

7

Macromolecular Architectures by Living and Controlled/Living Polymerizations

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7.1

Introduction

Homo- and copolymers, with high molecular weight (MW) as well as structural and compositional homogeneity, can be synthesized exclusively by living or controlled/living polymerizations. The way to living polymerization was opened in 1955 when the seminal work of Szwarc proved the livingness of macroanions and the term *living* was coined [1]. Szwarc's initial experiments, carried out under high vacuum conditions, proved the livingness of the anionic polymerization of styrene in an elegant but relatively simple way, i.e., the increase in viscosity (falling ball) by addition of new quantities of monomer. Furthermore, the critical contributions from Morton [2] and Bywater [3], to mention a few, propelled the field to its current state. New methods of controlled/living polymerizations were subsequently developed and led to the synthesis of well-defined materials composed of monomers noncompatible with anionic polymerization.

About 30 years after Szwarc's seminal work, the controlled/living routes for cationic polymerization were discovered. The highlights of the living cationic polymerization are presented in an elegant review by Kennedy, whose fundamental contributions to the field led to novel structures based on monomers not susceptible to anionic polymerization [4]. Simultaneously, the living/controlled group transfer polymerization of (meth)acrylates was developed by Webster [5].

Recently, several groups introduced controlled/living radical polymerization, and reviews on these new methods have been written by leading scientists in the field [6, 7]. The ground-breaking discovery of Szwarc together with subsequent developments inspired many researchers to apply the concept of livingness to other monomers such as ethylene, propylene, norbornene, etc. [8]. These methods and their combinations, together with a wide selection of monomers, serve as an arsenal for the synthesis of well-defined polymeric materials with predetermined properties and a rich variety of applications.

Representative syntheses of polymers with different macromolecular architectures (star, comb, cyclic, dendritic, hyperbranched, and other complex-branched), resulting from living and controlled/living methodologies and, in a few cases, with appropriate post-polymerization linking chemistry (e.g., chlorosilanes, “click”) are presented in this chapter.

7.2

Star Polymers

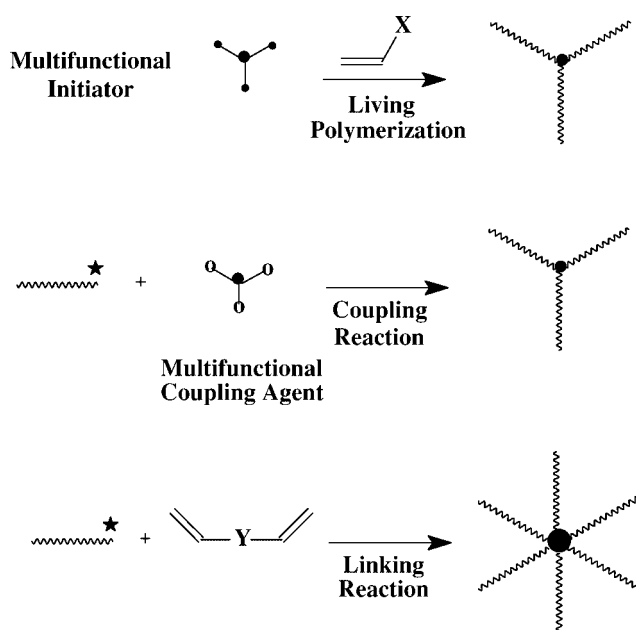
7.2.1

Symmetric Stars

Symmetric star polymers are branched polymers consisting of several identical linear chains linked to a central core. The synthesis of well-defined star polymers has been the subject of numerous studies to date [9–12]. Three general synthetic methods have been developed, as outlined in Scheme 7.1.

7.2.1.1 Multifunctional Initiators (MFIs)

Multifunctional initiators (MFIs) are compounds capable of simultaneously initiating several polymerizations to form the arms of the star polymer, while



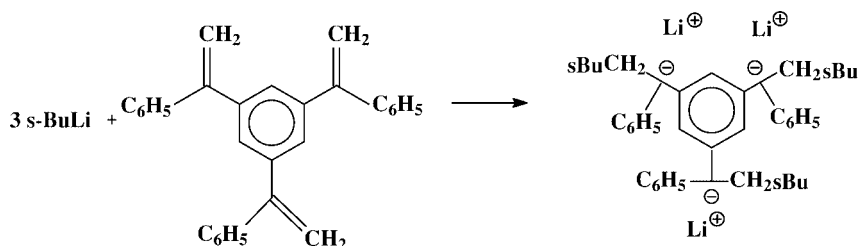
Scheme 7.1

the remaining moiety composes the core of the star. An MFI has to fulfill the following requirements to produce well-defined star polymers with uniform arms, low MW distribution, and controllable MWs: (i) all the initiation sites must be equally reactive and (ii) the initiation rate must be higher than the propagation rate.

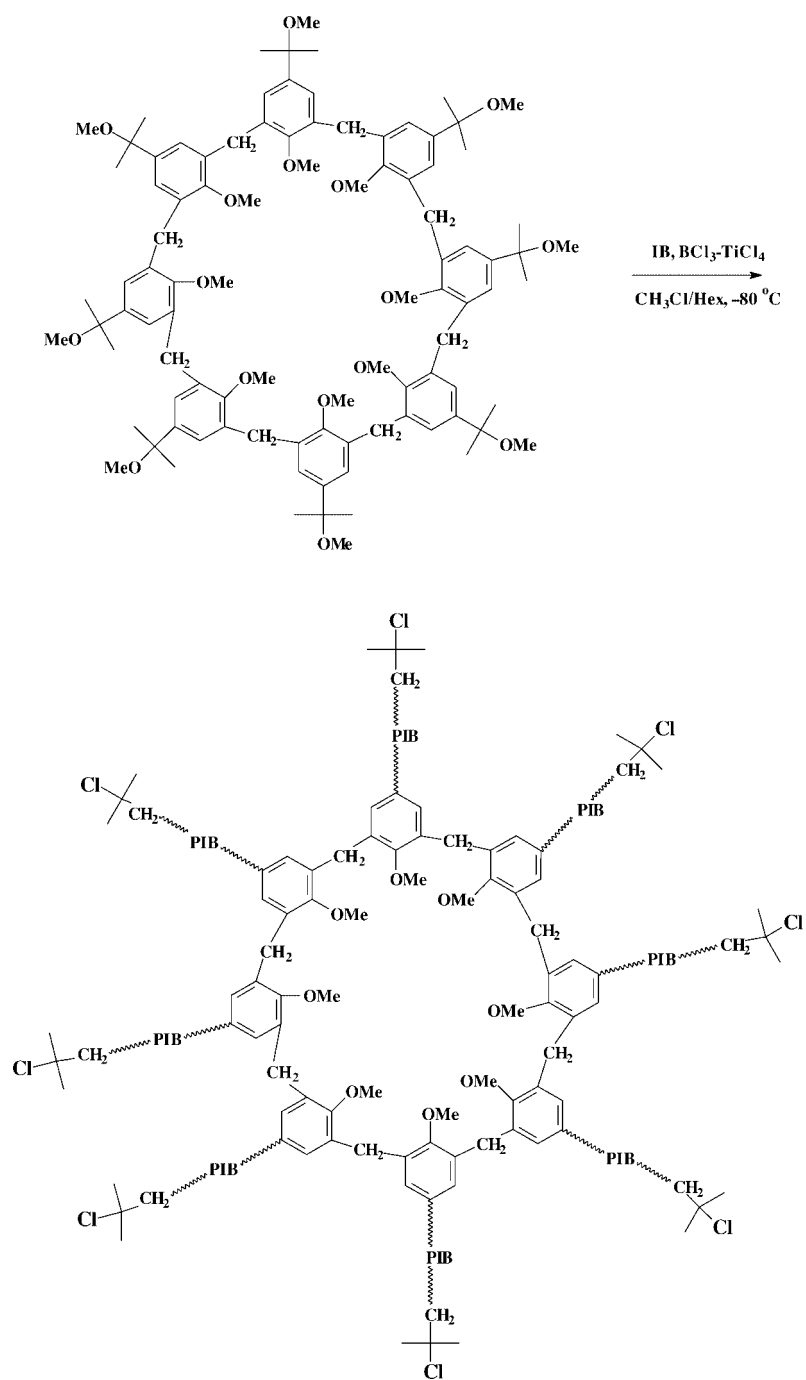
Burchard and colleagues [13, 14] first, and later Rempp and colleagues [15, 16] demonstrated that the reaction of divinyl benzene (DVB) with *n*-butyl lithium (*n*-BuLi) in dilute benzene solutions leads to MFIs (microgels) capable of polymerizing styrene, isoprene, and butadiene to produce star polymers. A slight variation was adopted by Funke [17, 18], where the polymerization of DVB was realized by low MW living poly(*t*-butylstyryl) lithium chains, instead of *n*-BuLi, to avoid the solubility problems arising from the strong association of the carbon-lithium functions in the nonpolar solvent.

A novel hydrocarbon-soluble trifunctional initiator was proposed by Quirk *et al.* [19] and 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 7.2. This initiator was found to be efficient for the polymerization of styrene only when tetrahydrofuran (THF) was added to the reaction mixture ($[\text{THF}]/[\text{s-BuLi}] = 20$). The same initiator was also used to produce a three-arm polybutadiene (PBd) star [20] in the presence of *sec*-lithium butoxide (*s*-BuOLi) in a ratio $[\text{s-BuLi}]/[\text{s-BuOLi}] = 2$ to disrupt the association of the initiator. The limitations of the method include the extreme care necessary to maintain the stoichiometry of the reaction between *s*-BuLi and tri-DPE and the fact that a minimum arm MW of approximately 6×10^3 is required for a successful synthesis. For arm MWs lower than 6×10^3 , incomplete initiation was observed. If these requirements are fulfilled, well-defined three-arm stars can be prepared.

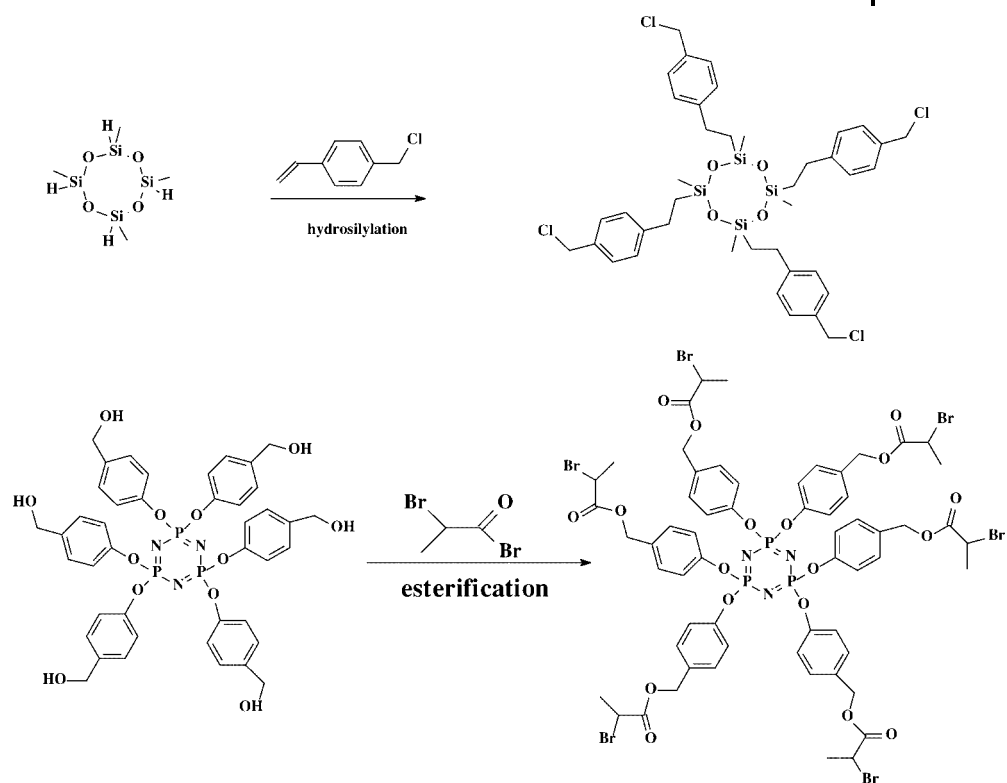
Well-defined eight-arm polyisobutylene (PIB) stars were synthesized using the *tert*-hydroxy and *tert*-methoxy derivatives of 5,11,17,23,29,35,41,47-octaacetyl-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene as octafunctional initiator and cationic polymerization (Scheme 7.3) [21]. The polymerization was performed in two steps in the same reactor. In the first step, the initiator along with BCl_3 and 25% of the IB monomer were added in CH_3Cl at -80°C , followed by the second step in which hexane, TiCl_4 , and the rest of the monomer were added. Size exclusion chromatography (SEC) with on-line refractive index



Scheme 7.2



Scheme 7.3

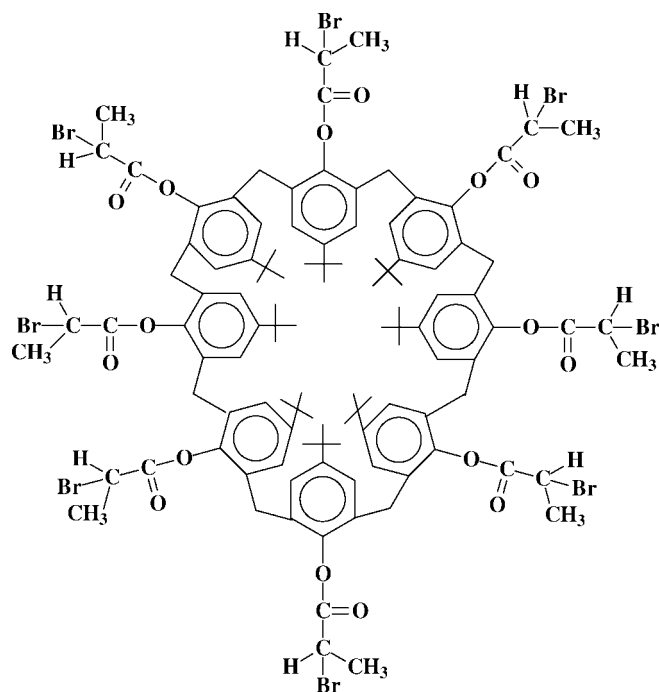


Scheme 7.4

(RI), ultraviolet (UV), and low angle laser light scattering (LALLS) detectors was used for the determination of the MWs and composition of the stars. The MWs obtained were close to the theoretically expected values.

Tetra- and hexafunctional initiators shown in Scheme 7.4 have been used for the polymerization of styrene and acrylates by atom transfer radical polymerization (ATRP) [22]. The resulting stars had low polydispersity indices, and the MWs obtained by SEC equipped with the LALLS detector and viscometry showed good agreement with the theoretical values. In addition, a six-armed star-block copolymer composed of poly(methyl methacrylate) (PMMA) internal and poly(isobornyl acrylate) external blocks was synthesized in this work.

A novel octafunctional calixarene derivative (Scheme 7.5) was prepared and utilized as an MFI for the bulk ATRP of styrene at 100 °C in the presence of CuBr/2,2-bipyridyl, leading to the synthesis of eight-arm star polymers [23]. Well-defined stars could be observed only at low polymerization conversion (up to 20%) since the irreversible coupling reactions that take place at higher concentrations are avoided.



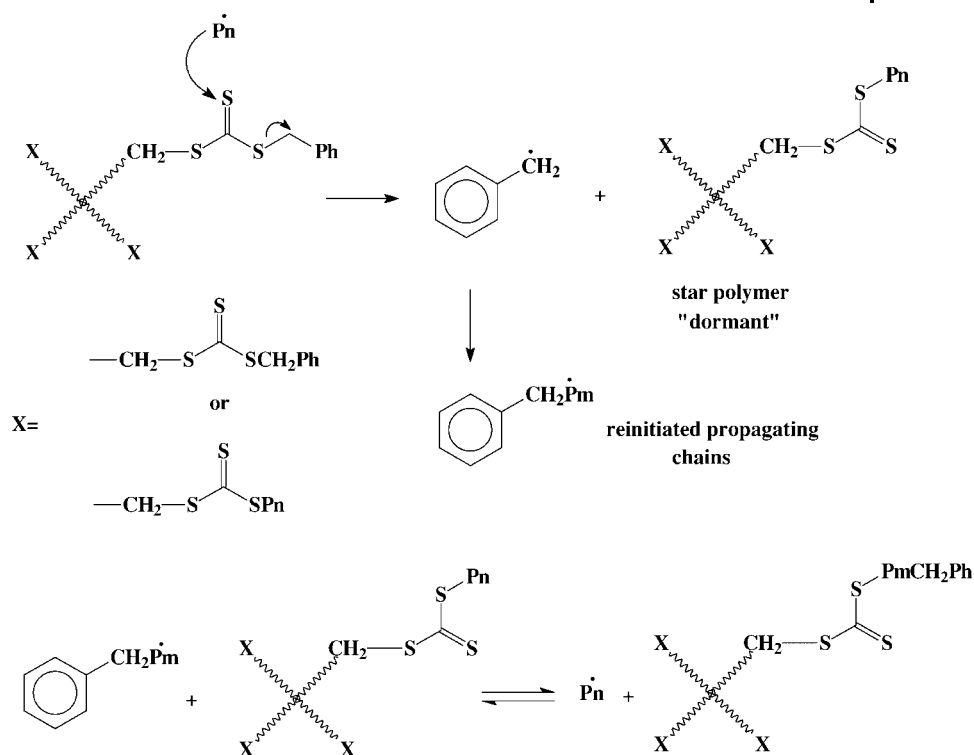
Scheme 7.5

The synthesis of dendritic multifunctional reversible addition-fragmentation chain transfer (RAFT) initiators carrying 6 and 12 external 3-benzylsulfanylthiocarbonylsulfanylpropionic acid groups has been reported [24]. These compounds, in combination with azo- α,α' -diisobutylnitrile (AIBN), have been used to polymerize *n*-butyl acrylate (*n*BA), in bulk at 60 °C, leading to star poly(*n*-butyl acrylate) (P*n*BuA) with moderate polydispersity (1.1–1.5). The star-shaped structure of the synthesized polymers has been confirmed through the cleavage of the arms from the core and characterization.

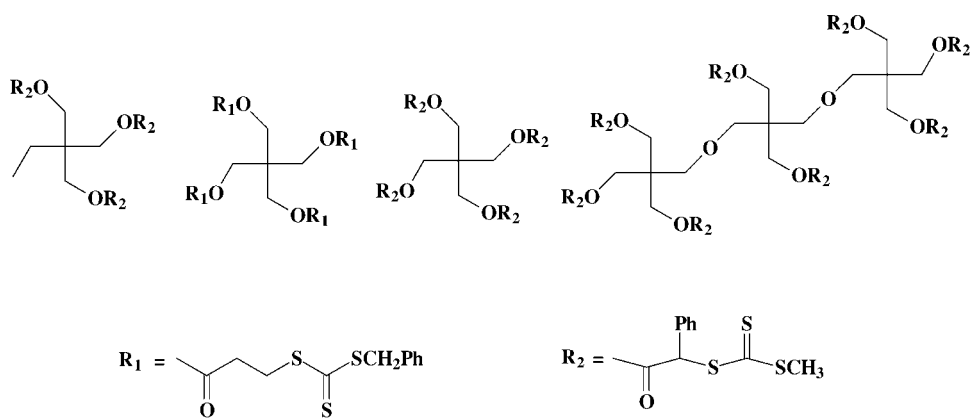
In the “arm-first” approach presented in Scheme 7.6, the fragmentation results in the formation of benzyl radicals, which are able to reinitiate polymerization of linear chains. The arms of the star polymer are dormant, and the growth of the arms always occurs away from the core. Using this methodology, four-arm polystyrene (PS) and PMMA stars were prepared [25].

A series of multi-thiocarbonyl thio compounds with three, four, six, or eight functional groups were prepared (Scheme 7.7) [26] and were subsequently employed as chain transfer agents for the synthesis of star polymers using the RAFT technique [27].

Four-arm hydroxyl-terminated poly(ϵ -caprolactone) (PCL) stars were synthesized by ring-opening polymerization (ROP) of ϵ -caprolactone (ϵ -CL), using pentaerythritol as the MF initiator [28] (Scheme 7.8). The terminal

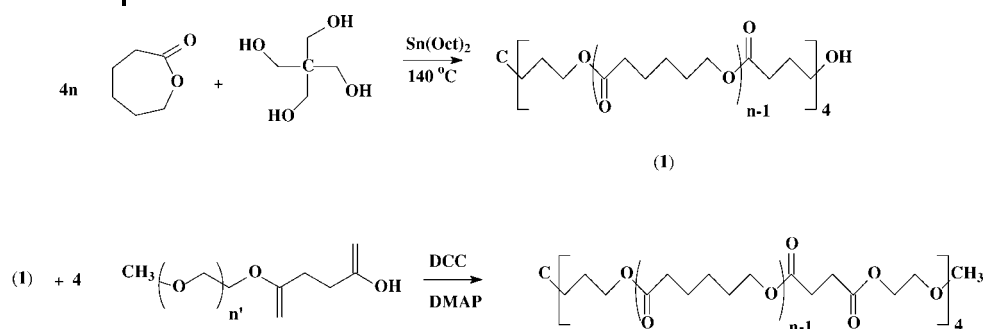


Scheme 7.6



Scheme 7.7

hydroxyl groups of the star were then reacted with an α -carboxy-functionalized poly(ethylene oxide) (PEO) to afford the four-arm PCL-*b*-PEO star-block copolymer. The linking efficiency was high ($\sim 95\%$). The PCL star



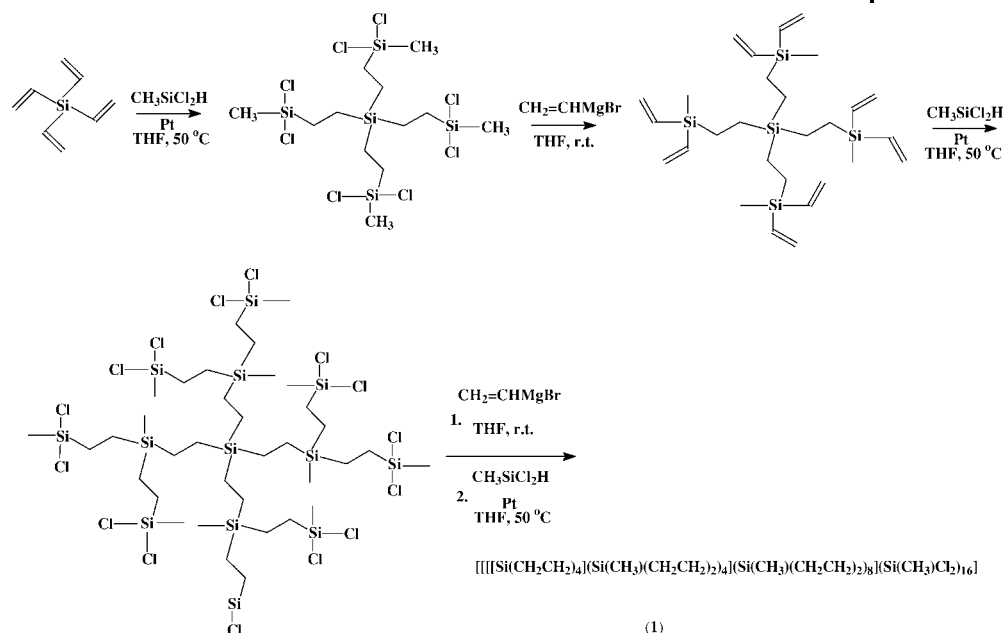
Scheme 7.8

homopolymer precursors along with the final star-blocks were characterized by nuclear magnetic resonance (NMR) spectroscopy and SEC. The star precursors exhibited higher MWs than those theoretically expected and the polydispersities were rather high (1.42–1.56). After reaction with the carboxy-PEO, the polydispersity indices of the star-block copolymers decreased (1.16–1.36).

7.2.1.2 Multifunctional Linking Agents (MFLAs)

Multifunctional linking agents (MFLAs) are compounds with several reactive sites that can react with living chains and represent the most efficient way to synthesize well-defined star polymers due to the absolute control afforded in all the synthetic steps. The functionality of the linking agent (LA) determines the number of the arms 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 accurately. Disadvantages of the method include the extensive amount of time often required for the linking reaction as well as the need to perform fractionation to obtain the pure star polymer since a small excess of the living arm is used, in almost all cases, to ensure complete linking.

Several LAs have been used for the synthesis of star polymers from living precursors synthesized by anionic polymerization [9]. The most important are the chlorosilanes [29] and the chloromethyl or bromomethyl benzenes [30, 31]. The linking reactions of the macroanions with the chlorosilanes proceed without any side reactions. However, the efficiency of the linking reaction depends on the steric-hindered character of the LA and the living macromolecular chain end. It was shown that the higher the steric hindrance of the reactants the lower the linking efficiency. 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 to reduce the steric hindrance and facilitate the linking reaction. Under these conditions, well-defined stars have been prepared with functionalities ranging



Scheme 7.9

from 3 up to 18 [32–38]. Recent advances in the synthesis of pure carbosilane dendrimers led to the preparation of LAs with functionalities as high as 128 [39]. These dendrimers were successfully used for the synthesis of PBd stars having 32, 64, and 128 branches [40, 41] (Scheme 7.9). The products were characterized by SEC, membrane osmometry (MO), vapor pressure osmometry, and light scattering (LS), and their dilute solution properties were extensively studied; low MW distribution polymers with functionalities close to the theoretical value were obtained in all cases. The validity of the chlorosilane LAs for the synthesis of star polymers was reevaluated recently using NMR [42] and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) [43] techniques.

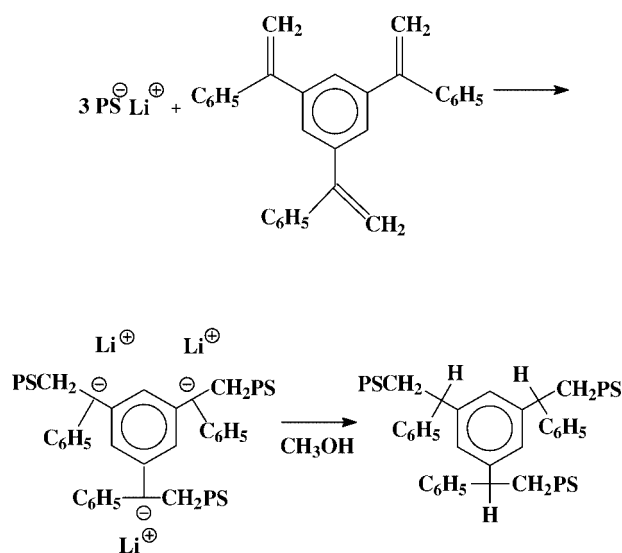
In the case of polyvinylpyridines (PVP) and poly(meth)acrylates, a chlorosilane LA cannot be used because either this agent reacts with the pyridine ring or the produced stars have hydrolyzable C–O–Si groups. In these cases, chloro(bromo)methyl benzenes are the most appropriate LAs.

The synthesis of three-arm poly(2-vinylpyridine) (P2VP) stars using 1,3,5-tri(chloromethyl)benzene have been reported [44]. The samples were characterized by SEC and viscometry. The chloromethylbenzenes suffer halogen–metal exchange leading to LAs with more or fewer chloromethyl groups and consequently to stars with more/fewer than the desired number of arms. The use of bromo instead of chloro derivatives in polar solvents as well as the low temperatures prevents the metal–halogen exchange.



Diphenylethylene derivatives constitute another class of LAs. 1,3,5-tris(1-phenylethenyl)benzene was used as a living LA for the synthesis of a three-arm PS star [19] (Scheme 7.11). Characterization results from SEC, MO, and LS revealed that a well-defined star was prepared by this procedure. Although the arm MW used was rather low ($M_n = 8.5 \times 10^3$), there was no steric limitation for the synthesis of three-arm PS stars using this coupling agent. Previous efforts to use methyltrichlorosilane (three chlorines on the same Si atom) as a LA for the synthesis of three-arm PS stars were not successful, due to incomplete coupling (steric hindrance effects) [29, 46].

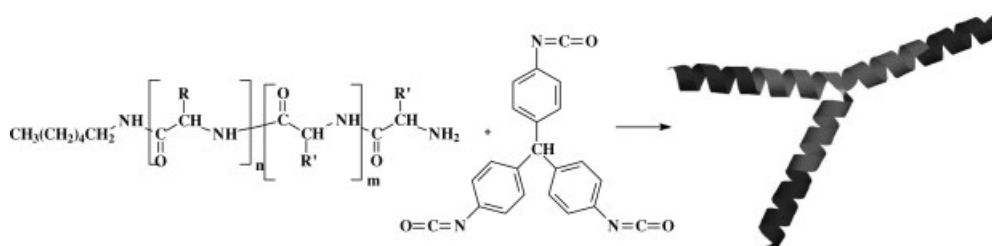
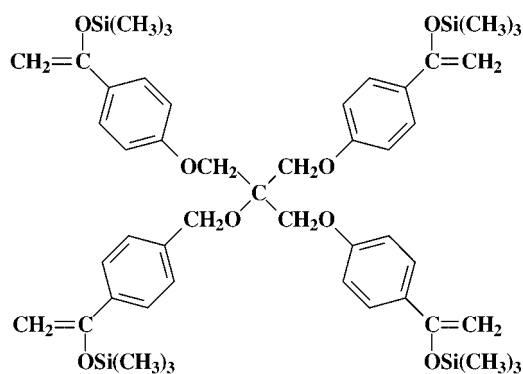
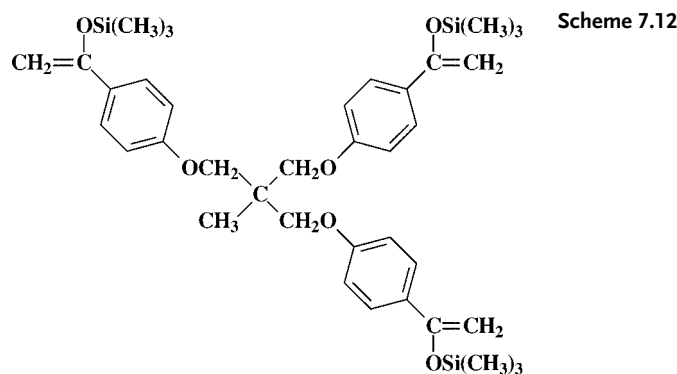
By employing tri- and tetrafunctional silyl enol ethers as coupling agents with living cationic polymerization (Scheme 7.12), three- and four-arm poly(isobutyl vinyl ether) (PIBVE) star homopolymers have been synthesized [47]. The living arms were produced at -15°C using the HCl/ZnCl_2 initiating system in methylene chloride. The coupling of relatively short chains of living PIBVE ($\text{DP} \sim 10$) was shown to occur nearly quantitatively, affording the multiarmed polymers in high yield ($>95\%$). The yield decreased slightly ($85\text{--}89\%$) with a longer living chain ($\text{DP} \sim 50$). The MW distribution of the final stars was low.



Scheme 7.11

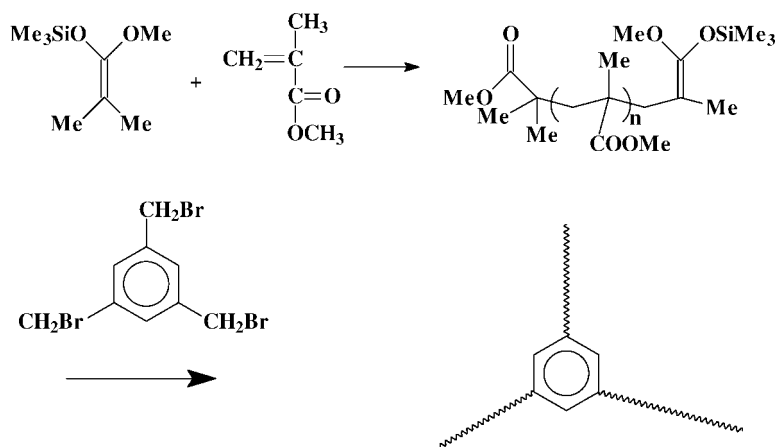
More recently, three-arm star homopolypeptides of poly(γ -benzyl-L-glutamate) (PBLG) and poly(ϵ -benzyloxycarbonyl-L-lysine) (PZLL), i.e., (PBLG)₃ and (PZLL)₃, were synthesized [48] by living ROP of the *N*-carboxyanhydride (NCA) of the corresponding α -amino acids and the linking methodology. The synthetic approach involves the preparation of the corresponding living arms, followed by linking with triphenylmethane 4,4', 4''-triisocyanate at room temperature (Scheme 7.13). The polymerization of the monomers γ -benzyl-L-glutamate NCA and ϵ -benzyloxycarbonyl-L-lysine NCA was performed using high vacuum techniques, with *n*-hexylamine as the initiator, leading to high MW, well-defined living polypeptides in $\sim 100\%$ yield with low polydispersity. A slight excess of living arms was used for the linking reaction and was subsequently fractionally removed. The polypeptides were extensively characterized by MO, SEC equipped with a LALLS detector, along with NMR spectroscopy. The polydispersity indices were lower than 1.1 and the observed MWs were very close to the theoretically expected ones. The characterization results revealed that the stars exhibited a high degree of molecular and compositional homogeneity.

1,3,5-Tris(bromomethyl)benzene was employed for the coupling of living PMMA chains obtained by group transfer polymerization, leading to three-arm stars [49] (Scheme 7.14). A reexamination of the reaction revealed that the linking efficiency was not quantitative. This behavior can be attributed to the fact that the reaction of the $-\text{CH}_2\text{Br}$ groups with the living chain ends occurs in a stepwise manner. Therefore, after each substitution of Br by a chain, the reactivity of the remaining $-\text{CH}_2\text{Br}$ groups is reduced as a result of steric hindrance, thus leading to lower conversions.



Scheme 7.13

Recently, “click” linking chemistry was applied for the synthesis of star polymers. Gao and Matyjaszewski prepared three- and four-arm PS stars by “clicking” 3- and 4-alkyne LA with azido-terminated PS chains (Scheme 7.15) [50]. The linking reactions were catalyzed by CuBr/*N, N, N', N', N''*-pentamethyldiethylenetriamine (PMDETA). The procedure was fast and efficient for low MW samples. However, upon



Scheme 7.14

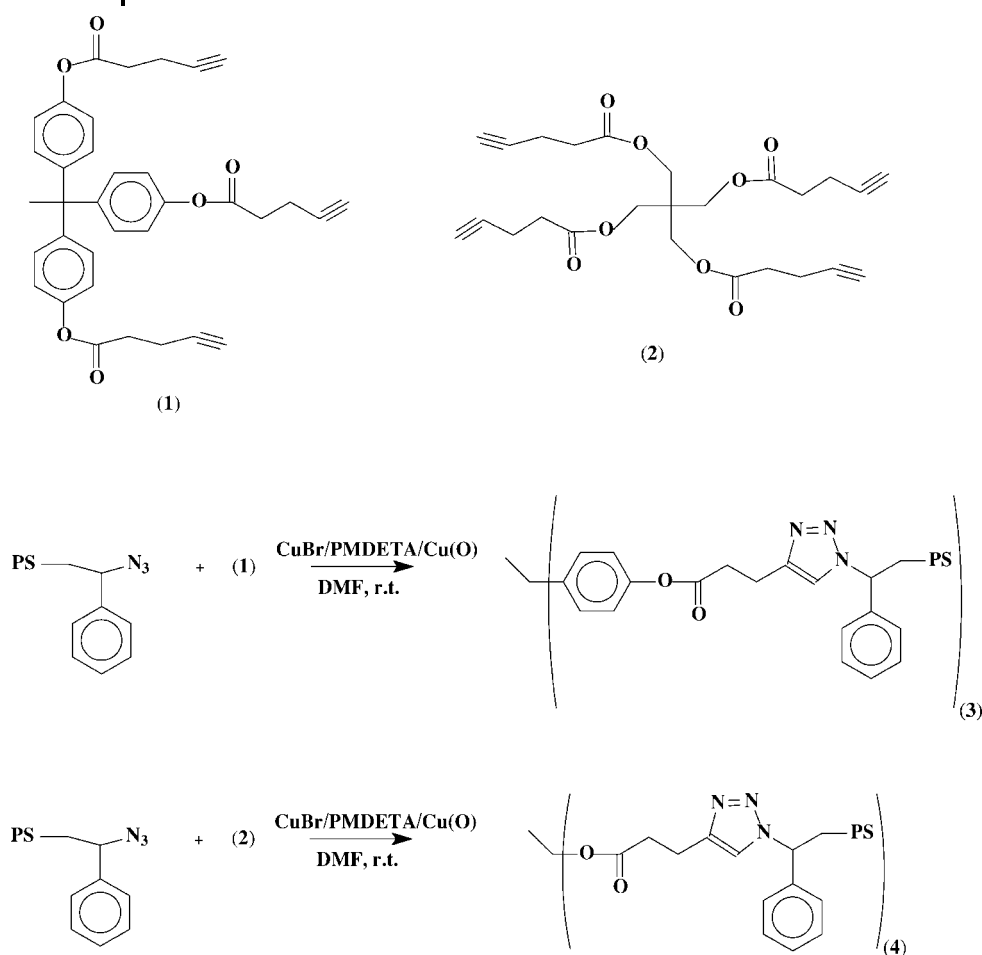
increasing the MW of the PS chains the efficiency was considerably reduced.

Schubert *et al.* [51] reported the synthesis of a seven-arm star PCL by “clicking” an acetylene-functionalized PCL precursor, prepared by ROP of ϵ -CL at 110 °C, with 5-hexyn-1-ol as initiator, with heptakis-azido- β -cyclodextrin (Scheme 7.16). The “click” reaction was performed under microwave irradiation at 100 °C. To induce complete functionalization of the β -cyclodextrin, 9 equivalents of the acetylene-functionalized PCL was used in the coupling reaction. After the reaction, the excess PCL was removed from the star by preparative SEC.

Tunca *et al.* [52] reported the synthesis of symmetric three-arm star polymers based on the arm-first technique, by “clicking” azide end-functionalized PS, poly(*tert*-butyl acrylate) (PtBuA), or poly(ethylene glycol) (PEG) with a trialkyne LA. The coupling efficiencies of PS-N₃, PtBuA-N₃, and PEG-N₃ with the trialkyne LA were 87, 85, and 82%, respectively.

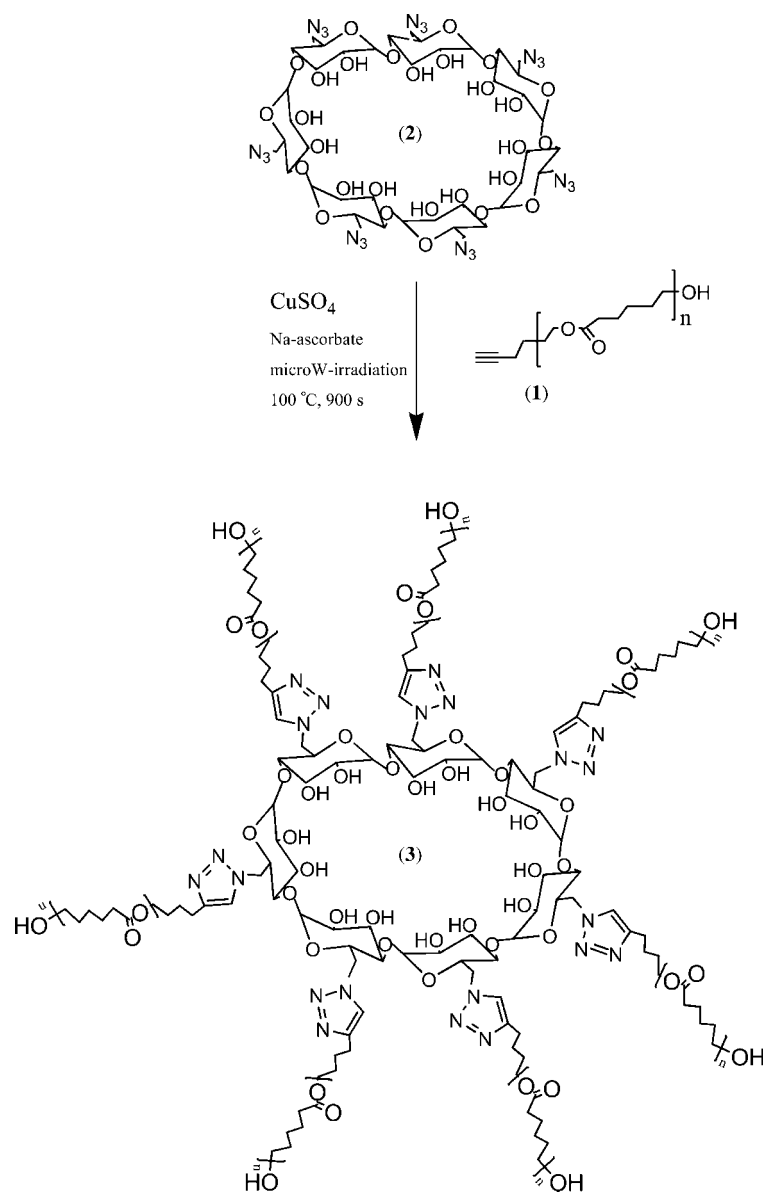
7.2.13 Difunctional Monomers (DFMs)

In this method, an end-reactive polymer precursor is used as initiator for the polymerization of a small amount of a suitable difunctional monomer (DFM). Microgel nodules of tightly cross-linked polymer are formed upon the polymerization. These nodules serve as the junction moiety from which the arms emanate. The functionality of the stars prepared by this method can be determined by MW measurements of the arms and the final star; however, it is very difficult to predict and control the number of arms. The number of arms incorporated in the star structure is influenced by many parameters. The most important is the molar ratio of the DFM over the living polymer. The functionality of the stars increases by increasing this ratio.



Scheme 7.15

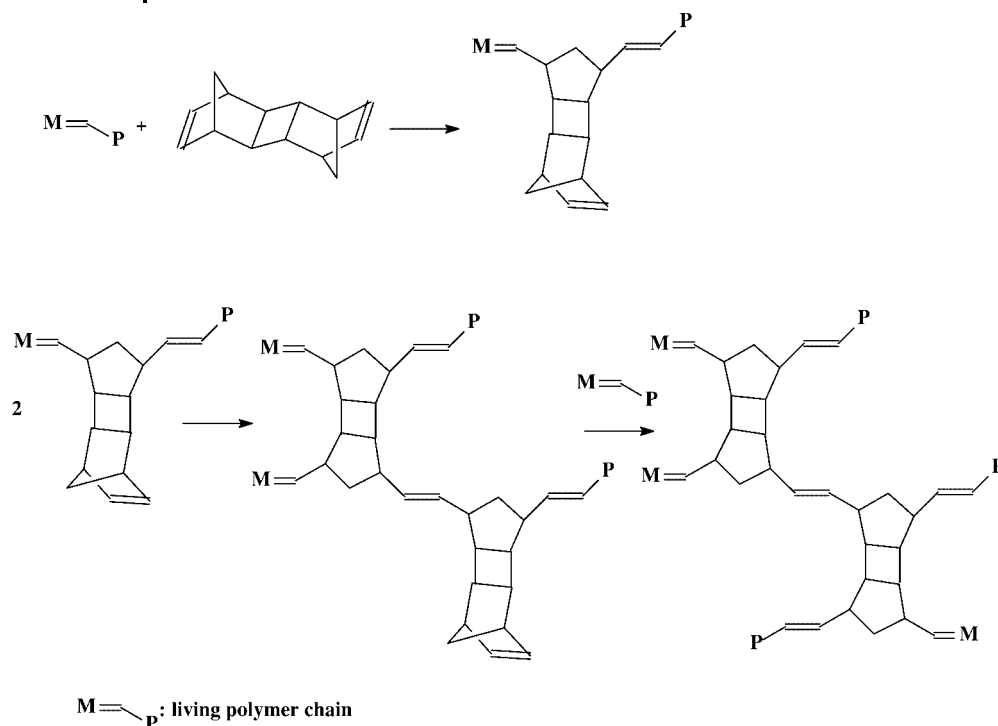
The norbornadiene dimer, *exo-trans-exo*-pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}] tetradeca-5,11-diene was employed as a DFM for the synthesis of star polynorbornene by ring-opening metathesis polymerization (ROMP). Norbornene was polymerized to afford the corresponding living polymer using M(CHR)(NAr)(O-*t*-Bu)₂ (M = W or Mo; NAr = *N*-2,6-C₆H₃-*i*Pr₂) as catalyst. The living polymer was then reacted with the DFM to produce the star polymers (Scheme 7.17). The linear living polymer was completely consumed, but the MW distribution of the final product was broader than that of the corresponding arms (mixture of stars with different functionality). The resulted stars are still living and bear active centers at the core of the structure. New arms can grow from these living sites giving rise to the formation of asymmetric stars. However, products with bimodal distributions were obtained, because of the



Scheme 7.16

slower initiation at the core of the star and the faster propagation as the reacting alkylidene centers move away from the sterically crowded core [53].

Several star polymers have been prepared by reacting living polymers synthesized by anionic polymerization with DVB. The method has been applied in the past for the synthesis of PS [54, 55] and polydiene [56] stars.



Scheme 7.17

Rather narrow MW distribution PS stars were obtained when the $[DVB]/[PSLi]$ ratio was varied from 5.5 to 30 and the corresponding functionality ranged from 13 to 39. A similar behavior was obtained for polydiene stars when the $[DVB]/[PDLi]$ ratio was between 5 and 6.5 and the functionality of the star was varied from 9 to 13.

Recently, PMMA stars were prepared by reacting PMMA chains, synthesized by anionic polymerization, with the DFM ethylene glycol dimethacrylate (EGDM) [57]. The polymers were characterized by SEC, LS, and viscometry. It was found that well-defined polymers can be prepared when the arm MW was rather high (e.g., $M_w = 40\,000$). It seems that this high MW is necessary to prevent intercore and gelation reactions from taking place. By reacting EGDM with isotactic living PMMA chains, obtained using *t*-butyl magnesium bromide as initiator in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene [58], a star polymer with 20–30 arms was synthesized. SEC connected with LS and viscometry detectors was used to characterize the sample. A similar reaction using syndiotactic living PMMA chains, obtained with the *tert*-butyllithium (*t*-BuLi)- R_3Al initiator system, failed to give star polymers. However, when EGDM was replaced by the butane-1,4-diol dimethacrylate, a PMMA star was obtained bearing 50–120 arms.

By using the DFM methodology and 2,2,6,6-tetramethyl-1-piperidinyloxy stable radical (TEMPO), star-block copolymers with a great variety of chemically different chains, in terms of MW and composition, were prepared [59]. The synthetic strategy involved the preparation of TEMPO-terminated linear chains and subsequent coupling with the DFMs divinylbenzene or a bis(maleimide) derivative.

The DFM methodology and ATRP were employed for the synthesis of PS [60] and PtBuA star homopolymers [61]. The DFMs used included DVB, 1,4-butanediol diacrylate, as well as EGDM. Several factors were investigated for the formation of nearly monodisperse stars, such as the choice of the exchanging halogen, the solvent, the addition of copper (II) species, the ratio of the coupling agent to the macroinitiator, and the reaction time. The highest efficiency (~95%) was obtained using a 10–15-fold excess of the DFM over chain ends.

Living PMMA chains, produced by the $\text{RuCl}_2(\text{PPh}_3)_3$ -catalyzed polymerization of MMA were reacted with the DFM bisphenol A dimethacrylate (BPDMA) to afford the corresponding PMMA star polymers [62]. The functionality of the products ranged from 4 to 63. The yield of the linking reaction was found to depend on the concentration and the degree of polymerization of the living arms, as well as the molar ratio of BPDMA over the living chains.

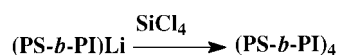
The DFM methodology and RAFT were utilized for the synthesis of PS star homopolymers [63]. The linear macro RAFT PS agent was synthesized in the bulk, at 110 °C, using benzyl dithiobenzoate and AIBN. DVB was used as the DFM. The stars were extensively characterized by NMR and infrared (IR) spectroscopy, as well as by SEC along with dynamic light scattering (DLS). It was found that the molar ratio of DVB/PS and polymerization time influenced the yield, MW, and the polydispersity index of the stars. In most cases, a significant amount of living linear macroagent remained unreacted and was separated from the star by preparative SEC.

7.2.2

Star-Block Copolymers

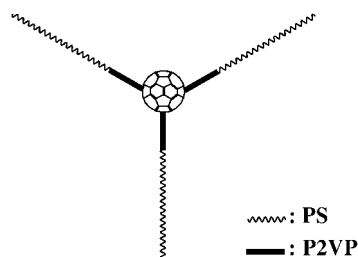
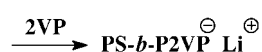
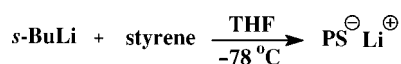
Star-block copolymers are star polymers in which each arm is a diblock (or a triblock) copolymer and can be prepared by all the methods reported above. The best route involves the linking reaction of a living diblock copolymer, prepared by sequential polymerization of the two monomers, with a suitable LA. Using anionic polymerization and chlorosilane LAs, Fetters *et al.* synthesized star-block copolymers (polystyrene-*b*-polyisoprene)_n [(PS-*b*-PI)_n] where $n = 4, 8, 12, 18$ [64, 65]. An example corresponding to four-arm star-block is given in Scheme 7.18. Well-defined structures of low polydispersities were obtained.

C₆₀ was also employed for the synthesis of star-block copolymers [66]. Living PS-*b*-P2VP diblocks, having short P2VP chains, were prepared by sequential anionic polymerization in THF. These living diblocks were reacted with a

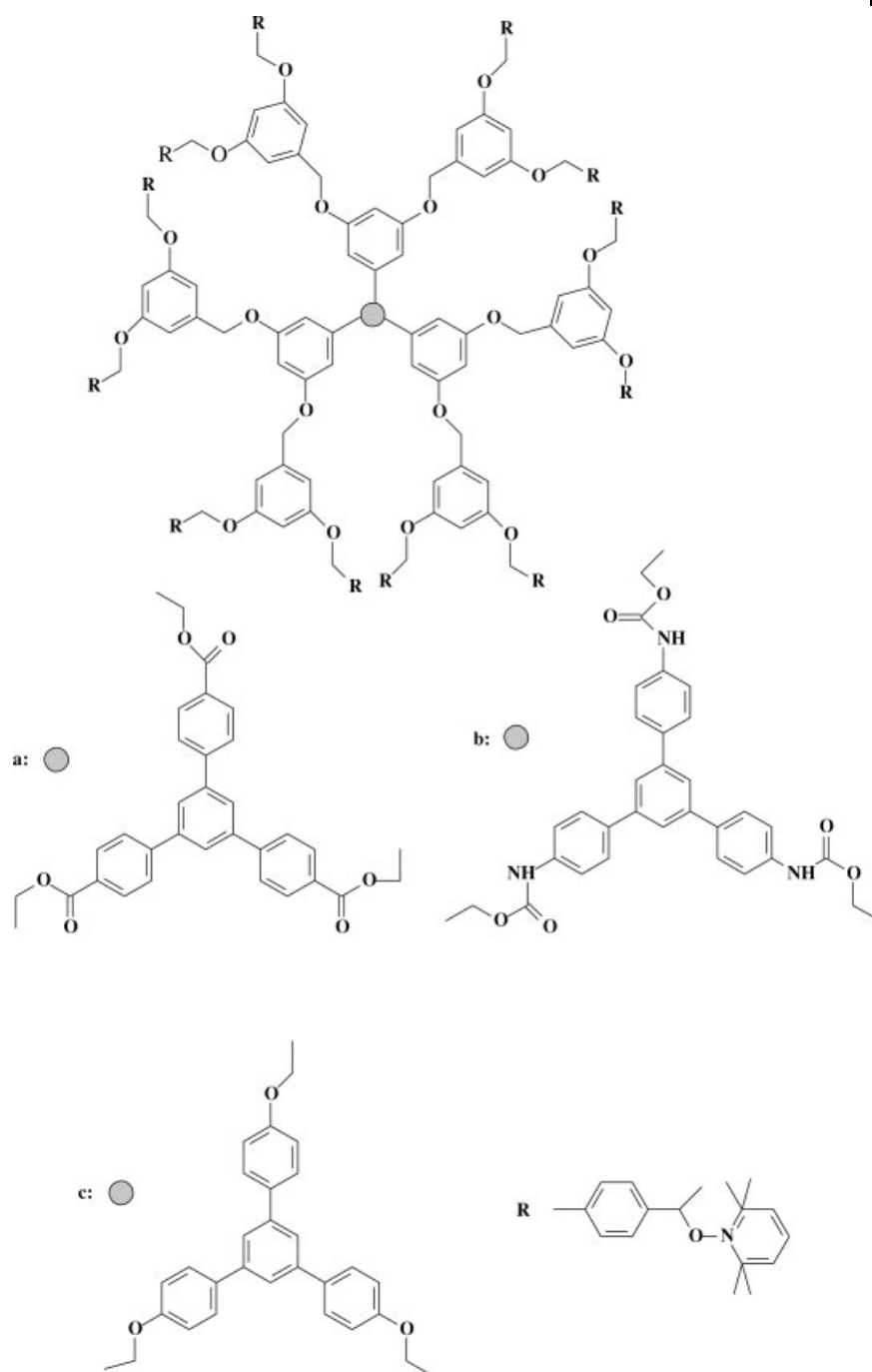


suspension of C_{60} in THF leading to the formation of a three-arm star-block copolymer (Scheme 7.19). The corresponding reaction with the living PS homopolymer resulted in the formation of a four-arm star. The lower reactivity of the 2VP anion seems responsible for this behavior. The SEC analysis of the product revealed a broad MW distribution, indicating that a mixture of stars with different functionalities was obtained.

Recently, 12-arm PS-*b*-poly(4-vinylpyridine) (P4VP) star-block copolymers were synthesized using dendritic dodecafunctional macroinitiators [67] and TEMPO-mediated radical polymerization (Scheme 7.20). The polymerizations were conducted in bulk at 120 °C, and the stars synthesized exhibited rather low polydispersity indices (1.06–1.26). In the cases where higher polydispersity indices were obtained, SEC profiles revealed the formation of a small amount of four-arm stars that was subsequently connected to form larger functionality stars. To evaluate the livingness for the TEMPO-mediated radical polymerization of styrene, hydrolysis of the ester central bonds and subsequent SEC measurements were performed. The analysis indicated that the functionality polydispersity was higher than the MW polydispersity (mixture of stars with different functionalities).



Scheme 7.19



Scheme 7.20

The DFM methodology and RAFT were utilized for the synthesis of PS-*b*-poly(*N*-isopropyl acrylamide) star-block copolymers [63], in a way similar to that already presented for the synthesis of PS star homopolymers. The synthesis of the precursor was performed by sequential polymerization in bulk at 110 °C, using benzyl dithiobenzoate and AIBN. DVB was used as the DFM. The stars were extensively characterized by NMR and IR spectroscopy, SEC along with DLS. It was found that the molar ratio of DVB/PS and the polymerization time influenced the yield, MW, and the polydispersity index of the stars. In most cases a significant amount of living linear macroagent remained unreacted and was consequently separated from the star by preparative SEC.

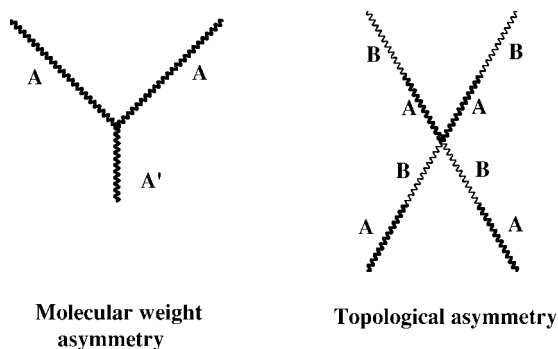
7.2.3

Asymmetric Stars

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

1. *MW*. All the arms of the star are identical in chemical nature but have different MWs (Scheme 7.21).
2. *Topology*. The arms of the star are block copolymers that may have the same MW and composition but differ with respect to the polymeric block that is covalently attached to the core of the star (Scheme 7.21).

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 MW, or topology is achieved. Efficient methods for the synthesis of asymmetric star polymers were developed only recently.



Scheme 7.21

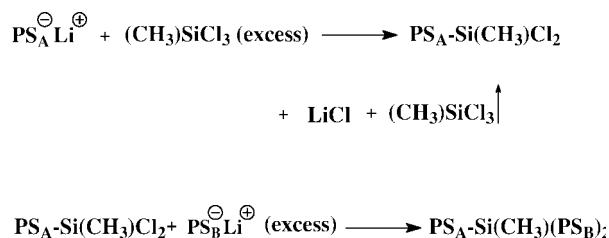
7.2.3.1 Molecular Weight Asymmetry

The chlorosilane method and anionic polymerization techniques for the synthesis of asymmetric stars were initially reported by Fetters and was later developed by Mays, Hadjichristidis, and collaborators [9–12]. Chlorosilanes are used as LAs for the stepwise selective 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 which 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 LA. The steric hindrance of living end increases (reactivity decreases) in the order $\text{BdLi} < \text{IsLi} < \text{SLi} < \text{DPELi}$. In the case of chlorosilanes, the closer the Si–Cl groups the more sterically hindered (reactivity decreases) 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 MW of the living chain, the polarity of the solvent in which 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.

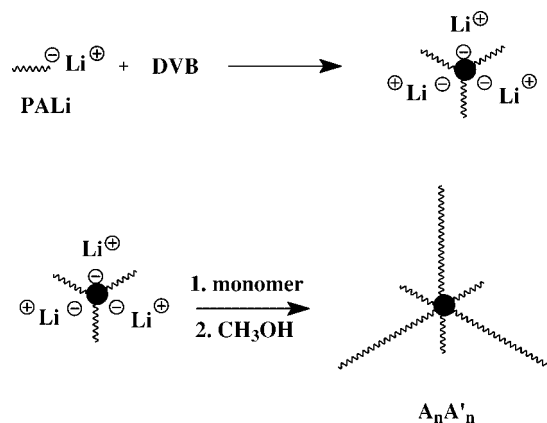
The method was first applied to the synthesis of asymmetric PS stars composed of two arms of equal MWs, PS_B , and a third one, PS_A , with a MW either half or twice that of the identical arms [68] (Scheme 7.22).

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 [68] and polyisoprene (PI) [69] stars.

When appropriate living polymer chains react with a small amount of DVB, a star polymer is formed consisting of a highly living cross-linked polydivinylbenzene core from which the arms emanate. The number of the living 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 in the formation of an asymmetric star of the type



Scheme 7.22

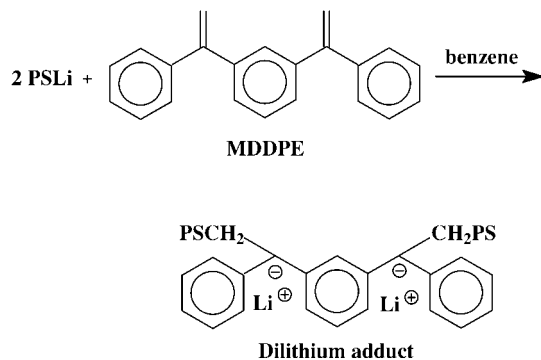
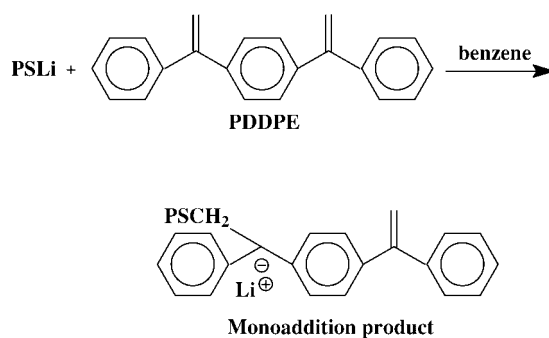


Scheme 7.23

$\text{A}_n\text{A}'_n$ (A and A' chains with different MW). This general procedure is depicted in Scheme 7.23.

The main drawback associated with the DVB method is the architectural limitation, i.e., only asymmetric stars of the type $\text{A}_n\text{A}'_n$ can be prepared. Furthermore, because of steric hindrance, in most cases, a fraction of the living arms A is not incorporated in the star structure, the active sites of the living A_n star are not equally accessible to the newly added A' monomers, and the initiation rate is not the same for all active sites. Consequently, 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 MW 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.

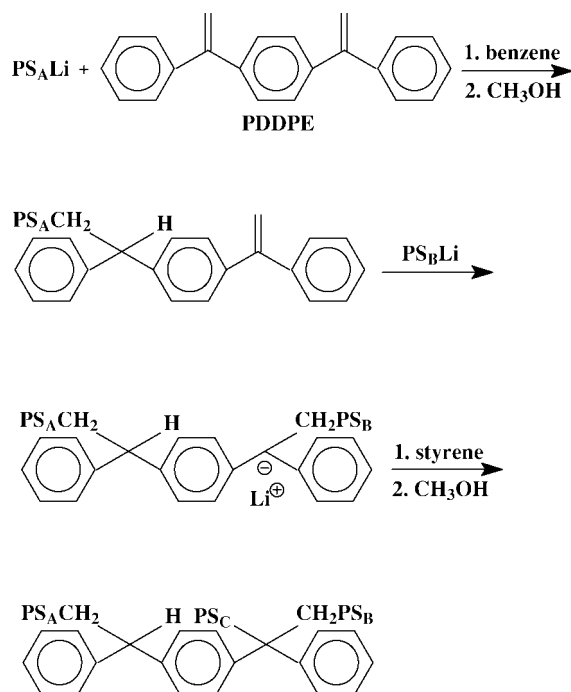
Using this methodology and anionic polymerization, asymmetric stars of the type $(\text{PS}_\text{A})_n(\text{PS}_\text{B})_n$ were prepared [70]. Living PS chains were obtained by *s*-BuLi initiation and reacted with a small amount of DVB to give a living star polymer. The anionic sites of the star 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 MW 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. In another example, mono-2-bromoisobutyryl PEO ester was used as macroinitiator for the ATRP of DVB, leading to the synthesis of the desired star polymers. Subsequent addition of styrene led to the synthesis of PEO_nPS_m miktoarm stars through the polymerization of styrene from the initiating sites located at the core of the PEO stars [71]. The styrene conversion

a. Reaction with MDDPE**b. Reaction with PDDPE****Scheme 7.24**

did not exceed 10% to avoid star–star coupling reactions and, therefore, the production of gels.

Rich chemistry was developed by Quirk and collaborators [72] leading to the formation of several types of asymmetric stars by reaction of living PS with either 1,3-bis(1-phenylethenyl)benzene (MDDPE) or 1,4-bis(1-phenylethenyl)benzene (PDDPE) according to Scheme 7.24.

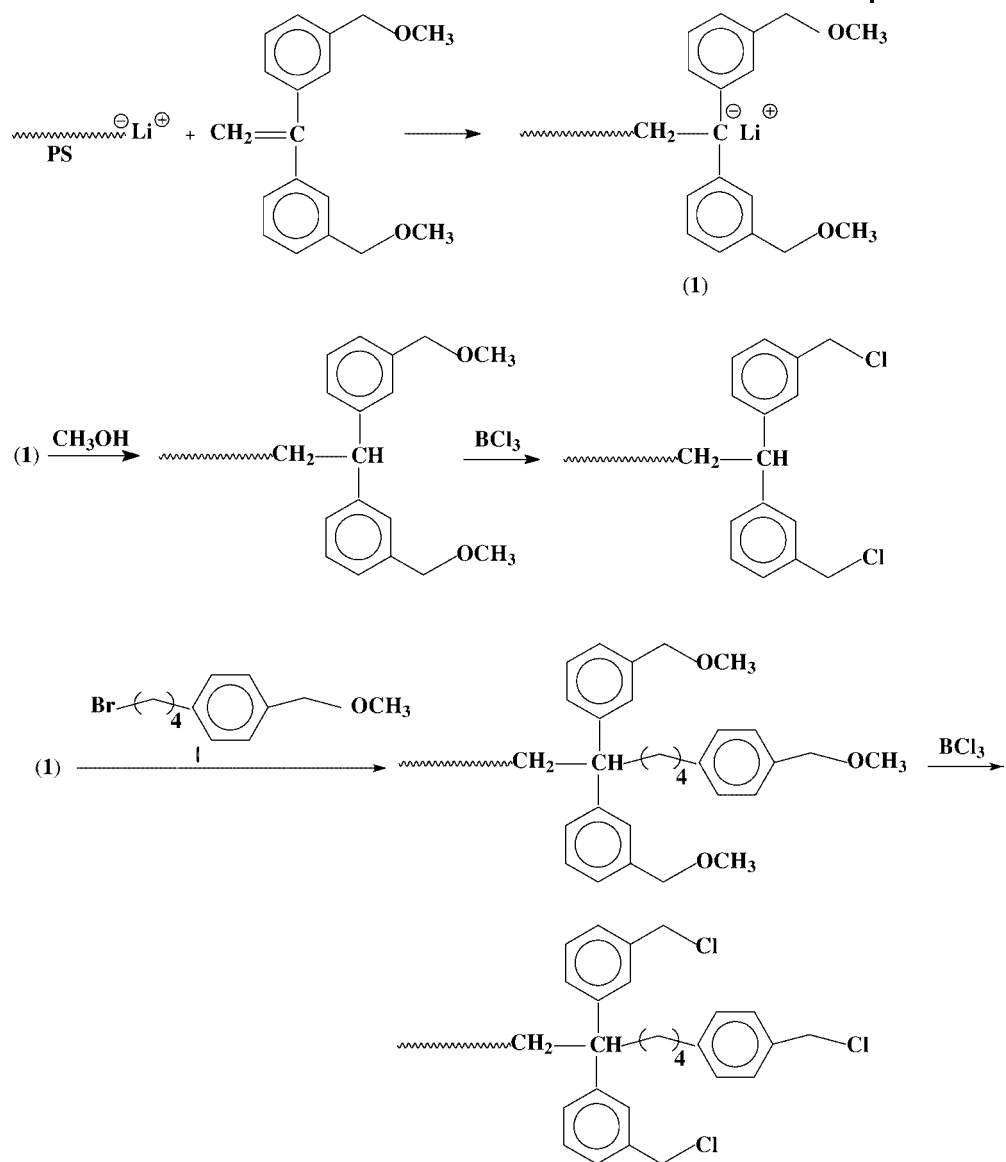
It was shown that 2 mol of the living polymer reacted rapidly with the MDDPE derivatives to form the dilithium adduct in hydrocarbon solvents, whereas in THF monoaddition was reported [73, 74]. This reaction was monitored by UV–visible spectroscopy. The analysis revealed that the stoichiometric addition of PSLi was quantitative. However, PDDPE exhibited a reduced tendency to form the diadduct both in polar and nonpolar solvents. This behavior can be attributed to the delocalization of the negative charge only in the para isomer. Mainly, low MW PSs have been used for these studies.



Scheme 7.25

On the basis of the observation above, a three-arm asymmetric PS star was successfully prepared [75] (Scheme 7.25). The monoadduct product was reacted with a second polystyryllithium chain of a different MW, 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 led to the formation of the product. The polymerization took place in the presence of THF to accelerate the crossover reaction. SEC analysis revealed the existence of a small quantity of the monoadduct product and the second arm of the PS homopolymer, due to incomplete linking reactions. The weak points of the method include the great care that should be exercised over the stoichiometry of the reactions and the difficulty in isolating and consequently characterizing 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.

Hirao *et al.* developed a general method employing 1,1-diphenylethylene (DPE) derivatives carrying protected (masked) chloromethyl groups to prepare PS asymmetric stars of the types AA'_2 , $\text{AA}'_2\text{A}''_2$, AA'_3 , AA'_4 , $\text{AA}'\text{A}''_2$, and $\text{AA}'_4\text{A}''_4$ [76, 77]. The procedure is based on the reaction sequence shown in Scheme 7.26. Living PS was reacted with

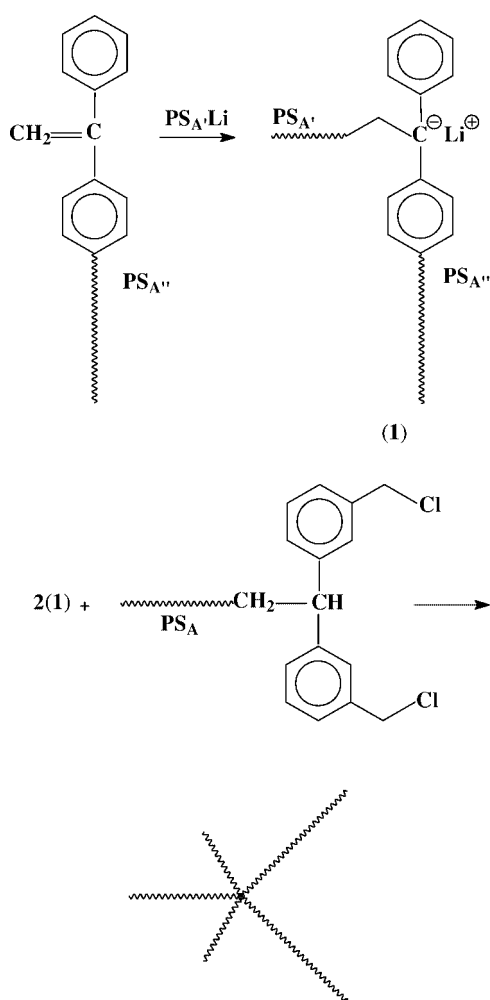


Scheme 7.26

1,1-bis(3-methoxymethylphenyl)ethylene followed by transformation of the methoxymethyl groups to chloromethyl groups by reaction with BCl_3 in CH_2Cl_2 at 0°C for 10–30 min. Prior to the reaction with BCl_3 , the living end-functionalized PS is able to react with other compounds such as 1-(4'-bromobutyl)-4-methoxymethylbenzene (Scheme 7.26). Despite the

difficult multistep procedure, it was shown that PSs with predictable MWs, narrow MW distributions, and almost nearly quantitative degrees of functionalization can be synthesized. Small amounts (<5%) of coupled PS by-products can be produced during the transformation reaction, due to a Friedel–Crafts side reaction among the polymer chains.

DPE-functionalized polymers were also used for linking reactions with living polymeric anions, 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 7.27 and 7.28, respectively. Well-defined star polymers with rather low MW arms were obtained with this method.

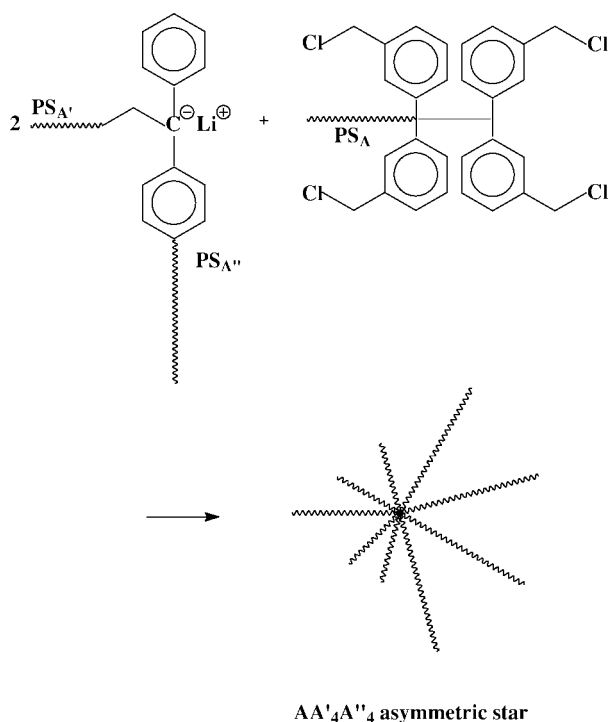


Scheme 7.27

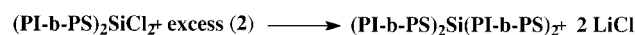
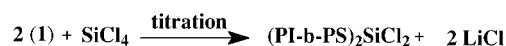
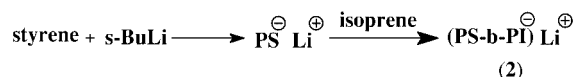
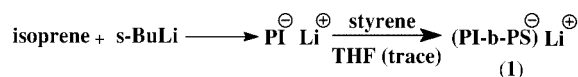
In addition to anionic polymerization, ATRP also led to the preparation of asymmetric stars [78]. ω -Bromopolystyrene was obtained using ethyl 2-bromoisobutyrate as initiator in the presence of the catalyst CuBr and the ligand pentamethyldiethylenetriamine. The end bromine group was reacted with 2-amino-1,3-propanediol leading to PS chains bearing two hydroxyl groups at the same chain end. These hydroxyl groups were subsequently transformed to bromines after reaction with 2-bromoisobutyryl bromide. The new initiating sites were used for the polymerization of styrene, leading to the synthesis of asymmetric PS(PS')₂ stars.

7.2.3.2 Topological Asymmetry

A novel star-block copolymer architecture, i.e., the inverse star-block copolymer, was reported [79]. These polymers are stars with four poly(styrene-*b*-isoprene) copolymers as arms. Two of these arms are connected to the star center by the PS block, whereas the other two through the PI block. The synthetic procedure is given in Scheme 7.29. 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



Scheme 7.28



Scheme 7.29

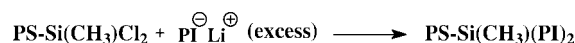
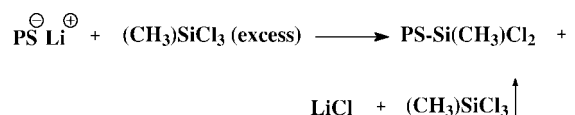
the polymerization of styrene, and the living diblock copolymer(I) was slowly added to a solution of SiCl_4 . The difunctional LA thus prepared was then reacted with a small excess of the living diblock copolymer(II) to produce the desired product. These living diblocks were end-capped with 3–4 units 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.

7.2.4

Miktoarm Star Polymers

The term miktoarm (from the Greek word $\mu\kappa\tau\acute{o}\varsigma$ meaning mixed) rather than heteroarm (from the Greek word $\acute{\epsilon}\tau\epsilon\rho\omicron\varsigma$ meaning the other) star polymers refers to stars consisting of chemically different arms. In the last decade, considerable effort has been made toward the synthesis of miktoarm stars, when it was realized that these structures exhibit very interesting properties [80–82]. The synthesis of the miktoarm star polymers can be accomplished by methods similar to those reported for the synthesis of asymmetric stars. The most common examples of miktoarm stars are the A_2B , A_3B , A_2B_2 , A_nB_n ($n > 2$), and ABCD types. Other less common structures, like the ABCD, AB_5 , AB_2C_2 , etc., are now also available.

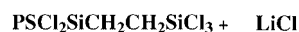
A near monodisperse miktoarm star copolymer of the A_2B type was first reported by Mays [83], with A being PI and B being PS. The synthetic method adopted was similar to that applied by Fetters [68] for the synthesis of the asymmetric PS and PBd stars. The living PS chains were reacted with an excess of methyltrichlorosilane to produce the monosubstituted macromolecular LA. The steric hindrance of the living polystyryllithium and the excess of the silane led to the absence of any coupled by-product. The excess silane was

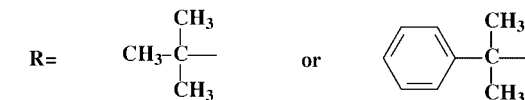
**Scheme 7.30**

removed, and then a slight excess of the living PI chains was added to produce the miktoarm star PS(PI)₂. Excess PI was then removed by fractionation. The reaction sequence given in Scheme 7.30 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 Hadjichristidis [84] to the synthesis of the A₂B stars, where A and B were all possible combinations of PS, PI, and PBd. In this case, a more sophisticated high vacuum technique was employed to ensure the formation of products characterized by high degrees of chemical and compositional homogeneity. This was tested using SEC, MO, LS, differential refractometry, and NMR spectroscopy. The method employed for the synthesis of the A₂B miktoarm stars can be expanded to the synthesis of A₃B structures using silicon tetrachloride (SiCl₄) instead of methyltrichlorosilane as the LA. The synthesis of PSPI₅ miktoarm stars [85] was accomplished by the reaction sequence outlined in Scheme 7.31.

Amphiphilic multiarm star copolymers of PIB and PEO bearing one PIB arm and two, three, and four PEO arms with identical length were reported





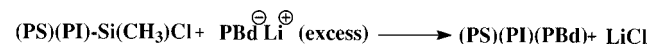
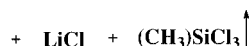
Scheme 7.32

by Lemaire *et al.* [86, 87]. End-chlorinated PIBs with controlled MW and narrow MW polydispersity were prepared by cationic polymerization, and the *tert*-Cl ω -end group was quantitatively converted to anhydride or dianhydride (Scheme 7.32). These species were used as macromolecular coupling agents for α -methoxy- ω -hydroxy PEOs leading to star-shaped polymers. It was found that the best coupling efficiency was obtained with *p*-toluenesulfonic acid as catalyst in mesitylene at 155 °C. The final products, characterized by SEC and MALDI-TOF MS, were mixtures of the stars with unreacted PEO and intermediate products.

Miktoarm star copolymers of the A_2B_2 type, where A is PIB and B is poly(MeVE), were prepared [88] via cationic polymerization. The synthetic strategy involved the reaction of 2,2-bis[4-(1-phenylethenyl)phenyl]propane (BDPEP) and 2,2-bis[4-(1-tolylenyl)phenyl]propane (BDTEP) with living PIB, resulting in a di-cationic in-chain initiator. This initiator was used for the polymerization of methyl vinyl ether to give the poly(isobutylene)₂(poly(methyl vinyl ether))₂, (PIB)₂(PMVE)₂, miktoarm copolymer. Purification of the crude A_2B_2 copolymer was performed on a silica gel column, and the purity of the resulting star was 93%.

The DFM methodology can be applied for the synthesis of miktoarm stars of the type A_nB_n in a manner similar to that of the asymmetric $A_nA'_n$ stars, involving a three-step procedure starting from the synthesis of the living chains A. These living chains initiate the polymerization of a small quantity of the DFM, leading to the formation of a living star polymer carrying a number of active sites within its core equal to the number of arms that have contributed

The synthesis of the (PS)(PI)(PBd) star terpolymer was accomplished by Hadjichristidis *et al.* [92] using anionic polymerization and controlled chlorosilane chemistry. Living PI chains reacted with a large excess of methyltrichlorosilane to produce the dichlorosilane end-capped PI. After 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 endpoint 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. The reaction sequence is outlined in Scheme 7.33.



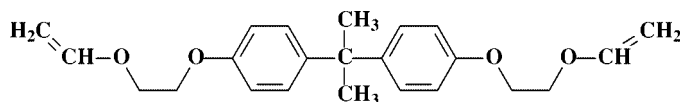
Scheme 7.33

linked in the titration step. Extensive characterization data for the arms as well as for the intermediate and the final product confirmed that the ABC star was characterized by high structural and compositional homogeneity. Two examples of the synthesis of ABCD miktoarm star quaterpolymers were reported in the literature [93, 94].

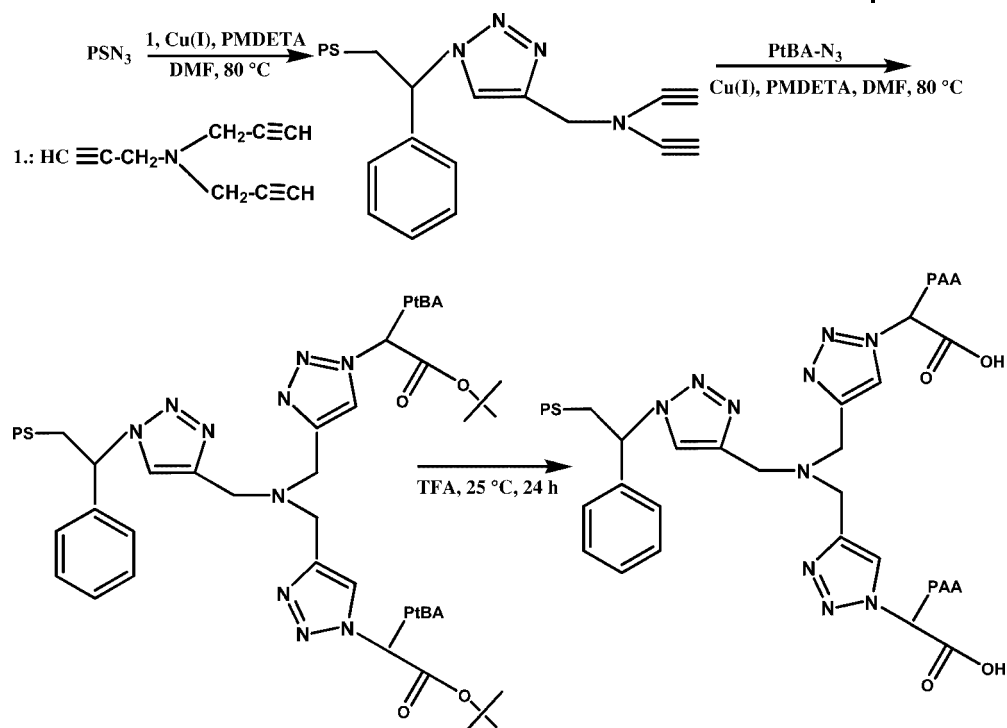
The DPE derivative methods and anionic polymerization were developed by Quirk and Hirao for the synthesis of miktoarm stars with complex architectures. The first procedure relies on the use of either MDDPE or PDDPE, whereas the second on the formation of polymers carrying DPE end groups with methoxymethyl moieties which 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. The synthesis of a wide variety of miktoarm stars with functionalized DPE derivatives and anionic polymerization has been reported recently in a detailed review by Hirao *et al.* [95]. Employment of the iterative methodology already presented for the synthesis of asymmetric stars, miktoarm stars of the type AB_4 , AB_8 , A_2B_4 , A_2B_8 , A_2B_{12} , ABC_2 , ABC_4 , $A_2B_2C_2D$, $A_4B_4C_4D$, ABC , A_3B , A_2B_2 , AB_3 , A_2BC , AB_2C , ABC_2 , and $ABCD$, where A is PS, B is PI or P α MS, C is PI or poly(4-(4-1,2:5,6-di-O-isopropylidene- α -glucofuranose-3-oxy)butoxy)styrene, and D is poly(4-trimethylsilylstyrene), have been prepared.

In addition to anionic polymerization, ATRP has also been used for the synthesis of miktoarm stars of the A_nB_m type. Using DVB, $(PnBuA)_n(PS)_m$ miktoarm stars were obtained. Bis(2-methacryloyloxyethyl)disulfide was also employed as a DFM for the synthesis of $(PMMA)_n(PnBuA)_m$ miktoarm stars [96]. In the last case, by using suitable reducing agents it is possible to degrade the core of the star structure. The formation of interstar and intrastar arm–arm coupling was observed. The initiating efficiency of the alkyl bromide sites in the core of the star polymers was determined after cleavage of the degradable stars and the corresponding miktoarm stars. It was found that only 19% of the initiation sites were active for the polymerization of the second monomer.

Cationic polymerization has also been applied in the synthesis of miktoarm stars of the type A_nB_n . Miktoarm stars of isobutyl vinyl ether (IBVE) and hydrolyzed 2-acetoxyethyl vinyl ether (AcOVE) or diethyl 2-(vinylxy)ethyl malonate (VOEM) [97] were prepared using the divinylether 1 of Scheme 7.34 as the DFM. The living chains of IBVE were used as macroinitiators for the polymerization of the diether, resulting in a star IBVE with a microgel core.



Scheme 7.34

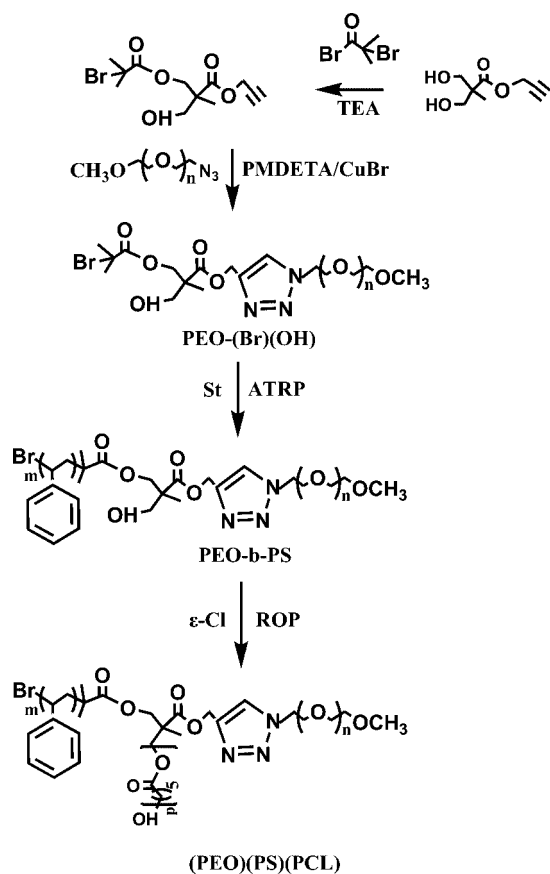


Scheme 7.35

The living sites in the core were used for the sequential polymerization of the other monomers.

Monteiro *et al.* [98] were the first to demonstrate the synthesis of a three-miktoarm star copolymer, (PS)₂PtBuA, using ATRP and “click” chemistry. A large excess of tripropargylamine was “clicked” with PS-N₃ to afford PS-(≡)₂ (Scheme 7.35). A solution of PS-(≡)₂ in dimethylformamide (DMF) was then added to a solution of PtBuA-N₃ in DMF at 80 °C to give the three-miktoarm star (yield: 92%). Conversion of the PtBuA to poly(acrylic acid) (PAA) with trifluoroacetic acid afforded an amphiphilic three-miktoarm star, PS(PAA)₂.

Deng *et al.* [99] reported the synthesis of ABC three-miktoarm star terpolymer by “click” chemistry, ATRP, and ROP. An azide-terminated poly(ethylene oxide) (PEO-N₃), was first synthesized and reacted with the trifunctional propargyl 2-hydroxyl-methyl-2-(α-bromoisobutyraloxymethyl)-propionate (PHBP), to generate a PEO macroinitiator (Scheme 7.36). The cycloaddition reaction of PEO-N₃ and PHBP was carried out using the CuBr/PMDETA catalyst at room temperature. It was found that 3.5 h was enough for completion of the reaction. Longer reaction times resulted in radical coupling between the PEO chains. The macroinitiator consisted of two functional groups, a hydroxyl group and an α-bromoisobutyryloxy group. Consecutive ATRP of styrene and



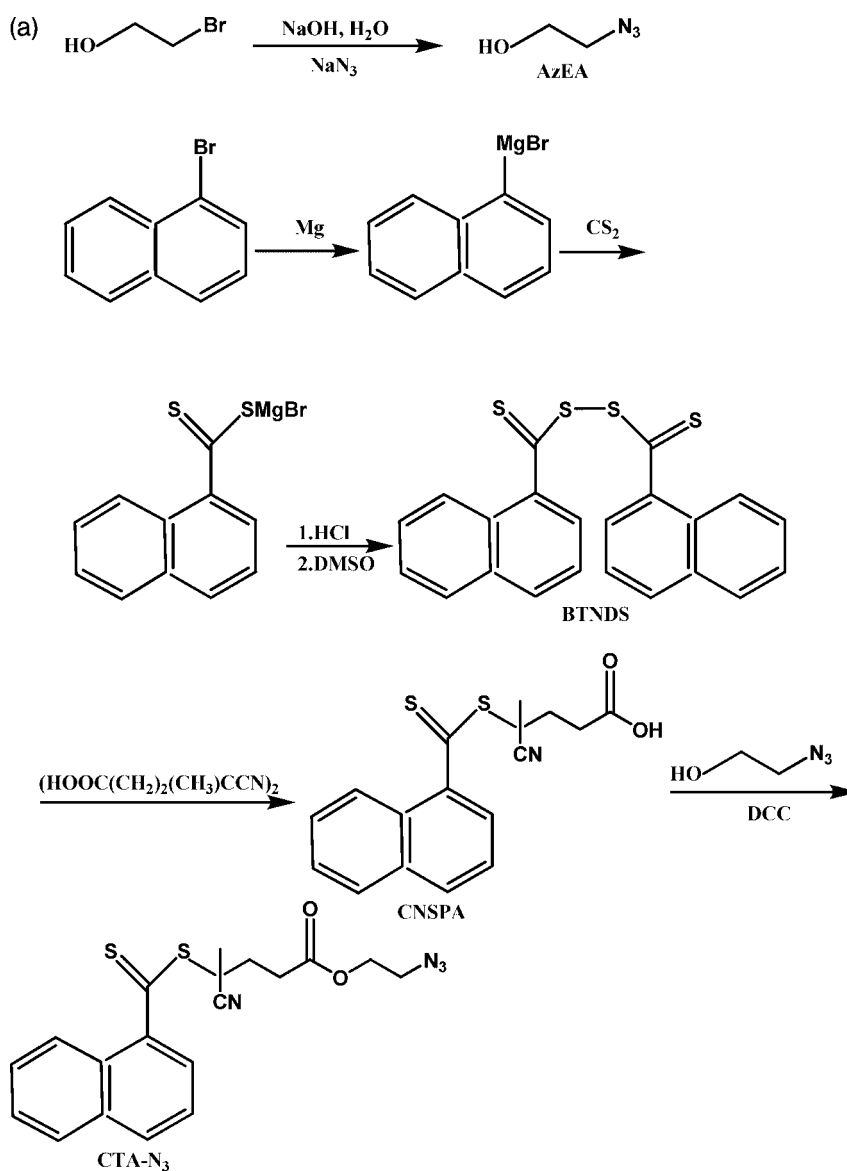
Scheme 7.36

ROP of ϵ -CL from the PEO macroinitiator produced an ABC three-miktoarm star terpolymer with narrow MW distribution.

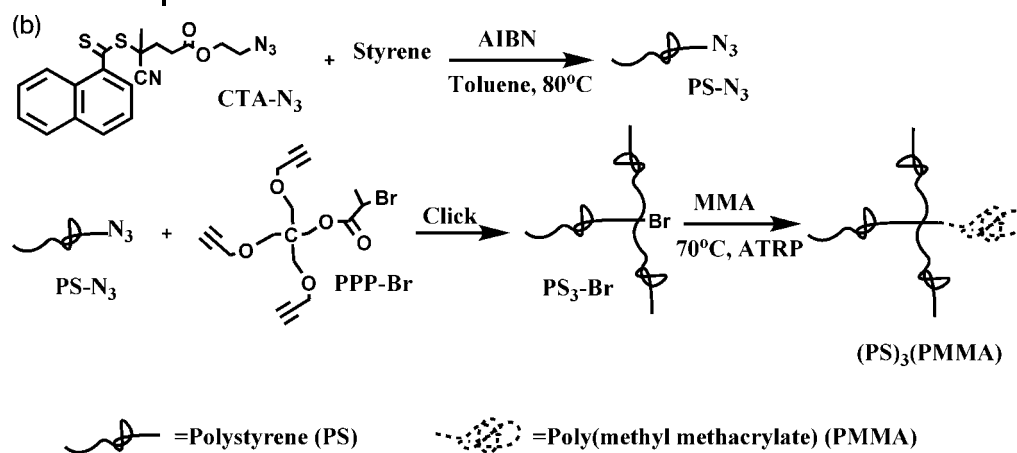
Kang *et al.* [100] reported an alternative approach for the synthesis of a four-miktoarm star copolymer (PS)₃PMMA by combination of controlled radical polymerizations and “click” chemistry. An azide-functionalized dithioester chain transfer agent (CTA-N₃) was first synthesized, according to Scheme 7.37a. CTA-N₃ was then used to RAFT polymerize styrene to afford PS-N₃. A three-arm star PS was then prepared via “click” reaction with a bromide-containing trialkyne coupling agent, followed by ATRP of MMA to afford the final four-miktoarm star copolymer (Scheme 7.37b).

Tunca *et al.* [101] published a series of papers dealing with the synthesis of three-miktoarm star terpolymers using combination of “click” chemistry and a MFI containing alkyne TEMPO and *tert*-bromide groups (Scheme 7.38). MMA was polymerized first by ATRP (CuCl/PMDETA as catalyst/ligand in

toluene, at 60 °C) followed by the nitroxide-mediated polymerization NMP of styrene at 125 °C. Finally, PMMA-*b*-PS with alkyne functionality at the junction point and an azide end-functionalized P*t*BuA (or PEG- N_3) were “clicked” in the presence of CuBr/PMDETA in DMF at room temperature for 24 h to afford the ABC miktoarm star terpolymer.



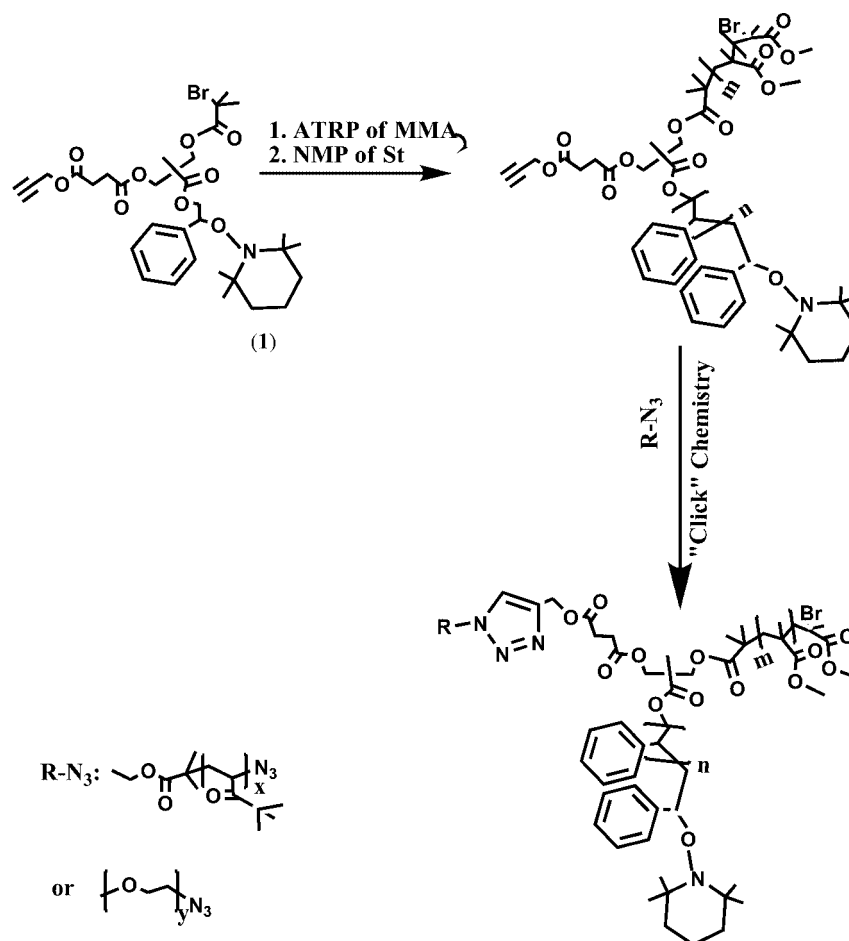
Scheme 7.37a



Scheme 7.37b

The same authors [102] utilized two different one-pot methods for the synthesis of ABC miktoarm star terpolymers. In the first (one-pot/one-step) method (Scheme 7.39), NMP of styrene, ROP of ϵ -CL, and “click” reaction between PMMA-N₃ or PEG-N₃ and the alkyne group of an MFI (TEMPO, alkyne and hydroxyl groups) were simultaneously carried out for 48 h at 125 °C. In the second (one-pot/two-steps) method, NMP of styrene and ROP of ϵ -CL were conducted, using the same MFI for 20 h at 125 °C, followed by “clicking” the product with PEG-N₃. In both techniques, the miktoarm star terpolymers were recovered by a simple precipitation in methanol without further purification. The second method resulted in lower polydispersity (~ 1.1) compared to the first one (~ 1.3).

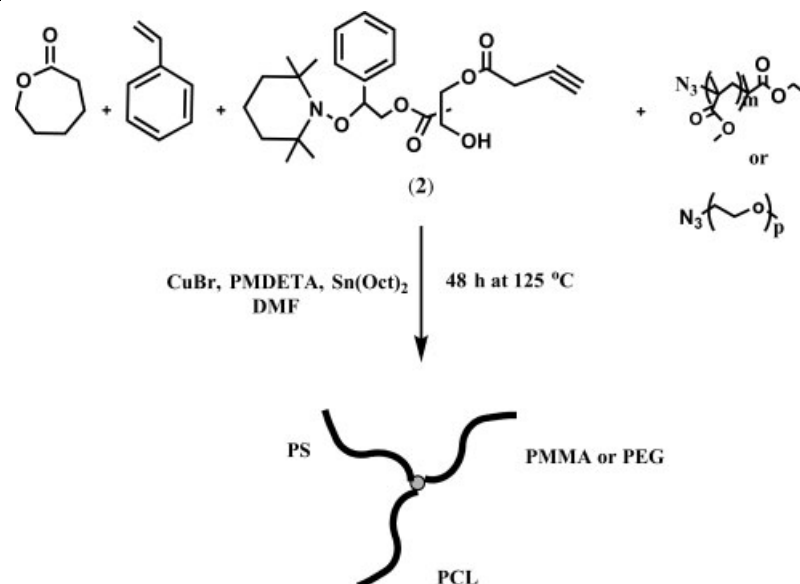
Tunca *et al.* also synthesized a four-miktoarm star quaterpolymer ABCD [103] by “clicking” two diblock copolymers having at the junction point either an alkyne or an azide group (Schemes 7.40a–c). An initiator containing TEMPO and hydroxyl groups **1** was used for the NMP of styrene and ROP of ϵ -CL at 120 °C (one-pot method) to give PS-*b*-PCL copolymer with bromine functionality at the junction point (Scheme 7.40a). The bromine at the junction point of PS-*b*-PCL was converted quantitatively into azide, using NaN₃ in DMF at room temperature, to afford the N₃ in-chain block copolymer. PEG macroinitiator was prepared via the condensation reaction of PEG-COOH and **2** in the presence of dimethylaminopyridine (DMAP)/dicyclohexylcarbodiimide (DCC) catalysts in CH₂Cl₂ at room temperature, followed by ATRP of MMA to afford the alkyne-in chain PEG-*b*-PMMA (Scheme 7.40b). The separately prepared N₃- and alkyne in-chain PS-*b*-PCL and PEG-*b*-PMMA copolymers were “clicked” (Scheme 7.40c) using CuBr/PMDETA in DMF at room temperature for 48 h to give the four-miktoarm star quaterpolymer (yield: 88%, $M_w/M_n = 1.22$).



Scheme 7.38

7.3 Comb Polymers

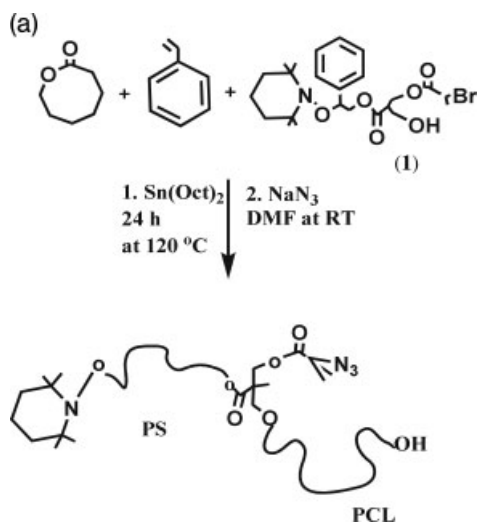
Comb polymers are composed of a main polymer chain, the backbone to which one or more side chains, the branches, are connected through covalent bonds. Comb polymers are homopolymers, i.e., both the backbone and the branches are of the same chemical nature, while graft polymers are composed of chemically different backbone and branches. The branches are usually randomly distributed along the backbone, because of the specific synthetic techniques used. However, more elaborate recent methods have allowed the synthesis of exact comb polymers, where all the molecular and structural parameters can be accurately controlled.



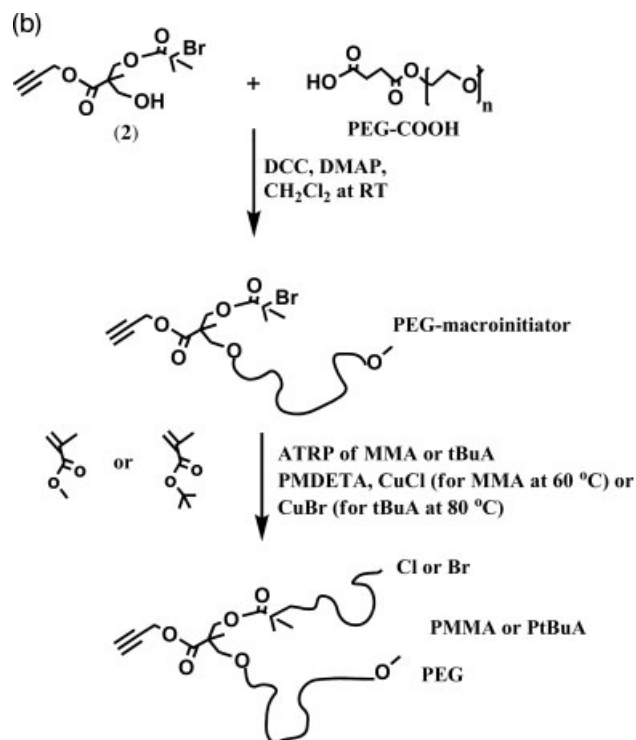
Scheme 7.39

Three general methods have been developed for the synthesis of randomly branched comb polymers: (i) the “grafting onto,” (ii) the “grafting from,” and (iii) the “grafting through” or macromonomer method (Scheme 7.41) [104].

The “grafting onto” method involves the use of a backbone chain containing functional groups X randomly distributed along the chain and branches having



Scheme 7.40a



Scheme 7.40b

reactive chain ends Y. The coupling reaction between the functional backbone and the end-reactive branches leads to the formation of comb polymers.

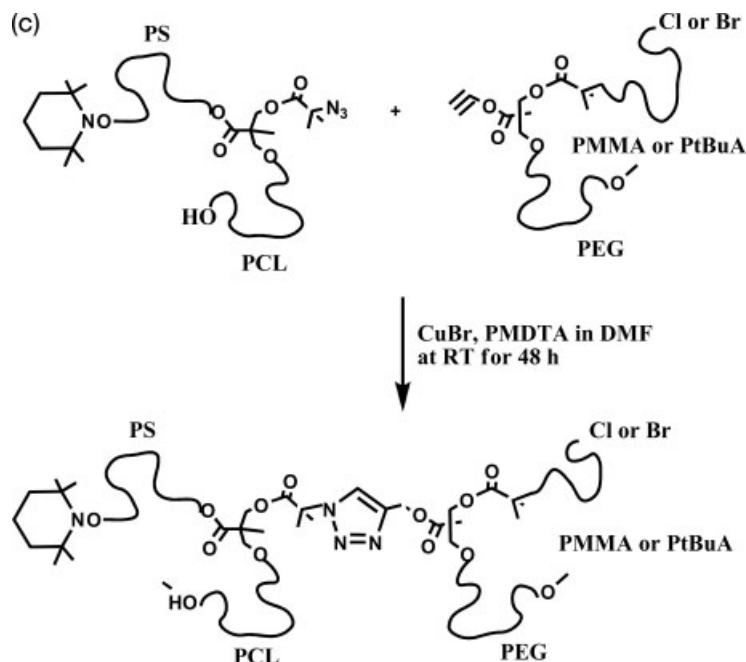
In the “grafting from” method active sites are generated randomly along the backbone. These sites are capable of initiating the polymerization of a second monomer, leading to the synthesis of comb polymers.

The most commonly used method for the synthesis of comb polymers is the “grafting through” or macromonomer method [105]. Macromonomer is an oligomeric or polymeric chain bearing a polymerizable end group. Macromonomers having two polymerizable end groups have also been reported [106]. Copolymerization of preformed macromonomers with the same monomer used to construct the macromonomer yields comb polymers.

7.3.1

“Grafting Onto” Methods

One of the methods widely used for the synthesis of comb polymers is the “grafting onto” method, i.e., reaction of preformed polymeric chains having functional groups, with other polymeric chains having active chain



Scheme 7.40c

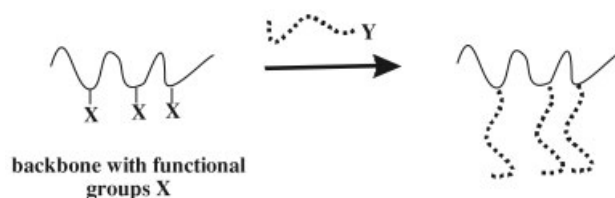
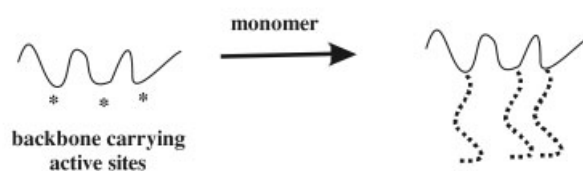
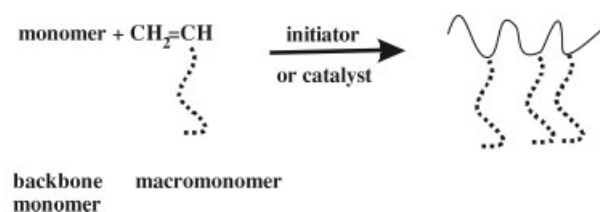
ends. In most cases, the incorporation of functional groups is performed by chemical modification of the backbone. Characterization of the backbone and the preformed side chains can be performed separately from the comb polymer, thus allowing for the detailed characterization of the final structure.

For example, anionically prepared linear PI was subjected to partial epoxidation, employing a suitable organic peracid, to introduce randomly grafting sites along the polymer chain. The epoxidized polymers were subsequently reacted with living polyisoprenyllithium to afford comb-branched PIs (Scheme 7.42) [107].

7.3.2

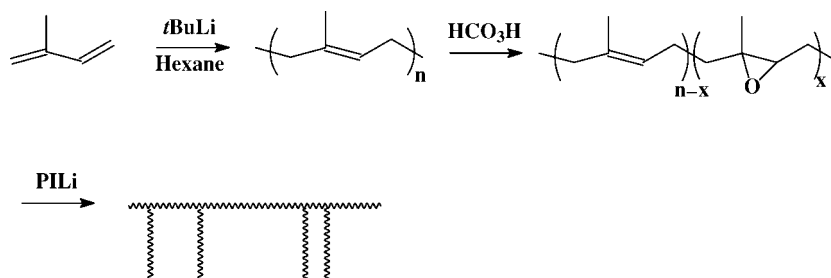
“Grafting from” Methods

In the “grafting from” method, the backbone is chemically modified to introduce active sites capable of initiating the polymerization of a second monomer. The number of grafted chains can be controlled by the number of active sites generated along the backbone, assuming that each one participates in the formation of one branch. Full structural characterization of the products obtained from a grafting from scheme is very difficult since neither the exact

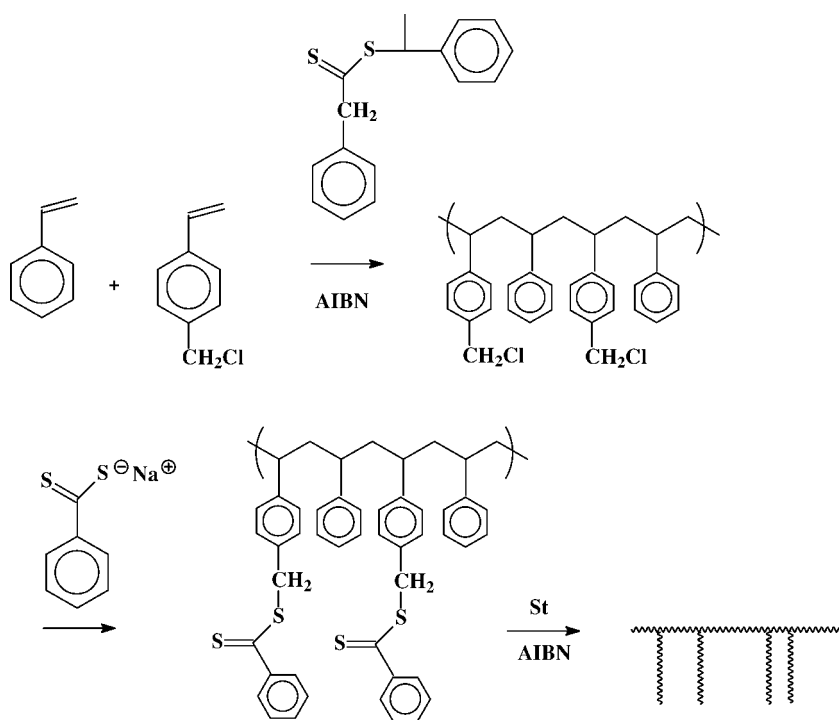
"Grafting onto" method*"Grafting from" method**Macromonomer method***Scheme 7.41**

number of side chains added nor their MW can be determined. Additionally, in the case of ionic copolymerization reactions, solubility may be a concern for highly charged macroinitiators, frequently leading to poorly controlled heterogeneous products.

For example, RAFT polymerization was employed for the synthesis of PS combs [108]. The reaction sequence involves the copolymerization of styrene and vinylbenzyl chloride (VBC) in the presence of AIBN and 1-phenylethyl phenyldithioacetate as initiator and chain transfer agent, respectively. The benzylic chloride groups were then reacted with sodium dithiobenzoate to afford PS chains bearing dithiobenzoate pendant groups. Subsequent addition of styrene and AIBN leads to the synthesis of PS combs, since the dithiobenzoate moieties serve as chain transfer agents (Scheme 7.43). The SEC traces were multimodal, indicating the existence of high molecular and structural heterogeneity of the combs.



Scheme 7.42

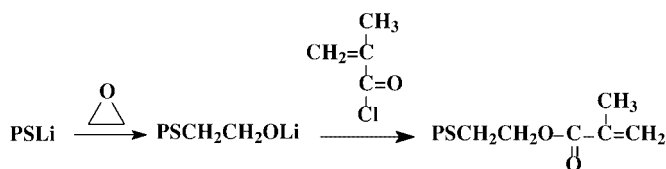


Scheme 7.43

7.3.3

“Grafting Through” or Macromonomer Method

The homopolymerization of macromonomers affords comb-shaped structures, polymacromonomers, or molecular brushes, with an extremely high density of branching, since each monomeric unit bears a polymeric chain as a side group [109]. Depending on graft length and degree of polymerization,



Scheme 7.44

the polymacromonomers may adopt several conformations in solution, such as starlike, comblike, bottlebrush, or flowerlike. The copolymerization of the macromonomers with another conventional monomer results in the formation of comb polymers.

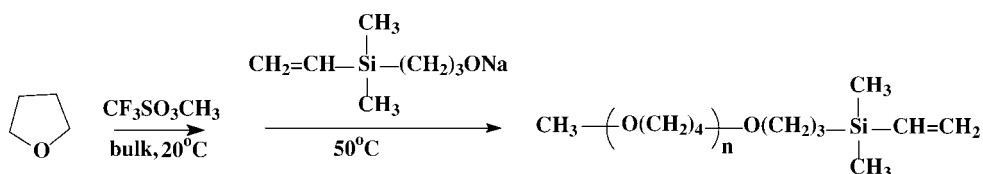
The synthesis of macromonomers can be accomplished by almost all the available polymerization techniques. Among them, living polymerization methods offer unique control over the MW, the MW distribution, and chain-end functionalization.

Anionic polymerization is one of the best methods for the synthesis of well-defined macromonomers. Functional initiation or termination by suitable electrophilic reagent is the best ways for the incorporation of the reactive end groups [110]. According to this methodology, living polystyryllithium was initially reacted with ethylene oxide to form the less reactive alkoxide followed by the reaction with methacryloyl chloride for the synthesis of the macromonomer (Scheme 7.44) [111].

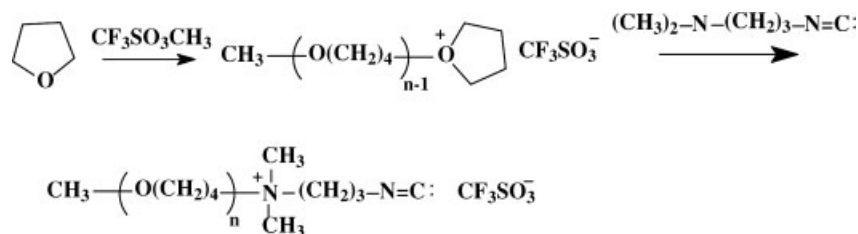
Cationic polymerization has also been used for the synthesis of macromonomers, especially after the development of living cationic polymerization techniques [112]. Macromonomers were prepared by the cationic ROP of THF using methyltrifluoromethane sulfonate followed by termination with 3-sodio-propyloxydimethylvinylsilane to give a macromonomer with vinyl silane end groups (Scheme 7.45) [113].

Termination of living polytetrahydrofuran (PTHF) with 3-(dimethylamino propyl) isocyanide leads to the formation of macromonomers having end isocyanide groups (Scheme 7.46) [114].

Free radical polymerization has been the most common technique for the synthesis of macromonomers, due to the facts that it is not a very demanding experimental method, there is no need for special purification of the reagents, and it is applicable to a wide variety of monomers. However, the method



Scheme 7.45



Scheme 7.46

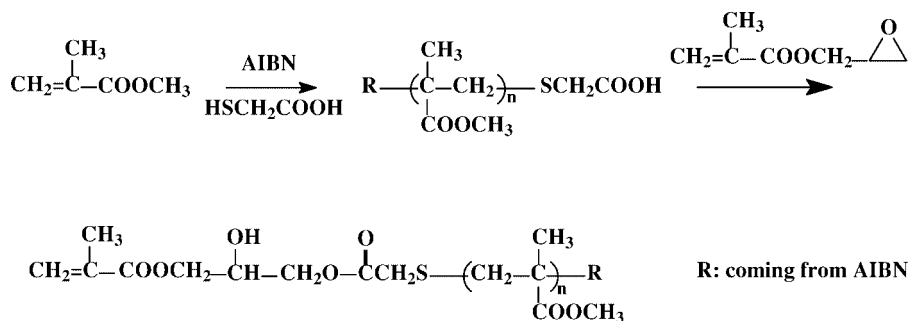
suffers from many disadvantages such as the poor control over the MW, the MW distribution, and the degree of functionalization. The basic method for the incorporation of the functional end groups involves the use of chain transfer agents [115].

PMMA macromonomers have been prepared using thioglycolic acid as a chain transfer agent, followed by reaction with glycidyl methacrylate (Scheme 7.47) [116].

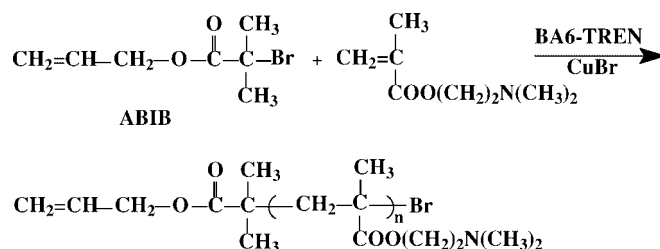
The evolution of the living/controlled radical polymerization techniques (mainly NMP and ATRP methods) very soon led to the synthesis of a wide range of macromonomers. These methods combine the advantages of the free radical polymerization with those of the living polymerization techniques, despite the fact that the control over the functionalization reaction is not always comparable to the anionic polymerization methods [117, 118].

Poly(dimethylaminoethyl methacrylate) macromonomers were prepared by ATRP using allyl 2-bromoisobutyrate (ABIB)/CuBr/tris[2-di(butyl acrylate) aminoethyl] amine (BA6-TREN) or allyltrichloroacetamide/CuBr/BA6-TREN as the initiation systems (Scheme 7.48) [119].

Group transfer polymerization has also been used for the synthesis of macromonomers. The functional end groups are incorporated mainly using the suitable initiation system [120]. Trimethylsilyloxy ethyltrimethylsilyl dimethyl ketene was used as initiator for the synthesis of PMMA macromonomers in the



Scheme 7.47

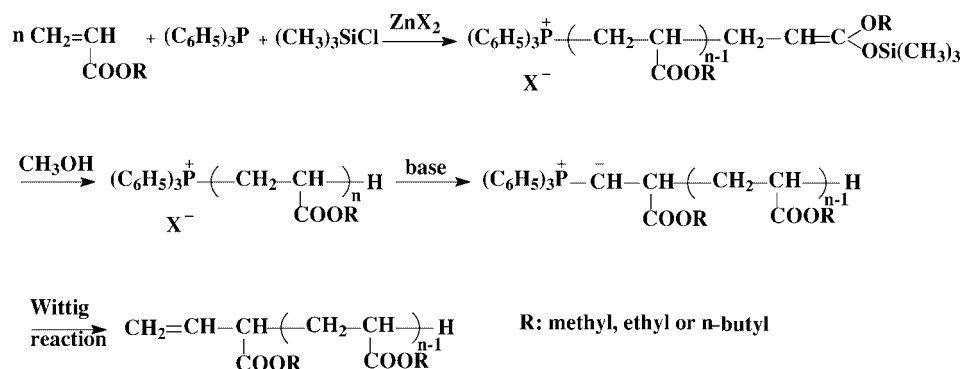


Scheme 7.48

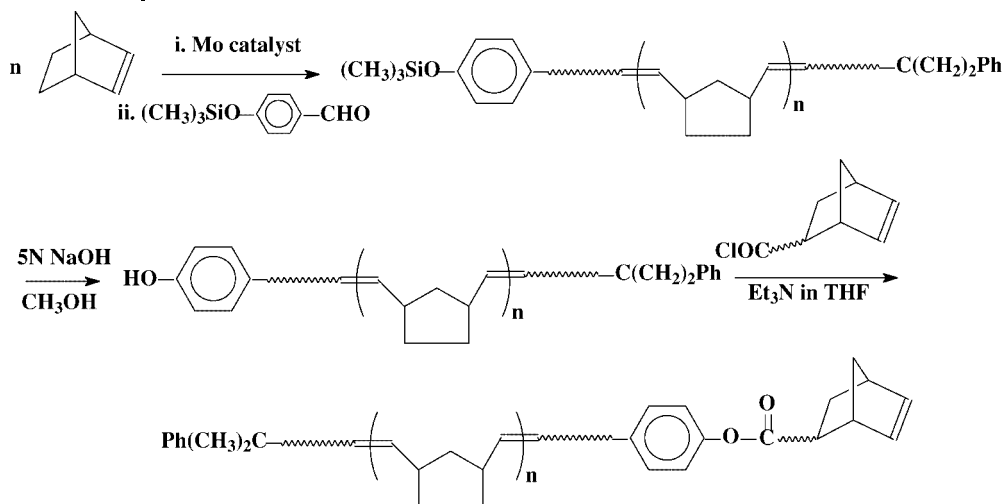
presence of tetrabutylammonium benzoate, which was the catalyst. Treatment with dilute HCl provided the –OH functional macromonomers, which was followed by the reaction with acryloyl chloride to give the final macromonomer structure (Scheme 7.49) [121].

ROMP was employed for the synthesis of polynorbornene macromonomers. A well-defined molybdenum initiator of the type $\text{Mo}(\text{CHCMe}_2\text{Ph})(N\text{-}2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{OR})_2$, [$\text{R}=\text{OCMe}_3$, $\text{OCMe}(\text{CF}_3)_2$] was used. The polymers produced were cleaved from the initiator fragment in a Wittig-like reaction using $p\text{-(CH}_3)_3\text{SiC}_6\text{H}_4\text{CHO}$, according to a well-established method. Deprotection under basic conditions gave macromonomers having phenyl end groups. Subsequent reaction with norbornene carboxylic acid chloride yields macromonomers with norbornene end groups (Scheme 7.50) [122].

One of the most widely used methods for the synthesis of comb polymers involves the use of macromonomers, through their copolymerization with the same monomer used to construct the macromonomer [123]. The method offers several advantages for the synthesis of well-defined combs: (i) all the possible polymerization techniques can be employed; (ii) the chain length of the side chains can be controlled by the synthesis of the macromonomers; (iii) the backbone length can be also controlled when a living polymerization method



Scheme 7.49



Scheme 7.50

is used for the copolymerization reaction; and (iv) the number of side chains per backbone can be controlled by the molar ratio of the macromonomer and the comonomer and by the reactivity ratios of the copolymerization system. However, there are several limitations that characterize the macromonomer method for the synthesis of combs. The most important is the lack of control over the spacing of the branches along the backbone. The spacing distribution is determined by the reactivity ratios of the macromonomer and the comonomer. The most important factors affecting the reactivity of the macromonomers are the following: (i) the chemical nature of the polymerizable end group, (ii) the MW of the macromonomer, and (iii) the conversion of the homo- or copolymerization. Among these parameters, the most important is without doubt the nature of the polymerizable end group. According to this statement, the reactivity of the macromonomer is identical to the reactivity of the corresponding low MW monomer. However, this is not always true, because of the increased importance of the above-mentioned parameters. It is well known that interactions between polymer chains are generally repulsive due to excluded volume effects. Consequently, the reactivity of the macromonomer is dramatically reduced during the polymerization upon increasing its MW. In this case, the excluded volume effects prevent the approach of the active center of the growing polymer chain to the polymerizable end group of the macromonomer. Since the above factors reduce the reactivity of the macromonomers, it can be concluded that during the copolymerization with a conventional monomer the comb structure will be very poor in branches at the initial stages of the copolymerization (high reactivity of the comonomer), whereas at the later stages of the copolymerization the structure will be richer in branches (excess of the unreacted macromonomers over the low

MW monomer). Therefore, in most cases, the final product will have a heterogeneous distribution of branches along the backbone.

All the available polymerization techniques can be employed for the synthesis of combs by the macromonomer method. The most common method is the free radical polymerization. The advantages and the drawbacks of the technique also apply in this case. The relative experimental simplicity, the lack of the need to perform exhaustive purifications of the monomers, solvents, etc., the application to an enormous number of macromonomers and monomers, and the possibility to expand the method to an industrial scale production of combs are the major advantages. However, the method suffers several drawbacks, such as the lack of control over the MW of the backbone and the increased polydispersity, as well as the chemical and compositional heterogeneity of the final products.

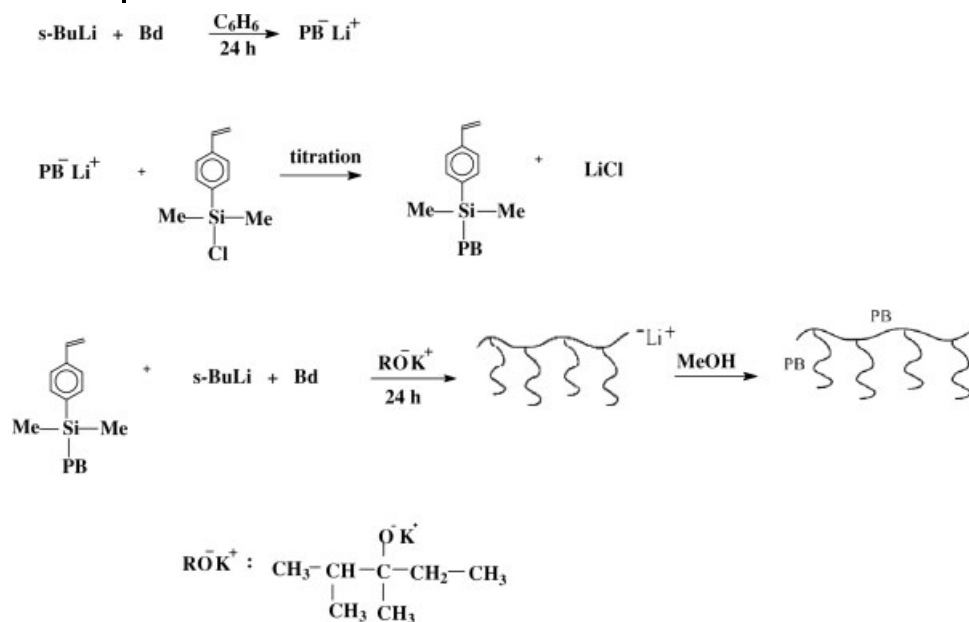
Although free radical polymerization has been the most widely used method for the synthesis of combs by the macromonomer method, the living polymerization techniques offer unique opportunities to control the molecular and structural characteristics of the structures. However, the superior behavior of the living polymerization methods is overbalanced to some extent by the demanding experimental effort needed to perform these kinds of reactions and the relatively small number of monomers that are susceptible to these polymerization reactions.

Among the living polymerization methods, anionic polymerization has been shown to be the most efficient method for the synthesis of complex macromolecular architectures. However, owing to the time-consuming and demanding experimental procedures [124] that are necessary to achieve truly living conditions, the method has not been broadly used for the synthesis of graft copolymers by the macromonomer method.

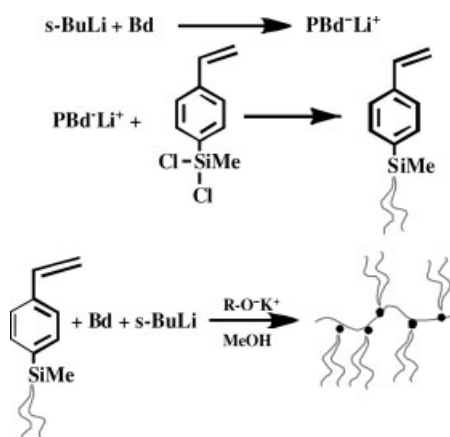
Stereoregular combs were prepared by copolymerization of stereoregular PMMA macromonomers (isotactic or syndiotactic) with MMA using *t*-BuMgBr in toluene at -78°C or diphenylhexyllithium (DPHLi) in THF at -78°C [125].

Well-defined PBd combs were prepared by Hadjichristidis *et al.* [126]. Living PBdLi chains were reacted with 4-(chlorodimethylsilyl)styrene (CDMSS) to afford the styrenic macromonomer. The efficiency of this approach relies on the much higher reactivity of the living polymer toward the chlorosilane group rather than the styrenic double bond. Subsequent copolymerization of the macromonomers with butadienes leads to the synthesis of PBd combs. To achieve the random placement of the branches along the backbone, the copolymerization was performed in the presence of potassium alkoxide of 2,3-dimethyl-3-pentanol, which equalizes the reactivity ratios of the styrenic macromonomers and butadiene (Scheme 7.51).

4-(Dichloromethylsilyl)styrene was also employed for the synthesis of double-tailed styrenic-tipped macromonomers (Scheme 7.52). The macromonomers were either copolymerized with Bd in the presence of potassium alkoxide of 2,3-dimethyl-3-pentanol, or homopolymerized to afford double-comb PBds or double macromolecular brushes, respectively [127]. The single or double-tailed



Scheme 7.51



Scheme 7.52

macromonomers were prepared and polymerized *in situ* without isolation and purification, thus avoiding the introduction of impurities and leading to well-defined products.

ATRP has emerged as an important method for the synthesis of a variety of complex architectures with controlled molecular characteristics and much less pronounced chemical and compositional heterogeneity than the

conventional free radical polymerization [128]. Therefore, a growing interest exists for the synthesis of combs using this method for the copolymerization of the macromonomers with other comonomers. PMMA macromonomers having methacryloyl end groups were copolymerized with MMA by ATRP to produce the corresponding combs [129]. Comparison with the conventional free radical copolymerization revealed that the reactivity of the PMMA macromonomer in ATRP is much higher, probably due to the different timescale of monomer addition in both processes. The free radicals exist for a few milliseconds, whereas the active radical species in ATRP may exist for several seconds, thus having the opportunity to react with the growing polymer chain.

Coordination polymerization using suitable catalytic systems offers the unique advantage to control polymer chain stereochemistry [130]. Furthermore, it can be applied on an industrial scale for the synthesis of valuable products. However, this method is not a living polymerization, meaning that there is no control over the MWs, and rather broad MW distributions are observed. Recently, with the use of metallocene catalysts it has been possible to achieve a much better control over the polymerization reaction leading to products of better quality [131].

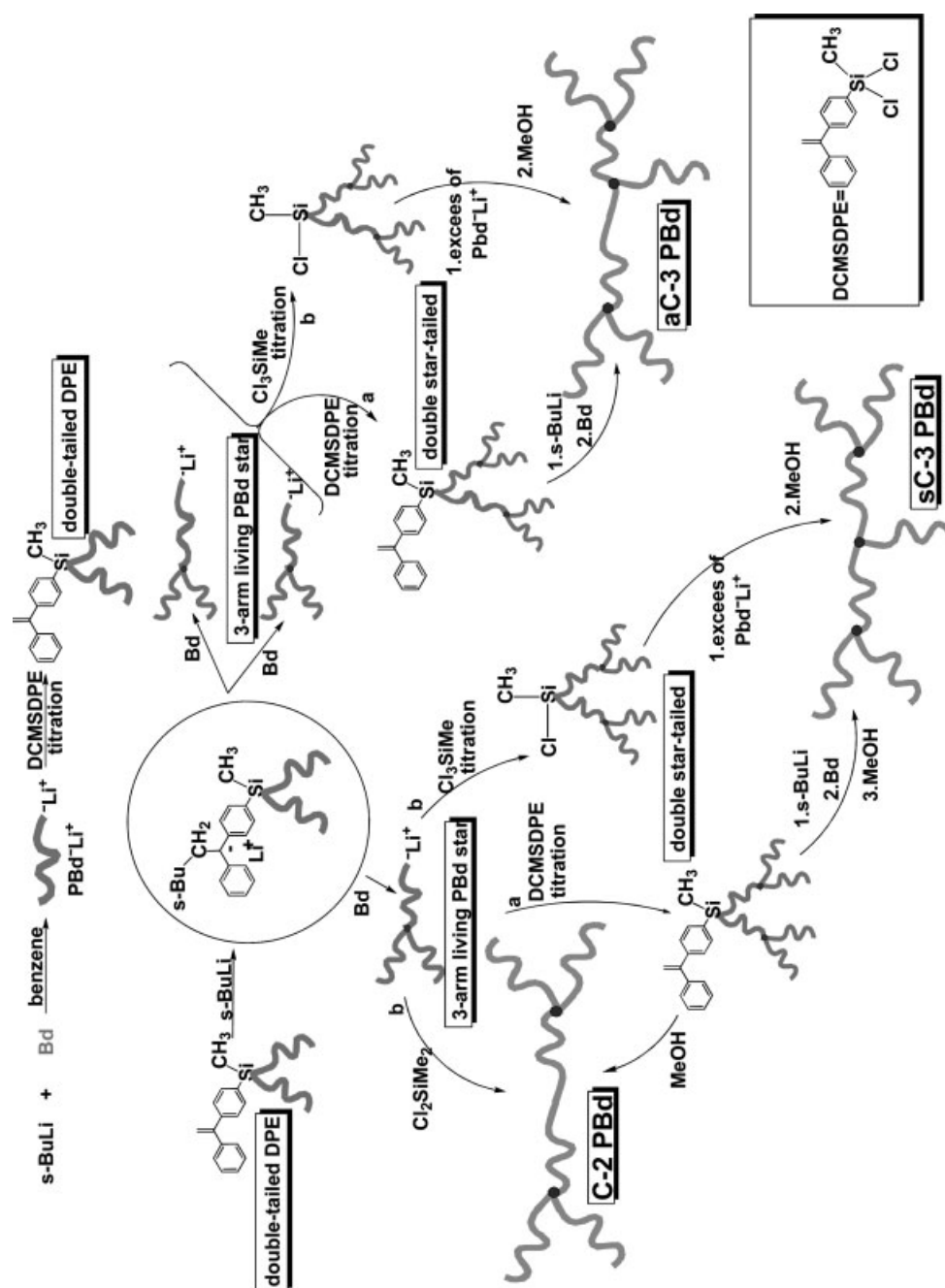
Shiono *et al.* prepared atactic polypropylene (PP) macromonomers through the polymerization of propene with bis(pentamethylcyclopentadienyl) zirconium dichloride/methylaluminoxane (MAO), $\text{Cp}_2^* \text{ZrCl}_2/\text{MAO}$, and termination by β -hydrogen elimination [132]. The PP macromonomers were copolymerized with propene using *rac*-[Me₂Si(2-Me-Benzind)₂]ZrCl₂/MAO as the catalytic system to produce atactic PP-*g*-isotactic PP stereo-comb polymers.

The macromonomer method was also employed by Endo *et al.* to prepare syndiotactic PS-*g*-atactic PS stereo-combs [133]. Anionic polymerization was used to prepare vinylbenzyl-terminated PS macromonomers, which were subsequently copolymerized with styrene using $\text{CpTiCl}_3/\text{MAO}$ as the catalyst. Low copolymerization yields (<20%) were obtained in this study.

The term *exact graft copolymers* refers to molecules where all the molecular and structural characteristics, such as the MWs of the backbone and the branches, the MW distributions, the number of branches and the specific grafting points on the backbone, can be controlled and varied at will. The parameters that are most difficult to be controlled are the number and the spacing distribution of branches along the backbone chain.

Exact comb PS polymers of the “H” shape have been prepared by anionic polymerization techniques and controlled chlorosilane chemistry [134].

Two methodologies, based on living star polymers and anionic polymerization high vacuum techniques, were used for the synthesis of exact comb PBds with two (C-2 or H-type) and three identical branches (symmetric, sC-3, H-type with an extra identical branch at the middle of the connector; and asymmetric, aC-3, H-type with the extra identical branch at any other position along the connector) (Scheme 7.53) [135]. The first methodology involves (i) the selective



Scheme 7.53

replacement of the two chlorines of 4-(dichloromethylsilyl)diphenylethylene (DCMSDPE, key molecule) with three-arm star PBds, by titration with identical (C-2, sC-3) or different (aC-3) living three-arm star PBds, (ii) the addition of *s*-BuLi to the double bond of DPE, and (iii) the polymerization of butadiene from the newly created anionic site (sC-3, aC-3). The second methodology involves the reaction of living stars with dichlorodimethylsilane (C-2) or the selective replacement of the three chlorines of trichloromethylsilane with star and linear chains (sC-3, aC-3). Intermediate and final products were characterized via SEC, LALLS, and ^1H NMR. The first methodology does not require fractionation, but in contrast to the second methodology cannot afford polymers with branches of identical MW. Both methods are general and can be extended to combs with two or three different branches at controllable positions along the backbone.

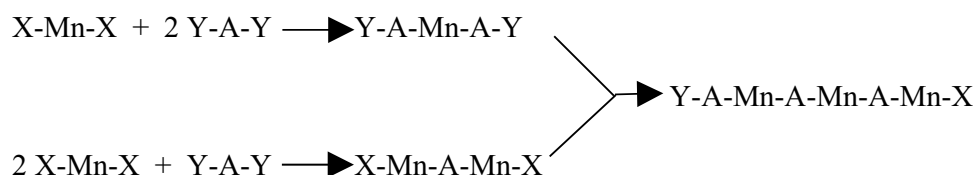
7.4 Cyclic Polymers

The first attempts to synthesize cyclic polymers involved ring–open chain equilibrium based on backbiting reactions of poly(dimethylsiloxanes) [136]. However, this method was limited to low MW and polydisperse cyclic polymers and is characterized by the inability to isolate the corresponding linear precursor to prove the cyclic structure by comparing the properties. Now, living polymerization processes leading to narrow MW distribution polymers are generally preferred. The linear precursor of the cyclic polymer had 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 LA. In the second case, an α,ω -heterodifunctional macromolecule was prepared using a functional protected initiator and by neutralizing the living site with the appropriate LA 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:

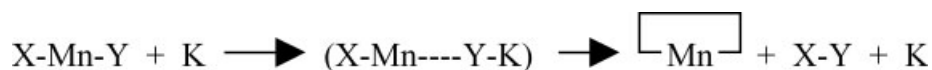


In addition to the intramolecular reaction, several intermolecular reactions can occur:



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

In the second case the cyclization requires an activation step:



This synthetic approach presents several advantages, e.g., 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 necessary. 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 $\langle r^2 \rangle^{3/2}$ 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 like is given by

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

This equation shows that (i) the more dilute the polymer solution, the more probable is the cyclization over the polycondensation and (ii) at the same MW, the doubled concentration (higher yield) can be used for heterodifunctional compared to homodifunctional polymers. The practical strategies used for the preparation of cyclic copolymers will be presented below.

7.4.1

Cyclic Polymers from Precursors with Homodifunctional Groups

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

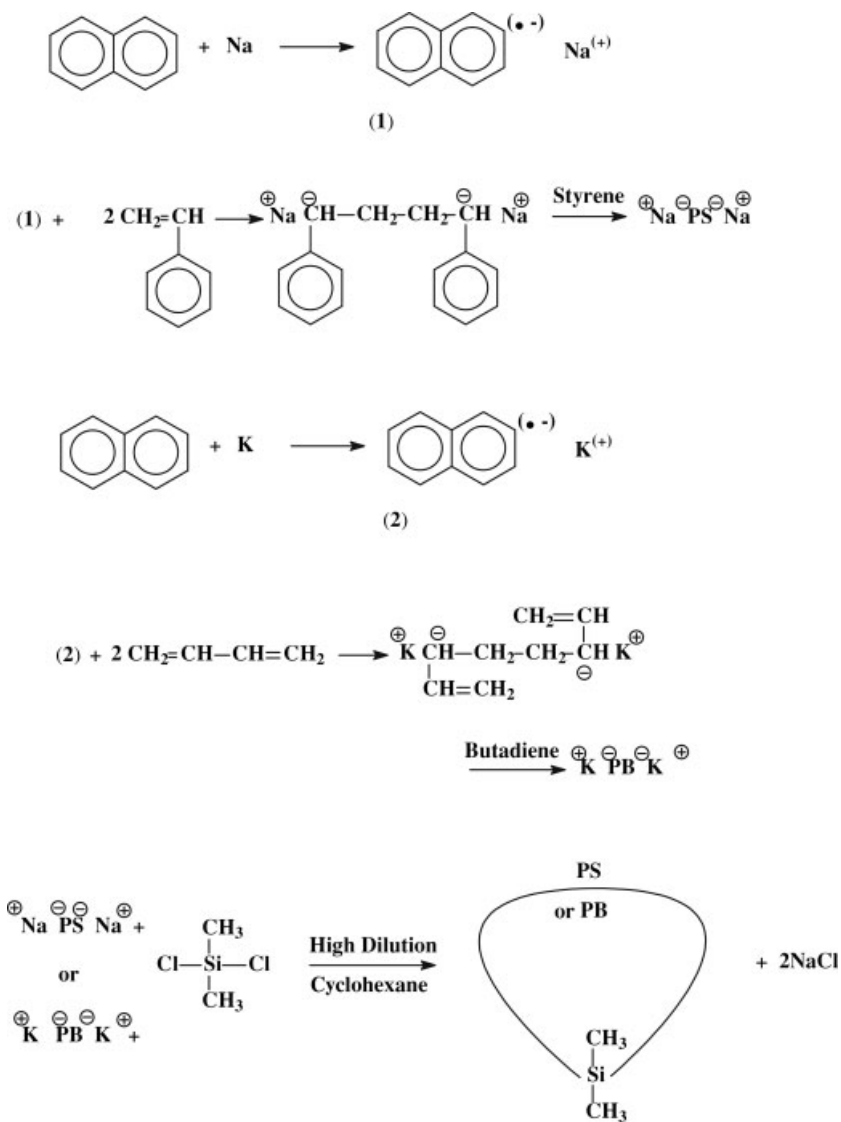
1. preparation of a monodisperse α - ω homodifunctional living polymer;
2. reaction of the living polymer with a homodifunctional LA;
3. fractionation for purification of the cyclic polymer.

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

7.4.2

Cyclic Homopolymers

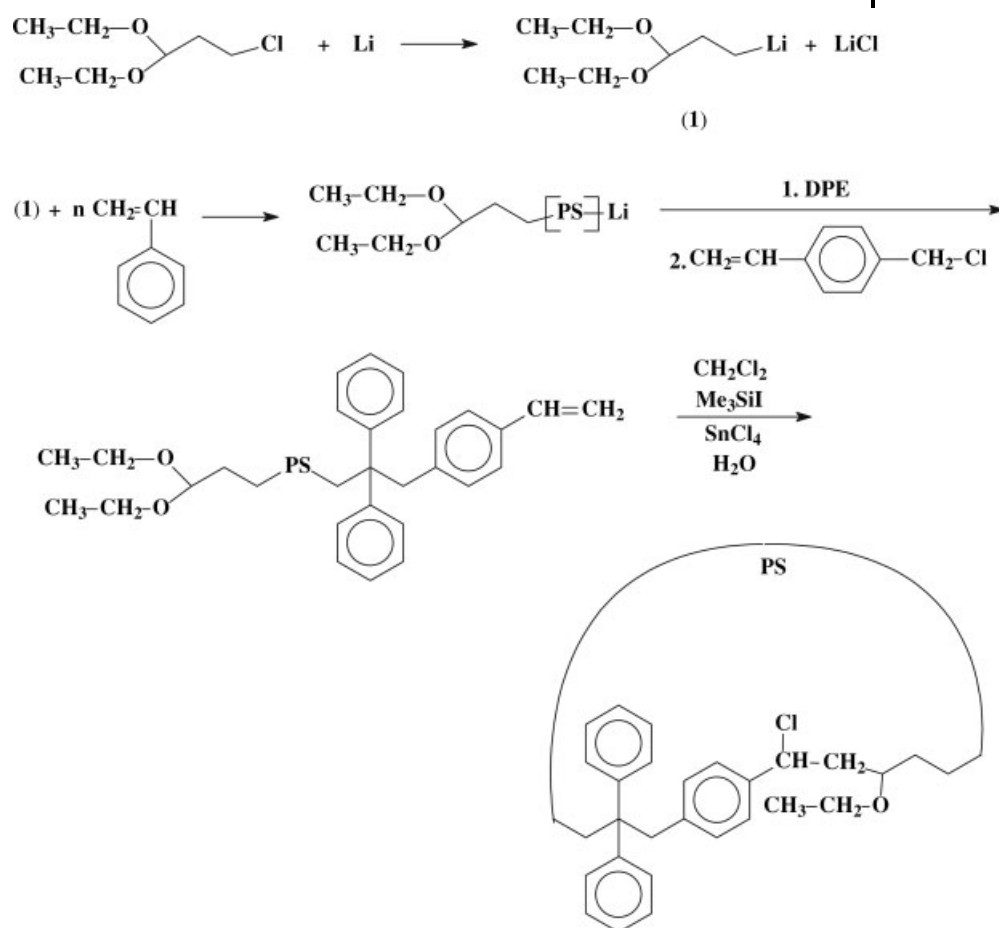
Roovers *et al.* [137] synthesized cyclic PS under high vacuum conditions using naphthalene sodium as a difunctional initiator. The polymerization solvent was a mixture of THF and benzene in a ratio of 1 : 1 (v/v). The LA was dichlorodimethylsilane, and the linking reaction was performed in cyclohexane at room temperature, close to theta conditions for PS. Roovers synthesized a series of cyclic PSs with MWs from 2.0 to 55×10^4 g mol⁻¹. The separation of the 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, in good agreement with the theoretically and experimentally reported values. A few years later and using the same experimental procedures, the same group prepared cyclic PBds [138] (Scheme 7.54). THF was the polymerization solvent, resulting in a 60% of 1,2 content. From the g' values, it was concluded



Scheme 7.54

that some of the cyclic PBds were contaminated by their linear precursors [139].

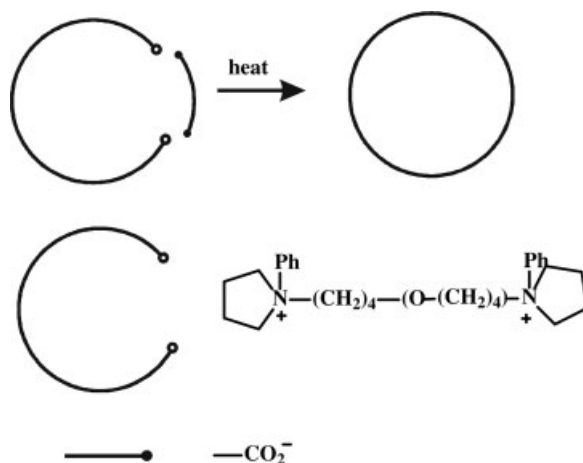
Deffieux was one of the first to use precursors with α,ω -heterodifunctional reactive groups. With his collaborators [140] he synthesized α -acetal-functionalized linear PS by using 3-lithiopropionaldehyde diethylacetal as initiator. After polymerization, the living anion was reacted first with DPE



Scheme 7.55

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 7.55. The yield was between 80 and 85%. The MW 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.

A novel methodology has been utilized by Tezuka [141] for the synthesis of various nonlinear polymer topologies with high efficiency, by exploiting the self-assembly principle to preorganize linear polymer precursors and subsequently convert them into covalently linked structures. Tezuka used self-assembly through coulombic interactions of hydrophobic macromolecules, bearing moderately strained cyclic onium salt end groups, with multifunctional low MW molecules bearing carboxylate groups as counterions.

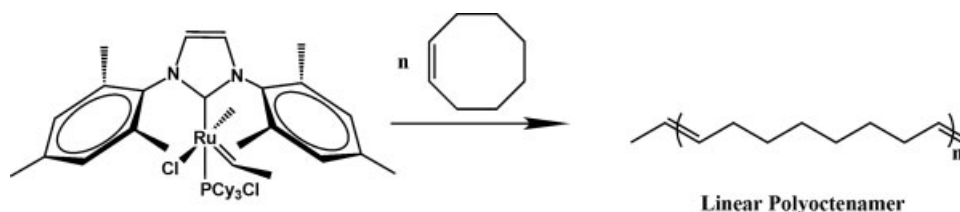


Scheme 7.56

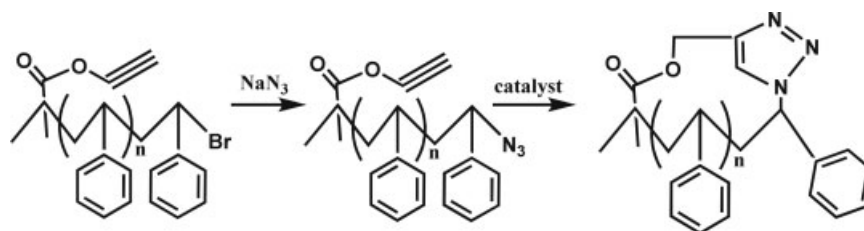
Under high dilution conditions, the aggregates were subjected to heat to convert the ionic interactions into covalent linkages by a ring opening reaction (Scheme 7.56). Using this strategy, poly(THF), PS, and poly(dimethylsiloxane) cyclic homopolymers were synthesized.

A new synthetic route to cyclic polymers was developed by Grubbs [142], in which the ends of growing polymer chains remain attached to a metal complex throughout the entire polymerization process (Scheme 7.57). The approach eliminates the need for linear polymeric precursors and high dilution, which are the drawbacks of traditional macrocyclization strategies, and also removes the barrier to producing large quantities of pure cyclic material. The potential of this strategy was demonstrated by the synthesis of cyclic polyethylenes (PEs), whose physical properties were found to be distinguishable from their linear analogs.

More recently, a novel approach for the synthesis of cyclic copolymers was reported by Matyjaszewski using “click” chemistry [143]. α -Alkyne- ω -azido-terminated PS chains were self-coupled in the presence of CuBr in dimethyl formamide solution at room temperature. Alternatively, α,ω -diazido-terminated PS was “clicked” with dipropargyl ether at room temperature. SEC



Scheme 7.57



Scheme 7.58

analysis revealed the presence of high MW polycondensation products. In addition, low MW materials with smaller hydrodynamic volumes than those of the corresponding linear functionalized precursors were also traced, providing direct evidence for the preparation of cyclic polymers by this procedure.

Grayson *et al.* [144] reported the synthesis of cyclic PS using “click” cyclization coupling (Scheme 7.58). Styrene was polymerized in bulk with the heterofunctional initiator propargyl 2-bromoisobutyrate in the presence of CuBr/PMDETA to produce Br-PS-alkyne. The Br end group was transformed to azide with sodium azide in DMF. For polymer concentrations above 0.1 mM in the presence of Cu(I) as catalyst in THF/water, condensation was favored. Dilution below that concentration favored intramolecular cyclization. The cyclization reaction was successfully carried out on two linear N₃-PS-alkyne with M_n of 2200 and 4200.

7.4.3

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 analogs are able to form loops and bridges. This significant difference is expected to give very interesting morphological properties to the cyclic copolymers.

Employing anionic polymerization and high vacuum techniques, Hadjichristidis *et al.* [145] synthesized cyclic block copolymers of PS-*d*₈ and PBd. The synthetic approach involved the reaction of (1,3-phenylene)-bis(3-methyl-1-phenylpentylidene) dilithium initiator with butadiene in the presence of *sec*-BuOLi, followed by polymerization of St (or St-*d*₈). The cyclization of the resulting α,ω -difunctional triblock copolymer was performed using bis(dimethylchlorosilyl) ethane under high dilution conditions. The copolymers were characterized by SEC, MO, NMR and UV spectrometry, and viscometry. The micelles formed in the selective solvents *n*-decane (for PBd) and dimethylformamide (for PS-*d*₈) were characterized by small-angle neutron scattering (SANS) and DLS. It was found that the aggregation number of the cyclic copolymers was the smallest among the different macromolecular

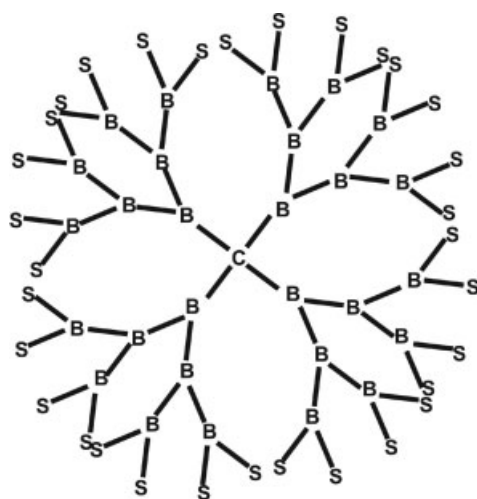
architectures. Moreover, the SANS data for the triblocks in *n*-decane indicated the presence of 37% dangling chains, which did not appear in the data for the corresponding cyclic copolymers. Considering that 5% of dangling chains can be detected, the data prove that the cyclic copolymers are at least 87% pure. A scaling model was used to justify the difference in the aggregation numbers between the four different copolymers.

7.5

Dendritic Polymers

The term *dendrimer* was originally coined by Tomalia *et al.* [146] to describe a family of regularly branched poly(amidoamines) (PAMAM) in which all bonds converge to a single point, each repeat unit contains a branch junction, and a large number of identical functional groups are present at the chain ends. The graphical representation of a dendrimer is shown in Scheme 7.59. A central core, or focal point, is connected to a number of layers, or generations of internal building blocks, which are in turn connected to numerous chain ends. The dendritic or dendrimer-like polymers are structurally analogous to regular dendrimers, but contain polymer chains of variable length between each branching unit rather than short spacers. Owing to their unique physical and chemical properties, dendrimers and dendritic polymers have found use in many industrial and academical areas.

For the synthesis of dendrimers and dendritic polymers, two fundamentally different strategies have been employed: the divergent approach (from inside out), and the convergent approach (from the outside in). In either route, dendrimers can be prepared with high regularity and controlled molecular weights. The main drawback of the divergent approach is that by increasing



Scheme 7.59

the number of reactions required to fully functionalize the chain ends during the growth of the dendrimers, maintaining and tracing perfect growth and removing the large excesses of reagents needed to force these reactions are difficult. The convergent growth method is the opposite of the divergent strategy; in this case, growth begins in the periphery of the dendrimer and proceeds inwards, with the final reaction being the attachment to a polyfunctional core. In this methodology, large parts of the dendrimer are synthesized separately, and are finally interconnected to form the dendrimer. The advantage of this approach over the divergent methodology is that if incomplete attachment of a large part occurs, it can be easily traced and corrected.

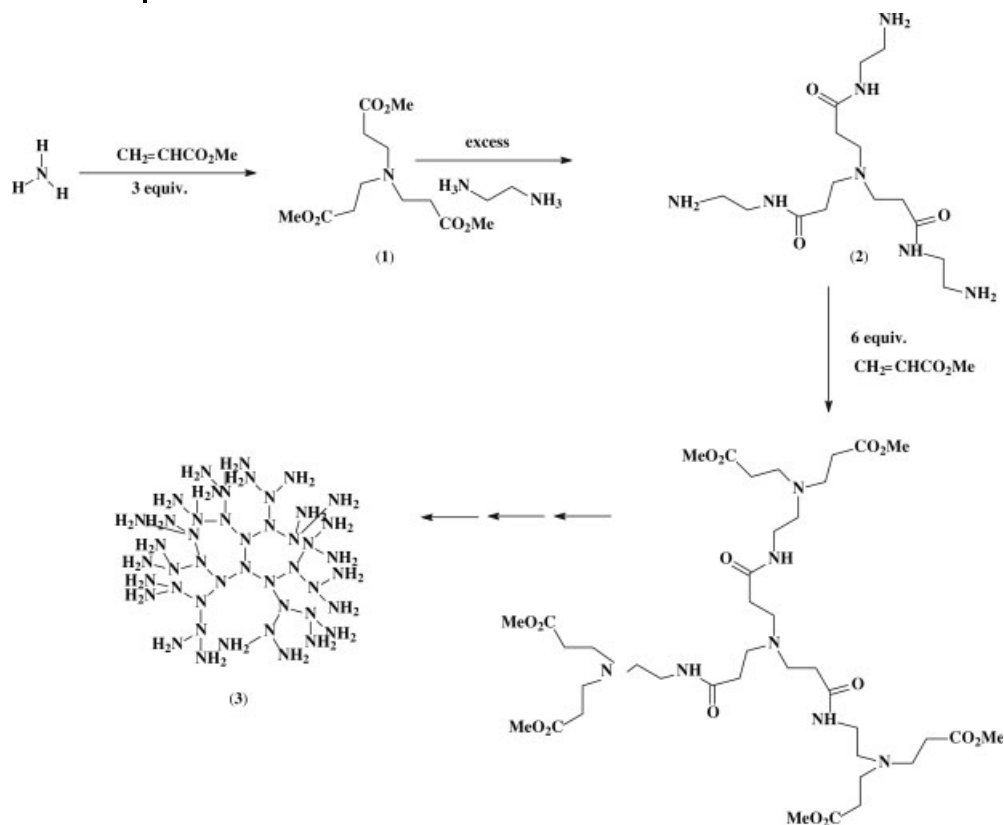
7.5.1

Dendrimers

A wide variety of dendrimers have been presented in the literature: PAMAM, poly(propyl imine) (diaminobutane-dendr-NH₂), polyethers, polyesters, poly(ester amides), poly(ether amides), polyalkanes, poly(phenylacetylenes), polysilanes, phosphorous dendrimers, and others [147–151]. The pioneering synthetic strategy developed by Tomalia *et al.* [146] for starburst dendrimers and of Newcome *et al.* [147] for cascade molecules is now recognized as the divergent growth approach. Perhaps, the most well-known divergent synthesis of dendritic macromolecules is the preparation of PAMAM by Tomalia *et al.* [146] (Scheme 7.60).

The synthesis starts with a polyfunctional core, in this case ammonia, and reaction with methyl acrylate results in the formation of the triester **1**. The second step of this two-step repetitive process is regeneration of the reactive amino groups at the chain ends accomplished by exhaustive amidation with a large excess of 1,2-diaminoethane to give the first-generation dendrimer, **2**, in which the number of reactive amino groups has doubled from three for ammonia to six for **2**. Repetition of the two-step process then leads to larger dendritic macromolecules, the structure of which follows a strict geometrical progression.

The convergent methodology was demonstrated by Fréchet *et al.* in 1989 [152]. The advantages of the convergent methodology were later demonstrated by Hawker and Fréchet [153] in the synthesis of a series of dendritic polyether macromolecules based on 3,5-dihydroxybenzyl alcohol as the monomer unit (Scheme 7.61). The starting material is the benzylic ether (**1**), which after reaction with carbon tetrabromide and triphenylphosphine regenerates the reactive bromomethyl group (**2**). Alkylation of **2** with the monomer unit under typical Williamson conditions leads to the next-generation dendron (**3**) in which the number of surface groups has doubled but there is still a single functional group at the focal point. The procedure has been repeated to the

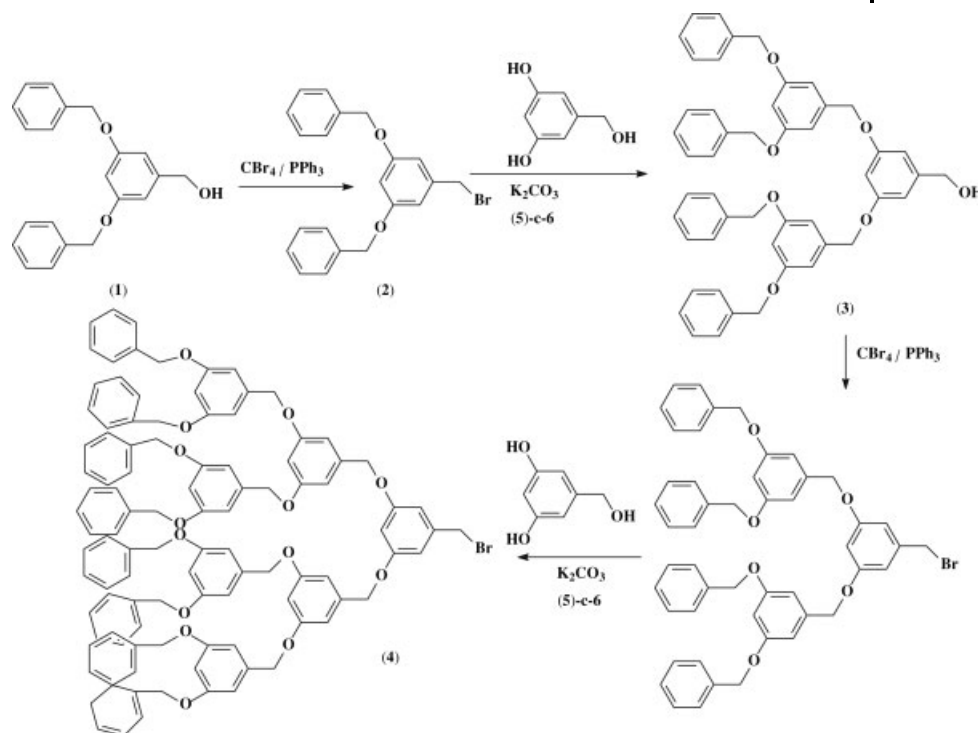


Scheme 7.60

sixth generation dendron which has 64 (2^6) surface benzyl groups, with a molecular formula of $\text{C}_{889}\text{H}_{763}\text{BrO}_{126}$ and a MW of 13 581.

“Click” chemistry has also been applied for the functionalization or even the synthesis of dendrimers. The traditional convergent approach was used for the synthesis of 3,5-dioxybenzyl ether dendrimers. Dendrons of different generations were synthesized and subsequently coupled to a central trifunctional core, affording dendrimers with 3, 6, 12, 24, and 48 chain-end acetylene groups [154] (Scheme 7.62a). A variety of azides incorporating reactive functional groups, such as nucleoside, carbohydrate, dye, or large dendrons (Scheme 7.62b), were subjected to “click” reactions with the acetylene-functionalized dendrimers, in the presence of $\text{Cu}(\text{PPh}_3)_3\text{Br}$ or $(\text{EtO})_3\text{PCuI}$, to afford the corresponding functionalized structures (overall yield: 85–90%) (Scheme 7.62c).

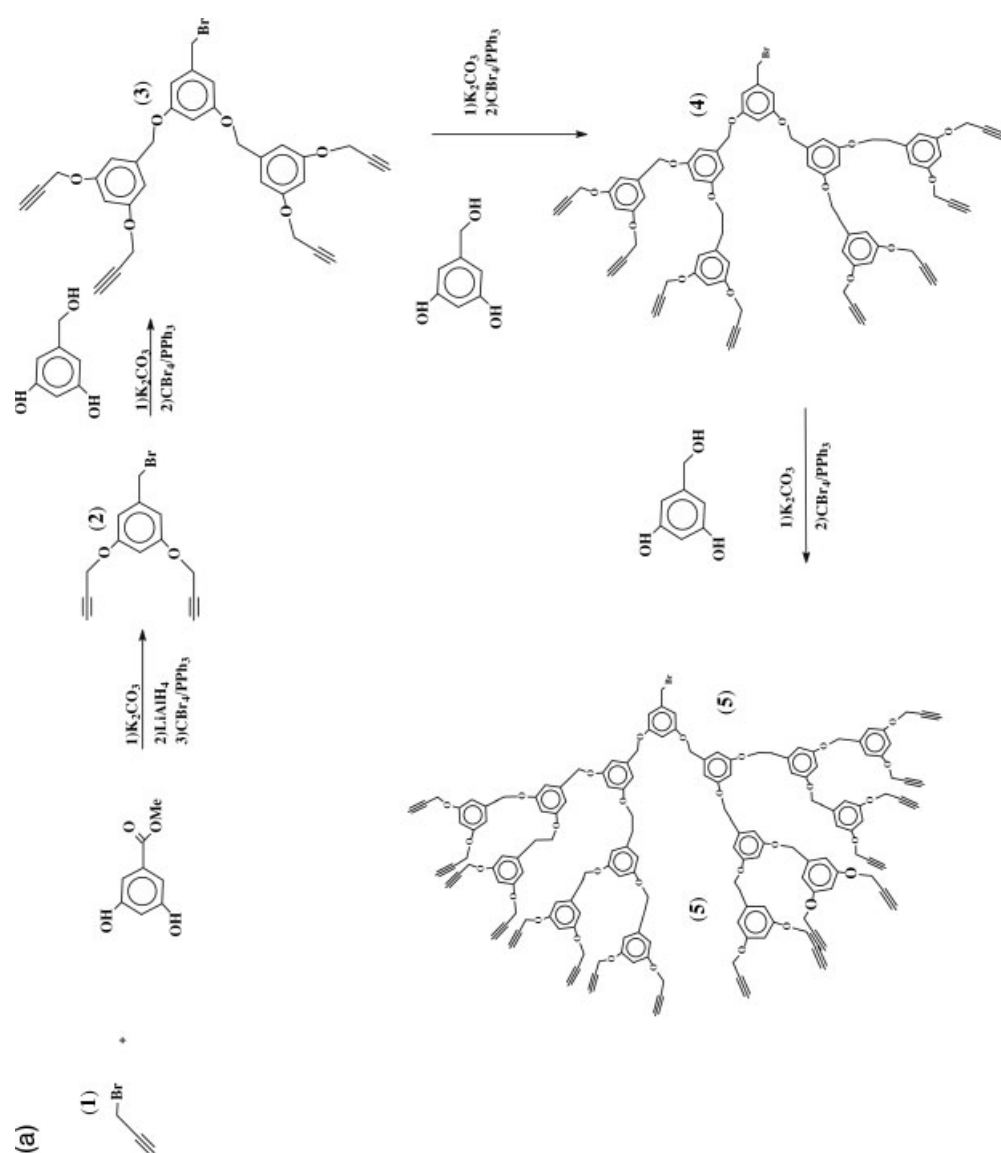
The convergent approach was employed for the synthesis of dendrimers using AB_2 monomers based on terminal alkynes and alkyl halide functionalities. Separate dendrons were synthesized employing “click” reactions and



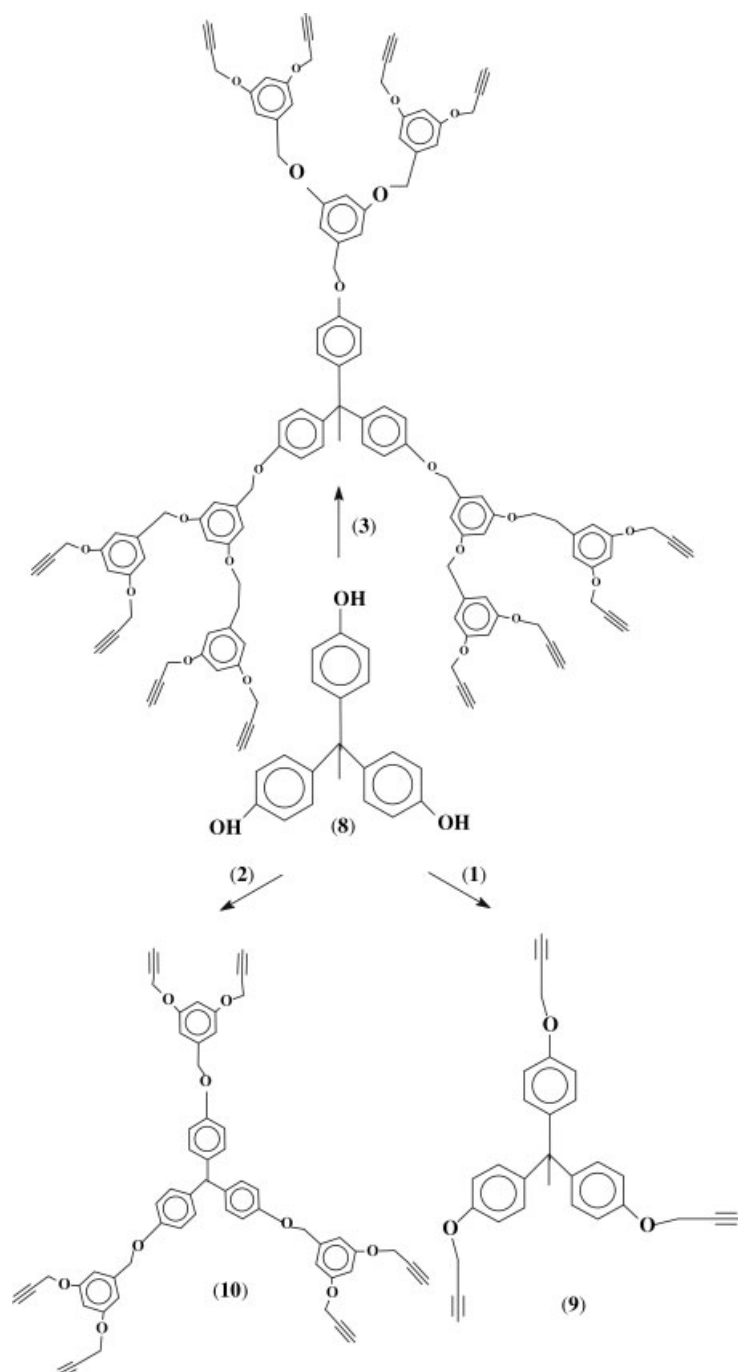
Scheme 7.61

were then coupled to a central core to provide the final dendritic structure [155] (Scheme 7.63). The alkyne groups of the AB_2 monomer were reacted with a suitable azide in the presence of CuSO_4 and sodium ascorbate in a mixture of water and *tert*-butyl alcohol to afford the desired bistriazoles in near quantitative yields. The chloride groups were then transformed to azides by reaction with sodium azide. Subsequent reaction with the AB_2 monomer generated the second-generation dendron. These steps were repeated for the synthesis of higher generation materials. Owing to the insolubility of the higher MW products in water, the “click” reaction was performed with $\text{Cu}(\text{PPh}_3)_3\text{Br}$. The triazole dendrons of the third and fourth generation, having an azide focal point, were finally coupled to a variety of trifunctional cores carrying alkyne functions, leading to the synthesis of the desired dendrimers.

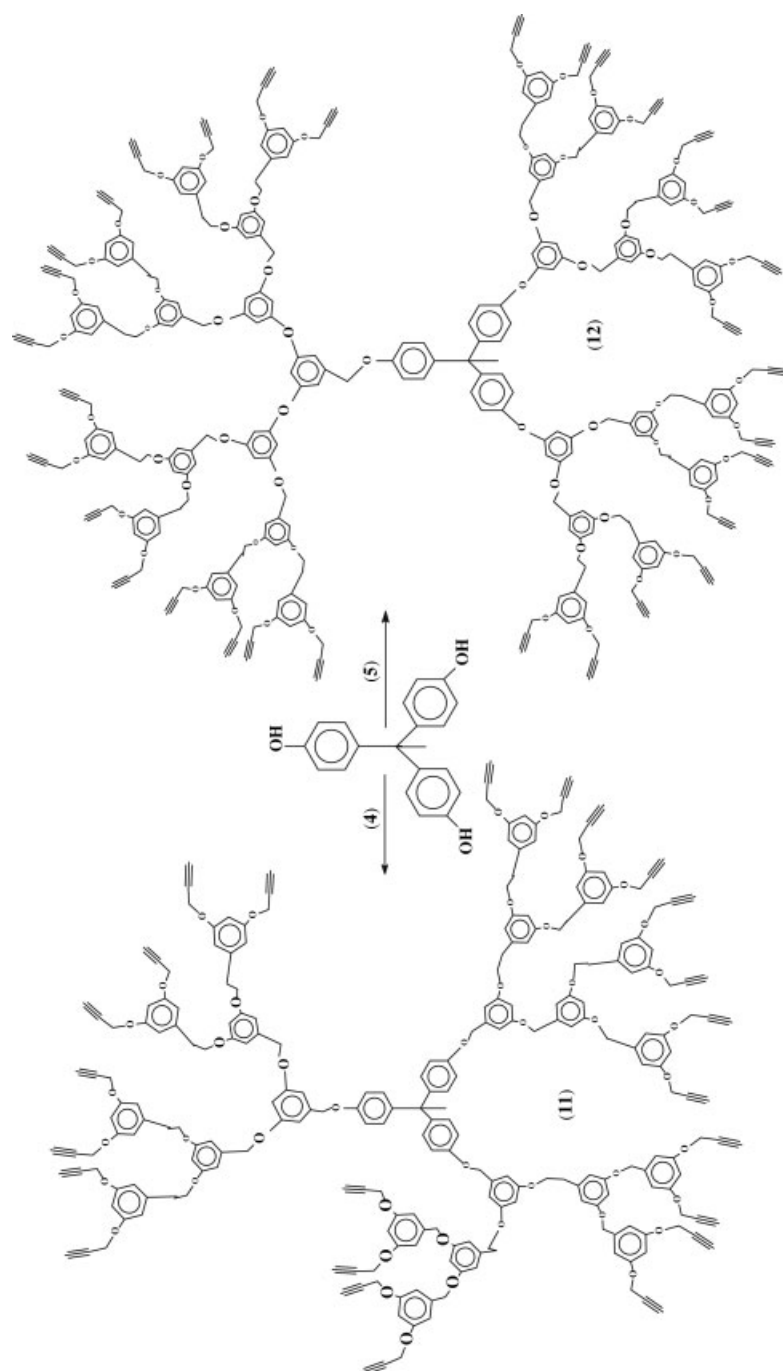
The divergent methodology and “click” reactions were also applied for the synthesis of dendrimers. 4-Carboxy-4'-[bis(2-chloroethyl)amino]azobenzene was synthesized and was subsequently either esterified with propynol to afford the corresponding molecule with an available triple bond, or reacted with NaN_3 to substitute the chloride groups with azides (Scheme 7.64) [156]. These products were used as building blocks for the construction of dendrimers



Scheme 7.62a



Scheme 7.62a (continued).



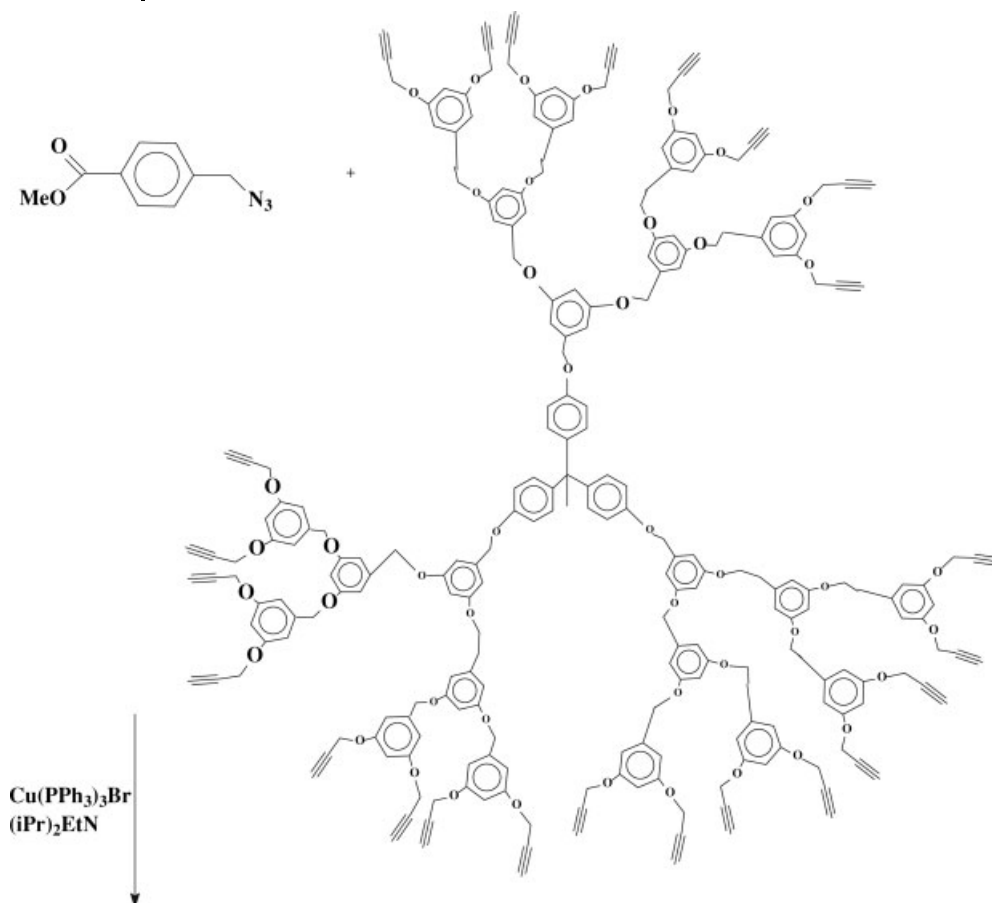
Scheme 7.62a (continued).



Scheme 7.62b

through an iterative sequence involving “click” reactions between the azide-terminated dendrons with the alkyne-functionalized compounds.

1,2-Bis(2-azidoethoxy)ethane and 1-propargyl-3,5-dihydroxymethylene benzene were reacted under typical “click” chemistry conditions to give the first-generation dendrimer [157] (Scheme 7.65). The hydroxymethylene groups were then converted to chlorides by treatment with SOCl_2 and finally to azides after reaction with NaN_3 . Dendrimer growth then proceeded through a reaction sequence involving “click” reactions between the azido end groups of the growing dendrimer and the alkynyl group of the monomer followed by the reactivation and transformation of the hydroxyl groups to azides. Using this divergent approach, dendrimers of up to the third generation were prepared.

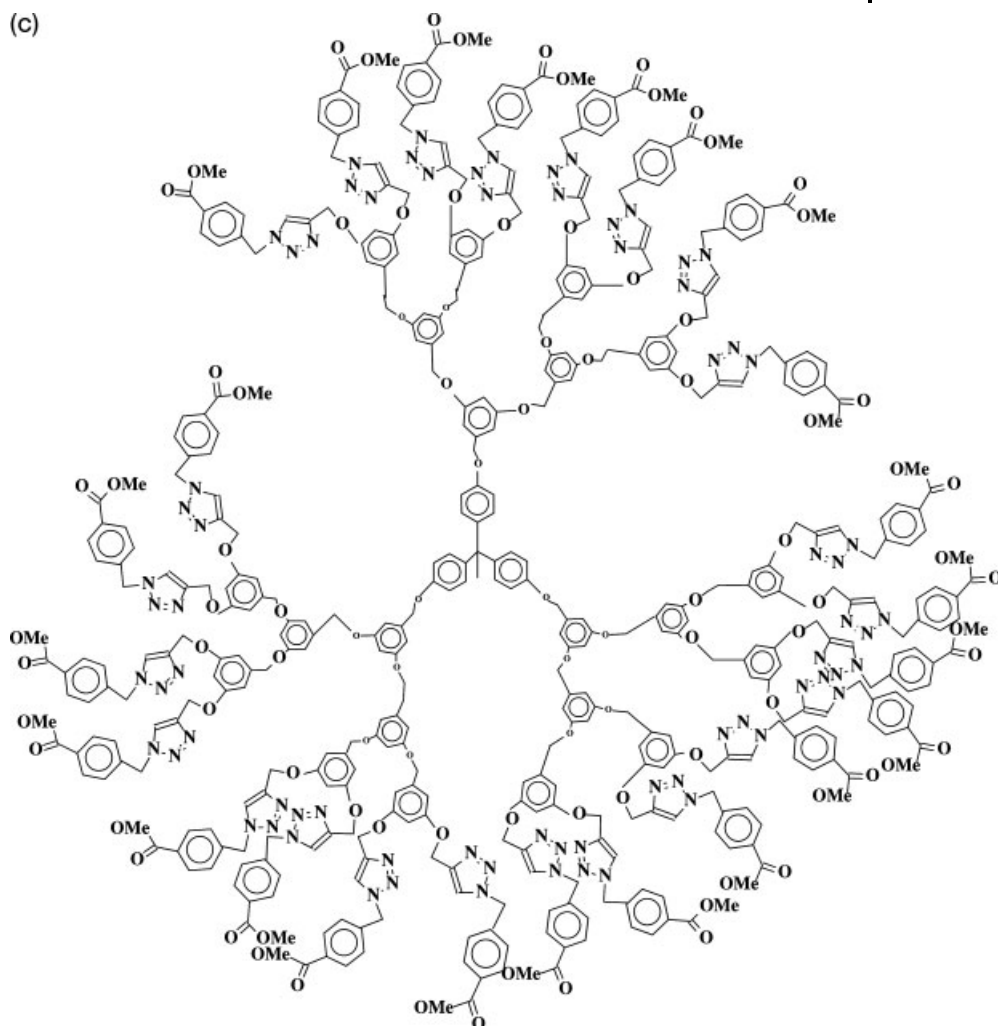


Scheme 7.62b (continued).

7.5.2

Dendritic Polymers

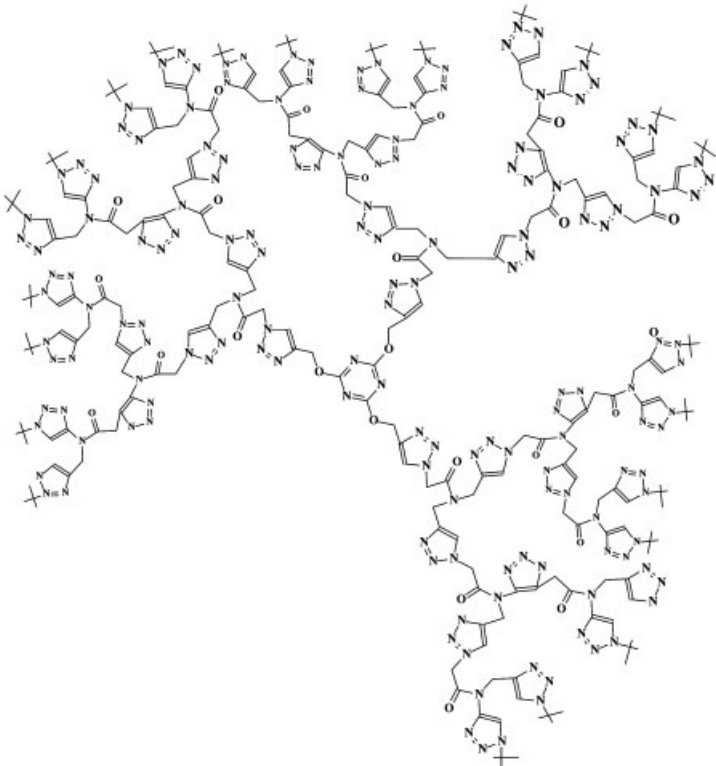
The preparation of well-defined G-2 dendritic homo- and copolymers of isoprene and styrene was reported by Chalari and Hadjichristidis [158] via stepwise convergent anionic polymerization. The synthesis of second-generation (G-2) dendritic polymers of isoprene (I) and styrene (S) was achieved with anionic polymerization high vacuum techniques and the following steps: (i) selective reaction of a living chain with the chlorosilane group of CDMSS (a dual-functionality compound) to produce a macromonomer; (ii) addition of a second living chain (same or different) to the double bond of the macromonomer; (iii) polymerization of I with the anionic sites; and (iv) reaction of the produced off-center living species with



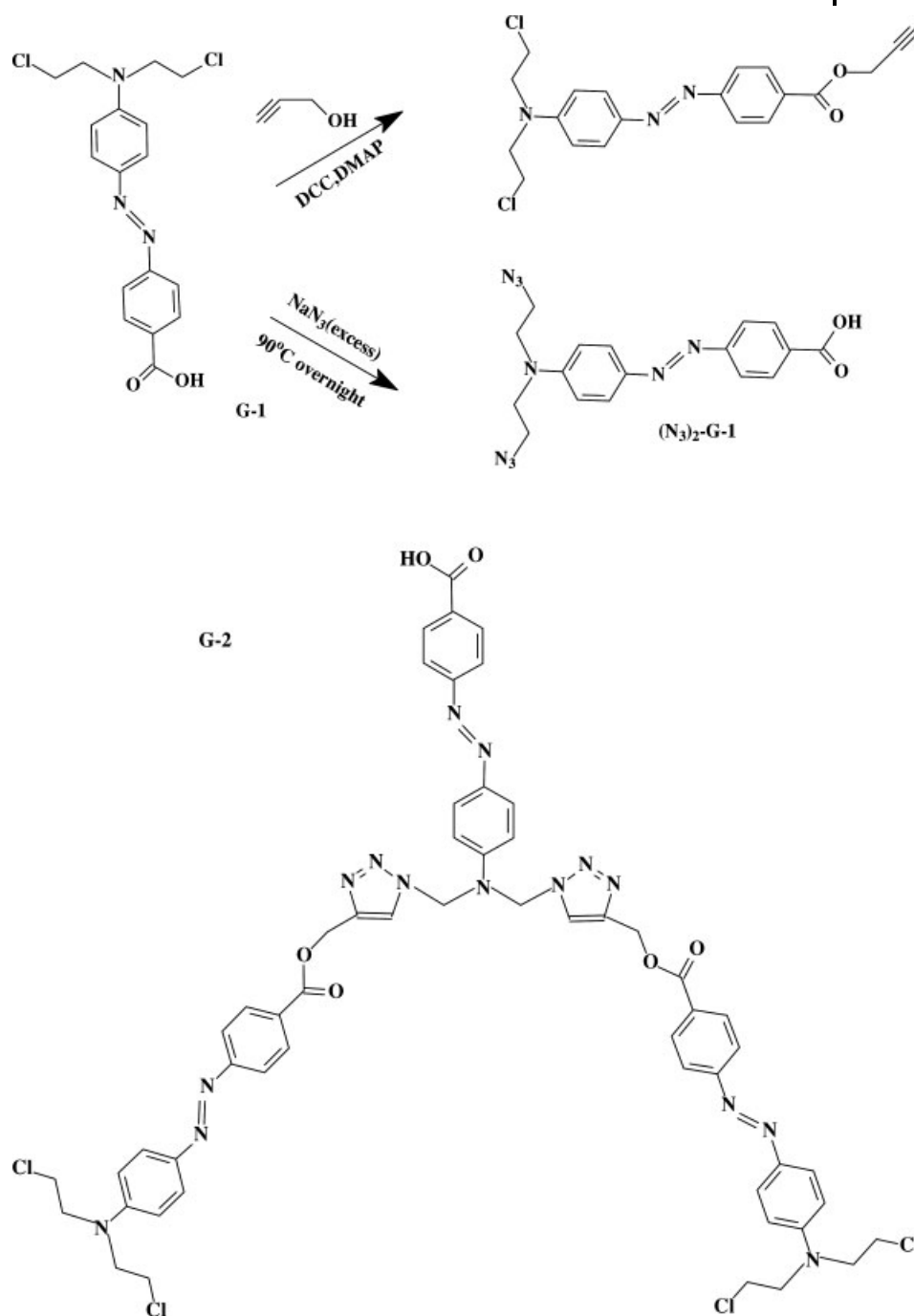
Scheme 7.62c

trichloromethyl silane or tetrachlorosilane (CH_3SiCl_3 or SiCl_4). The combined characterization results indicated that the G-2 dendritic macromolecules synthesized, i.e., $(\text{S}_2\text{I})_3$, $(\text{SI}'\text{I})_3$, $(\text{I}''\text{I}'\text{I})_3$, $(\text{I}'_2\text{I})_4$, had high molecular and compositional homogeneity. The success of the synthesis relied on the selective reaction between living chains and the dual-functionality compound CDMSS. This stepwise synthesis provides good control over the reaction, leading to dendritic polymers with structural and compositional homogeneity.

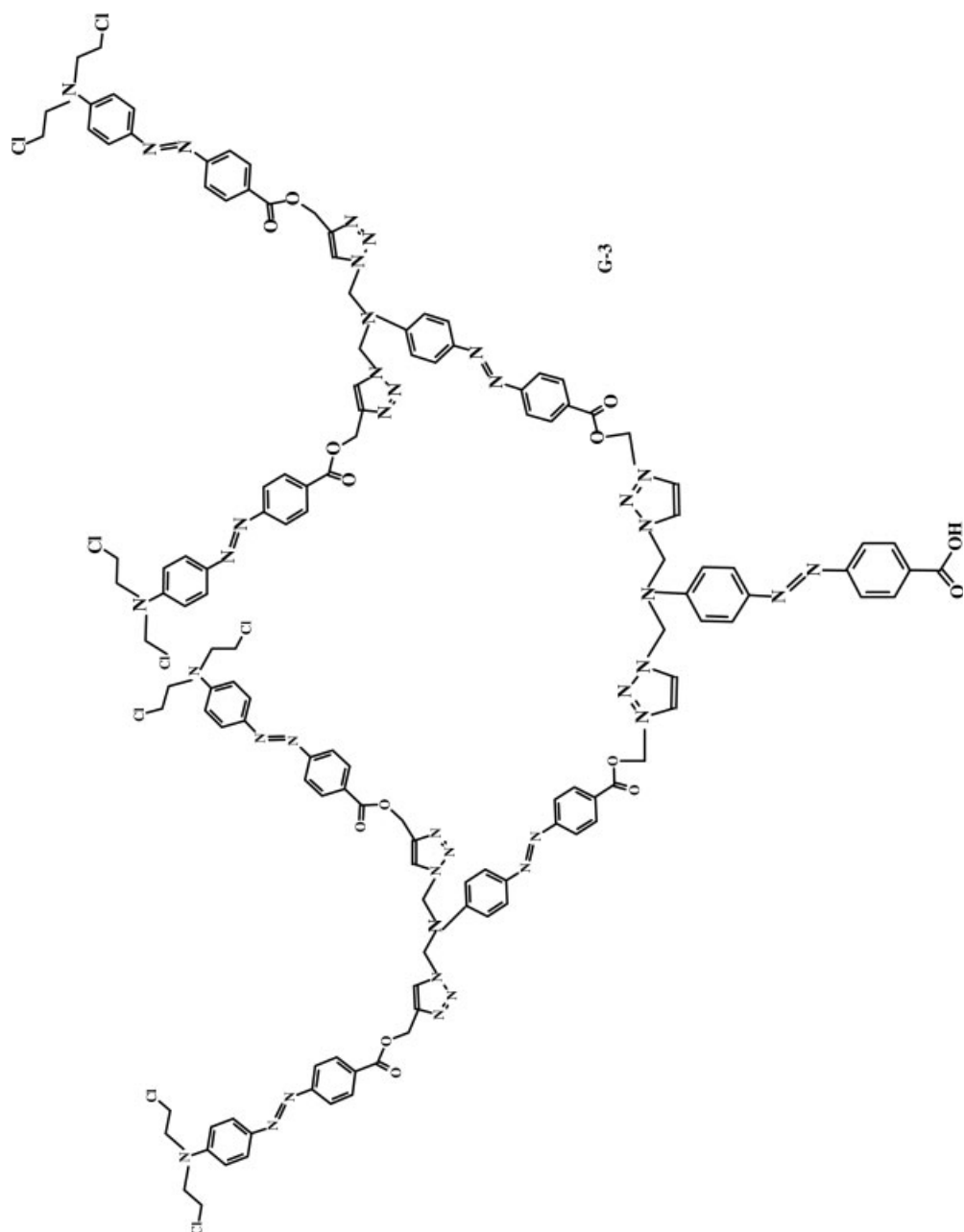
A better control for the synthesis of dendritic PBd polymers was adopted using the nonhomopolymerizable dual-functional LA, DCMSDPE. Living



Scheme 7.63

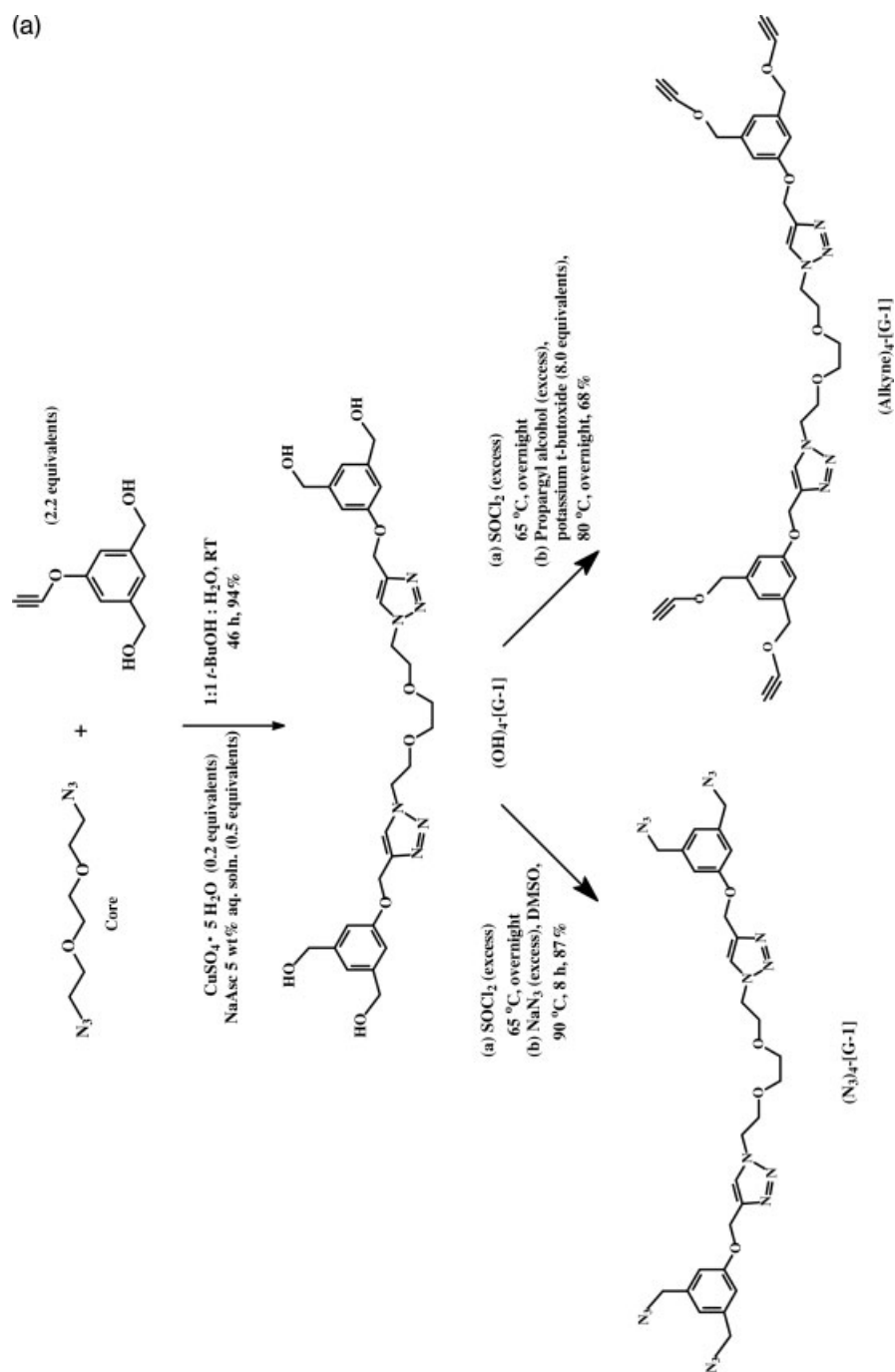


Scheme 7.63 (continued).



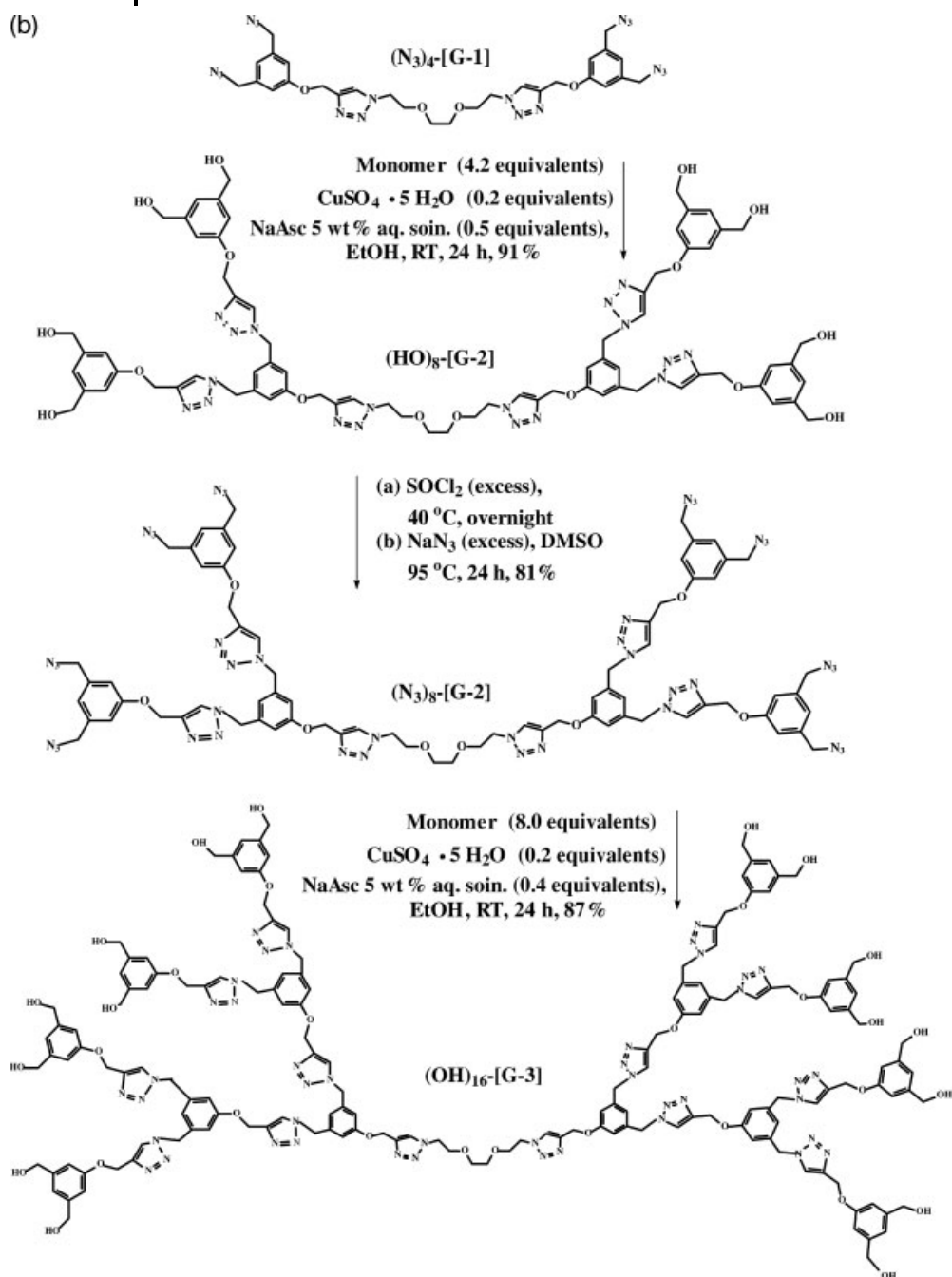
Scheme 7.64

(a)



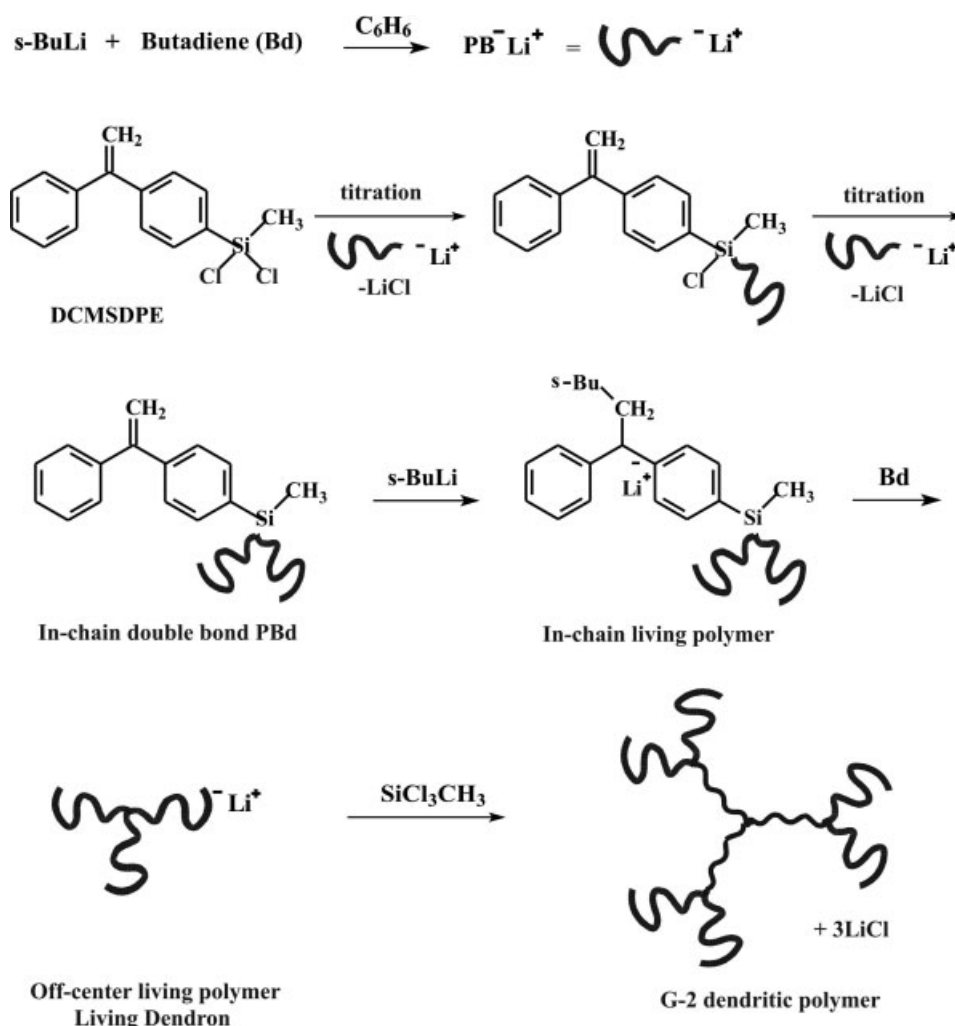
Scheme 7.65a

(b)



Scheme 7.65b

PBdLi chains were linked selectively with the two chlorosilyl groups, leading to the synthesis of PBds bearing in-chain double bonds. The steric hindrance of the two phenyl groups of DCMSDPE prevented the reaction of the double bond with the living polymers. The remaining double bond was subsequently activated by *s*-BuLi to afford the in-chain living polymer. Addition of a new quantity of Bd resulted in the formation of a living three-arm star polymer, which was then linked to trichloromethylsilane to give the second-generation dendritic polymer (Scheme 7.66) [159]. Using the same methodology, the third-generation dendritic PBd was also prepared.



Scheme 7.66

7.6

Complex Macromolecular Architectures

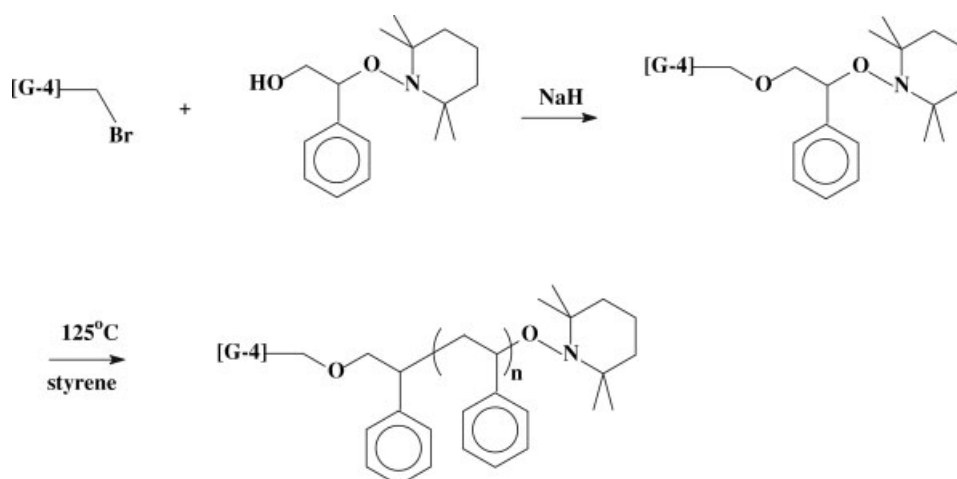
Recent developments in synthetic methodologies have allowed the synthesis of novel macromolecular structures with excellent control over the topology, microstructure, and composition [1, 8, 160]. The application of organic chemistry reactions for the transformation of the macromolecular chains as well as the synthesis of new initiators and LAs along with the combination of different polymerization methods are the main tools for the synthesis of complex macromolecular architectures.

7.6.1

 ω -Branched Polymers

These polymers can be considered linear chains having a number of covalently attached chains at one of their ends. Such products are called *palm-tree* or even *umbrella* polymers and their synthesis can be achieved either by a divergent or a convergent method. According to the divergent method, the linear polymer has a number of initiating sites located at the chain end. Through these sites, new polymer chains can grow, leading to the formation of a ω -branched structure. Alternatively, the branched structure may act as initiator for the synthesis of the linear chain. An example is given in Scheme 7.67 [161].

The convergent method involves the linking of preformed chains to suitable linking sites located at the main chain end. This approach was applied for the synthesis of the umbrella copolymers. PS-*b*-PBd block copolymers with a short PBd block of the 1,2 microstructure were prepared by anionic polymerization.



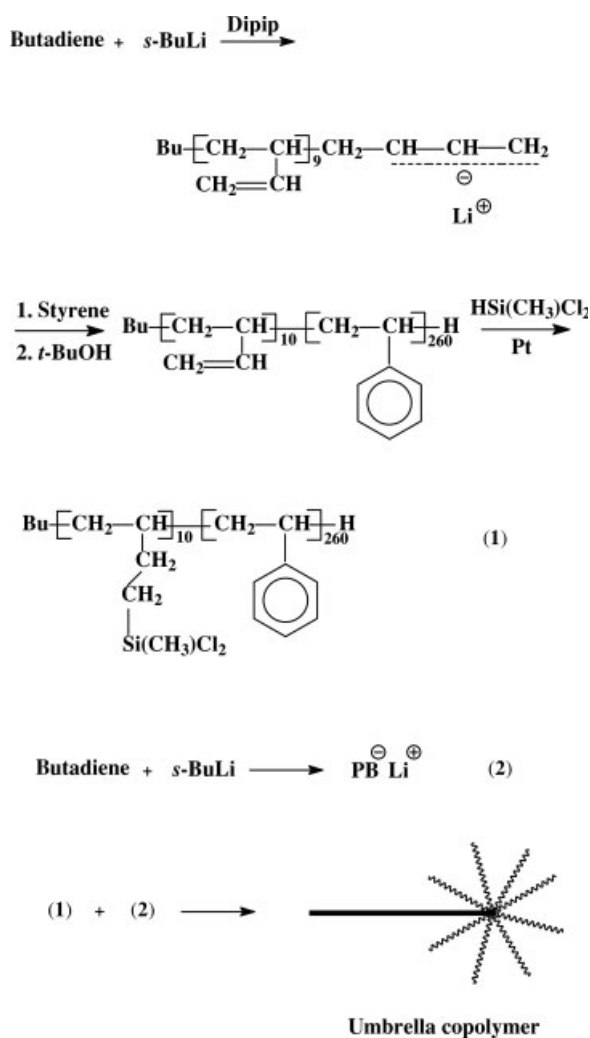
Scheme 7.67

The polydiene block was hydrosilylated for the introduction of Si–Cl groups. Subsequent linking of these groups with living P2VP chains afforded the desired PS(P2VP)_x structures [162] (Scheme 7.68).

7.6.2

α,ω-Branched Polymers

These polymers can be considered linear macromolecules having a number of covalently attached chains at both chain ends. Their synthesis can be achieved



Scheme 7.68

employing methods similar to those used for ω -branched polymers, except that the reactions are performed at both chain ends. Copolymers of the type B_3AB_3 are termed *super-H shaped copolymers* and, more generally, copolymers of the type B_nAB_n are characterized in the literature as “pom–pom” or “dumbbell” copolymers.

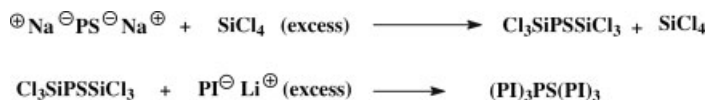
Using a convergent approach and anionic polymerization techniques associated with suitable chlorosilane chemistry, $(PI)_3PS(PI)_3$ super-H shaped copolymers were prepared [163]. A difunctional PS chain, derived from the polymerization of styrene in THF using sodium naphthalene as initiator, was reacted with a large excess of $SiCl_4$, leading to the synthesis of PS chain end functionalized at both ends with $-SiCl_3$ groups. After elimination of the excess $SiCl_4$ and addition of living PI arms, the desired super-H structure was achieved (Scheme 7.69).

Employing a similar method, $(PI)_5PS(PI)_5$ copolymers (pom–pom shaped) were synthesized [85]. Living PI chains were reacted with a hexafunctional chlorosilane in a $SiCl : Li$ ratio = 6 : 5, giving the five-arm star with a remaining $SiCl$ group at the central point. Subsequent reaction with a difunctional PS led to the synthesis of the pom–pom copolymer (Scheme 7.70).

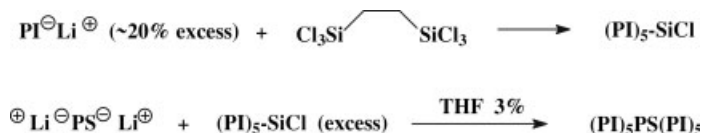
The divergent methodology was applied for the synthesis of pom–pom or dumbbell copolymers with higher functionalities. Triblock copolymers $PBd-b-PS-b-PBd$ containing short PBd blocks with 1,2 microstructure were prepared by anionic polymerization techniques [164]. The vinyl side groups of the PBd blocks were subjected to the hydroboration–oxidation reaction for the incorporation of hydroxyl groups. These groups were subsequently transformed to alkoxides to initiate the polymerization of ethylene oxide, leading to the synthesis of $(PEO)_nPS(PEO)_n$ dumbbell copolymers (Scheme 7.71).

Structures resembling dumbbell copolymers have also been prepared. In this case, a living anionic difunctional PS connector was linked with polyether dendritic groups [165] (Scheme 7.72).

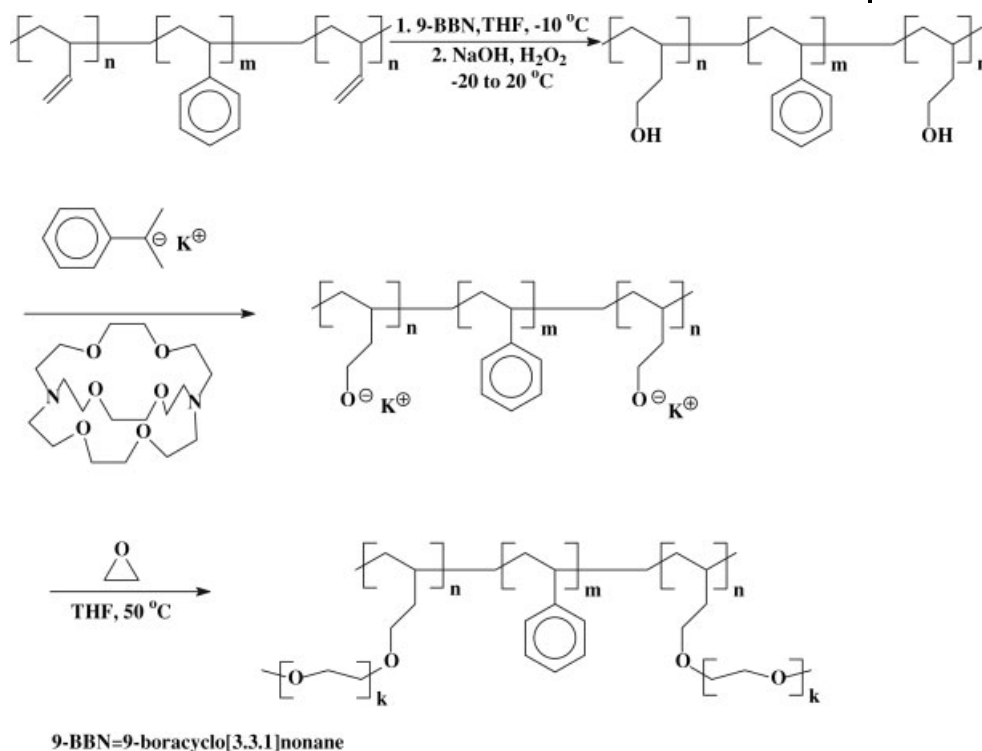
A barbell-like ABA-type triblock copolymer, comprised of poly(L-lysine) (PLL) dendrimers (A) and PEG connector (B) was reported [166]. The synthetic



Scheme 7.69



Scheme 7.70

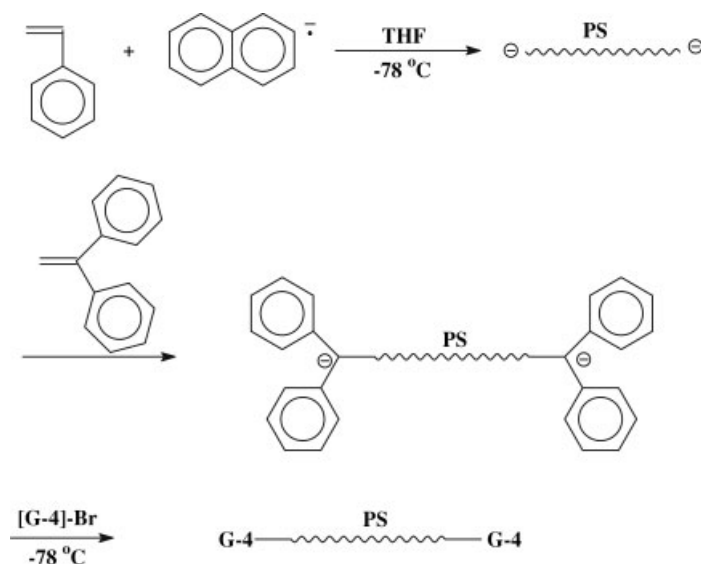


Scheme 7.71

route involved the use of an α,ω -diamino-functionalized PEG as the polymeric support for the attachment of $-\text{NH}_2$ -protected lysine via an amidation reaction. The PLL dendrimer was generated at both ends of B by repeated liquid-phase peptide synthesis, as shown in Scheme 7.73. The intermediate products along with the final copolymers were characterized by MALDI-TOF MS. The results revealed that narrow MW dispersity copolymers were synthesized having low MWs.

The convergent approaches offer a better structural control provided that the linking reactions are efficient and free of steric hindrance effects. On the other hand, the divergent methods usually lack the precise control over the structure, since they require the generation of initiation centers at both ends of a polymer chain. The growth of polymer chains through these initiation sites may not be uniform, because of steric hindrance, association phenomena, kinetic differentiations, etc., leading to products with structural defects and chemical inhomogeneities.

Macromonomers can also be used for the synthesis of α,ω -branched polymers. A difunctional living polymer chain can be used as a macroinitiator to polymerize macromonomers to produce a pom–pom (or dumbbell) copolymer,



Scheme 7.72

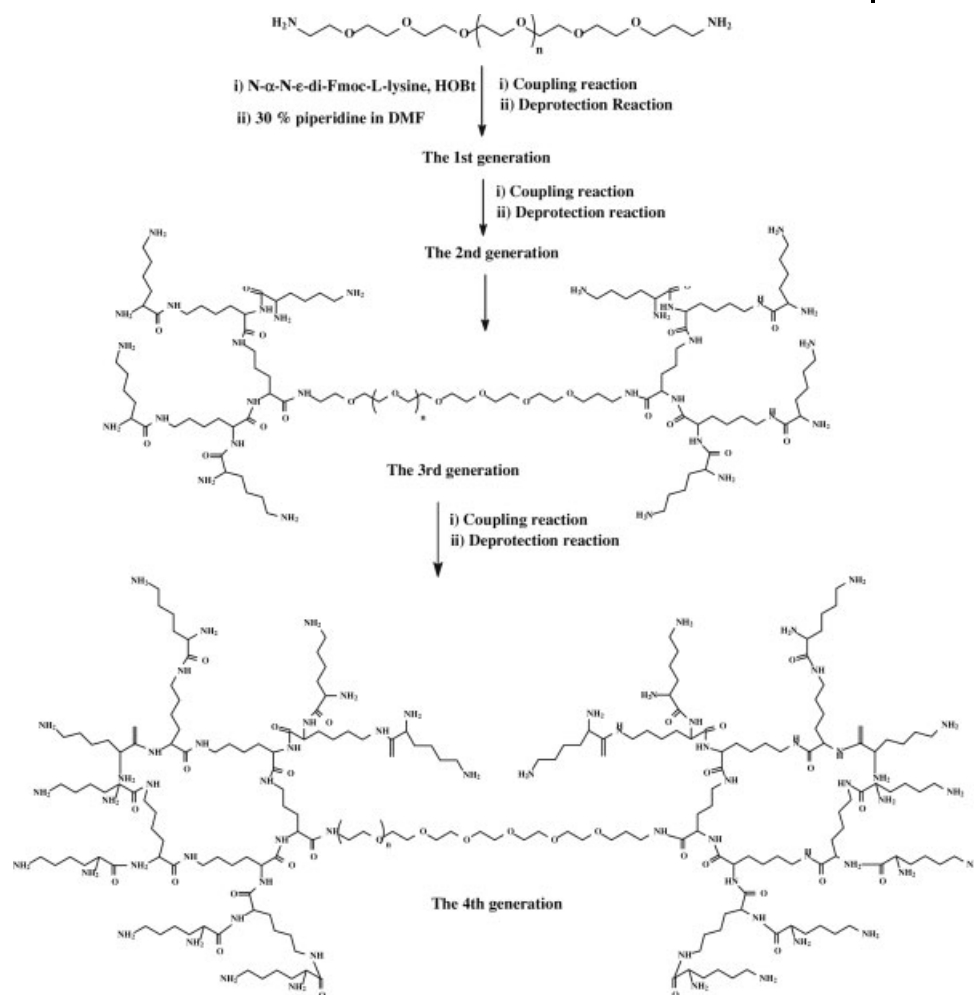
if a small number of macromonomers is added at the end of the living polymer chain (Scheme 7.74) [105].

In an extension of the methodology involving DPEs, the preparation of chain-end functionalized polymers with a definite number of bromomethylphenyl (BnBr) end groups and their utilization in the synthesis of dumbbell polymers has been reported [167]. The synthesis of linear PS chain capped at each end with 2, 4, 8, or 16 BnBr groups is illustrated in Scheme 7.75. A living difunctional PS chain was reacted with DPE, a derivative bearing one *tert*-butyldimethylsilyloxymethylene group. Subsequent reaction with $\text{LiBr}/(\text{CH}_3)_3\text{SiCl}$ transformed the end groups to BnBr moieties. DPE carrying two *tert*-butyldimethylsilyloxymethylene groups was activated with *s*-BuLi and reacted with the bromomethyl units of the telechelic PS chains. Subsequent transformation to BnBr functions affords a linear PS macromolecule with two end groups at each chain end. The procedure can be repeated for the incorporation of up to 16 BnBr groups at each chain end. Linking of living PS polymers end-capped with a DPE unit resulted in the formation of well-defined dumbbell polymers with a predetermined number of branches.

7.6.3

Hyperbranched and Dendrigraft Polymers

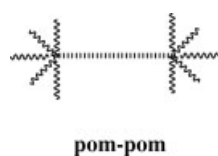
Hyperbranched and dendrigraft polymers belong to the family of dendritic polymers [168]. However, they are not characterized by the strict structural and



Scheme 7.73

molecular control attained from dendrimers [169]. Hyperbranched polymers are obtained using two different approaches. The first involves the use of single monomers (single monomer methodology, SMM) of the general type AB_n and can be subdivided to one of the following procedures: (i) polycondensation of AB_n monomers, (ii) self-condensing vinyl polymerization (SCVP), and (iii) self-condensing ring opening (SCROP) and proton transfer polymerization (PTP). The second approach involves the use of two types of monomers (double monomer methodology, DMM).

The one-pot polycondensation reaction of AB_n monomers, according to the SMM, led to the synthesis of a wide variety of hyperbranched structures, such as



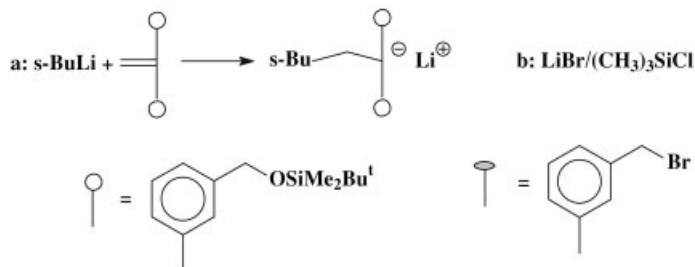
Scheme 7.74

poly(phenylenes) [170], polyesters [171], polyethers [172], poly(ether ketones) [173], and polycarbonates [174]. The products are characterized by limited control over the structure and broad MW distributions ($M_w/M_n \approx 2$) [175].

SCVP was initially proposed by Fréchet [176], and involves the use of vinyl monomers of the AB type. A stands for the vinyl group and B is a group that can be activated to form an initiating site B*, capable of initiating the polymerization of the vinyl A groups. Therefore, the AB molecules can act simultaneously as monomers and initiators and therefore are usually called *inimers*. Several living or controlled polymerization techniques have been employed leading to a variety of hyperbranched structures [177]. ATRP techniques have been employed as well for the synthesis of hyperbranched polymers. A one-pot polymerization procedure using *p*-(chloromethyl)styrene in the presence of Cu(I) and 2,2-bipyridyl was reported [178]. In this case, *p*-(chloromethyl)styrene acts both as the monomer and the initiator, since the chlorine atom can be abstracted homolytically to form benzyl radicals. 2-[(2-Bromopropionyl)oxy]ethyl acrylate was also homopolymerized using CuBr and di-*tert*-butyl-2,2'-bipyridine or 4,4'-di-5-nonyl-2,2'-bipyridine [179]. Hyperbranched polymers of rather broad MW distributions were obtained in both cases.

SCROP has been applied for the synthesis of polyethers, polyesters, and polyamines [180], whereas PTP led to the synthesis of hyperbranched polysiloxanes and polyesters bearing hydroxyl and epoxy end groups [181].

The DMM involves the polycondensation of A_2 and B_3 (or generally B_n , $n > 2$) monomers. The disadvantage of this procedure is that it usually leads to gelation. To obtain soluble products, the polymerization should be conducted in dilute solutions and terminated before reaching the critical gelation point. In addition, the monomer feed ratio and the monomer addition manner dramatically affect the properties of the final products. Examples of hyperbranched polymers prepared by this methodology include the products of the reactions between *p*-phenylene diamine and trimesic acid [182], 1,2,7,8-diepoxyoctane and 1,1,1-tris(hydroxymethyl)ethane [183], 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and tri-(*p*-aminophenyl)amine [184], etc. It is generally considered that the reactivity of the A and B groups is identical. However, in several monomer pairs, nonequal reactivity of the functional groups was observed [185]. In this case, the monomers can be described as AA' and $B'B_2$, where the reactivity of the A' and B' groups is higher than that of the A and B groups. Owing to this inherent difference in reactivity, AB_2 intermediate monomers are formed

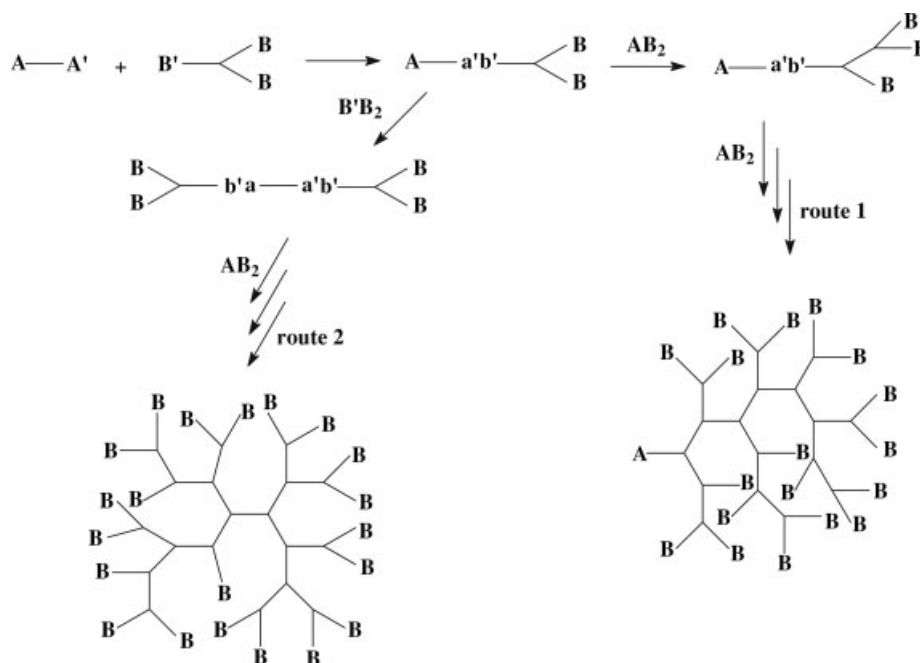


Scheme 7.75

in situ. Further reaction of these AB_2 species results in the formation of hyperbranched polymers (Scheme 7.76).

Dendrigraft polymers are produced following the generation-based growth system but are constructed from polymeric building blocks [186]. Therefore, high MWs can be obtained after only a few generations. Each grafting step can be considered as a new generation. The grafting reaction is a random process and, consequently, dendrigraft polymers are not strictly defined as dendrimers. However, much narrower MW distributions ($1.1 \leq M_w/M_n \leq 1.5$) are obtained compared to the hyperbranched polymers. These structures are also referred to in the literature as *comb-burst* [187] or *arborescent* [188] polymers.

The dendrigraft polymers can be prepared by all the reported methods available for the synthesis of comb polymers and graft copolymers, i.e., “grafting onto,” “grafting from,” and “grafting through” procedures. The “grafting onto” scheme relies on the generation of grafting sites along a polymer backbone followed by coupling with living polymer chains. The “grafting from” methodology involves the formation of active polymerization sites onto the polymeric backbone and the growth of side chains from these sites. Both procedures can be considered as divergent approaches for the synthesis of dendrigraft polymers. However, the “grafting through” procedure is envisioned as a convergent approach and involves the reaction of living



Scheme 7.76

Arborescent PS homo- and PS-g-P2VP copolymers have been synthesized [189] via an approach that combines the repetitive anionic polymerization of styrene, the attachment of acetyl groups by partial acetylation of the benzene rings of styrene, and reaction of living anionic polymeric chains with the acetyl groups. For the synthesis of the arborescent copolymers, P2VPLi chains were used in the final linking reaction. It was found that quantitative grafting occurred when the active sites were transformed to -2VPLi instead of $-\text{SLi}$. The polymerizations along with the coupling reactions were conducted in a mixture of THF/toluene at -78°C to afford arborescent polymers with two generations and low polydispersity indices.

“Grafting from” procedures were performed for the synthesis of highly branched poly(2,3-epoxypropan-1-ol) by anionic ROP [190] (Scheme 7.77).



Scheme 7.77

Linear poly(2,3-epoxypropan-1-ol) was initially prepared by polymerizing glycidol acetal using potassium *tert*-butoxide as initiator followed by deprotection of the acetal groups with formic acid and KOH/methanol/1,4-dioxane mixtures. Partial titration of the pendent hydroxyl groups with potassium *tert*-butoxide formed new initiating sites capable of initiating the anionic polymerization of a new portion of glycidol acetal. Additional cycles afforded highly branched polyglycidols.

Macromonomers have also been used as intermediate structures for the synthesis of highly branched or dendritic macromolecules by means of the convergent approach. When a bifunctional compound carrying a polymerizable vinyl group and a group capable of linking a living polymer chain is slowly added into a living polymer solution, consecutive macromonomer formation and macromonomer addition reactions can take place. Bifunctional compounds that have been used are CDMSS, and VBC [191]. Depending on the degree of branching and the MW of the living polymers, the final product may be a dendrigraft structure. Possible reactions involving the reaction of polystyryllithium with VBC are given in Scheme 7.78.

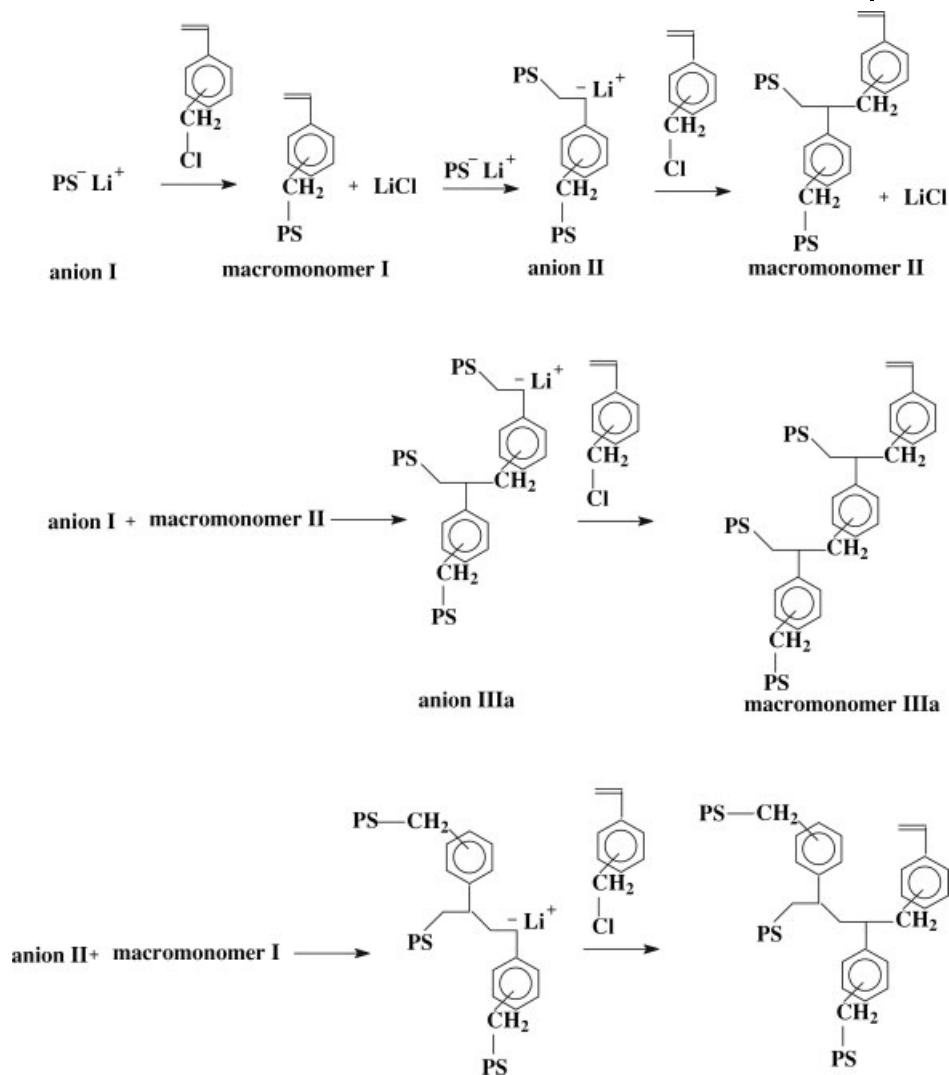
The characteristic of this procedure is that the complex architectures are formed in a one-pot reaction. However, there is no absolute control during the progress of the synthesis, and the products are rather polydisperse with high MW heterogeneity. Especially in the case of VBC, several side reactions may take place, imposing extra difficulties in obtaining well-defined polymers. Monomeric or dimeric terminations of the living PS chains, α -proton abstraction from VBC, and lithium–halogen exchange are possible side reactions. By choosing the suitable reaction conditions (solvent, temperature, reaction time, etc.), these side reactions can be minimized but not eliminated. The dendritic structures prepared were characterized from the existence of a functional styryl group at the focal point or the core, respectively. It was therefore possible to copolymerize these complex macromonomers with styrene or MMA for the synthesis of graft copolymers, imposing star polymers or dendrimers as side chains [192]. The products, shown in Scheme 7.79, had very broad MW distributions and were characterized by increased compositional and molecular heterogeneity.

7.6.4

Other Complex Architectures

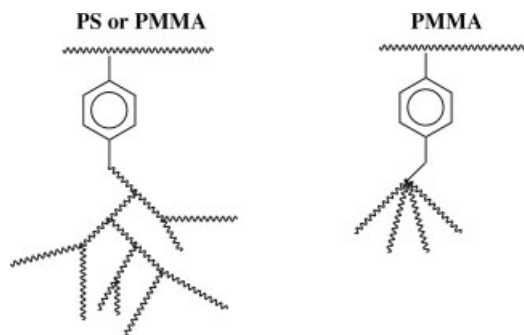
The DPE methodology and anionic polymerization techniques were adopted for the synthesis of linear-star-linear PSs of the types PS-(PS)_{*n*}-PS (*n* = 2, 4, 8, 16) and PS-(PS)_{*n*}-PS-(PS)_{*n*}-PS (*n* = 2, 4, 8) [167]. The synthesis involved the preparation of the corresponding in-chain functionalized polymers with a definite number of BnBr groups, as shown in Schemes 7.80 and 7.81.

Living PS macroanion was reacted with a PS chain end functionalized with a DPE unit, resulting in the synthesis of a linear PS macromolecule with an



Scheme 7.78

in-chain anionic center, which was deactivated *in situ* with 1-(4-bromobutyl)-4-(*tert*-butyldimethylsilyloxymethyl)benzene. The silyl ether groups were further transformed to BnBr moieties by treatment with LiBr/(CH₃)₃SiCl. Using the PS-(BnBr)-PS intermediate, the coupling and transformation reactions in the iterative reaction sequence were repeated four more times to synthesize the PS-(BnBr)_{*n*}-PS (*n* = 2, 4, 8, 16) in-chain functionalized polymers. Subsequent coupling with living PS chains end-capped with a DPE unit produced the desired PS-(PS)_{*n*}-PS (*n* = 2, 4, 8, 16) structures.



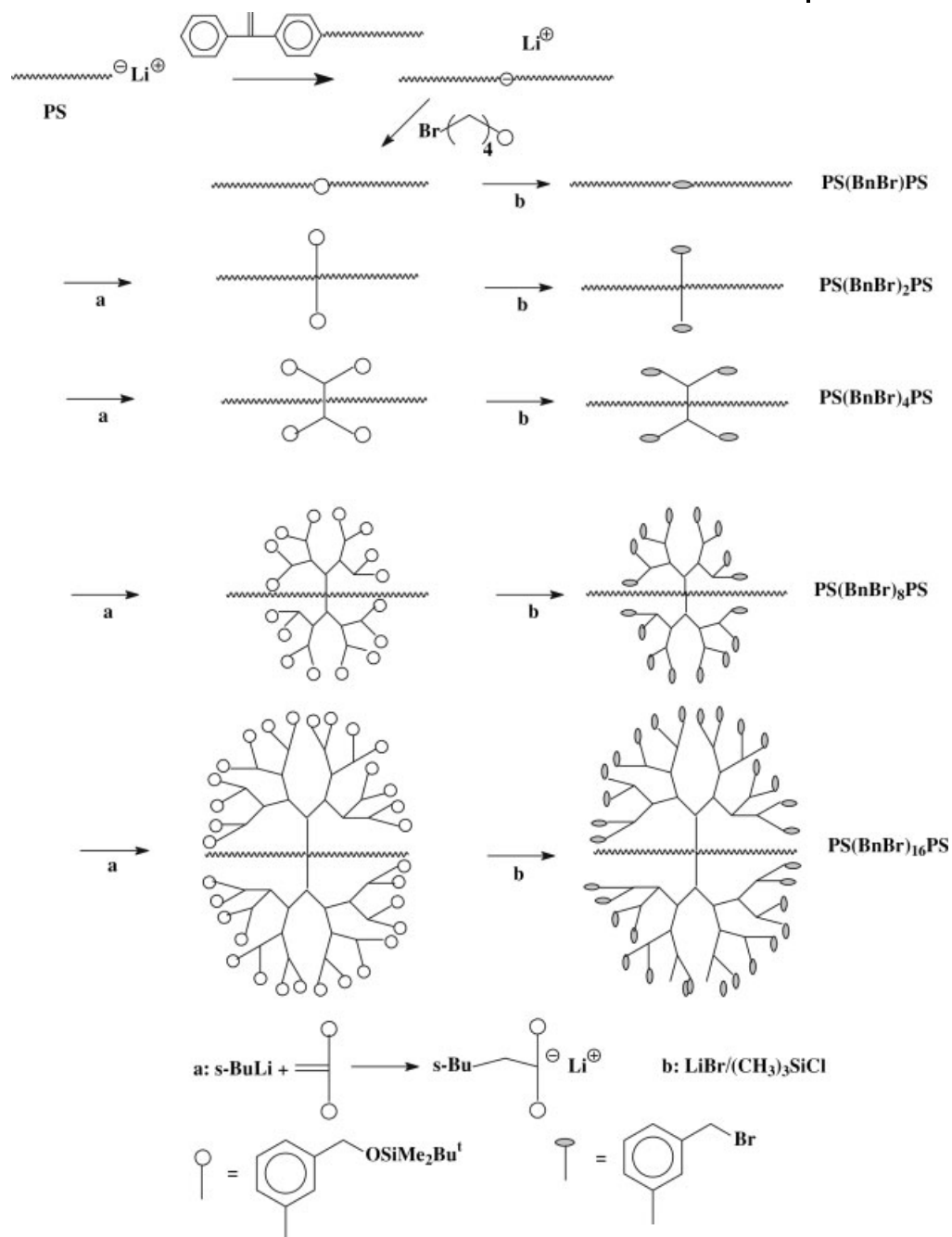
Scheme 7.79

A similar method was adopted for the synthesis of the PS-(PS) $_n$ -PS-(PS) $_n$ -PS ($n = 2, 4, 8$) polymers. Living PSLi was reacted with an α,ω -chain end-functionalized PS with DPE moieties followed by reaction with 1-(4-bromobutyl)-4-(*tert*-butyldimethylsilyloxymethyl)benzene to deactivate the generated two anionic sites. The same procedure as previously reported was employed for the introduction of BnBr functions, and by employing the iterative reaction sequence, the synthesis of the PS-(BnBr) $_n$ -PS-(BnBr) $_n$ -PS ($n = 2, 4, 8$) functionalized polymers was achieved. Coupling with PSLi end-capped with DPE afforded the PS-(PS) $_n$ -PS-(PS) $_n$ -PS ($n = 2, 4, 8$) structures.

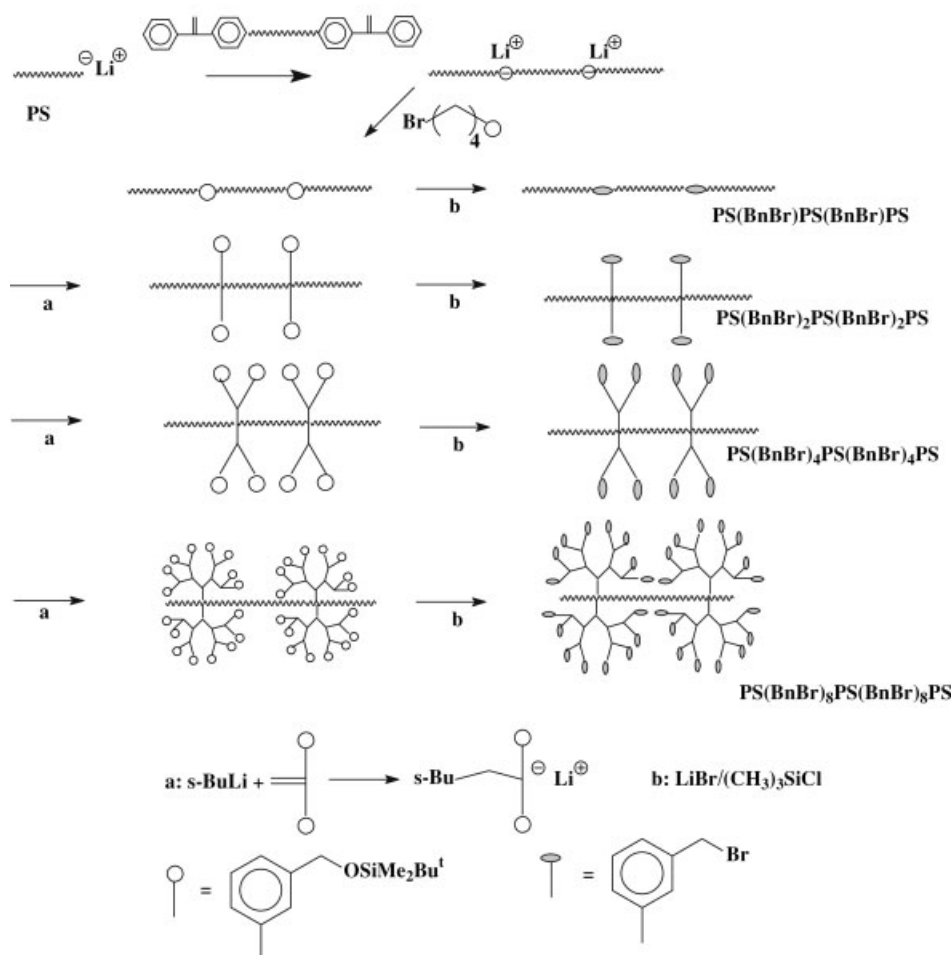
The electrostatic self-assembly and covalent fixation method has been utilized for the synthesis of complex macromolecular architectures, as shown in Scheme 7.82. Telechelic PTHF bearing *N*-phenylpyrrolidinium groups was aggregated with the suitable tetra- and hexacarboxylate counterions in dilute solutions and were subsequently heated to promote the ring opening of the end groups, leading to the covalent fixation of the polymer chains to the carboxylate moiety core and the formation of the desired polycyclic polymers [141, 193].

Θ -shaped PTHF was also obtained by the same method. A trifunctional three-arm PTHF star polymer with *N*-phenylpyrrolidinium end groups was subjected to the covalent conversion process in the presence of a tricarboxylate to afford the Θ -shaped structure [193].

A five-step strategy was reported by Jérôme *et al.* [194] for the synthesis of a two-tail tadpole-shaped copolyester, whose tails were grafted with PEO chains (Scheme 7.83). ϵ -CL was initially polymerized using the cyclic tin dialkoxide 2,2-dibutyl-2-stanna-1,3-dioxepane. A small amount of α -(1-acryloxyethyl)- ϵ -caprolactone (α A ϵ CL) was subsequently added to incorporate a few monomer units. The pendant acrylic unsaturated units were then subjected to cross-linking reaction by UV irradiation, leading to a macrocyclic polyester free of any endocyclic tin alkoxide. This structure was further employed as a macroinitiator for the copolymerization of ϵ -CL and α -chloro- ϵ -caprolactone (α Cl ϵ CL). The side chloride groups were quantitatively transformed into azides



Scheme 7.80



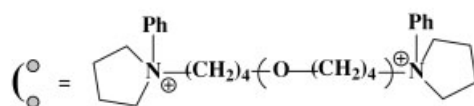
Scheme 7.81

through reaction with sodium azide, without degrading the polyester chains. Alkynyl end-capped PEO was prepared by esterification of the end hydroxyl group of PEO monomethyl ether with 4-pentynoic acid in the presence of DCC and DMAP. The azide groups of the tadpole-shaped copolyester were finally subjected to “click” reaction with the alkynyl end-capped PEOs in the presence of CuI and triethylamine. It was found that each arm of the copolyester was grafted with 53 PEO chains. SEC analysis revealed that rather broad MW distributions were obtained.

This work was further expanded to the synthesis of eight-shaped tadpole copolyesters with each arm being grafted with PEO chains [195] (Scheme 7.84).



Scheme 7.82

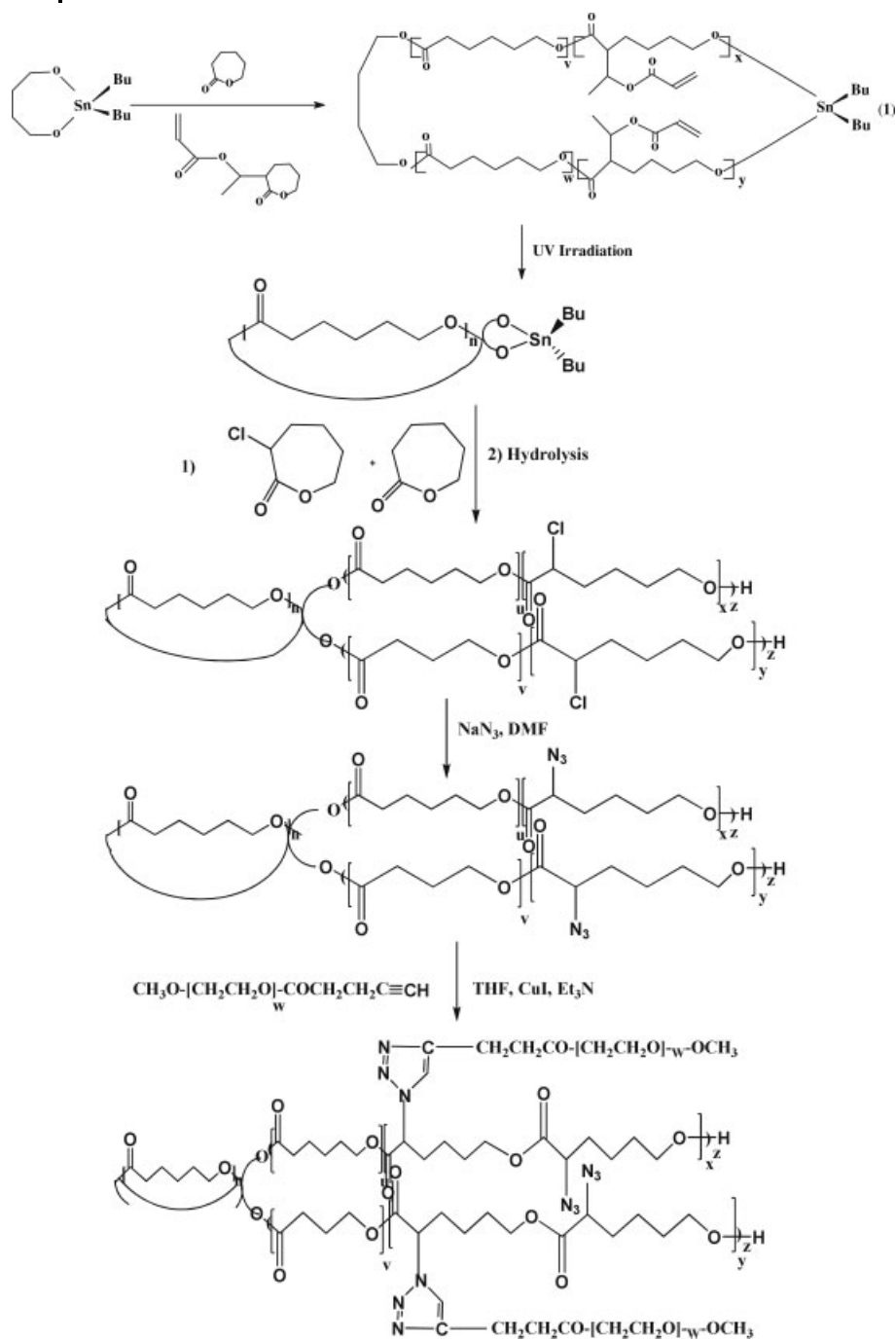


The spirocyclic initiator **1** was employed for the polymerization of ϵ -CL, followed by the addition of α A ϵ CL to form a short block. UV irradiation was then performed to cross link the acrylic pendant groups followed by the hydrolysis of the endocyclic tin alkoxides, thus providing “8”-shaped copolyesters having four available hydroxyl groups, which can be subsequently used for the copolymerization of ϵ -CL and α Cl ϵ CL. The chlorine moieties were converted to azides, as previously reported, and were then subjected to “click” reaction with alkynyl end-capped PEOs to afford the desired tadpole structures. The grafting efficiency at the final synthetic step was found to be equal to 61%. The products were characterized by rather broad MW distributions.

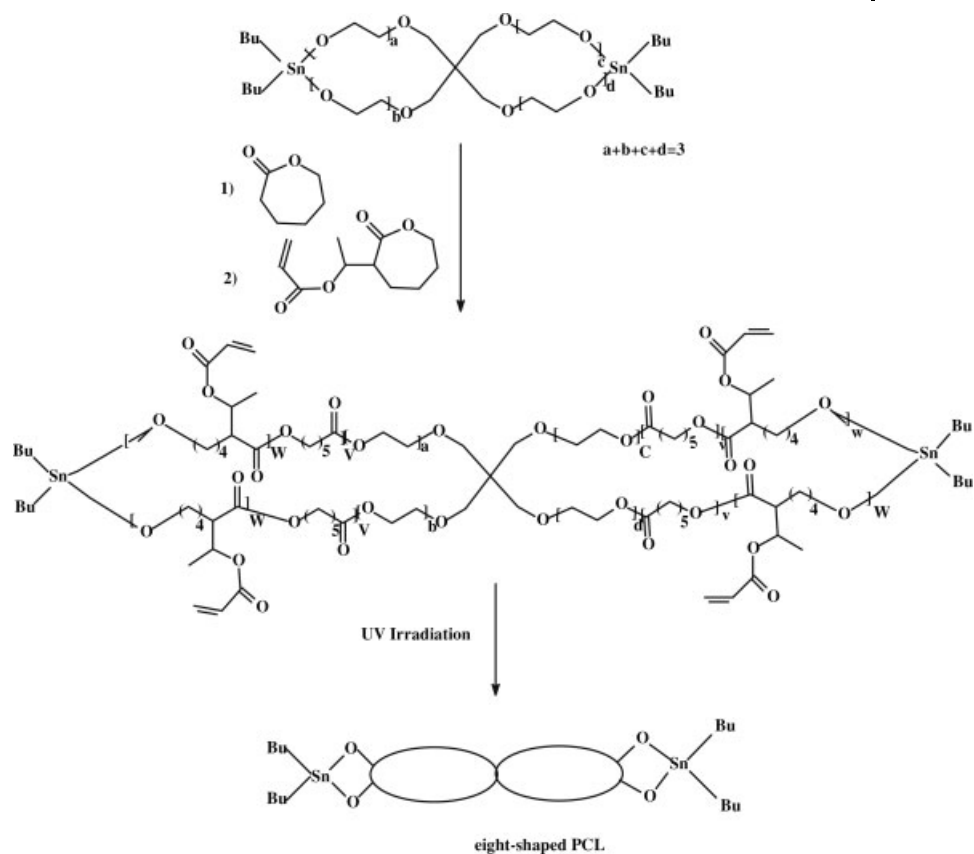
The same spirocyclic initiator **1** was used for the polymerization of ϵ -CL followed by the addition of a mixture of ϵ -CL and α Cl ϵ CL. The tin alkoxides were subsequently hydrolyzed, leading to the synthesis of four-arm star-block copolymers. The pendant chlorine groups were then transformed to azides and reacted with alkynyl end-capped PEOs in a similar fashion, as previously reported, giving the final star-graft copolymers (Scheme 7.85).

7.7 Applications

The well-defined molecules presented above, with high MW, as well as structural and compositional homogeneity, could find many industrial applications, but their transfer to industrial production is difficult. The demanding synthetic procedures, in particular for living anionic polymerization, are not readily applied in industrial settings, thus justifying the limited number of industrial



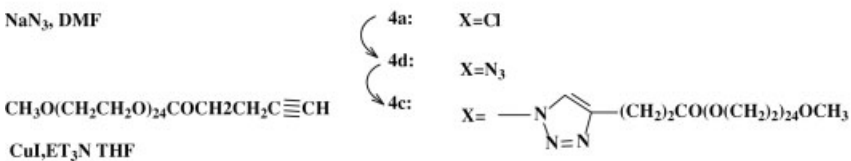
Scheme 7.83



Scheme 7.84

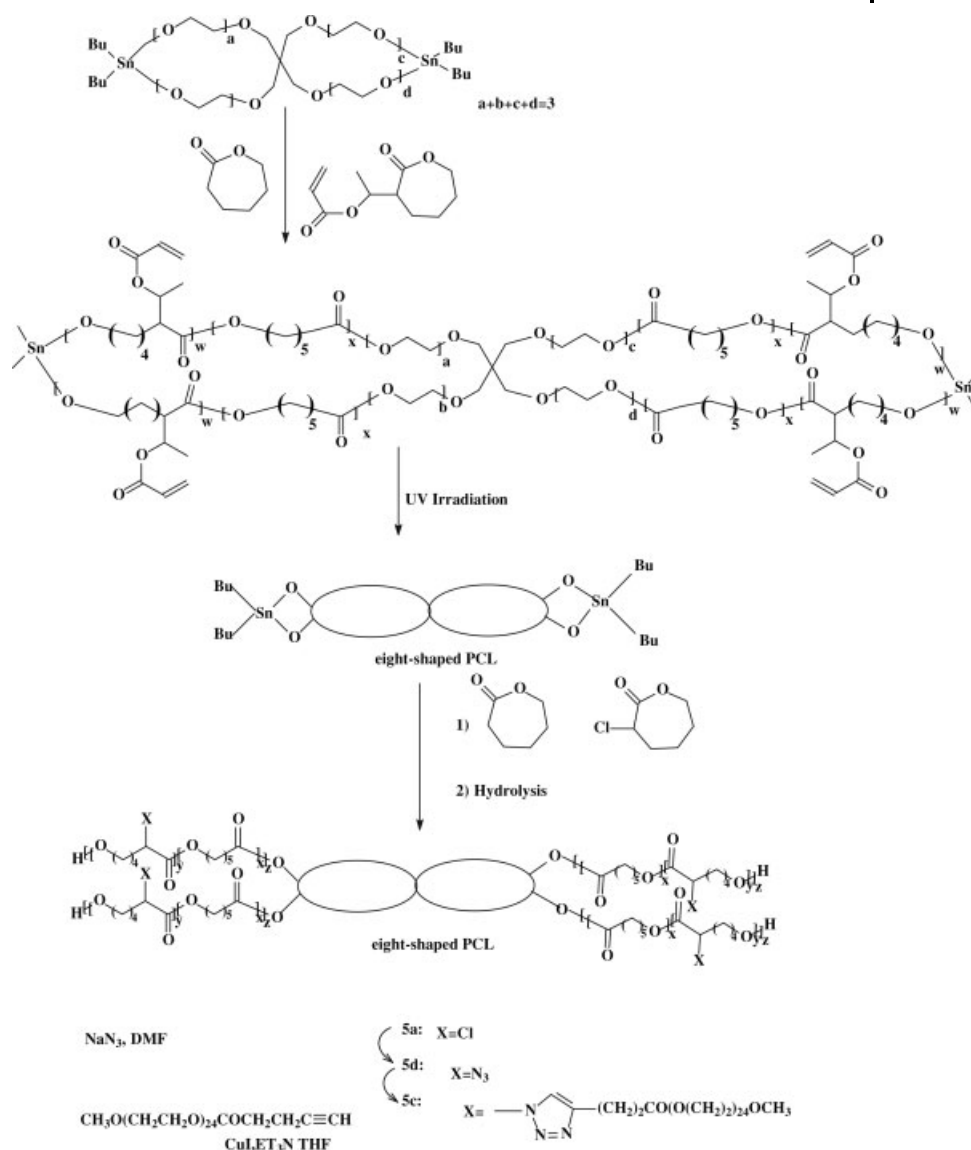
polymeric products in use. For example, star-block copolymers of butadiene and styrene, symmetric (e.g., Solprene) and asymmetric (e.g., Styrolux), have found commercial applications as adhesives and sealants, as blending agents of different homopolymers for producing materials with different properties, as surface modifiers for fillers and fibers to improve dispensability in the matrix, as surfactants for phase stabilization, as viscosity improvers of lubricating oils, as membranes for desalination, in biomedical applications, etc [196].

Well-defined molecules are mainly used to establish structure–property relationships, to select the appropriate structure for a particular application. The preparation of such selected materials is subsequently adapted to industrial conditions, by means of either a similar or different synthetic methodology. For example, low density polyethylene (LDPE), used for plastic film production, is easily processed in extruders and possesses good bubble stability, but the final film does not have the mechanical strength required for certain products. On the other hand, high density metallocene polyethylene (mPE) films are



Scheme 7.84 (continued).

characterized by high strength, but low processability. The question is, how can mPE processability be improved by mixing with appropriate additives? To answer this question, PBds with different macromolecular architectures (star, H-shape, super-H, pom-pom, and comb) have been synthesized by anionic



Scheme 7.85

polymerization high vacuum technique and appropriate linking chemistry, followed by hydrogenation, to produce the corresponding PEs. Shear [197] and elongational viscosity studies [198,199] were carried out on these PEs and on their mixtures with mPE (3%) to determine the shear thinning (η_0/η^* , where η_0 is the zero shear viscosity and η^* the complex viscosity at 100 rad s^{-1} at 190 °C, standard industrial film extrusion conditions) and the

strain hardening ($\eta_{\text{ext}}/\eta_{\text{ext,lin.}}$, where η_{ext} is extensional viscosity and $\eta_{\text{ext,lin.}}$ the extensional viscosity predicted by linear viscoelasticity at strain rate: 1 s^{-1} ; time: 3 s; and T : 190°C). It should be noted that the higher the shear thinning, the easier the extrudability; and the higher the strain hardening, the higher the bubble stability. From these rheological studies, the mixture of mPE and PE comb (3%) was found to be the most appropriate. For the industrial synthesis of the PE comb, rather than applying anionic polymerization high vacuum techniques an alternative methodology involving the copolymerization of an ethylene-macromonomer with ethylene was used.

Thus, the ability of living and controlled/living polymerizations to produce a wide variety of well-defined architectures has made it an invaluable tool to enable us to understand the behavior and improve the properties of industrially important polymeric materials.

7.8

Conclusions

The rich variety of macromolecular architectures (star, comb, cyclic, dendritic, hyperbranched, and other complex-branched) described in this chapter represents only a small fraction of those structures achievable from living and controlled/living polymerization methods. The seed that Szwarc sowed 55 years ago gave fruit not only to developments in polymer chemistry, but also in other branches of polymer science including polymer physics and materials science, and enabled us to understand the behavior and improve the properties of industrially important polymeric materials.

List of Symbols and Abbreviations

AcOVE	Acetoxyethyl vinyl ether
AIBN	azo- α,α' -Diisobutylnitrile
BDPEP	2,2-Bis[4-(1-phenylethenyl)phenyl]propane
BDTEP	2,2-Bis[4-(1-tolylenyl)phenyl]propane
BnBr	Bromomethylphenyl group
BPDMA	Bisphenol A dimethacrylate
CDMSS	4-(Chlorodimethylsilyl)styrene
DFM	Difunctional monomers
DLS	Dynamic light scattering
DPE	1,1-Diphenylethylene
ϵ -CL	ϵ -Caprolactone
EGDM	Ethylene glycol dimethacrylate
IR	Infrared spectroscopy
Is	Isoprene
LA	Linking agent

LALLS	Low-angle laser light scattering
LS	Light scattering
MDDPE	1,3-Bis(1-phenylethenyl)benzene
MFI	Multifunctional initiator
MFLA	Multifunctional linking agent
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
<i>n</i> -BuLi	<i>n</i> -Butyllithium
NCA	<i>N</i> -carboxyanhydride
NMR	Nuclear magnetic resonance
NMP	Nitroxide mediated polymerization
P2VP	Poly(2-vinylpyridine)
P4VP	Poly(4-vinylpyridine)
PAMAM	Polyamidoamine dendrimers
PBd	Polybutadiene
PBLG	Poly(γ -benzyl-L-glutamate)
PCL	Poly(ϵ -caprolactone)
PDDPE	1,4-Bis(1-phenylethenyl)benzene
PE	Polyethylene
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PI	Polyisoprene
PIB	Polyisobutylene
PIBVE	Poly(isobutyl vinyl ether)
PLL	Poly(L-lysine)
PMMA	Poly(methyl methacrylate)
PMVE	Poly(methyl vinyl ether)
<i>Pn</i> BuA	Poly(<i>n</i> -butyl acrylate)
PS	Polystyrene
<i>Pt</i> BuA	Poly(<i>tert</i> -butyl acrylate)
<i>Pt</i> BuMA	Poly(<i>tert</i> -butyl methacrylate)
PZLL	Poly(ϵ -benzyloxycarbonyl-L-lysine)
RAFT	Reversible addition-fragmentation chain transfer
RI	Refractive index
ROMP	Ring opening metathesis polymerization
ROP	Ring opening polymerization
SANS	Small-angle neutron scattering
<i>s</i> -BuLi	<i>sec</i> -Butyllithium
<i>s</i> -BuOLi	<i>sec</i> -Lithium butoxide
SEC	Size exclusion chromatography
<i>t</i> -BuLi	<i>tert</i> -Butyllithium
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy stable radical

THF	Tetrahydrofuran
UV	Ultraviolet spectroscopy
VBC	Vinyl benzyl chloride
VOEM	2-(Vinylloxy)ethyl malonate

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