PI)(PS)-Si(CH₃)Cl was synthesized in benzene solution. Benzene was then evaporated and the linking agent was dissolved in THF, followed by the addition of the living P2VPLi chains, prepared in THF at -78 °C. The linking was conducted at -78 °C to avoid side reactions with the living P2VP chains. Well-defined stars were prepared as shown by the extensive molecular weight characterization data given in this study.

A (PI)(PS)(PDMS) miktoarm star terpolymer was synthesized by the same method.⁹⁷ The (PI)(PS)Si(CH₃)Cl macromolecular linking agent was prepared as previously mentioned, followed by the addition of the living PDMSLi chains to give the desired product. Also in this case a well-defined polymer with narrow molecular weight distribution was obtained.

The same route was adopted for the synthesis of asymmetric AA'B star polymers.¹¹⁰ The two A arms were PIs having different molecular weights, and B

Scheme 45



was deuterated polystyrene (dPS). The higher molecular weight PI branch was introduced first, followed by the slow stoichiometric addition (titration) of the living dPS chains. The lower molecular weight PI branch was incorporated at the end of the procedure.

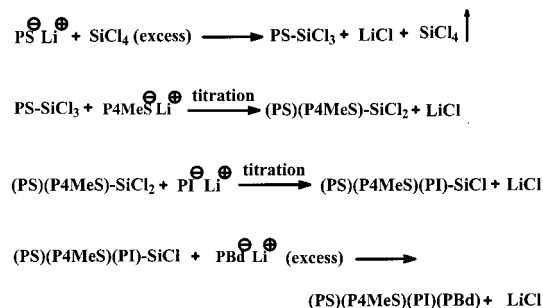
A different approach was employed for the synthesis of (PI)(PS)(PMMA) miktoarm star terpolymers,^{111,112} as outlined in Scheme 45. It is well-known that the reaction between living PMMA chains with Si-Cl bonds fails to give the linked product. Therefore, after the monofunctional macromolecular linking agent (PI)(PS)Si(CH₃)Cl was formed, it was reacted with a dilute solution containing a stoichiometric amount of a difunctional initiator, synthesized by the reaction between DPE and Li. According to this procedure, one of the active centers of the difunctional initiator was linked to the remaining Si-Cl bond, whereas the other one was used to initiate the polymerization of MMA, resulting in the formation of the desired product. It is obvious that the PMMA branches cannot be isolated and characterized independently. This method is very demanding, and extreme care has to be taken for the control of the different reaction steps. It was found that during the synthesis of the difunctional initiator a large amount of the monofunctional byproduct (as high as ~30%) was also obtained. This byproduct does not interfere with the synthesis of the ABC star, since it reacts with the macromolecular linking agent (PI)(PS)Si(CH₃)Cl to give the terminated PS-*b*-PI diblock,

which can be removed by fractionation. Nevertheless, it reduces the yield of the desired product and makes the control of its composition more difficult. Despite these difficulties, well-defined structures were obtained.

vi. ABCD Miktoarm Star Quaterpolymers.

Only one example of the synthesis of ABCD miktoarm star quaterpolymers is reported in the literature.¹⁰⁴ It consists of four different arms, PS, PI, PBd, and poly(4-methylstyrene) (P4MeS). A step by step incorporation of the branches was adopted in this case, as shown in Scheme 46. The synthetic proce-

Scheme 46



cedure involved two titration steps. Therefore, the order of linking of the different branches plays an essential role in controlling the reaction sequence. PS was chosen to react first with an excess of SiCl₄, followed after the evaporation of the excess silane by the slow stoichiometric addition of the living P4MeS chains in order to form the difunctional linking agent (PS)-(P4MeS)SiCl₂. A second titration step was then performed with the addition of the living PI chains to form the monofunctional linking agent (PS)-(P4MeS)(PI)SiCl. The fourth arm, namely PBdLi, was added in the last step to give the desired product. Complete linking was observed in all the reaction steps by SEC. Combined characterization results from several methods revealed that a well-defined star was produced.

2. Divinylbenzene Method

The DVB method can be applied for the synthesis of miktoarm stars of the type A_nB_n in a similar manner as in the case of the asymmetric A_nA'_n stars. It is a three-step procedure starting from the synthesis of the living chains A. These living chains initiate the polymerization of a small quantity of DVB, leading to the formation of a living star polymer carrying within its core a number of active sites equal to the number of arms that have contributed to its formation. During the third step, these active sites are used to polymerize the monomer B, thus producing the miktoarm star A_nB_n.

This method for the synthesis of miktoarm stars was first reported by Funke^{17,18} and then extended and improved by Rempp et al.¹⁰ In all cases published in the literature, the A arms are PS chains, whereas a variety of B chains has been used such as PtBuMA, PtBuA, PEO, P2VP, and PEMA^{58,113–115}. Special care was given to the synthesis of amphiphilic stars carrying both hydrophobic and either cationic or anionic branches. The polymerization of the sty-

rene was initiated with *s*-BuLi, except in the case of the PS_nPEO_n stars, where cumyl potassium was used. After the formation of the living PS star the SEC analysis showed that a considerable part (as high as 15%) of the PS chains was not incorporated in the star structure, mainly due to accidental deactivation. When the second monomer was a (meth)acrylate, the active sites were first capped with one unit of DPE to reduce their nucleophilicity. The final stars usually had *n* values between 4 and 20.

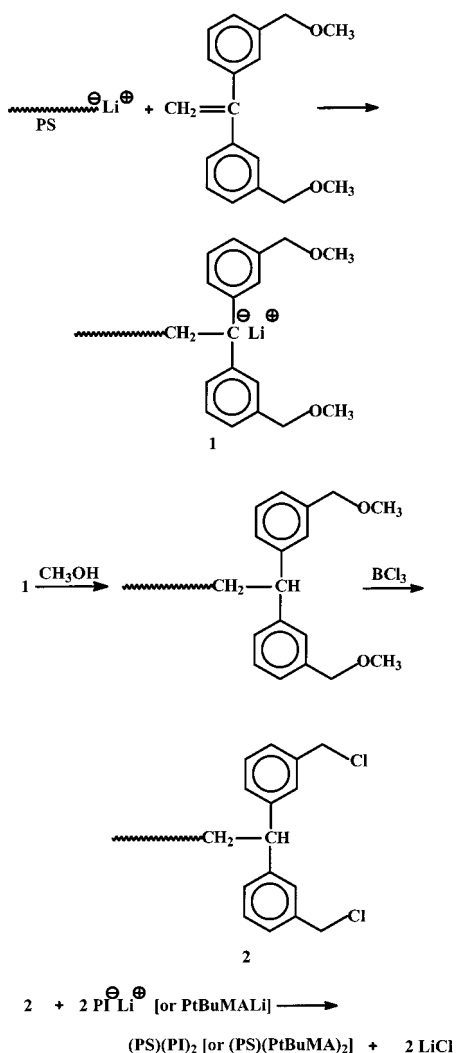
An important feature of this method is that the second-generation branches growing from the living core are living and therefore are susceptible to end-functionalization reactions or can be potentially used to initiate the polymerization of another monomer, leading to the formation of a A_n(B-*b*-C)_n structure. All the drawbacks of the method reported earlier in the discussion concerning the asymmetric stars and the use of DVB as a multifunctional initiator apply in this case as well. The poor control over the structural parameters (*n* values, composition, molecular weights of the B chains), the inability to independently characterize the B arms, and the existence of a distribution in the number of arms within the same sample indicate that the products have rather poor molecular and compositional homogeneity.

3. Diphenylethylene Derivative Method

The DPE derivative methods are based on the procedures developed by Quirk and Hirao, as was previously reported in the case of the asymmetric stars. The first procedure relies on the use of either 1,3-bis(1-phenylethenyl)benzene (MDDPE) or 1,4-bis(1-phenylethenyl)benzene (PDDPE), whereas the second relies on the formation of macromonomers carrying DPE end groups with methoxymethyl moieties that can be transformed to chloromethyl groups. Other specific methods have also been developed utilizing DPE derivatives for the synthesis of miktoarm stars. The discussion given in the case of the asymmetric stars concerning the advantages and limitations of the methods apply here as well. The recent achievements using this methodology will be presented in the following paragraphs.

i. A₂B Miktoarm Star Copolymers. A₂B miktoarm stars, where A is PS and B is PI or PtBuMA, were synthesized by Hirao et al.^{116,117} according to the reaction in Scheme 47. Living PS chains were reacted with a 1.2-fold excess of 1,1-[bis(3-methoxymethylphenyl)]ethylene in THF at -78 °C for 1 h. Only the monoadduct product was obtained under these conditions. The end-methoxymethyl groups were then transformed to chloromethyl moieties by reaction with BCl₃ in CH₂Cl₂ at 0 °C for 2 h. NMR studies showed that this transformation reaction goes to completion. The macromolecular linking agent was then carefully purified by repeated precipitation and freeze-drying from benzene solution and then reacted with living PILi or PtBuMALi chains to give the desired products. 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. SEC and NMR methods have been only used for the

Scheme 47



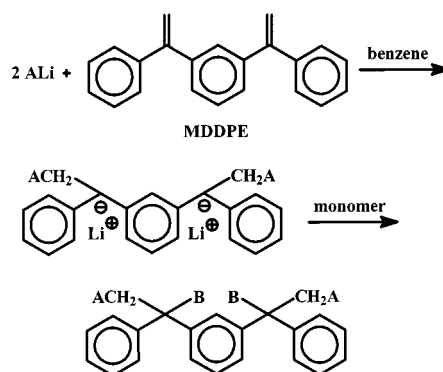
molecular characterization of these structures. Low molecular weight arms were employed to facilitate the NMR analysis.

ii. A₂B₂ Miktoarm Star Copolymers. The use of MDDPE for the synthesis of A₂B₂ type of miktoarm stars has been extensively investigated.²⁶ The method involves the reaction of the living A arms with MDDPE in a molar ratio 2:1, leading to the formation of the living dianionic coupled product. The active sites are subsequently used as initiator of another monomer to give the A₂B₂ structure, as shown in Scheme 48.

The coupling reaction of the living A chains can be monitored by UV-vis spectroscopy and SEC. This step can be very efficient, although careful control over the stoichiometry is needed. The efficiency of the coupling reaction is reduced on increasing the molecular weight of the arm. Only living PS chains have been successfully used for this coupling reaction. It was found that the poly(dienyl)lithium compounds are not reactive enough and the presence of Lewis bases is required in order to accelerate the coupling reaction. However, in this case the subsequent addition of another diene for further polymerization leads to polydienes exhibiting high vinyl contents.

The crossover reaction used to initiate the polymerization of the B monomers has to proceed in such

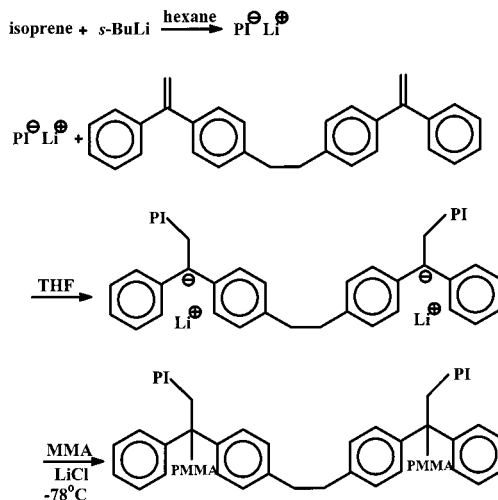
Scheme 48



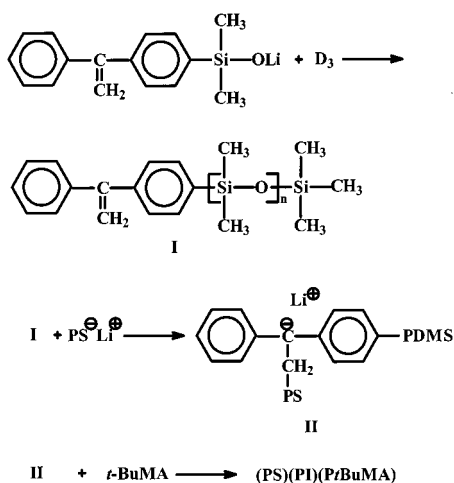
a way that the rate constants of the two active centers should be similar. Only in this way is the formation of uniform chains obtained. This result can only be achieved when a polar compound is added prior to the crossover reaction. It was found that among the different polar additives *s*-BuOLi does not appreciably affect the polydiene's microstructure. The growing B arms cannot be isolated and characterized independently. Miktoarm stars PS₂PI₂ and PS₂PbD₂ were prepared by this method.^{80,118} An advantage of this procedure is that the growing B chains are living, thus leaving the opportunity to introduce end-functional groups by reaction with a suitable electrophile or to continue the polymerization with the addition of another monomer. Taking advantage of this fact, the synthesis of the miktoarm star PS₂(PS-*b*-PbD)₂ was reported.¹¹⁹

A similar method was employed for the synthesis of PI₂PMMA₂ miktoarm stars,¹²⁰ shown in Scheme 49. 1,1-(1,2-Ethanediy)bis[4-(1-phenylethenyl)benzene] (EPEB) was used as the linking agent in this case. A solution of EPEB was slowly added to the solution of the living PI chains, leading to the formation of the coupled product. LiCl was then added and the polymerization of MMA was initiated at -78 °C to give the desired product. Unreacted PI chains formed by accidental deactivation during the coupling reaction were removed by fractionation. Molecular characterization data showed that well-defined stars were prepared by this method.

Scheme 49



Scheme 50

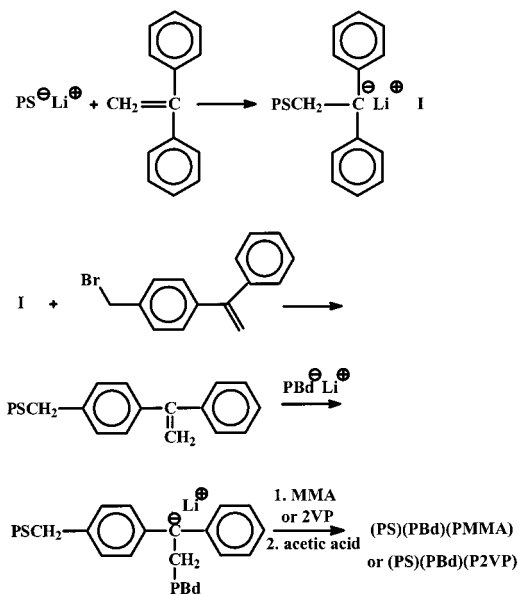


iii. ABC Miktoarm Star Terpolymers. Several approaches have been developed for the synthesis of ABC miktoarm star terpolymers. A (PS)(PDMS)-(PtBuMA) star was prepared¹²¹ according to the method shown in Scheme 50. The lithium salt of the *p*-(dimethylhydroxy)silyl- α -phenylstyrene was prepared and consequently used as initiator for the polymerization of hexamethylcyclotrisiloxane (D_3). Living PS chains were then reacted with the double bond of the end-reactive PDMS, leading to the formation of the living coupled product. The active sites were used for the polymerization of *t*BuMA for the synthesis of the final star.

The molecular weight distribution of the original PDMS was rather broad ($M_w/M_n = 1.3\text{--}1.4$). Therefore, fractionation was performed in order to reduce the polydispersity of the product before conducting the subsequent steps of the synthesis. Despite the fact that the living PS chains were reported to attack the PDMS chains, no side reactions were detected in this study.

A similar synthetic route was adopted by Stadler et al. for the synthesis of the (PS)(PBd)(PMMA)¹²²

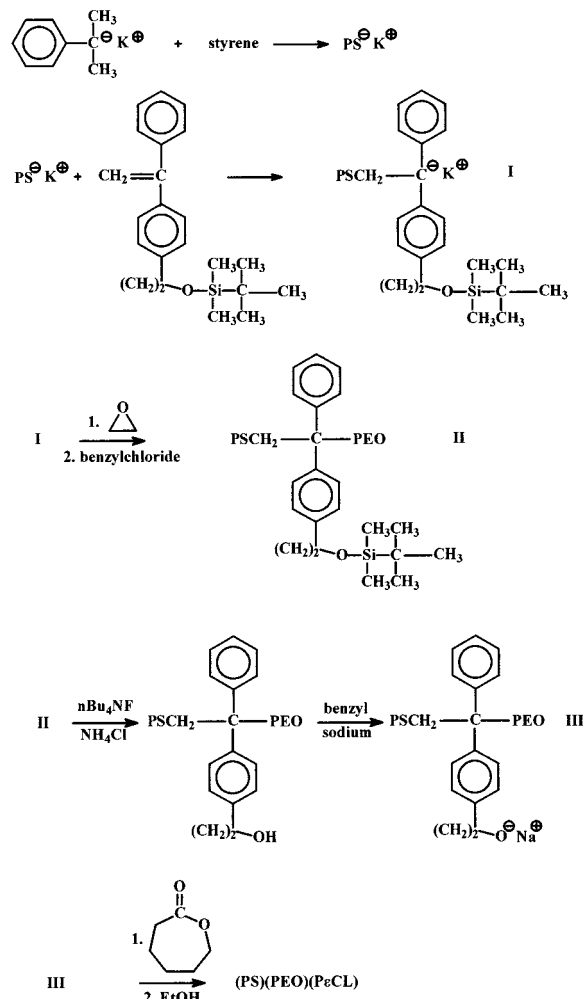
Scheme 51



and (PS)(PBd)(P2VP)¹²³ stars (Scheme 51). Living PS chains were reacted with 1-(4-bromomethylphenyl)-1-phenylethylene to produce DPE end-functionalized PS. The living PS chains were first end-capped with a DPE unit to reduce their reactivity and increase the steric hindrance of the living chain end. Under these conditions, the addition of the PSLi chains to the DPE derivative and the halogen–lithium exchange reactions are minimized. The functionalization of the PS was reported to be quantitative, as judged by UV spectroscopic analysis. The next step involved the linking of living PBdLi chains, prepared in THF at $-10\text{ }^\circ\text{C}$, to the double bond of the end-reactive PS. A living diblock copolymer was thus prepared. The active site was finally used to polymerize MMA or 2VP to produce the miktoarm star terpolymer. A multippeak product, especially in the case of the (PS)(PBd)(PMMA) star, was revealed by SEC analysis. The pure product was obtained after fractionation.

Dumas et al.^{124,125} have developed a procedure for the synthesis of ABC miktoarm star terpolymers containing amphiphilic branches. Styrene was polymerized in THF at $-78\text{ }^\circ\text{C}$ using cumylpotassium as initiator. The living chains were then reacted with 1-[4-(2-*tert*-butyldimethylsiloxy)ethyl]phenyl-1-phenylethylene, as illustrated in Scheme 52. The living center was then used to initiate the polymerization

Scheme 52

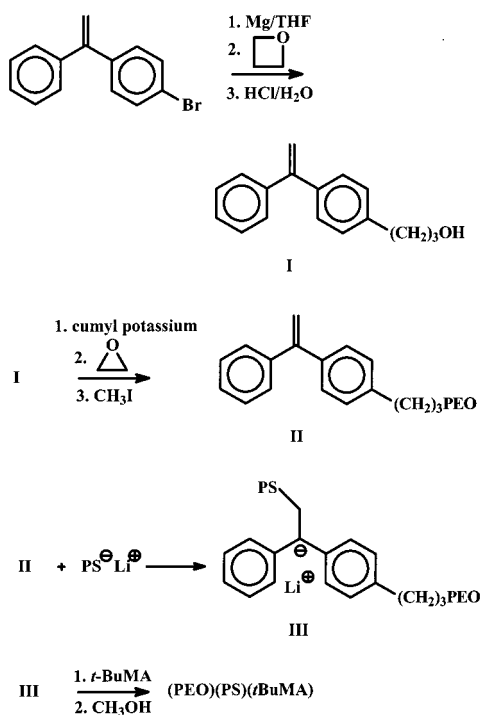


of ethylene oxide. After removal of the protecting group with tetrabutylammonium fluoride, the corresponding alcoholate was formed in the presence of diphenylmethylsodium and used for the polymerization of ϵ -caprolactone (ϵ -CL). Rather broad molecular weight distributions were obtained ($M_w/M_n = 1.2-1.4$). Only SEC and NMR analysis have been reported.

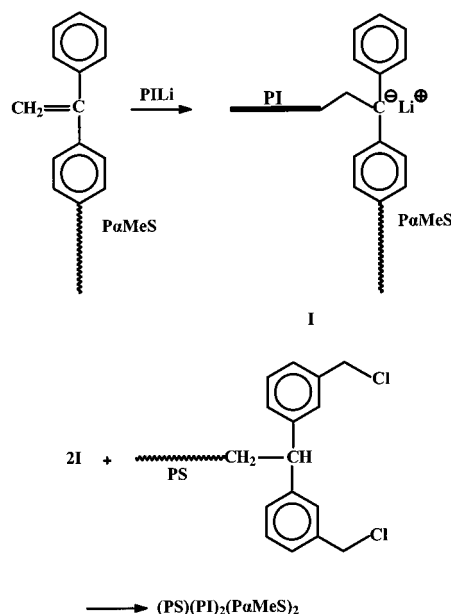
The alcoholate was alternatively reacted with tin octoate to initiate the polymerization of L-lactide (LL) and produce (PS)(PEO)(PLL) star terpolymer. In another application of the method, the 1,1-diphenylalkylpotassium intermediate (I) was used to initiate the polymerization of MMA at -78°C . After deprotecting and activating the hydroxyl group, the polymerization of ethylene oxide was initiated, leading to the formation of the (PS)(PMMA)(PEO) star terpolymer. If ϵ -CL is polymerized instead of EO, then (PS)(PMMA)(P ϵ -CL) stars are produced. Limited characterization data were given for these stars. In all cases two of the arms grow from the star center and thus cannot be isolated and characterized. However, interesting amphiphilic structures were obtained.

The potassium salt of 1-(4-hydroxypropylphenyl)-1-phenylethylene was used to initiate the polymerization of ethylene oxide, leading to the formation of a PEO chain having an end-DPE group.²⁶ The macromonomer was then quantitatively reacted with PSLi to form the living diblock copolymer. The active site was used to polymerize tBuMA after the temperature was reduced to 5°C (Scheme 53). Only SEC and NMR spectroscopy were employed for the characterization of the star structure. This technique has not been used for the synthesis of stars having high molecular weights, raising questions about the efficiency of the method in this case.

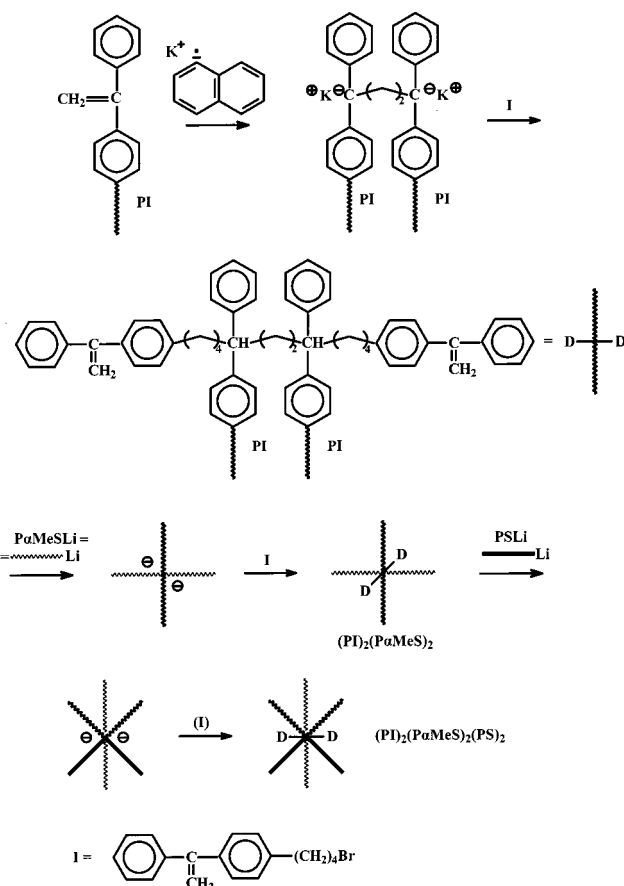
Scheme 53



Scheme 54



Scheme 55



iv. More Complex Architectures. A new methodology that permits the synthesis of a variety of miktoarm stars was developed by Hirao as described in the case of the asymmetric stars. In a series of papers the synthesis of the following structures has been reported: AB_3 , AB_4 , A_2B_4 , A_2B_{12} , ABC_2 , ABC_4 , AB_2C_2 , and $A_2B_2C_2$, where A is PS, B is PI, and C is poly(α -methyl styrene) (P α MeS).^{82-86,116,117} Characteristic examples are given in Schemes 54 and 55. It

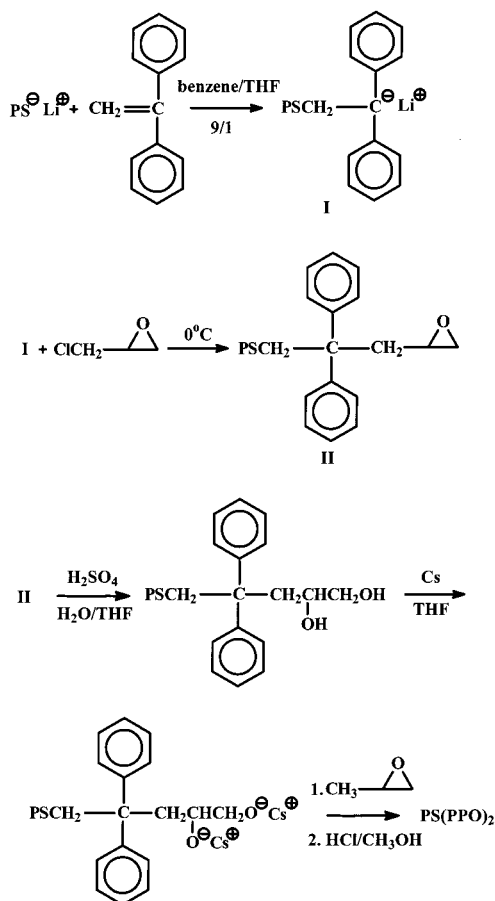
was shown that this methodology is very powerful with respect to the variety of structures that can be obtained, and it offers the possibility to prepare even more complex products. However, this multistep procedure is time-consuming and extra care is needed to avoid the presence of side reactions. The formation of byproducts was minimized by the choice of reaction conditions, leading to the formation of well-defined products. The exclusive use of low molecular weight arms poses questions about the efficiency of the method when higher molecular weight arms, having more sterically hindered chain ends, are used.

4. Synthesis of Miktoarm Stars by Other Methods

Several other specific methods have been reported in the literature for the synthesis of miktoarm stars. Usually they do not have general applicability, but most of them lead to products that cannot easily be obtained by the more general methods described earlier. Therefore, these techniques are valuable tools in polymer synthesis.

A miktoarm star copolymer carrying one PS arm and two poly(propylene oxide) arms¹²⁶ was prepared by the method given in Scheme 56. Living PS chains were end-capped with one unit of DPE, to reduce the reactivity of the chain end, followed by the addition of epichlorohydrin to produce the epoxide functionalized polymer. It was shown by SEC analysis and chemical titration that the epoxide content of the final product was 95 wt %. The desired functionalized

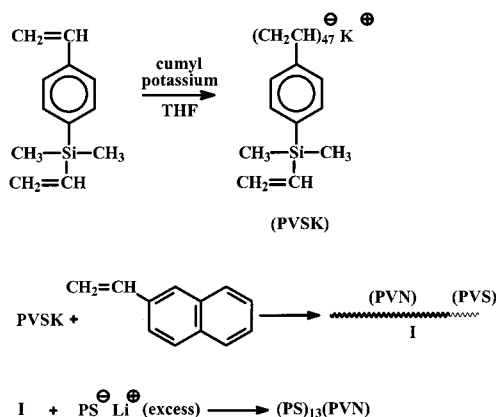
Scheme 56



product was isolated by silica gel thin-layer chromatography. The epoxide group was then hydrolyzed under acidic conditions to give the ω -dihydroxyl-functionalized PS. The pure product was obtained by silica gel chromatography. The hydroxyl groups were reacted with cesium metal in THF at room temperature for 5 h to give the cesium alkoxides, which were subsequently used as initiators for the polymerization of propylene oxide. The crude product contained 36 wt % of the desired PS(PPO)₂ star and 64 wt % of PPO homopolymer, as a result of chain transfer to the PPO monomer. The homopolymer was removed by fractionation in a methanol/water mixture. Only SEC and ¹H NMR analysis were given, making it difficult to prove that the final product contains two equal PPO arms.

Star polymers carrying one poly(2-vinylnaphthalene) (PVN) and several PS arms were prepared by Takano et al.¹²⁷ according to Scheme 57. (4-Vinyl-

Scheme 57

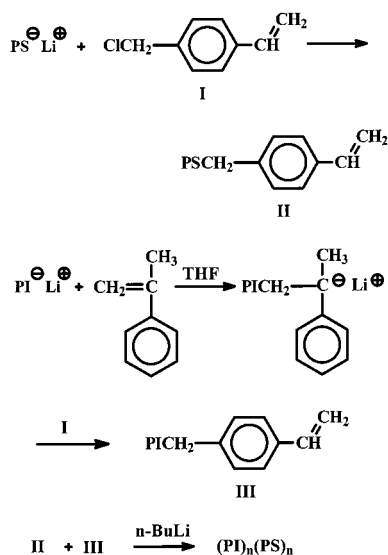


phenyl)dimethylvinylsilane (VS) was oligomerized using cumyl potassium as initiator, followed by the polymerization of vinylnaphthalene. The vinylsilyl double bonds of the monomer remained unaffected during the polymerization of VS. This was accomplished by carrying out the reaction in THF and using short polymerization times. These double bonds were subsequently used as linking agents with living PSLi chains. The characterization results showed that on average 13 PS arms were incorporated into the star structure. This method does not provide the best control over the number of PS arms since, probably for steric hindrance reasons, only one out of 3.6 silylvinyl groups was used for the PS arms.

A macromonomer technique was employed by Ishizu and Kuwahara to prepare miktoarm star copolymers of the (PS)_n(PI)_m type.¹²⁸ PS and PI macromonomers were prepared by coupling the living chains with *p*-chloromethylstyrene. The PS and PI macromonomers (vinyl end-capped chains) were copolymerized anionically in benzene using *n*-BuLi as initiator. The products are comb-shaped copolymers, but they behave as miktoarm stars of the type A_nB_m. The reaction sequence is given in Scheme 58.

Miktoarm stars containing PS and PMMA branches were synthesized using C₆₀ as the linking agent.¹²⁹ Living PSLi chains were added to C₆₀ to form the

Scheme 58



living star with six arms. Subsequent addition of MMA resulted in the grow of PMMA branches. The sample was characterized only by SEC. The chromatogram was bimodal, indicating that a mixture of products was obtained. Judging from the SEC data, it was concluded that six PS and at least two PMMA branches were incorporated in the star structure. It is obvious that this method does not produce well-defined polymers, and more efforts are needed to understand the linking chemistry of living carbanionic species with C_{60} .

A similar synthetic route was adopted for the synthesis of $(\text{PS})_6(\text{PI})$ miktoarm stars, also reported as palm tree structures.¹³⁰ The living star carrying six PS branches was formed by the reaction of living PS chains with C_{60} . Isoprene was subsequently added. It was claimed that only one PI arm can grow from the core, although six C-Li species are available. A considerable increase in the molecular weight distribution was observed during the formation of the PS_6 star ($M_w/M_n = 1.07\text{--}1.14$ compared to values of 1.04 for the PS arm) and the miktoarm star ($M_w/M_n = 1.2\text{--}1.3$). Slow initiation was blamed for the broad molecular weight distribution of the final structure. However, the existence of a mixture of stars containing more than one PI arm cannot be ruled out.

III. Comb-Shaped Polymers

Graft polymers consist of a main polymer chain, the backbone, with one or more side chains attached to it through covalent bonds, the branches. Graft copolymers are comb-shaped polymers where the chemical nature of the backbone and the branches differs. The chemical nature and composition of the backbone and the branches differ in most cases. Branches are usually distributed randomly along the backbone, although recently advances in synthetic methods allowed the preparation of better defined structures.^{88,90}

Randomly branched comb-shaped polymers can be prepared by three general synthetic methods: the "grafting onto", the "grafting from", and the "grafting through" or macromonomer method.⁸⁸

A. "Grafting Onto"

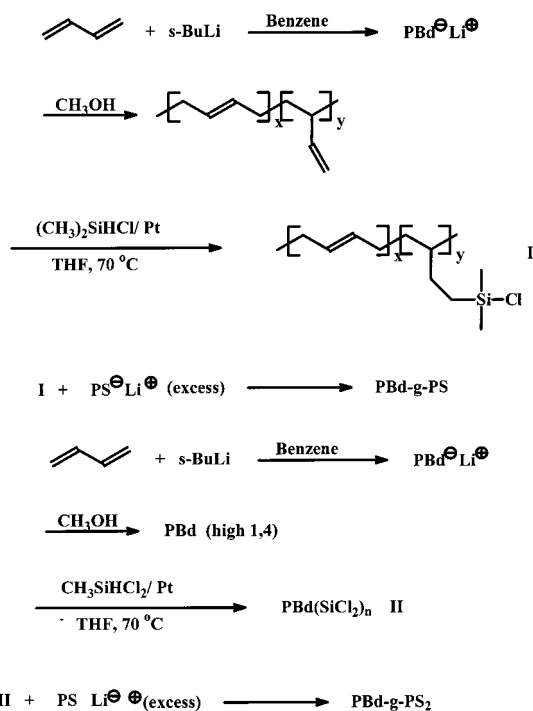
In the "grafting onto" method the backbone and the arms are prepared separately by a living polymerization mechanism. The backbone bears functional groups distributed along the chain that can react with the living branches. Upon mixing the backbone and the branches in the desired proportion and under the appropriate experimental conditions, a coupling reaction takes place resulting in the final comb-shaped polymers.

By the use of an anionic polymerization mechanism, the molecular weight, molecular weight polydispersity, and the chemical composition of the backbone and branches can be controlled. Additionally, both backbone and branches can be isolated and characterized separately. The average number of branches can be controlled primarily by the number of the functional groups (branching sites) present in the backbone and sometimes by the ratio of the functional groups to the active chain end concentration of the branches used in the coupling reaction.

The branching sites can be introduced onto the backbone either by postpolymerization reactions or by copolymerization of the main backbone monomer(s) with a suitable comonomer, with the desired functional group (unprotected or in a protected form if this functional group interferes with the polymerization reaction). Branches of comb-shaped polymers are commonly prepared by anionic polymerization, and backbones with electrophilic functionalities such as anhydrides, esters, pyridine, or benzylic halide groups are employed.⁸⁸ The actual average number of branches in the final copolymer can be found by the determination of the overall molecular weight of the copolymer and the known molecular weights of the backbone and the branches.

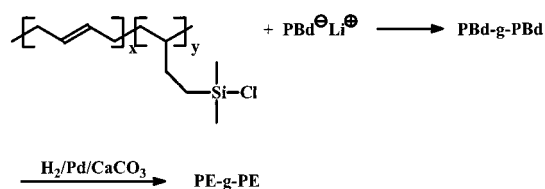
A representative example is the preparation of poly(butadiene-*g*-styrene) graft copolymers¹³¹ (Scheme

Scheme 59



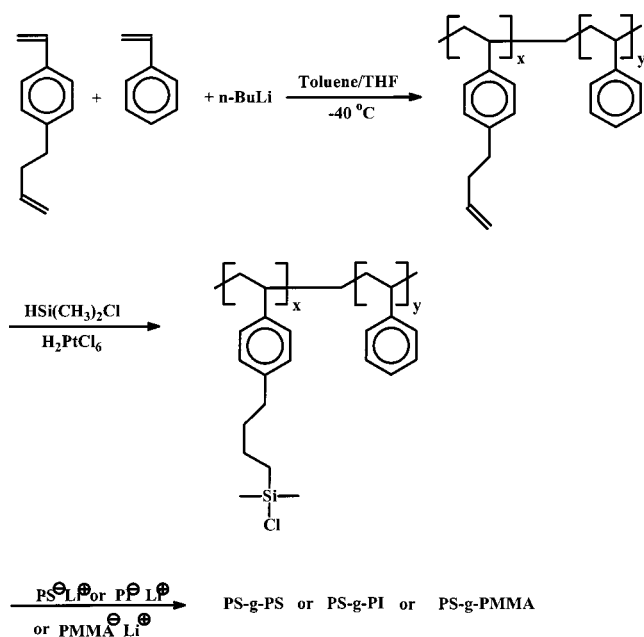
59). The PBd backbones were synthesized by anionic polymerization in benzene, resulting in PBds with high 1,4-addition (1,2-addition was lower than 10%). Postpolymerization catalytic hydrosilylation using $(\text{CH}_3)_2\text{SiHCl}$ was used for introduction of chlorosilane groups, preferentially at the 1,2-double bonds. Finally, a linking reaction between living polystyrene anions and the Si-Cl groups of the PBd backbone gave poly(Bd-*g*-S) graft copolymers with randomly placed single PS branches. When $\text{HSiCl}_2\text{CH}_3$ was used in the hydrosilylation step, difunctional branching sites were introduced in the backbone. Subsequent reaction with excess PSLi afforded graft copolymers with randomly distributed double PS branches (PBd-*g*-PS₂). Characterization of the final products showed that they possessed a high degree of molecular weight and compositional homogeneity. By the same synthetic scheme, PBd comb polymers were prepared, and after catalytic hydrogenation, well-defined graft polyethylenes were obtained¹³² (Scheme 60).

Scheme 60



Ruckenstein and Zhang reported that the anionic copolymerization of 4-(vinylphenyl)-1-butene with styrene in toluene/THF at $-40\text{ }^{\circ}\text{C}$ gives well-defined polymers,¹³³ since under these experimental conditions the vinylic double bond is selectively polymerized. The copolymers were subjected to hydrosilylation for the introduction of Si-Cl groups at the olefinic double bonds. These groups were used as grafting sites for the linking of PSLi, PILi, and PMMALi living chains in order to synthesize PS-*g*-

Scheme 61

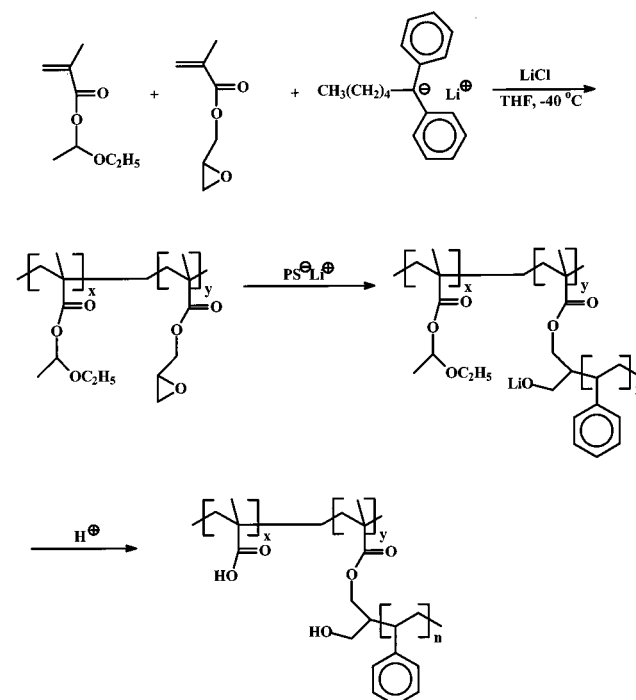


PS, PS-*g*-PI, and PS-*g*-PMMA comb-shaped polymers with well-defined molecular characteristics (Scheme 61). The PS-*g*-PMMA graft copolymers were found to decompose in proton-containing media, while they were stable in organic solvents.

Anionically prepared and subsequently hydrosilylated PBds were also used for the formation of PBd-*g*-poly(sodium methacrylate) graft copolymers.¹³⁴ The precursors were PBd-*g*-poly(*tert*-butyl methacrylate) graft copolymers. These were prepared by reaction of the hydrosilylated PBd backbone with living PtBuMA anions end capped with *tert*-butyl 4-vinylbenzoate. This modification of the living end proved to be necessary, since in this way the expected C-silylation stable product is obtained instead of the O-silylated one, when uncapped living PtBuMA is used. Hydrolysis of the graft copolymers followed by neutralization with sodium hydroxide yielded the amphiphilic analogues.

Ruckenstein and Zhang presented the synthesis of amphiphilic graft copolymers with poly(methacrylic acid) hydrophilic backbones and hydrophobic PS side chains.¹³⁵ The precursors of the backbones were random copolymers of 1-(ethoxy)ethyl methacrylate (EEMA) and glycidyl methacrylate (GMA) prepared by anionic copolymerization of the two monomers. These copolymers had narrow molecular weight and composition polydispersities as well as predetermined molecular weights and compositions. The amount of GMA in the copolymers determines the number of grafting sites in the backbone, and it was kept low in all cases. In the next step a predetermined amount of a solution of living PSLi was added to the solution of the living backbone, resulting in a rapid reaction between PSLi active chain ends and the epoxy groups of GMA in the backbone. Unreacted epoxy groups were neutralized by 1,1-diphenylhexyllithium. The final graft copolymers had relatively narrow molec-

Scheme 62

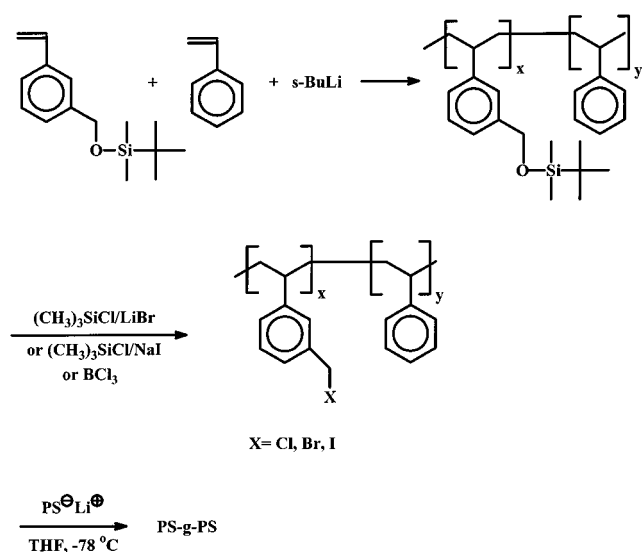


ular weight distributions. The EEMA units were then subjected to hydrolysis, and the desired amphiphilic comblike copolymers were obtained (Scheme 62). It is characteristic that no excess of PSLi was used in this work, introducing another way of controlling the number of grafted chains per backbone through control of the stoichiometry between potential grafting sites and number of living side chains.

Using the same methodology, PMMA-*g*-PS and poly(allyl methacrylate)-*g*-Ps graft copolymers were prepared.¹³⁶ In all cases GMA was anionically copolymerized with the appropriate methacrylic monomer in order to produce the backbone of the graft. In the case of poly(allyl methacrylate)-*g*-PS, the allylic groups of allyl methacrylate were converted to hydroxyl groups by hydroboration–oxidation reaction, giving amphiphilic graft copolymers with hydrophilic backbones and hydrophobic branches. Reaction of GMA homopolymers with a PSLi, PILi, and PSLi/PILi mixture resulted in the formation of PGMA-*g*-PS, PGMA-*g*-PI, and PGMA-*g*-(PS,PI) graft copolymers.¹³⁷

Hirao and Ryu synthesized PS graft copolymers with one side chain in almost every monomeric unit.¹³⁸ They used anionically synthesized poly(*m*-*tert*-butyldimethylsilyloxy)styrene)s as precursors for the preparation of *m*-halomethylstyrenes by reaction with BCl₃, (CH₃)₂SiCl/LiBr, and (CH₃)₂SiCl/NaI for the introduction of Cl, Br, and I, respectively. The transformation reactions were quantitative. The halomethylstyrenes, having well-defined molecular weights and low molecular weight polydispersities, were subsequently used as backbones for the preparation of comb-shaped polymers. Reaction of the highly reactive benzyl halides with living PSLi chains in THF gave the aforementioned PS combs (Scheme 63). The final products, isolated after fractionation, were similar in respect to their molecular characteristics with the polymer obtained when living PSLi was coupled with poly(*m*-chloromethylstyrene) at -78 °C or diphenylethylene-capped PSLi at -40 °C. Reaction times were shorter in the former case, due to the higher reactivity of PSLi. PS combs were also pre-

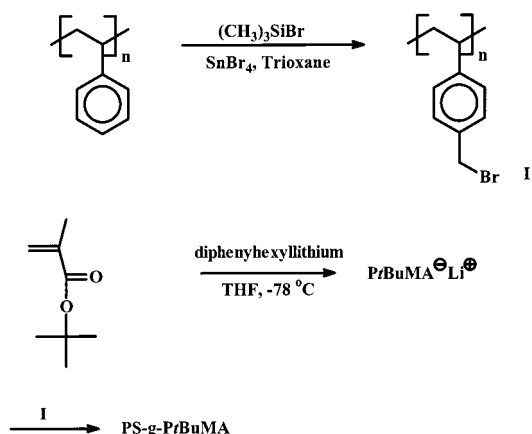
Scheme 63



pared by reaction of poly(*m*-bromomethylstyrene) with PSLi end-capped with DPE.

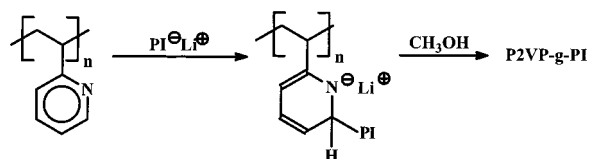
Partially chloromethylated or bromomethylated anionically prepared polystyrenes have been used for the preparation of several graft copolymers containing PS backbones and PI,⁴³ P2VP,^{45,139} P4VP,¹⁴⁰ PtBuMA,⁴⁵ and PEO^{141,142} branches. Some of these copolymers are precursors for amphiphilic graft copolymers (Scheme 64).

Scheme 64



Watanabe et al. reported the synthesis of P2VP-*g*-PS and P2VP-*g*-PI copolymers.¹⁴³ The P2VPs used as the backbones were prepared by anionic polymerization. After thorough purification for complete removal of terminating impurities, these homopolymers were directly reacted with living PILi and PILi to give the desired graft copolymers (Scheme 65). The final products had narrow molecular weight distributions. No grafting was observed when the side chains were end-capped with DPE.

Scheme 65



B. "Grafting From"

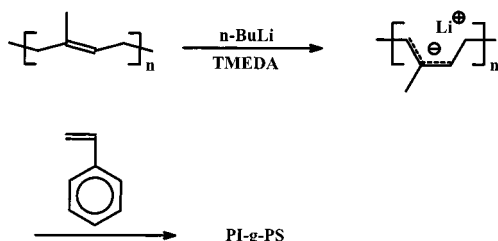
In the "grafting from" method, after the preparation of the backbone, active sites are produced along the main chain that are able to initiate the polymerization of the second monomer(s). Polymerization of the second monomer results in the formation of branches and the final graft copolymer. The number of branches can be controlled by the number of active sites generated along the backbone, assuming that each one of them initiates the formation of one branch. Obviously, the isolation and characterization of each part of the graft copolymer in this case is almost always impossible. Knowledge of precursor molecular characteristics is limited to the backbone. Isolation of the branches can be achieved only in some cases and usually involves selective chemical decomposition of the backbone, e.g., ozonolysis of polydiene backbone in poly(diene-*g*-styrene) graft copolymers.¹³³ Following this methodology, several

graft copolymers were synthesized by the use of anionic polymerization.

Anionic active sites can be generated by metalation of allylic, benzylic, or aromatic C–H bonds, present in the backbone, by organometallic compounds, such as *s*-BuLi, in the presence of strong chelating agents that facilitate the reaction. The metalation of polydienes with *s*-BuLi in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) presents a representative example.^{144–146}

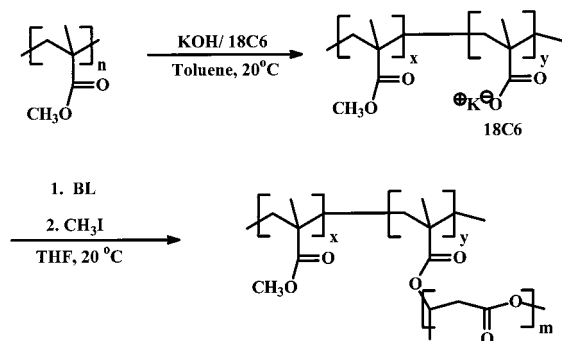
Metalation of PI and PBd by this procedure and subsequent polymerization of styrene led to the formation of PI-*g*-PS and PBd-*g*-PS copolymers with well-defined molecular characteristics^{144–148} (Scheme 66).

Scheme 66



In another approach, PMMA-*g*-poly(β -butyrolactone) copolymers were synthesized using the “grafting from” technique.¹⁴⁹ Anionically polymerized PMMA was treated with the 18-crown-6 complex of potassium hydroxide in toluene, resulting in a macromolecular initiator (Scheme 67). The average number

Scheme 67



of grafting sites per macroinitiator was determined by reaction of the modified PMMA with benzyl bromide and subsequent characterization of the copolymer. The carboxylate active groups formed were used as initiating sites for the anionic polymerization of β -butyrolactone in THF at room temperature. The grafting process was followed by ¹H NMR and the final copolymers, obtained after termination with methyl iodide, were characterized by SEC, VPO, and NMR. The grafting efficiency was determined to be high and the density of the grafting sites could be controlled easily.

C. “Grafting Through”

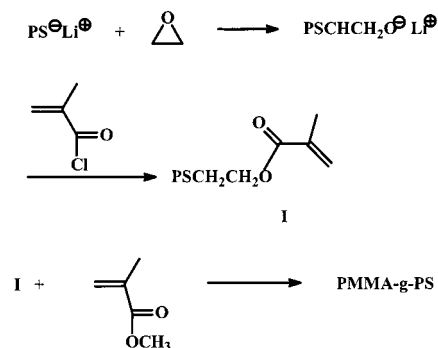
In the grafting through method, preformed macromonomers are copolymerized with another monomer in order to produce the graft copolymer. Macromono-

mers are oligomeric or polymeric chains that have a polymerizable end group. In this case, the macromonomer comprises the branch of the copolymer and the backbone is formed in situ. The number of branches per backbone can be generally controlled by the ratio of the molar concentrations of the macromonomer and the comonomer. Several other factors have to be considered. Among them the most important one is the copolymerization behavior of the macromonomer and the comonomer forming the backbone. Depending on the reactivity ratios, r_1 and r_2 , of the reacting species, different degree of randomness can be achieved, with respect to the placement of the branches. Since macromonomer and comonomer incorporation in the graft copolymer can vary in the course of the copolymerization reaction due to changes in the concentration of the two compounds in the mixture, different kinds of graft copolymers are formed as a function of time. Phase separation can also occur in these systems, due to the formation of the copolymers, leading to increased compositional and molecular weight heterogeneity of the final product.

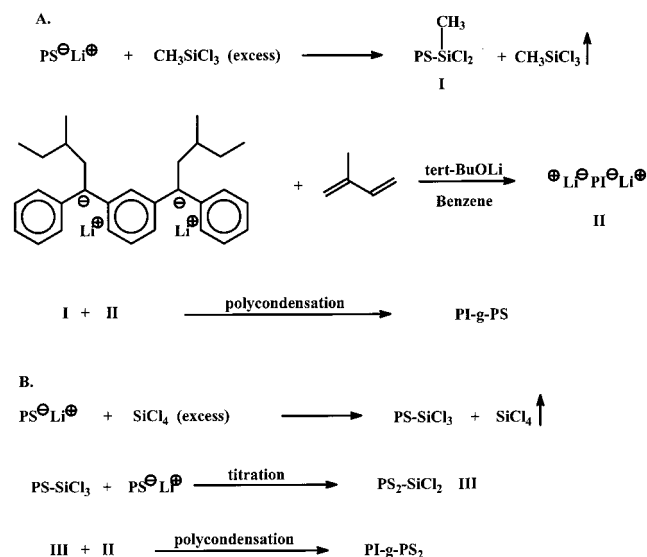
PS macromonomer formation by anionic polymerization has been described in several cases.^{150–153} In one of them styrene was polymerized by *s*-BuLi, and once the monomer has been consumed completely, a slight excess of ethylene oxide was added.¹⁵⁰ The oxirane end-capped living polymer is then reacted with methacryloyl chloride to give a PS macromonomer with a methacrylate type polymerizable end unit. If the oxirane end-capped living polymer is reacted with benzyl bromide (or chloride), PS macromonomer with a styrenic polymerizable end unit is produced. Alternatively, living PS was end-capped with 1,1-diphenylethylene and then reacted with vinyl benzyl bromide (chloride). In a similar way, living PMMALi anions can be end-capped with methacryloyl chloride or vinyl benzyl bromide (chloride) by direct reaction. These macromonomers were used, after complete removal of protonic impurities, in subsequent anionic copolymerization with MMA or styrene to give the corresponding PMMA-*g*-PMMA, PMMA-*g*-PS, and PS-*g*-PS comb-shaped polymers (Scheme 68). Direct polymerization of the macromonomers results in the formation of polymacromonomers, i.e., graft copolymers with a side chain on every backbone monomer.¹⁵⁴

Graft copolymers of St and Is, with trifunctional or tetrafunctional branching points, situated equi-

Scheme 68



Scheme 69

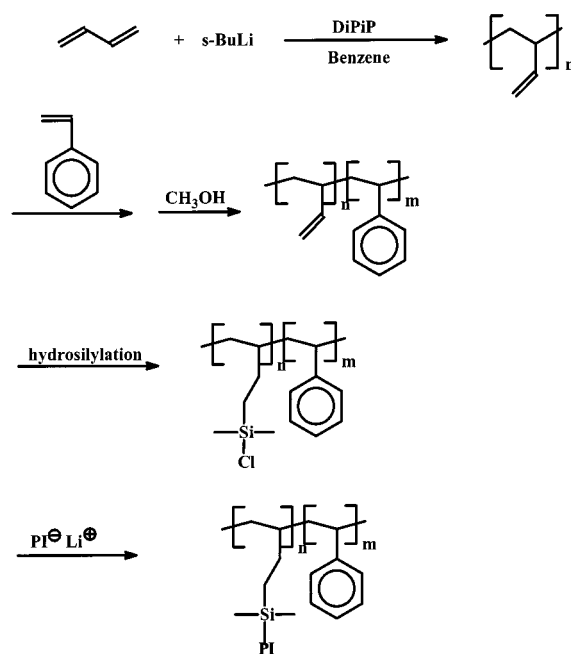


distantly on the backbone, were synthesized by a combination of living anionic and condensation polymerization methodologies¹⁵⁵ (Scheme 69). In the case of graft copolymers with the trifunctional branching points, a living PSLi was reacted with excess MeSiCl₃ to give a macromolecule with two terminal SiCl bonds. This was reacted, after removal of excess silane, with a difunctional PI produced by the difunctional initiator derived from MDDPE and *s*-BuLi, following a polycondensation reaction scheme, giving a well-defined graft copolymer with PI backbone and PS branches. In this way, the length of the branches and the distance between them on the backbone could be controlled. Some control over the average number of branches could also be exercised by the molar ratio of the difunctional macromonomers. In the case of the grafts with tetrafunctional branching points, the PS branch was reacted with SiCl₄ in a controllable way to give (PS)₂SiCl₂ (Scheme 69). The first branch was introduced by reaction with excess SiCl₄, which was subsequently removed, and the second PS was introduced via a titration procedure in order to avoid substitution of the third Cl. The macromolecular linking agent was reacted with a predetermined amount of a difunctional PI to give the desired graft copolymer. In both cases, crude reaction products had relatively wide molecular weight distributions as a result of the condensation mechanism of the second synthetic step, but after fractionation, narrow molecular weight distribution products were obtained.

IV. Block-Graft Copolymers

Block-graft copolymers, having a PS–PB diblock as a backbone and PS, PI, PB and PS-*b*-PI branches, were prepared by anionic polymerization and hydrosilylation reactions.¹⁵⁶ The diblock copolymer backbone was prepared by sequential addition of styrene and butadiene. The polymerization of butadiene took place in the presence of dipiperidinoethane, resulting in high 1,2-content. The backbone was then subjected to hydrosilylation in order to incorporate the desired amount of SiCl groups on the PB block. These groups were then used as branching sites, where PSLi, PILi,

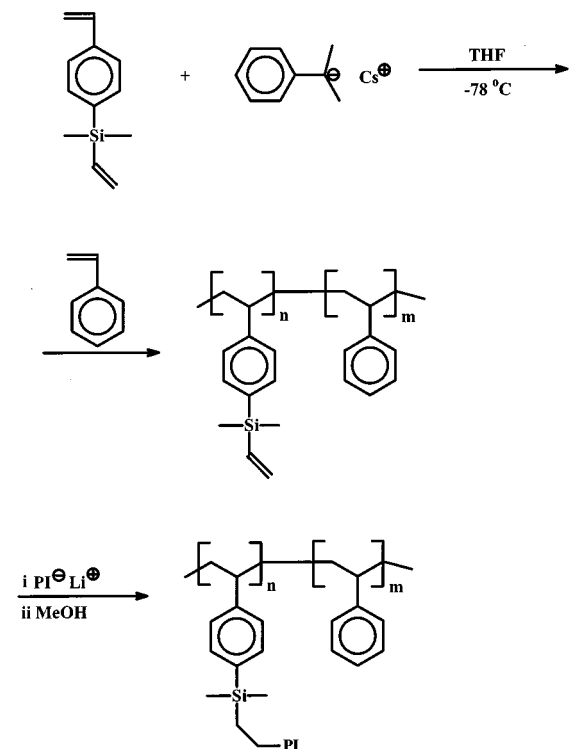
Scheme 70



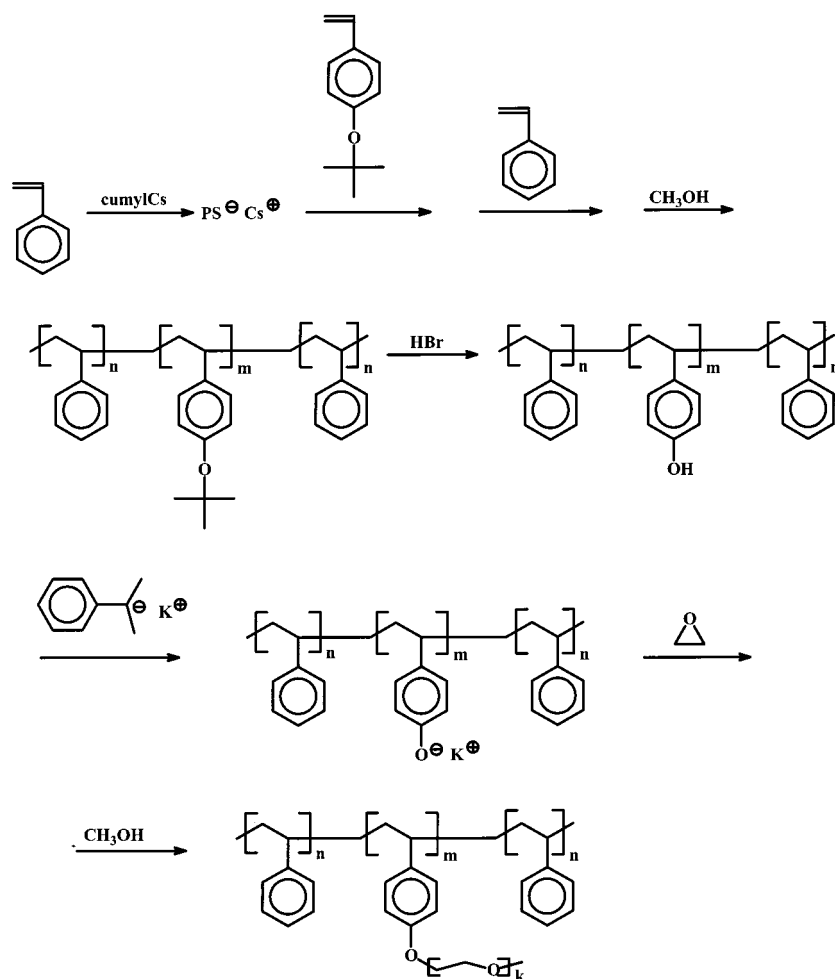
PBLi, and PSPILi living chains were linked (Scheme 70). The use of MeSiHCl₂ instead of Me₂SiHCl in the hydrosilylation step produced difunctional branching sites along the PB part of the backbone, leading to the formation of block-graft copolymers with two chains grafted on each branching point.

Se et al. presented the synthesis of poly[(*VS-g-I-b-S*)] block-graft copolymers.¹⁵⁷ The backbone, a diblock copolymer of 4-(vinyl dimethylsilyl)styrene (VS) and styrene, was prepared first by anionic polymerization. The VS monomer was polymerized selectively through the styryl double bond at low

Scheme 71



Scheme 72



temperature in THF using cumylcesium as initiator followed by the addition of styrene. Living PILi was then allowed to react with the vinylsilyl groups of the VS block, giving the final graft copolymer (Scheme 71). Detailed characterization of the polymers obtained by SEC, osmometry, and ultracentrifugation techniques proved their high molecular weight and compositional homogeneity, as well as their desired architecture.

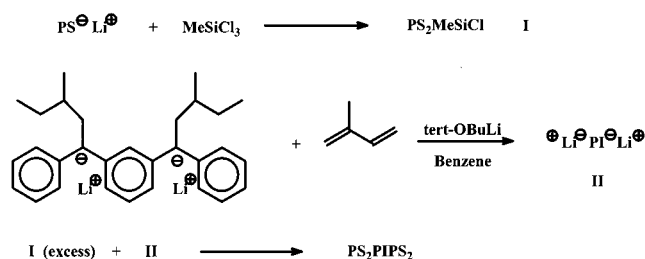
The synthesis of block-graft copolymer containing styrene, hydroxystyrene, and ethylene oxide of the types $\text{PS-}b\text{-(PHS-}g\text{-PEO)}$ and $\text{PS-}b\text{-(PHS-}g\text{-PEO)-}b\text{-PS}$, where PHS is poly(*p*-hydroxystyrene), has been reported.¹⁵⁸ The ABA triblock copolymer comprising the backbone was synthesized by a three-step sequential addition of monomers i.e., styrene and *p*-*tert*-butoxystyrene (the precursor to hydroxystyrene). The PBS blocks were converted to poly(*p*-hydroxystyrene), by reaction with hydrogen bromide. The OH groups thus formed were transformed to potassium alkoxide groups by reaction with cumyl potassium or 1,1-diphenylethylene potassium. The resulting macromolecular initiators were used for the polymerization of EO, forming the branches of the block-graft-block copolymers (Scheme 72). Molecular characterization of the products by SEC and osmometry indicated that they possessed narrow molecular weight distributions and predictable molecular weights and compositions.

Ruckenstein et al. reported the preparation of $\text{PMMA-}b\text{-(PGMA-}g\text{-PS)}$ and $\text{PMMA-}b\text{-(PGMA-}g\text{-PI)}$ block-graft copolymers, where PGMA is poly(glycidyl methacrylate).¹³⁷ The $\text{PMMA-}b\text{-PGMA}$ diblock was obtained first by anionic polymerization through sequential addition of monomers. Then living PSLi and PILi chains were linked to the diblock backbone by reaction with the glycidyl groups of the GMA block. Molecular characterization of the final products confirmed the intended architecture and relatively narrow molecular weight distributions.

V. α,ω -Branched Architectures

By the use of anionic polymerization and controlled chlorosilane chemistry, the exact placement of the side chains along the backbone is possible. Using this combination, H- and super-H-shaped copolymers were synthesized. In the case of H-shaped copolymers,¹⁵⁹ living PSLi and MeSiCl_3 were reacted in a ratio $\text{SiCl:Li} = 3:2.1$. Due to the sterically hindered PSLi anion, only two Cl atoms were substituted, resulting in a PS dimer having an active Si-Cl bond at the center. The macromolecular linking agent was reacted with a difunctional PI chain (the connector), synthesized using the difunctional initiator derived from MDDPE and *s*-BuLi in benzene solution and in the presence of lithium-*tert*-butoxide, giving the

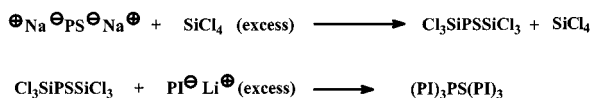
Scheme 73



H-copolymer as shown in Scheme 73. This synthetic scheme is an extension of the one used for the preparation of H-shaped polystyrene homopolymers.¹⁶⁰

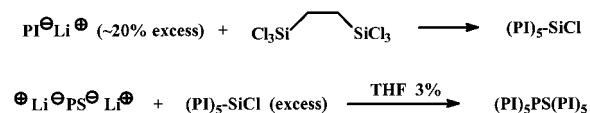
For the synthesis of the $(\text{PI})_3\text{PS}(\text{PI})_3$ super-H copolymers,¹⁶¹ a difunctional PS chain, derived from the polymerization of isoprene in THF using sodium naphthalene as initiator, was reacted with a large excess of SiCl_4 , giving a PS chain with three Si-Cl active bonds at each end. After elimination of excess SiCl_4 and the addition of excess P ILi living arms, the $(\text{PI})_3\text{PS}(\text{PI})_3$ super-H shaped copolymer was isolated (Scheme 74). Using the same synthetic strategy, $(\text{PS}-\text{PI})_3\text{PS}(\text{PI}-\text{PS})_3$ block copolymers were also synthesized.¹⁶²

Scheme 74



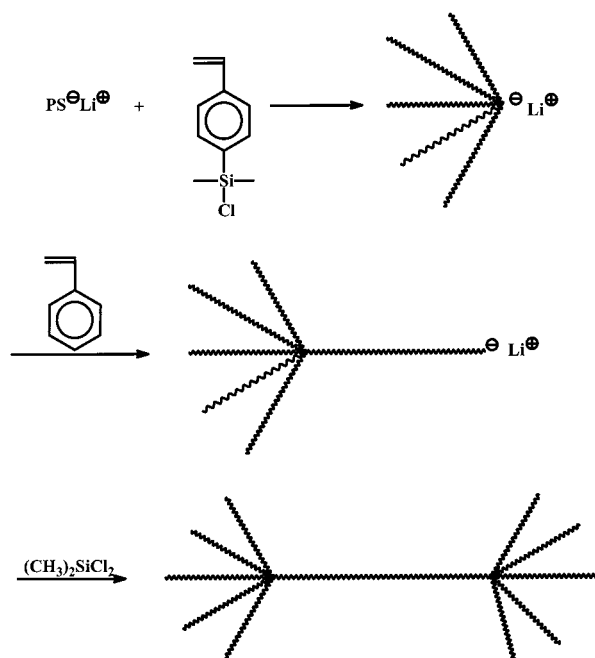
$(\text{PI})_5\text{PS}(\text{PI})_5$ copolymers (pom-pom shaped) were synthesized in a way similar to the preparation of H-shaped copolymers¹⁰¹ (Scheme 75). A hexafunctional silane was reacted with P ILi in a ratio $\text{SiCl}:\text{Li} = 6:5$, giving the five-arm star having a SiCl group at the central point. These functional stars were reacted in a second step with a difunctional PS, giving the desired pom-pom copolymers.

Scheme 75



$(\text{PS})_n\text{PS}(\text{PS})_n$ homopolymers were prepared by a synthetic scheme involving anionic polymerization of styrene followed by addition of 4-(chlorodimethylsilyl)styrene (CDMSS) in the first step.¹⁶³ By controlling the amount of CDMSS added to the solution of the living PS relative to the amount of the initial chain ends, the extent of coupling (number of arms, n) can be controlled. The star PS thus formed contains one living chain end that can be used for the polymerization of additional styrene in the second step. Coupling of the living stars with $(\text{CH}_3)_2\text{SiCl}_2$ in the third step results in the formation of $(\text{PS})_n\text{PS}(\text{PS})_n$ pom-pom polymers (Scheme 76). Due to the statistical nature of the first step, there is a distribution in the number of arms connected to the ends of the main PS chain.

Scheme 76

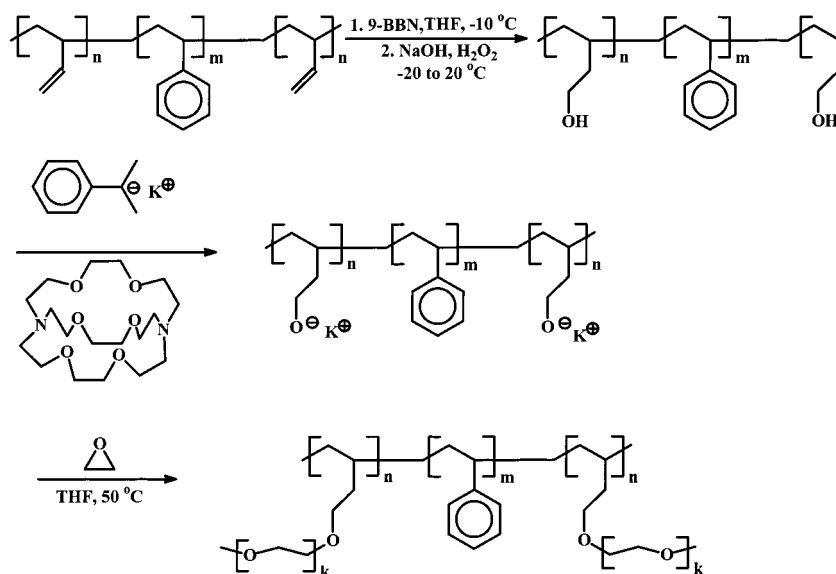


Pom-pom or dumbbell copolymers with a high functionality of the end-grafted chains were synthesized by first preparing a P Bd -1,2-PS-P Bd -1,2 triblock copolymer having short P Bd blocks by anionic polymerization, using naphthalene potassium as difunctional initiator.¹⁶⁴ The pendant double bonds in the P Bd blocks were subjected to hydroboration-oxidation, producing OH groups. These groups were transformed to alkoxides, by reaction with cumylpotassium in the presence of cryptant(kryptofix-[2.2.2]). In this way, precipitation of the polyfunctional initiator was avoided. The alkoxide groups were subsequently used as initiating sites for the polymerization of ethylene oxide. The dumbbell-shaped $(\text{PEO})_n\text{PS}(\text{PEO})_n$ copolymer was prepared in this way (Scheme 77). Characterization of the obtained polymers indicated a low degree of molecular weight and compositional heterogeneity.

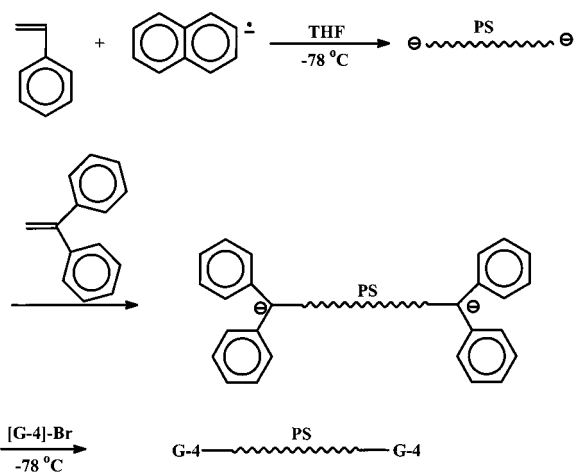
Dumbbell copolymers were also synthesized by Frechet et al.¹⁶⁵ A difunctional PS living chain, prepared in THF using potassium naphthalenide as initiator, was end-capped with DPE and subsequently reacted with a fourth-generation dendrimer having a bromomethyl group at its converging point (Scheme 78).

π -Shaped graft copolymers, i.e., graft copolymers with a PI backbone and two identical PS branches, were synthesized by anionic polymerization.¹⁵⁹ P ILi was reacted with excess MeSiCl_3 in order to produce the macromolecular linking agent P ISiCl_2 . P SLi was slowly added to P ISiCl_2 in order to replace the second Cl atom. The course of the reaction was followed by SEC. The junction point functionalized $(\text{PS})(\text{PI})\text{SiCl}$ diblock was subsequently reacted with a difunctional living PI in a 2.1:1 ratio to give the π -shaped copolymer after fractionation (Scheme 79). In this case the length of the PS branches of the connecting part of the backbone, the length of the two backbone parts between the branching points, and the ends of

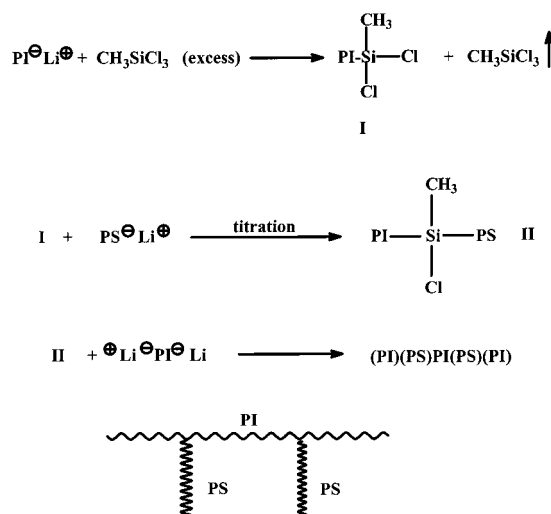
Scheme 77



Scheme 78



Scheme 79



the main chain could be controlled, leading to a well-defined graft architecture.

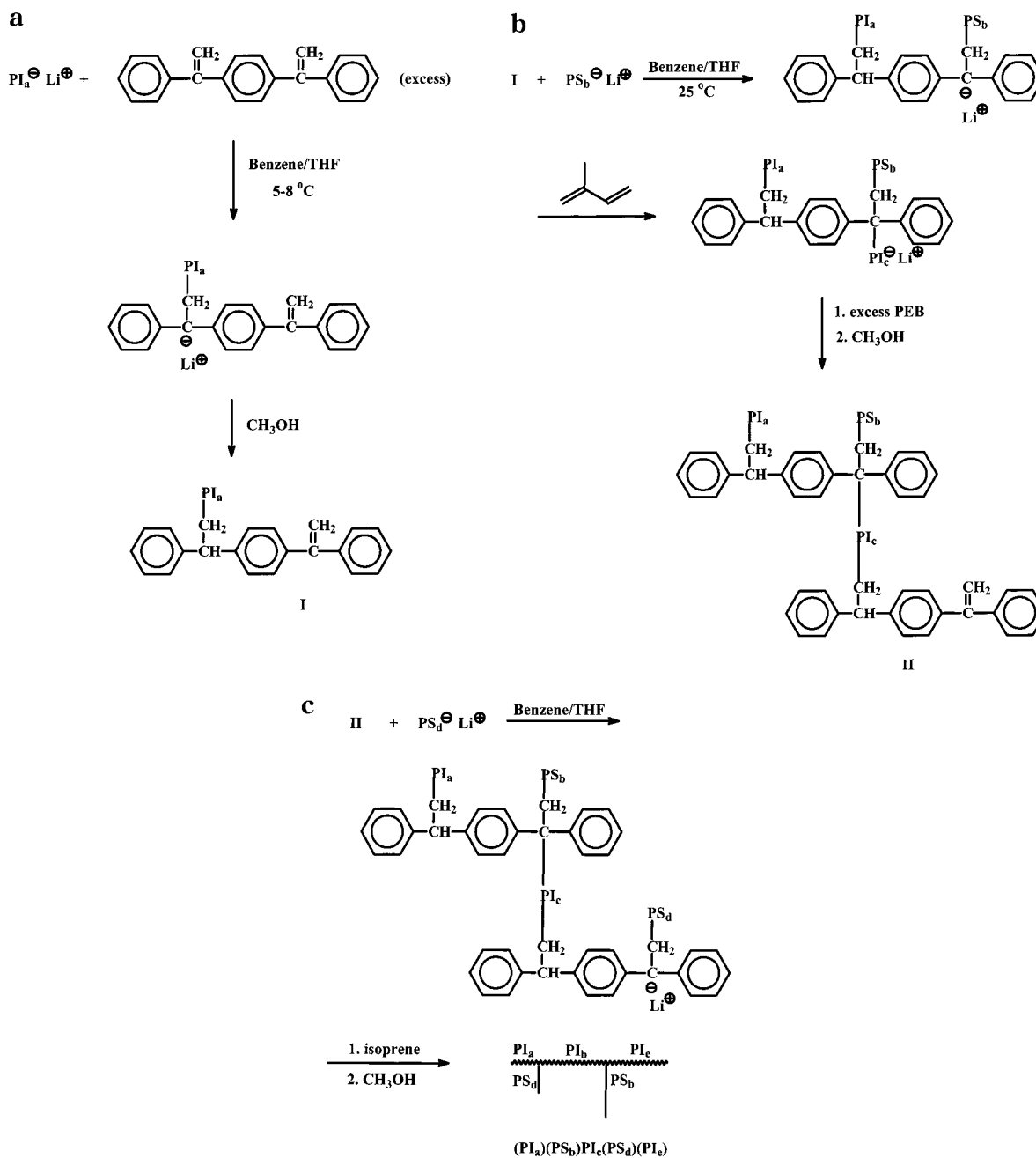
Exact graft copolymers¹⁶⁶ with a PI backbone and two PS branches, where the position of the branching points along the backbone and the length of each branch could be controlled exactly, were synthesized using anionic polymerization methodology and non-polymerizable DPE derivatives for branching point formation (Scheme 80). Living PILi is produced and reacted with PDDPE in the presence of a small amount of THF. By taking advantage of the differences in the reactivity of the two double bonds and the appropriate stoichiometry, monitored by titration, only one chain is introduced on PDDPE. The product is isolated and purified. Then it is reacted with living PSLi in order to introduce the second part of the molecule. After complete reaction, the living centers on PDDPE are used to polymerize Is in the presence of THF. The resulting ABB' star has an anionic active center on the end of the B' branch, which can react with PDDPE again, giving a star-shaped, double-bond-functionalized polymer. After isolation and thorough purification of the intermediate, another PS branch is introduced by reaction with the remaining

double bond. The active site is used for the formation of the last part of the molecule by polymerization of Is. Despite the numerous reaction steps and the demanding purification of the intermediate products, the method allows control over almost all molecular characteristics of the final graft copolymer and can be extended to the preparation of grafts with a higher number of branches.

VI. Cyclic Polymers

The first attempts to synthesize cyclic polymers involved a ring-open chain equilibrium based on backbiting reactions of poly(dimethylsiloxanes).¹⁶⁷ However, this method was limited to low molecular weight and polydisperse cyclic polymers and was characterized by the inability to isolate the corresponding linear precursor in order to prove the cyclic structure by comparing the properties. Now a days living polymerization processes leading to narrow molecular weight distribution polymers are generally preferred. The linear precursor of the cyclic polymer

Scheme 80

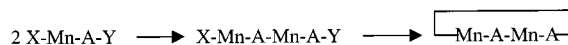
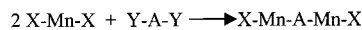
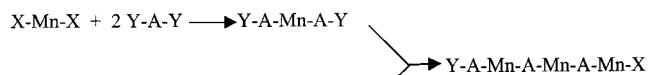


has either two identical or two different functional groups capable of reacting with each other. In the first case, an α,ω -homodifunctional macromolecule was synthesized first, followed by the reaction with an appropriate difunctional linking agent. In the second case, an α,ω -heterodifunctional macromolecule was prepared by using functional protected initiator and by neutralizing the living anion with the appropriate linking agent containing another protected group. The cyclic structure is formed by the coupling reaction of the two reactive groups.

The first case is shown below schematically:

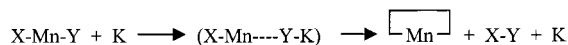


Besides the intramolecular reaction, several intermolecular reactions can occur:



These reactions lead to undesirable, high molecular weight polycondensates, which are either linear or cyclic and should be removed from the low molecular weight desirable cyclic product.

In the second case, the cyclization requires an activation step:



This synthetic approach presents several advantages, such as an exact stoichiometry of addition of the two reagents is not required, since the two reactive groups are in the same molecule and only a catalytic amount of the activator K is needed. In both cases, the possibility of intramolecular versus intermolecular reaction depends on their effective concentration. The probability of intramolecular reaction, i.e., of finding the ω -end of a chain within a small reaction volume v_e close to the α -end is given by

$$P_i = (3/2\pi)^{3/2} v_e / \langle r^2 \rangle^{3/2}$$

where $\langle r^2 \rangle$ is the mean square end-to-end distance of the chain in the reaction medium. The probability of the intermolecular reaction, i.e., of finding the chain end of another molecule is given by

$$P_e = (N_A c / M) v_e$$

where N_A is Avogadro's number, c the concentration of the polymer, and M the molecular weight. The concentration at which the intra- and intermolecular reaction are equally likely is given by

$$c_{\text{equal}} = [(3/2\pi) / \langle r^2 \rangle]^{3/2} M / N_A$$

This equation shows that (a) the more dilute the polymer solution, the more probable the cyclization over the polycondensation is, and (b) at the same molecular weight, double the concentration (higher yield) can be used for heterodifunctional than for homodifunctional polymers. The practical strategies used for the preparation of cyclic copolymers will be presented below.

A. Cyclic Homopolymers from Precursors with Homodifunctional Groups

Many different linking agents and functional groups have been proposed for the synthesis of cyclic polymers using homodifunctional groups. However, the general strategy followed by most authors is similar and can be outlined as follows:

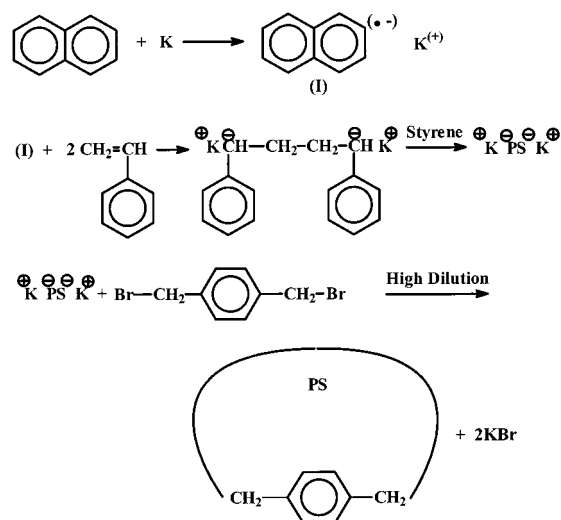
- preparation of a monodisperse α, ω -homodifunctional living polymer,
- reaction of the living polymer with a homodifunctional linking agent,
- and (c) fractionation for purification of the cyclic polymer.

In all cases a high dilution of the linking reaction was used in order to increase the yield of cyclization.

1. Cyclic Homopolymers

Hild et al.¹⁶⁸ prepared ring polystyrenes under argon atmosphere by reacting α, ω -dipotassium polystyrene, synthesized by potassium naphthalenide, with dibromo-*p*-xylene in a mixture of THF:benzene or cyclohexane in a ratio 1:1 (v/v) (Scheme 81). The addition of the reagents was made by using two dropping funnels. After fractional precipitation, the yield of the synthetic procedure was between 30% and 46%. The apparent molecular weight obtained by SEC was about 20% lower than that obtained by

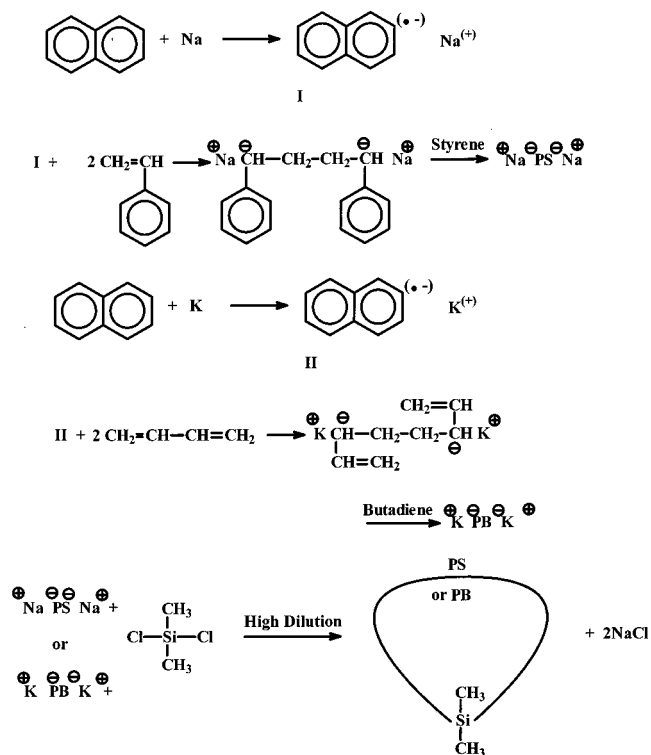
Scheme 81



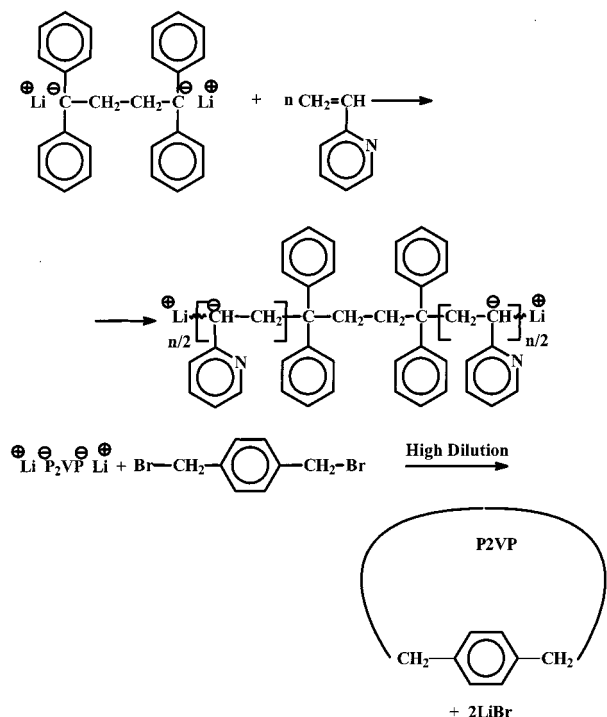
light scattering, and this was attributed to the lower hydrodynamic volume that is expected for a cyclic polymer when compared to the corresponding linear material.

Roovers et al.¹⁶⁹ synthesized cyclic PS under high-vacuum conditions by using naphthalene sodium as a difunctional initiator. The polymerization solvent was a mixture of THF:benzene in a ratio of 1:1 (v/v). The linking agent was dichlorodimethylsilane, and the linking reaction was performed in cyclohexane at room temperature, which is close to θ conditions for PS (Scheme 82). Although the procedure has been questioned by some authors due to the higher possibility of forming permanent "knots", no clear evidence of this conjecture has been forthcoming. Roovers synthesized a series of cyclic PSs having molecular weights $(2.0-55) \times 10^4$ g/mol. The separation of the

Scheme 82



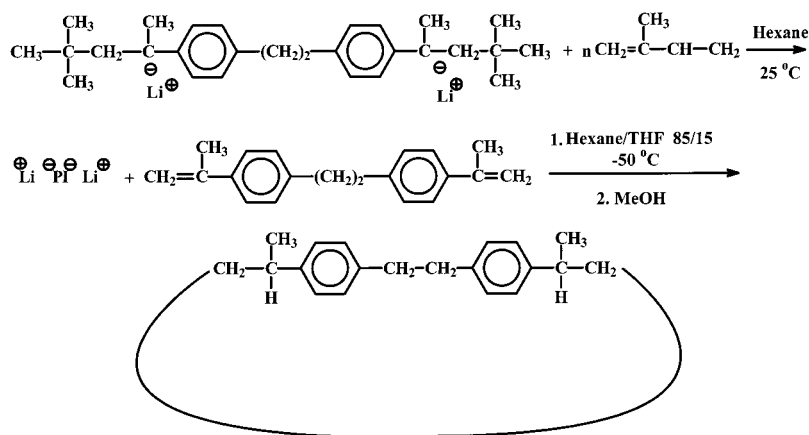
Scheme 83



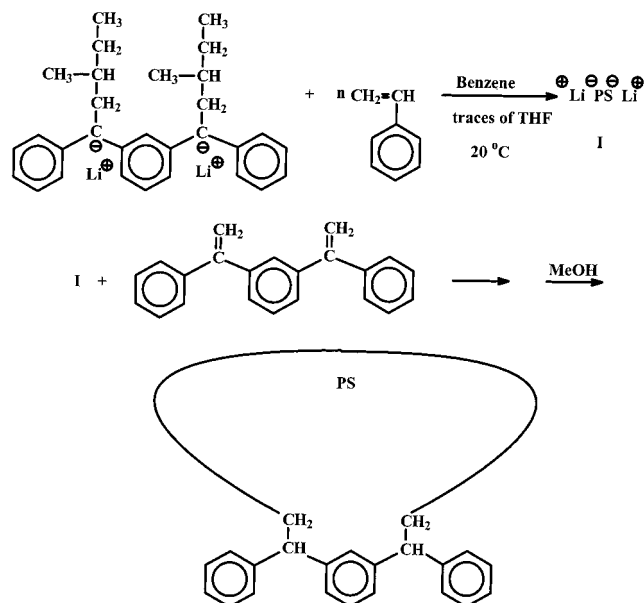
cyclic from the linear precursor was achieved by ultracentrifugation. The $g' = [\eta]_r/[\eta]_l$ values, where $[\eta]_r$ and $[\eta]_l$ are the intrinsic viscosities of the cyclic and the corresponding linear polymer, respectively, varied from 0.58 to 0.68, which is in good agreement with the theoretically and experimentally reported values.

A few years later, by using the same experimental procedures, the same scientists prepared cyclic polybutadienes¹⁷⁰ (Scheme 82). THF was the polymerization solvent, which results in a 60% 1,2-content. From the g' values was concluded that some of the cyclic polybutadienes (PBd) were contaminated by their linear precursors. A high-resolution column set was used in order to separate the linear from the cyclic polymer. In this work the characterization analysis was the most comprehensive presented so far. Recently, these cyclic PSs were analyzed by high-pressure liquid chromatography under critical conditions, which is a method that can separate linear and cyclic macromolecules according to their archi-

Scheme 84



Scheme 85

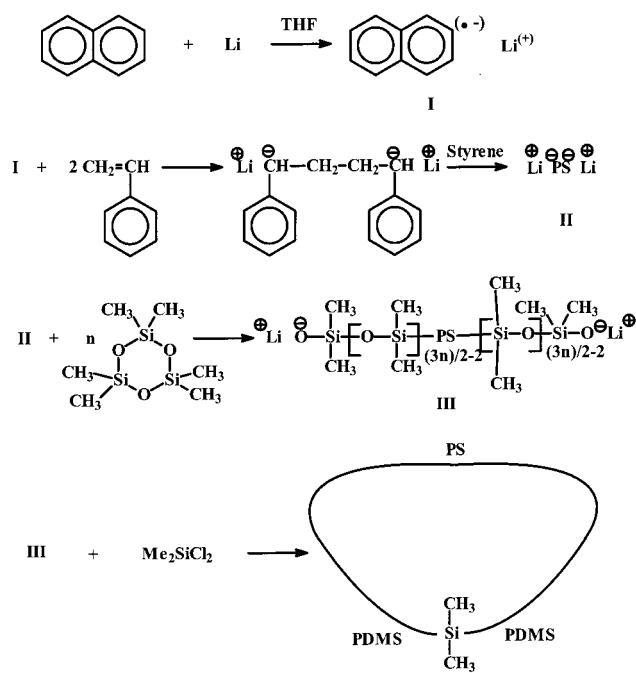


itecture and not according to their hydrodynamic volume, and verified the low degree of contamination.¹⁷¹

Hogen-Esch et al.¹⁷² synthesized α,ω -dilithium poly(2-vinylpyridine) by anionic polymerization of 2-vinylpyridine with 1,4-dilithio-1,1,4,4-tetraphenylbutane, in THF at -78°C under inert atmosphere. The cyclization reaction was performed in high dilution by adding 1,4-bis(bromomethyl)benzene (Scheme 83). The main indication for the formation of the cyclic polymers was the significant difference in the T_g value between the cyclic and the linear precursor.

A few years later the synthesis of cyclic polyisoprenes with high 1,4-content was presented by Madani et al.¹⁷³ They used hexane as polymerization solvent at -40°C , and a difunctional initiator formed by the reaction of 1,2-bis(4-isopropenylphenyl)ethane with 2 mol of *t*-BuLi. This initiator was soluble in organic solvents. The linking agent was a nonconjugated diene, 1,2-bis(isopropenyl-4-phenyl)ethane. The cyclization was performed in the presence of 15% THF at -50°C (Scheme 84). Under the same conditions they tried to synthesize bicyclic and tadpole molecules. They found a high yield of cyclization by using only SEC analysis. The high yield was attributed to

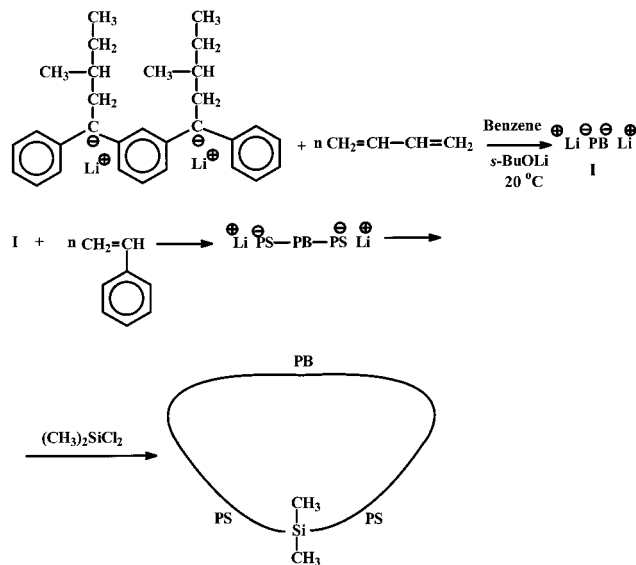
Scheme 86



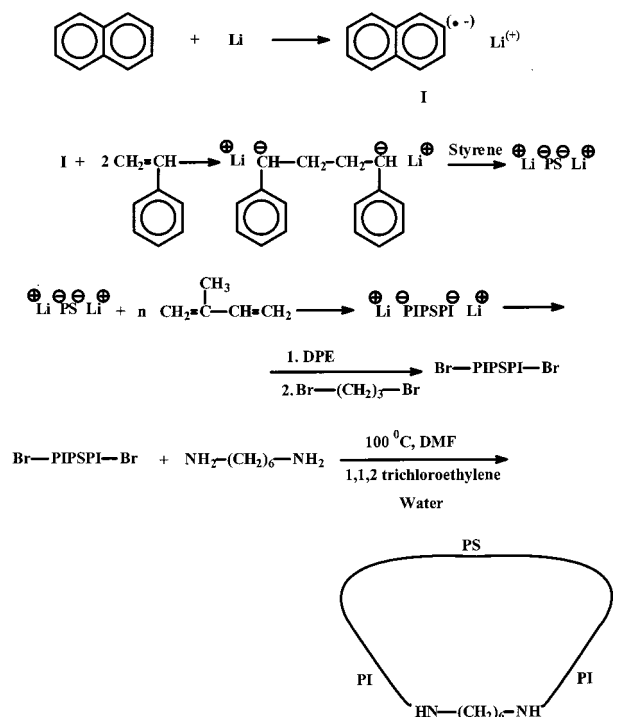
the association of the lithium carbanions under the cyclization conditions that favors the intramolecular reaction.

Leppoittevin et al.¹⁷⁴ synthesized ring-shaped polystyrenes by using 1,3-bis(1-phenylethylenyl)benzene (MDDPE) activated by *s*-BuLi. The polymerization solvent was benzene, and a trace of THF was used in order to accelerate the initiation reaction. The polymerization and cyclization reactions were performed in a drybox. MDDPE was used as the linking agent for the cyclization reaction (Scheme 85). The cyclic polymers were deactivated with methanol. The macrocyclic products were separated from the linear precursors and polycondensates by preparative high performance liquid chromatography at the exclusion-adsorption transition point. Further information on the purity of the cyclic polymers was obtained by MALDI-TOF MS. The above techniques seem to

Scheme 87



Scheme 88



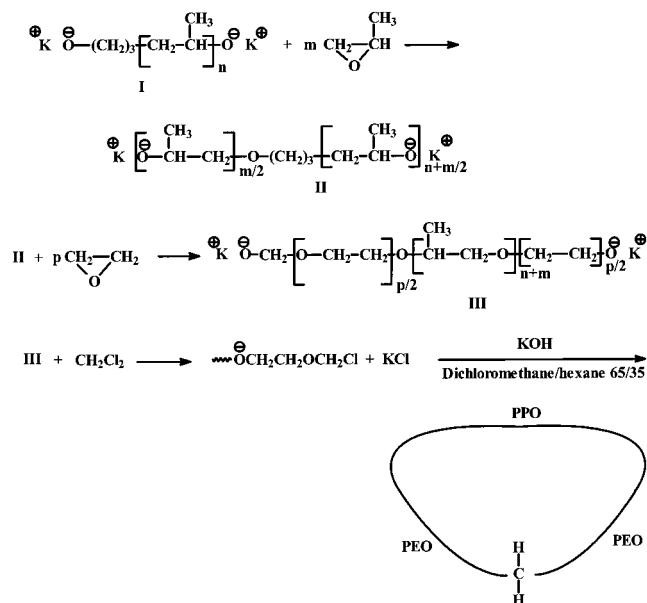
be efficient for the verification of the cyclic structure. An additional verification was the determination of the g' ratio value, which was found to be equal to 0.67.

2. Cyclic Block Copolymers

Cyclic block copolymers with blocks that microphase separate in bulk are expected to form only loops at both sides of the interface, while their linear triblock analogues are able to form loops and bridges. This significant difference is expected to give very interesting morphological properties to the cyclic copolymers.

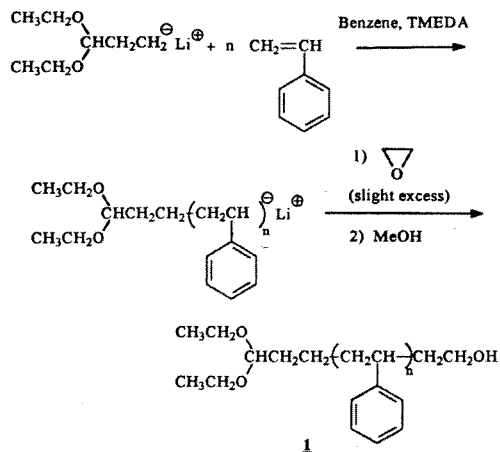
The first well-defined cyclic block copolymers of poly(dimethylsiloxane) and PS were made by Yin et

Scheme 89

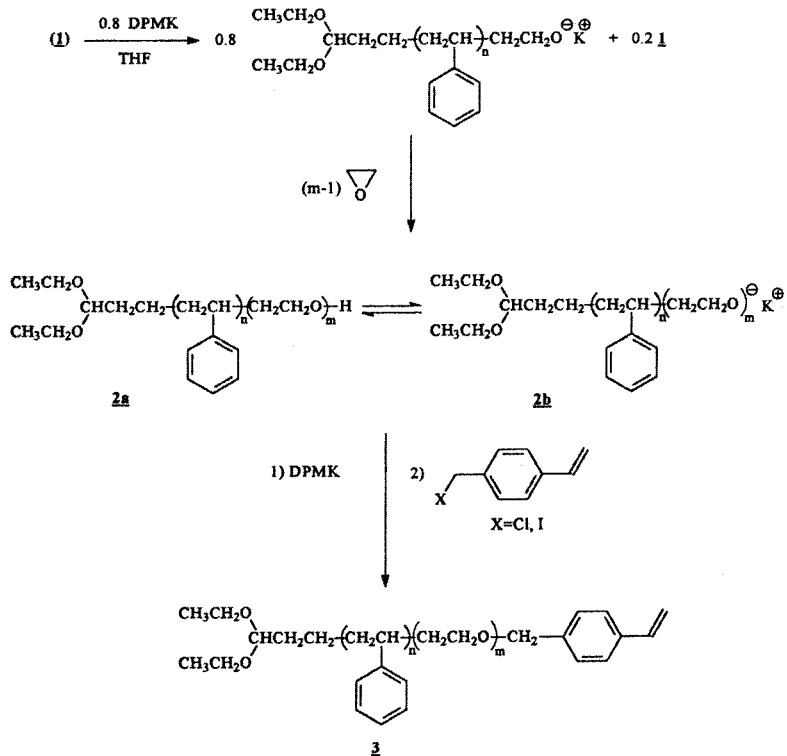


Scheme 90

Part a

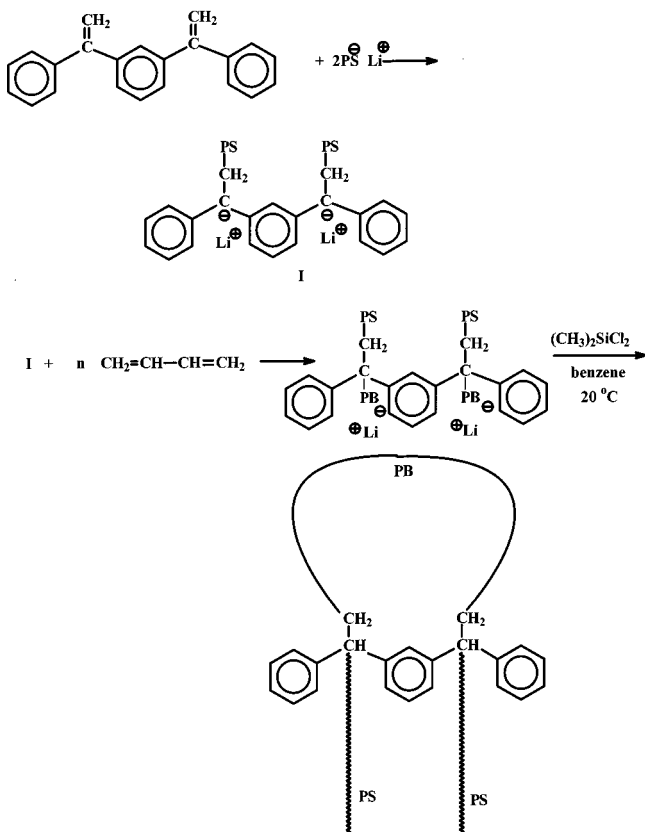


Part b



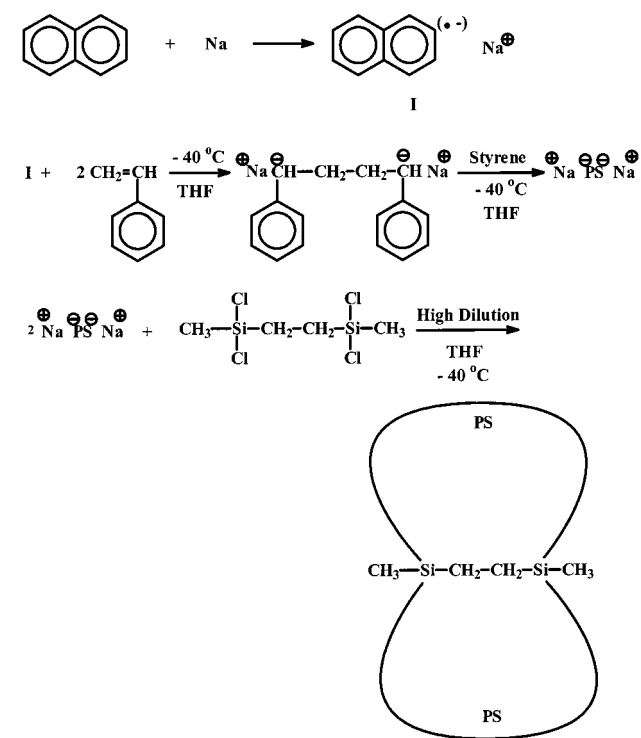
al.^{175,176} Styrene was polymerized by lithium naphthalenide initiator at -78°C in THF, followed by the polymerization of hexamethylcyclotrisiloxane (D_3). The resulting α,ω -living triblock PDMS-PS-PDMS was cyclized with dichlorodimethylsilane at $5-10^\circ\text{C}$

Scheme 91



under high dilution conditions (Scheme 86). The purity of the cyclic copolymers was investigated by ^1H NMR, ^{29}Si NMR, and FTIR. The lack of SiOH or SiCl groups in the final copolymers was a direct indication of the high purity of the cyclics. However, due to the backbiting reaction of the living PDMS under the conditions used for the cyclization reaction, the quality of the cyclics is questionable. In the same

Scheme 92



study the synthesis of a linear CBABC and the corresponding cyclic ABCB is described, where A is PS, B is 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane, and C is PDMS.

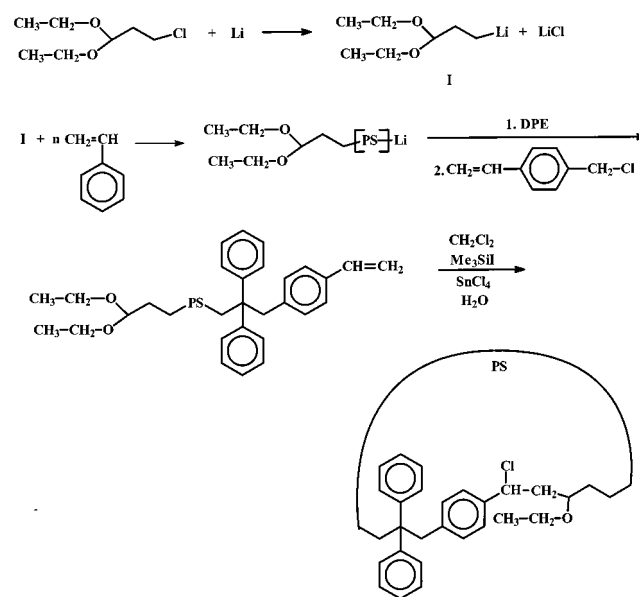
Ma et al.¹⁷⁷ synthesized α,ω -dilithium poly(styrene-*b*-butadiene-*b*-styrene)s (PS-*b*-PBd-*b*-PS) by using 1,3-bis(1-phenylethenyl)benzene activated with 2 mol of *s*-BuLi as initiator for the sequential polymerization of butadiene and styrene in the presence of *s*-BuOLi in benzene. The cyclization reaction was performed under high dilution in cyclohexane with either dichlorodimethylsilane or MDPPE (Scheme 87). The cyclic copolymer was isolated by fractional precipitation. The only indication of the formation of this architecture was the lower intrinsic viscosity.

Ishizu et al.^{178,179} synthesized poly(I-*b*-S-*b*-I) triblock copolymer by the sequential polymerization of styrene and isoprene, using lithium naphthalenide as initiator in a mixture of THF:benzene equal to 8:2 (v/v) at -78°C . The α,ω -living triblock was reacted first with 1,1-diphenylethylene followed by a reaction with a large excess of 1,3-dibromopropane. The cyclization reaction was performed by reacting the α,ω -dibromofunctional triblock copolymer with 1,6-diaminohexane (Scheme 88) in a mixture of dimethylformamide (DMF)/1,1,2-trichloroethylene/water (interfacial condensation). The cyclics were characterized only by SEC. The morphology study has shown that the cyclic copolymers exhibited smaller domain spacings compared to the corresponding linear copolymers.

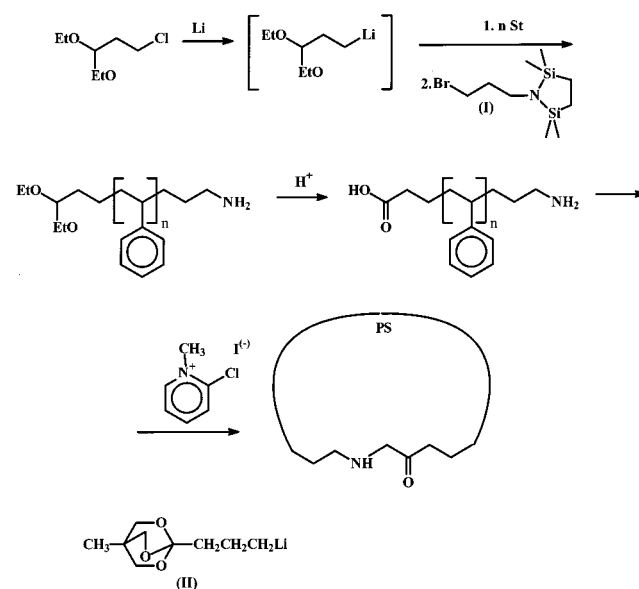
Yu et al.¹⁸⁰ have synthesized cyclic diblock copolymers of ethylene oxide and propylene oxide. They polymerized sequentially propylene oxide and ethylene oxide by using the difunctional initiator (I) shown in Scheme 89. The cyclization reaction of the α,ω -hydroxyl-ended diblock macromolecules was carried out under Williamson conditions. A solution of the triblock precursor in a mixture of dichloromethane and hexane 65:35 (v/v) was added to a stirred suspension of powdered KOH (85% w/v) in the same dichloromethane/hexane mixture (Scheme 89). After separation and evaporation of the organic phase, the cyclic diblocks were isolated by fractional precipitation. The dilute solution properties of the cyclics and the corresponding linear triblock and diblock copolymers with the same composition and total molecular weight were compared. By examining the micellar behavior in water they found that the aggregation numbers were on the order $N_T < N_C < N_D$, where N_T , N_C , and N_D , are the aggregation numbers of the triblocks, cyclic, and diblocks, respectively.

Recently, the group of Deffieux¹⁸¹ presented the synthesis and solution properties of macrocyclic poly(styrene-*b*-ethylene oxide). The synthetic route involved the preparation of a linear α -diethylacetal- ω -styrenyl poly(styrene-*b*-ethylene oxide) precursor and cyclization by cationic activation with SnCl_4 catalyst. The α -diethylacetal- ω -styrenyl poly(styrene-*b*-ethylene oxide) precursor was synthesized by using α -diethylacetalpropyllithium as initiator of styrene. The functional living PS was end-capped with ethylene oxide, and the resulted ω -hydroxyl group was reacted with diphenylmethylpotassium. The potassium alkox-

Scheme 93



Scheme 94

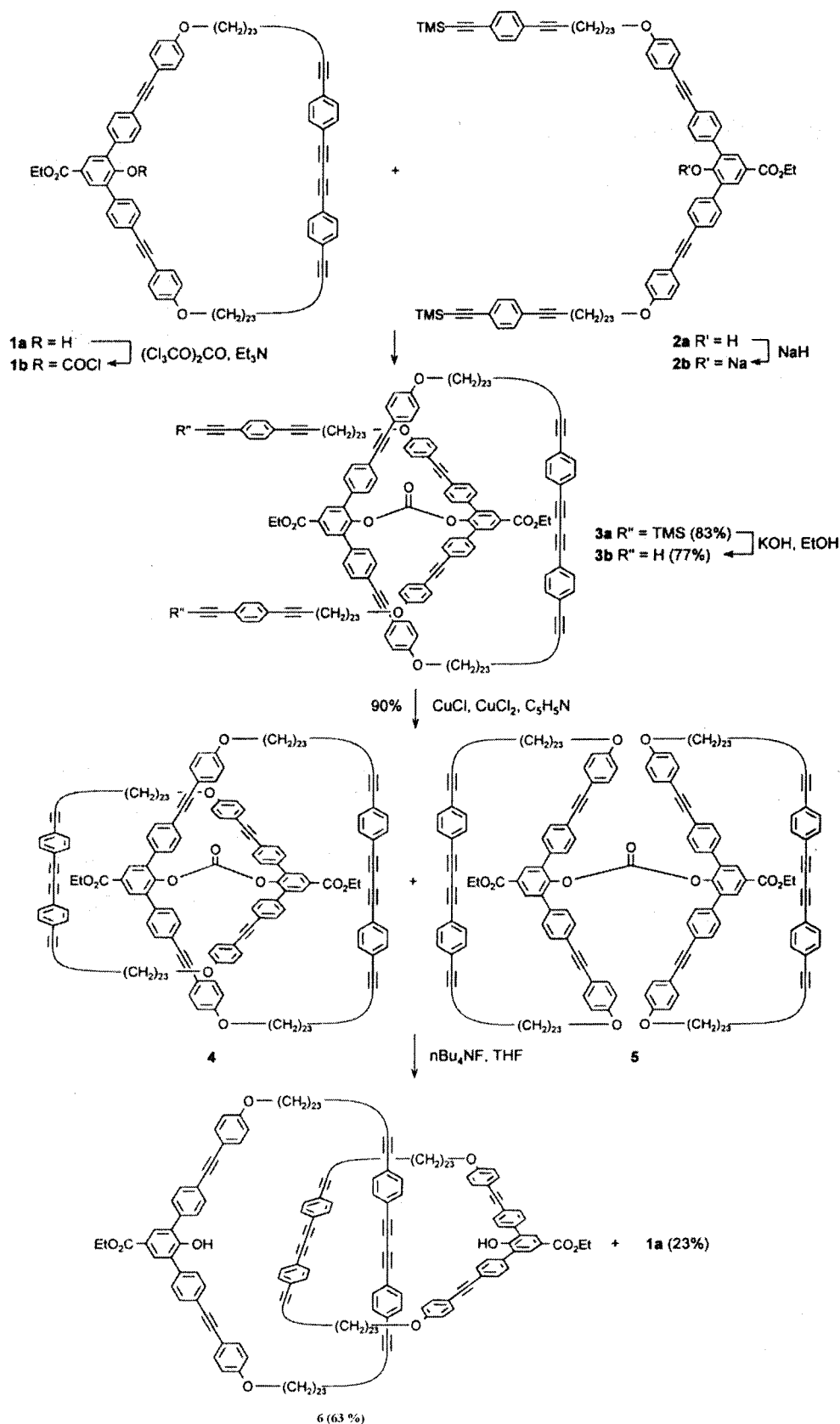


ide was used to initiate the polymerization of ethylene oxide. Finally, the potassium alkoxide group was reacted with *p*-chloromethyl styrene to anchor a styrenyl group at the ω -end of the copolymer chains (Scheme 90b). The cyclization procedure was performed under high dilution conditions.

3. Tadpole and Bicyclic Polymers

Tadpole polymers are polymers consisting of one cyclic chain and one or more linear chains. Quirk and Ma¹⁸² prepared a tadpole copolymer consisting of a cyclic PBd and two linear PS chains. First they reacted PDPPE with two monofunctional living PS chains. The resulting difunctional PS was used to initiate the polymerization of butadiene. The living PBd chains were then cyclized with dichlorodimethylsilane in benzene as shown in Scheme 91. The separation of the tadpole copolymer from the polycondensates was achieved by fractional precipitation.

Scheme 95



The smaller the ring fraction in the copolymer, the more difficult the separation. Insufficient characterization results were given.

Antonietti et al.¹⁸³ synthesized bicyclic PS homopolymers. They prepared difunctional PS initiated by sodium naphthalene in THF at -40°C . The cycliza-

tion reaction was performed in a 0.5% solution of linear precursor by using 1,2-bis(methyldichlorosilyl)ethane (Scheme 92). Although the final product was proved to have double the molecular weight, sufficient characterization results to prove the architectures claimed were not presented.

Along the same lines, Mandani et al.¹⁷³ reacted a difunctional polyisoprene with silicon tetrachloride, to prepare bicyclic polyisoprenes. The only indication for the formation of the bicyclic homopolymer was the lower hydrodynamic volume obtained by SEC. However, the final polymer was not isolated for further characterization.

B. Cyclic Homopolymers from Precursors with Heterodifunctional Groups

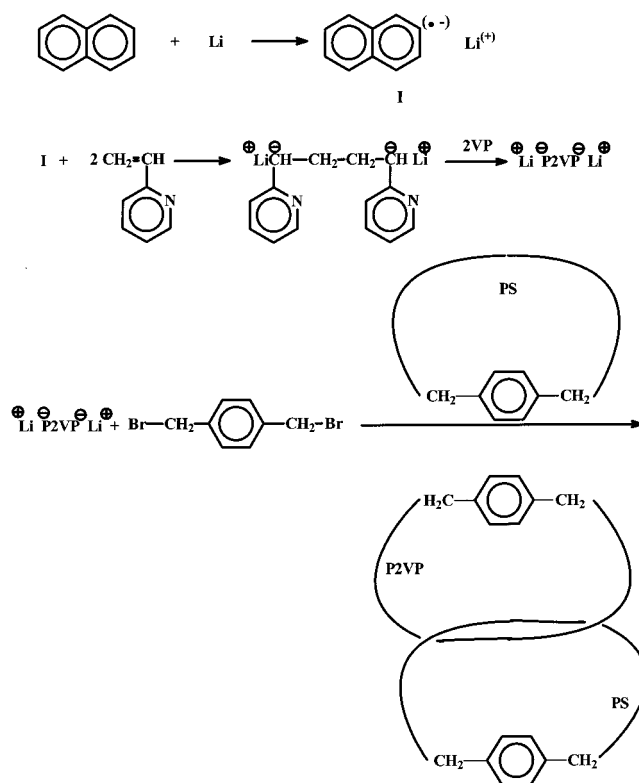
Deffieux was one of the first to use precursors with α,ω -heterodifunctional reactive groups. With his collaborators¹⁸⁴ he synthesized α -acetal-functionalized linear PS by using 3-lithiopropionaldehyde diethylacetal as initiator. After polymerization, the living anion was reacted first with 1,1-diphenylethylene and then with *p*-chloromethylstyrene. The acetal group of the initiator was converted into the α -iodo ether group with trimethylsilyliodide. The cyclization was performed as shown in Scheme 93. The yield was between 80% and 85%. The molecular weight range of the cyclics prepared was between 2000 and 6700. The presence of 10% linear precursor in the final product was detected by NMR spectroscopy. More recently, Pasch et al.¹⁸⁵ analyzed the cyclic PS with liquid chromatography under critical conditions. They found that the higher the molecular weight of the polymer, the higher the contamination with linear precursor. The cyclic structure was also confirmed by MALDI-TOF MS experiments.

Kubo et al.¹⁸⁶ prepared cyclic PS from α -carboxyl- ω -amino bifunctional linear PS. The linear precursor was synthesized by using 3-lithiopropionaldehyde diethylacetal as the carboxyl-protected functional initiator and 2,2,5,5-tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disila-cyclopentane (Scheme 94 (I)) as the amino-protected terminating agent of the living anions. The preparation of the linear polymer for the cyclization involved five steps in order to deprotect the reactive groups and four purifications on silica gel to give the α -carboxyl- ω -amino bifunctional linear PS. The cyclization was performed under high dilution conditions by intramolecular amidation with an overall yield of 30–35% (Scheme 94). More recently, another approach for the preparation of α -carboxyl- ω -amino bifunctional linear PS was presented by Kubo et al.¹⁸⁷ 1-(3-Lithiopropyl)-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane was used as initiator (Scheme 94 (II)) and 2,2,5,5-tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopentane (I) for neutralization of the living ends. The former is a carboxyl-protected initiator, while the latter is an amino-protected linking agent. After deprotection of the functional groups, the cyclization was performed under the same conditions presented above. The molecular weight of the samples prepared was between 1700 and 2700. The overall yield of their approach was 81%. The authors performed NMR spectroscopy and MALDI-TOF analysis of the cyclics in order to determine their purity.

C. Catenanes

Catenanes consist of two or more chemically independent cyclic molecules that penetrate each other

Scheme 96

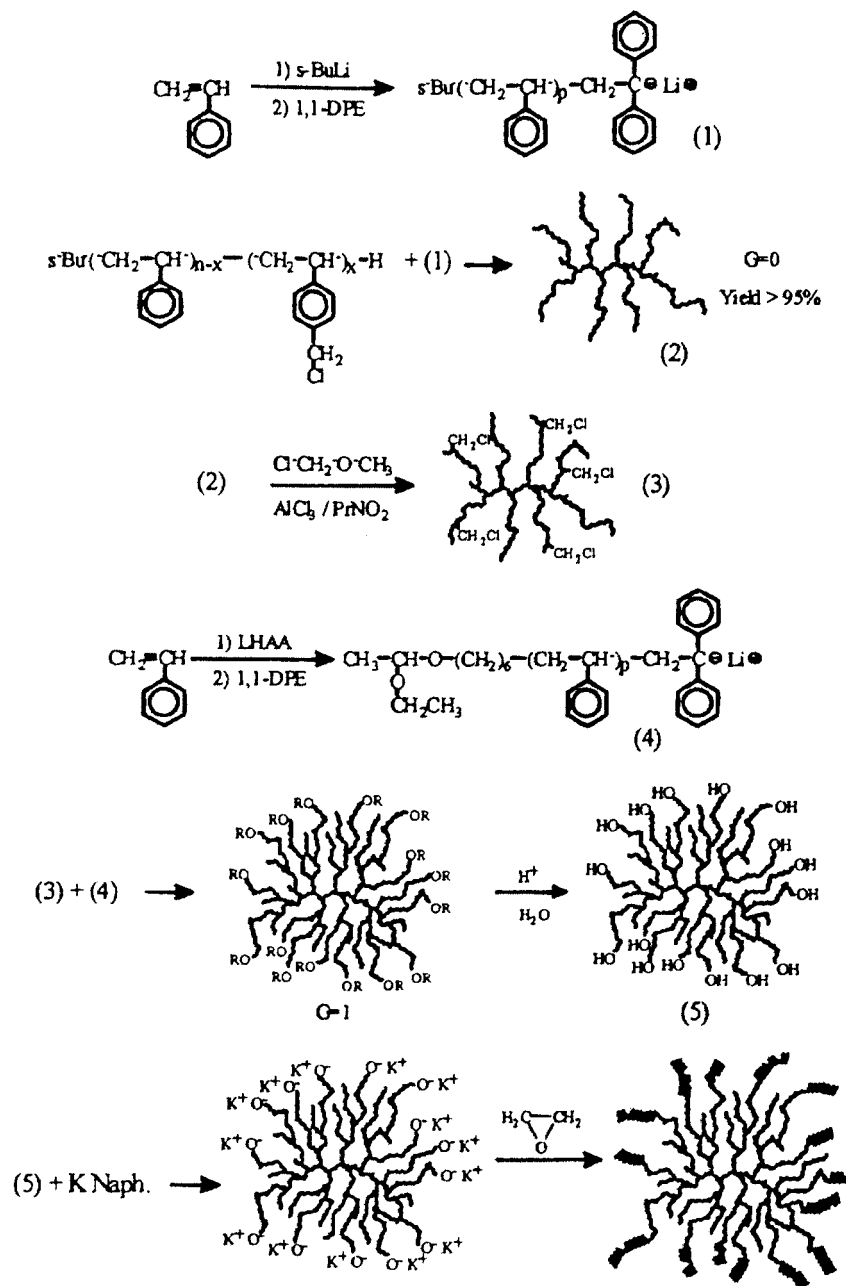


and therefore are not covalently but only topologically linked. The ring molecules are allowed to rotate independently of each other.

Unsal et al.^{188,189} synthesized a catenane consisting of two interpenetrating rings. They used a cyclic oligomer of polyethylene that contains one 4-hydroxybenzoate group that carries toluene units in the 3- and 5-positions (Scheme 95). The polyethylene chains are connected with this group through ether bonds. The linear precursor of the next cycle that will be connected to the first was a similar molecule containing the latter group and polyethylene oligomers prepared by anionic polymerization and hydrogenation, and in the chain ends were acetylene units (**2a**, Scheme 95). The cyclic compound was transformed into the chloroformate **1b** by reaction with triphosgene in the presence of triethylamine. The cycle precursor was deprotonated with sodium hydride and reacted with **1b** to form **3a**, which was purified by column chromatography and desilylated to give product **3b**, followed by cyclization by oxidative acetylene dimerization under high dilution conditions. Treatment of **4** with *n*-Bu₄NF in THF gave the catenane **6**. The SEC analysis showed that low molecular weight products that were identical to the cyclic compound **1a** were also formed. From this it was concluded that on cyclization of **3b**, the dumbbell-shaped carbonate **5** was formed in addition to the intended catenane precursor **4**. The intermediate products were characterized by NMR spectroscopy. The catenanes were characterized only by SEC and NMR spectroscopy.

Gan et al.¹⁹⁰ synthesized catenated copolymers containing one cyclic PS and one cyclic poly(2-vinylpyridine) (P2VP). The preparation involved the cyclization of a difunctional P2VP polymeric chain in

Scheme 97



the presence of cyclic PS. The polymerization of 2-vinylpyridine was performed in THF by using lithium naphthalenide as initiator. The cyclization reaction was performed at room temperature at relatively high concentration of cyclic PS in order to increase the possibility of the formation of catenanes (Scheme 96). The catenanes were isolated from the side products and cyclic PS homopolymer by treating the crude product with cyclohexane, which is a poor solvent for P2VP, and methanol, which is poor solvent for PS. Indications for the formation of the catenanes were obtained only by NMR spectroscopy.

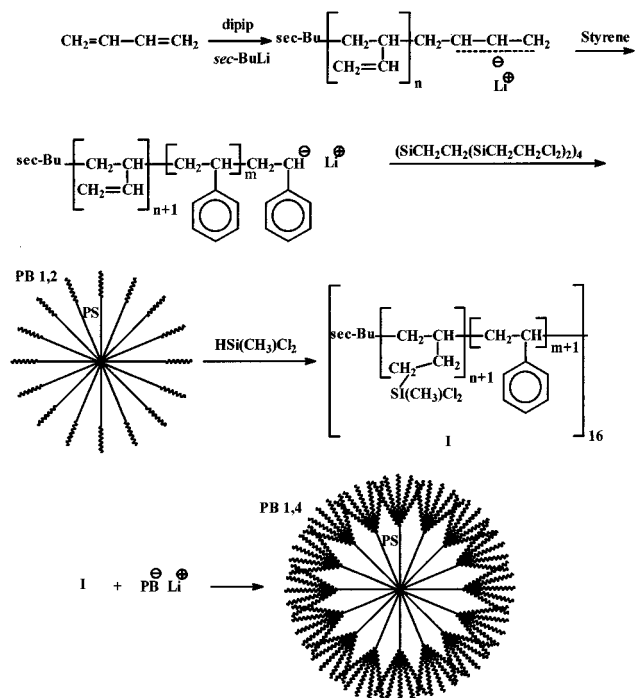
VII. Hyperbranched Architectures

Branched polymers have physical properties distinct from their linear analogues, both in solution and in the melt. However, the more complicated the structure, the more difficult the development of

techniques for synthesizing polymers with well-defined molecular characteristics and the more difficult to characterize them. Many synthetic approaches have been presented for the preparation of hyperbranched polymers, mainly by polycondensation reactions.^{191,192} In most cases the resulting polymers exhibited high molecular and compositional polydispersity, and their molecular architectures could not be exactly defined. Even so, their properties were very interesting, and therefore these polymers can be used in many technological applications. Here several synthetic approaches to the synthesis of hyperbranched polymers by anionic polymerization will be presented.

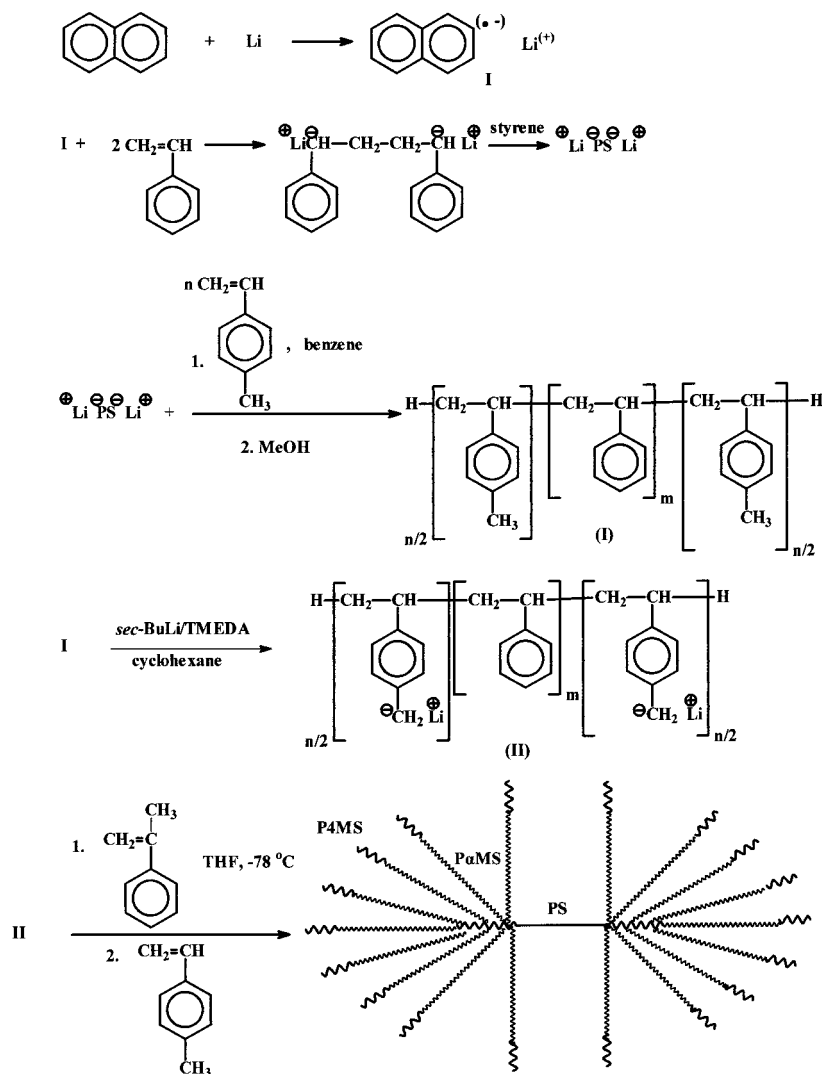
Gauthier et al.¹⁹³ prepared highly branched arborescent graft copolymers of PS and poly(ethylene oxide). Their synthetic approach involved the reaction of living PS end-capped with DPE with chlorometh-

Scheme 98

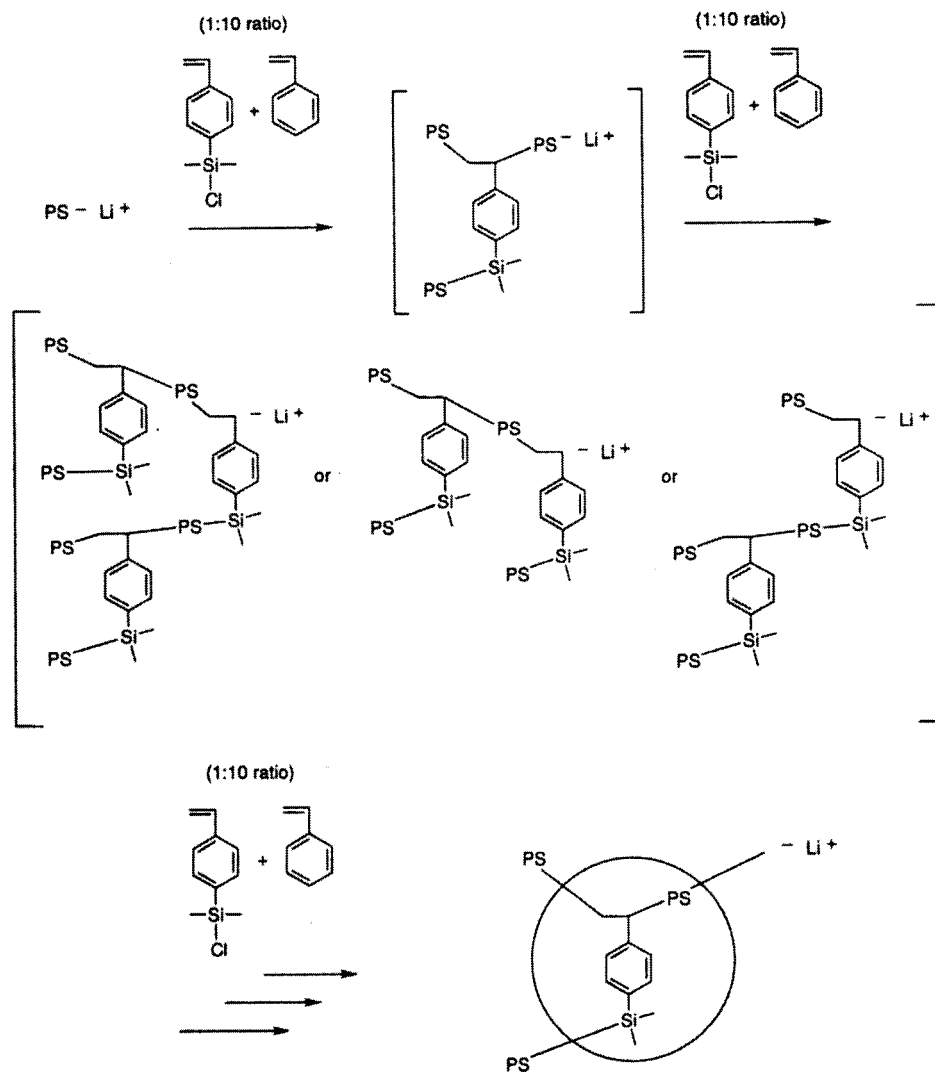


ylated linear polystyrene. The produced graft polymer was further chloromethylated and was reacted with living PS end-capped with DPE that contains a hydroxyl-protected group. The hydroxyl groups of the resulting graft polymer were deprotected and titrated by potassium naphthalenide in order to transform the hydroxyl to $-\text{O}^{\ominus}\text{K}^{\oplus}$ groups. These anions are capable of polymerizing ethylene oxide. The resulted copolymer exhibits a PS core and long arms (shell) of poly(ethylene oxide). The hyperbranched materials were isolated by fractional precipitation. The composition analysis of the copolymers were performed by FTIR and NMR spectroscopies. SEC was used for the evaluation of the polydispersities of the final products. Dynamic light scattering experiments of the intermediate PS core and the final copolymer were performed in order to demonstrate the incorporation of the poly(ethylene oxide) chains. Roovers et al.^{102,103} prepared umbrella star copolymers of PS and PBd or P2VP. The structure of these copolymers can be described as a multiarm star in which each arm, instead of a free end, connects to another star molecule. The core of the umbrella polymers was PS chains, while the shell was either PBd or P2VP. The synthesis of these copolymers involved the preparation of 1,2-PBd-*b*-PS polymeric chains in which the

Scheme 99



Scheme 100



1,2-PBd block is short, followed by coupling with an appropriate chlorosilane linking agent, depending on the desired number of arms. After isolation of the star by fractional precipitation, the double bonds of the 1,2-PBd were hydrosilylated in order to incorporate $-\text{Si}(\text{CH}_3)_2\text{Cl}$ or $-\text{Si}(\text{CH}_3)_2\text{H}$, followed by reaction with living PBd or P2VP chains (Scheme 98).

Ishizu et al.¹⁹⁴ synthesized hyperbranched macromolecules that resemble dendrimers. The synthetic approach involved the preparation of poly(4-methylstyrene-*b*-PS-*b*-poly(4-methylstyrene)) triblock copolymer by using naphthalene lithium as difunctional initiator. The 4-methyl groups of the terminal blocks were metalated with *s*-BuLi/tetramethylethylenediamine (TMEDA) complex in a molar ratio of 1:2. After removal of the excess *s*-BuLi by repeated precipitation of the living polymer and transfer of supernatant solution to another flask under high vacuum conditions, the polymer was dissolved in THF and was used as the initiator of α -methylstyrene at -78°C . After the polymerization of α -methylstyrene, a small amount of 4-methylstyrene was added. The procedure of metalation of the α -methyl groups and polymerization of α -methylstyrene can be repeated many times to form a dendritic type hyperbranched polymer (Scheme 99). The characterization of the inter-

mediate polymers was performed by SEC and static light scattering. It was found that an average number of 29 arms of poly(α -methylstyrene) was attached to each initial poly(4-methylstyrene) block. The intrinsic viscosity of the hyperbranched copolymers was measured, and the g' values were calculated.

Recently Hasan et al.¹⁹⁵ synthesized hyperbranched copolymers by using a dendritic type initiator. Low molecular weight living PS chains were reacted with a mixture of vinylbenzyl chloride or 4-(chlorodimethylsilyl)styrene and styrene in a molar ratio 1:10. The living ends of polystyrene chains can polymerize the styrene monomer and at the same time can react with the $-\text{SiCl}$ or $-\text{CH}_2\text{Cl}$ group of the or 4-(chlorodimethylsilyl)styrene or vinylbenzyl chloride, as shown in Scheme 100. A dendritic type initiator is obtained for polymerization of either styrene or isoprene. The weak point of this approach is that the positions of the grafting points of the macromolecular initiator are randomly distributed along the PS chains. Moreover, the number of the linear PS or PI chains cannot be controlled. The molecular weight of the resulting polymer was characterized by SEC coupled with multiangle laser light scattering. In the case of the copolymers, the composition was determined by ^1H NMR.

VIII. Concluding Remarks

Anionic polymerization has proven to be a very powerful tool for the synthesis of well-defined macromolecules with complex architectures. Although, until now, only a relatively limited number of such structures with two or three different components (star block, miktoarm star, graft, α,ω -branched, cyclic, hyperbranched, etc. (co)polymers) have been synthesized, the potential of anionic polymerization is unlimited. Fantasy, nature, and other disciplines (i.e., polymer physics, materials science, molecular biology) will direct polymer chemists to novel structures, which will help polymer science to achieve its ultimate goal: to design and synthesize polymeric materials with predetermined properties.

Furthermore, anionic polymerization will lead to well-defined multicomponent multiblock copolymers. A plethora of novel multiphase morphologies will be hopefully discovered. The potentiality of these multicomponent multiblock copolymers to be used as multifunctional smart materials is enormous.

Finally, combination of anionic with other polymerization methods (cationic, living radical, ROMP, metallocenes, etc.) will open new horizons for the synthesis of more complex and more fascinating macromolecular structures.

In the years to come there will be a new thrust in polymer synthesis like the one in the early 1960s, on the condition that characterization techniques for complex architectures will be also advanced.

IX. List of Symbols and Abbreviations

$[\eta]_l$	intrinsic viscosity of a linear polymer
$[\eta]_r$	intrinsic viscosity of a ring polymer
$\langle r^2 \rangle$	mean square end-to-end distance
c	polymer concentration
CDMSS	4-(chlorodimethylsilyl)styrene
c_{equal}	polymer concentration at which intra- and intermolecular reactions of α,ω -difunctional polymers are equally likely
D ₃	hexamethylcyclotrisiloxane
DIB	<i>m</i> -disopropenylbenzene
DLS	dynamic light scattering
DMAPLi	3-dimethylaminopropyllithium
DMF	dimethylformamide
d-PBd	deuterated polybutadiene
DPE	1,1-diphenylethylene
DPMP	diphenylmethylpotassium
d-PS	deuterated polystyrene
DVB	divinylbenzene
EEMA	1-(ethoxy)ethyl methacrylate
EGDM	ethylene glycol dimethacrylate
EPEB	1,1-(1,2-ethanediyl)bis[4-(1-phenylethenyl)-benzene]
FTIR	Fourier transform infrared spectroscopy
g'	the ratio $[\eta]_r/[\eta]_l$
GMA	glycidyl methacrylate
HPLC	high performance liquid chromatography
Is	isoprene
LALLS	low angle laser light scattering
LL	poly(L-lactide)
LS	light scattering
MALDI-TOF-MS	matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy
MDDPE	1,3-bis(1-phenylethenyl)benzene
M_n	number-average molecular weight

MO	membrane osmometry
M_w	weight-average molecular weight
M_w/M_n	molecular weight distribution
N_A	Avogadro's number
NMR	nuclear magnetic resonance
Ns	nosyl group
P ϵ -CL	poly(ϵ -caprolactone)
P2VP	poly(2-vinylpyridine)
P2VPK	poly(2-vinylpyridinyl) potassium
P4MeS	poly(4-methylstyrene)
P4VP	poly(4-vinylpyridine)
PBd	polybutadiene
PBdLi	polybutadienyllithium
PBS	poly(<i>p</i> - <i>tert</i> -butoxystyrene)
PDDPE	1,4-bis(1-phenylethenyl)benzene
PDMS	poly(dimethylsiloxane)
PDMSLi	poly(dimethylsiloxanyl) lithium
P_e	probability of intermolecular reaction of α,ω -difunctional chains leading to the formation of polycondensates
PEMA	poly(ethyl methacrylate)
PEO	poly(ethylene oxide)
PHS	poly(<i>p</i> -hydroxystyrene)
PI	polyisoprene
P_i	probability of intramolecular reaction of an α,ω -difunctional chain leading to the formation of a cyclic polymer
PILi	polyisoprenyllithium
PMMA	poly(methyl methacrylate)
PMMALi	poly(methyl methacrylyl) lithium
PPO	poly(propylene oxide)
PS	polystyrene
PS- <i>b</i> -PILi	polystyrene- <i>block</i> -polyisoprenyllithium
PSLi	polystyryllithium
<i>P</i> <i>t</i> BuA	poly(<i>tert</i> -butyl acrylate)
<i>P</i> <i>t</i> BuMA	poly(<i>tert</i> -butyl methacrylate)
<i>P</i> <i>t</i> BuMALi	poly(<i>tert</i> -butyl methacrylyl) lithium
PVN	poly(2-vinylnaphthalene)
r_1, r_2	copolymerization reactivity ratios
<i>s</i> -BuLi	<i>sec</i> -butyllithium
<i>s</i> -BuOLi	lithium <i>sec</i> -butoxide
SEC	size exclusion chromatography
SLS	static light scattering
St	styrene
<i>t</i> -BuLi	<i>tert</i> -butyllithium
THF	tetrahydrofuran
TMEDA	<i>N,N,N,N</i> -tetramethylethylenediamine
tri-DPE	1,3,5-tris(1-phenylethenyl)benzene
v_e	reaction volume of an end-functionalized group
VPO	vapor pressure osmometry
VS	(4-vinylphenyl)dimethylvinylsilane

X. References

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