Star-Branched Polymers (Star Polymers)

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Abstract The synthesis of well-defined regular and asymmetric mixed arm (hereinafter miktoarm) star-branched polymers by the living anionic polymerization is reviewed in this chapter. In particular, much attention is being devoted to the synthetic development of miktoarm star polymers since 2000. At the present time, the almost all types of multiarmed and multicomponent miktoarm star polymers have become feasible by using recently developed iterative strategy. For example, the following well-defined stars have been successfully synthesized: 3-arm ABC, 4-arm ABCD, 5-arm ABCDE, 6-arm ABCDEF, 7-arm ABCDEFG, 6-arm $A_2B_2C_2$, 9-arm $A_3B_3C_3$, 12-arm $A_4B_4C_4$, 13-arm $A_4B_4C_4D$, 9-arm AB_8, 17-arm AB_{16}, 33-arm AB_{32}, 7-arm AB_2C_4, 15-arm $AB_2C_4D_8$, and 31-arm $AB_2C_4D_8E_{16}$ miktoarm star polymers, most of which are quite new and difficult

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to synthesize by the end of the 1990s. Several new specialty functional star polymers composed of vinyl polymer segments and rigid rodlike poly(acetylene) arms, helical polypeptide, or helical poly(hexyl isocyanate) arms are introduced.

Keywords Living anionic polymerization • Star polymer • Regular star polymer • Asymmetric star polymer • Miktoarm star polymer • μ-Star polymer • Iterative strategy • Multicomponent and multiarmed star polymer

1   Introduction

The availability of star-branched polymers (hereinafter star polymers) with well-defined architectures and low degrees of molecular weight and compositional heterogeneity is essential for fundamental understanding regarding the relationships among the star-branched structure and their basic properties as well as morphologies. If such relationships can be understood and predetermined, new specialty polymers based on star-branched structures are created, because it has long been known that the branched structure significantly influences various physical properties and morphologies.

A star polymer, recognized as the simplest branched polymer among the various branched polymers so far synthesized, consists of three or more linear polymer chains linked together at one end of each chain by a single or junction point. In general, star polymers are categorized into two types, that is, regular and asymmetric star polymers. Regular star polymers are composed of all the same arm segments in molecular weight and chemical structure. Because of several arm segments connected at the single point and the same number of chain ends, these polymers have characteristic features, such as lower viscosities in the bulk and solution, better solubility, smaller hydrodynamic volumes, lower crystallinities, and lower glass transition temperatures (T_g) and melting points (T_m), in comparison to linear polymers with the same molecular weights.

Asymmetric star polymers, whose arms differ in chemical structure, are generally called mixed-arm or miktoarm (coming from the Greek word μικτός meaning mixed) star polymers, abbreviated as μ-star polymers. This type of polymer belongs to a star with a composition asymmetry. Furthermore, there are two additional different asymmetric star polymers as follows: the first example is a star polymer with molecular weight asymmetry, whose arms are identical in chemical structure, but differ in molecular weight. The other one is a star polymer with topological asymmetry, in which the arms are block copolymers, but differ with respect to the block sequence connected to the branch point. Such three asymmetric star polymers are illustrated in Fig. 1 to clearly understand their structures.

Among such asymmetric star polymers, μ-star polymers have received much attention in recent years because they exhibit unique and unusual morphologies in bulk and selected solvents, either by moving the borders of the classical morphology map of linear block polymers or by tremendously increasing the variety of new morphological structures [1–3]. Thus, μ-star polymers are expected as promising
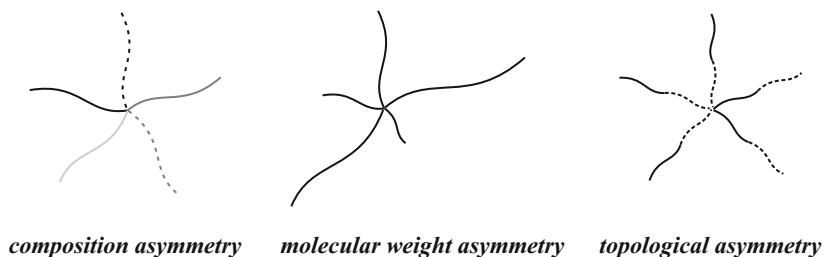
composition asymmetry   *molecular weight asymmetry*   *topological asymmetry*

Fig. 1 Three asymmetric star polymers

nonlinear multiphase polymers next to linear block polymers with many potential applications in the fields of nanoscience and nanotechnology such as electronic and optical nanodevices, nanomaterials for lithography, nanoreactors carrying metal catalysts and enzymes, nanoscale microfilters, self-assembled materials for drug and genetic materials delivery, etc.

In this chapter, we will briefly describe the general and basic synthesis of star polymers established until the 1990s to avoid the duplication of previous reviews and books [4–13]. Our attention will focus on the recent developments of multiarmed and multicomponent μ-star polymers synthesized by the living anionic polymerization *"with emphasis on the precise control of synthetic factors involving the molecular weight, molecular weight distribution, arm number, and composition."* The rapid progress in living/controlled radical polymerization systems as well as several living polymerization systems via cationic, transition-metal-mediated, and other mechanisms also enables the synthesis of various different μ-star polymers, which cannot be obtained by anionic polymerization. However, such star polymers, although interesting, are beyond the scope of this chapter and may be covered elsewhere.

2 Regular Star Polymers

2.1 Regular Star Polymers Synthesized Until the 1990s

In order to synthesize regular as well as asymmetric star polymers with well-defined structures, the use of living polymerization systems is essential. Although several living polymerization systems via different active species and reaction mechanisms have been significantly developed, particularly in the last 25 years, the living anionic polymerization of styrene, 1,3-butadiene, isoprene, 2-vinylpyridine, alkyl methacrylates, and their derivatives with certain functional groups [14–18] is still the best system based on the following viewpoints: first, the molecular weight can be precisely controlled in a wide range from 10^3 to even 10^6 mol/l. Second, an extremely narrow molecular weight distribution can be realized, M_w/M_n values being 1.05 or even lower. Finally, the resulting living anionic polymers have chain-

Scheme 1 Synthesis of
regular star polymer by
"core-first" initiation
method
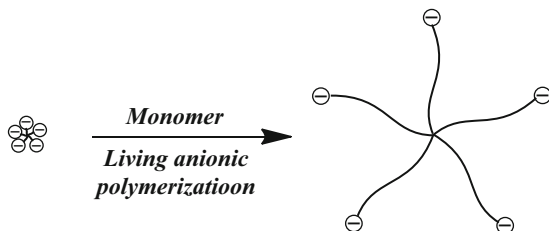
end anions, which are highly reactive, but stable under appropriate conditions. Such
characteristics are ideally suited for the synthesis of star polymers with well-defined
structures.

Two strategies were proposed for the synthesis of regular star polymers as early
as the 1960s soon after the discovery of the living anionic polymerization in 1956.
They were strategies based on the "core-first" initiation and "arm-first" termination
methodologies. Scheme 1 shows the synthesis of star polymers by the core-first
initiation method. A multifunctional anionic initiator having three or more anionic
sites exactly defined in number is prepared in advance and used as the initiator for
the living anionic polymerization of an appropriate monomer to grow the arm
segments. The number of arms in the resulting star corresponds to the number of
anionic sites if all of the sites efficiently work. There are advantageous points where
steric hindrance is reduced as the polymerization proceeds and fractionation is
basically not needed. The most successful examples by this method were the
synthesis of polystyrene (PS), poly(ethylene oxide) (PEO), and poly(dimethyl-
siloxane) (PDMS) star polymers having 4–16 arms by the polymerization of the
corresponding monomers with the multifunctional anionic initiators based on
carbosilane dendrimers of several generations [19, 20]. A hydrocarbon-soluble
trifunctional anionic initiator was prepared from 1,3,5-tris(1-phenylethenyl)ben-
zene and sec-BuLi and found to be an effective initiator for the synthesis of 3-arm
PS and poly(1,3-butadiene) (PB) star polymers [21, 22].

A serious problem, however, exists regarding the uniformity of the arm seg-
ments in molecular weight. Due to the ionic repulsion among several anionic sites
that influences the degree of ion dissociation, it is highly probable that the propa-
gation reaction heterogeneously proceeds, resulting in a large molecular weight
distribution of the arm segments. Furthermore, it is difficult or nearly impossible to
know how many reaction sites participate in the polymerization. Thus, star archi-
tectures including arm the lengths and numbers cannot be always unambiguously
defined. For these reasons, the agreement between the calculated and observed
molecular weights is not a guarantee to demonstrate the well-defined structures of
the resulting polymers. In addition, the insolubility and synthetic difficulty of
highly purified multifunctional anionic initiators often prevents the practical syn-
thesis of star polymers.

The second strategy based on the arm-first termination methodology utilizes a
multifunctional terminator having the exact number of reaction sites in the linking
reaction with living anionic polymers for the star polymer synthesis, as shown in
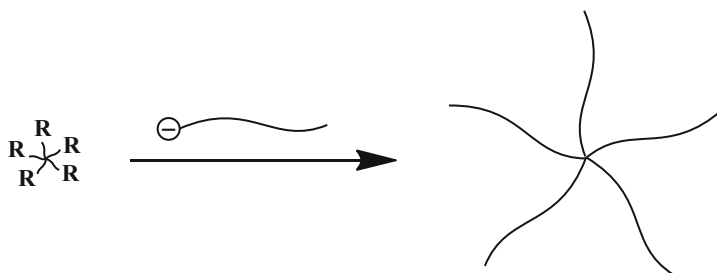
Scheme 2 Synthesis of regular star polymer by "arm-first" termination method
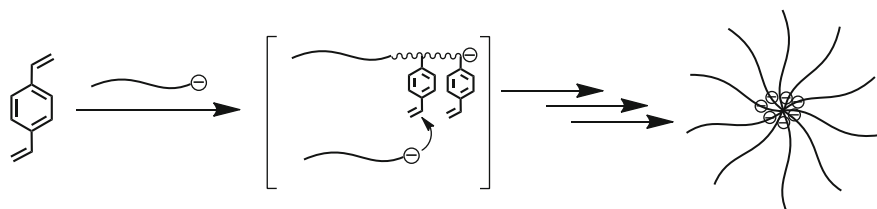
Scheme 2. The premade living anionic polymer with a known molecular weight and a narrow molecular weight distribution is employed in the linking reaction. The number of arms in the resulting star polymer is readily determined by comparing the molecular weight of the final polymer to that of the premade living polymer. Agreement between the molecular weight of the final polymer and the molecular weight calculated by multiplying the M_n value of the premade living polymer by the arm number is direct evidence for the well-defined and expected structure. The uniformity and molecular weight of the arm segment are always guaranteed by the use of the premade living polymer. Thus, the arm-first termination methodology is quite superior to the core-first initiation one with respect to the well-defined star polymer synthesis.

During the early stage of the star polymer synthesis, the use of a wide variety of multifunctional terminators was attempted in the linking reaction with living anionic polymers [23]. These terminators involved 1,3,5-trichloromethylbenzene, 1,3,5-tribromomethylbenzene, 1,2,4,5-tetrabromobenzene, hexa(4-chloromethylphenyl)-benzene, MeSiCl$_3$, SiCl$_4$, SnCl$_4$, PCl$_3$, hexachlorocyclic triphosphazene, 2,4,6-triallyloxytriazine, dimethyl terephthalate, tetrekis((phenyl-1-vinyl)-4-phenyl) plumbane, 1,1,4,4-tetraphenyl-1,4-bis(allyloxytriazine)butane, 1,3,5-tris (phenylethenyl)benzene [22], and even C$_{60}$ [24, 25]. Unfortunately, insufficient linking and undesired side reactions often occurred in the linking reactions of most of these terminators with the living anionic polymers to afford mixtures of target stars, less or extra-armed stars, and other by-products. Moreover, the number of arms was generally limited in range from 3 to 6. Such difficulties and limitations were overcome by developing several functional dendrimer-based multifunctional terminators. The arm-first termination methodology using such multifunctional terminators is currently the most promising procedure for the synthesis of well-defined multiarmed star polymers and will be introduced in the next sections "Arm-first termination methodology using multifunctional chlorosilane reaction site," "Arm-first termination methodology using BnBr reaction site," and "Arm-first termination methodology using DPE reaction site."

The third strategy initially reported by Burchard et al. [26, 27] since the 1970s and later developed by Rempp et al. [28, 29] utilizes certain divinyl monomers either with anionic initiators, followed by polymerization, or with living anionic
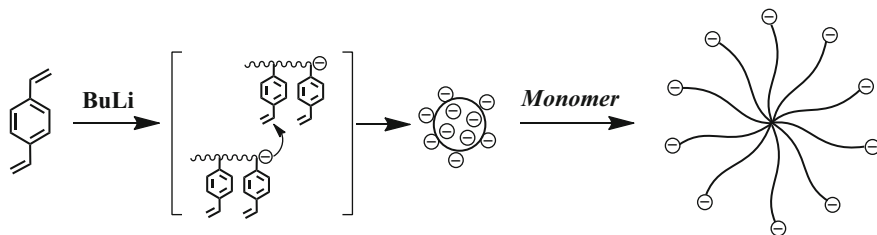
Scheme 3 Synthesis of star polymer by the polymerization with multifunctional initiator prepared from BuLi with 4-DVB


Scheme 4 Synthesis of star polymer by reacting living anionic polymer with 4-DVB

polymers. The typical divinyl monomers used are 4-divinylbenzene (4-DVB), a commercially available mixture of 3- and 4-DVBs, and several bis(methacrylate) monomers. In the former case as shown in Scheme 3, an anionic initiator like BuLi reacts with 4-DVB to polymerize and subsequently undergoes the addition reaction between the chain-end anion and the pendant vinyl group, resulting in the production of a soluble microgel-like multifunctional compound with many anionic reaction sites. This multifunctional compound is used as the anionic initiator in the polymerization of the appropriate monomer. Thus, a variety of PS, PB, poly-isoprene (PI), poly(*tert*-butyl acrylate) (P^{t}BA), and PEO star polymers were synthesized [29–34]. The number of arms can be controlled by the ratio of [4-DVB]/ [BuLi] in the range from 5 to even the high number of 1,300. Moreover, the reaction of the growing chain-end anions with either suitable electrophiles or the addition of other monomers allows access to a variety of end-functionalized stars or star block copolymers.

A star polymer can also be synthesized by directly reacting a living anionic polymer with 4-DVB, as illustrated in Scheme 4. Similar to the reaction of BuLi with 4-DVB mentioned above, the living anionic polymer polymerizes a few 4-DVB molecules, followed by the addition reaction of the chain-end anion with the pendant vinyl group, forming a 4-DVB micro gel nodule that serves as the branch point for the produced star polymer. PS, PB, and PI star polymers are typical examples synthesized by this methodology [35–39]. The number of arm segments can also be changed from 5 to 56 by the ratio of [4-DVB] to [chain-end anion].

Since a number of anionic sites are produced by the above reaction, subsequent addition of the same monomer or another monomer yields regular star polymers
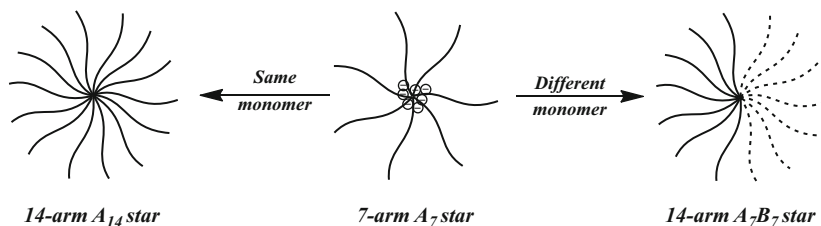
Scheme 5 Synthesis of more armed regular star and A_nB_n μ-star by the polymerization of the same or different monomer with the polymer anion

having more number of arms or μ-star polymers (see Scheme 5). For example, a variety of A_nB_n μ-star polymers composed of PS (A) and poly(*tert*-butyl (meth) acrylate) (P^tB(M)A) (B), PEO (B), or poly(2-vinylpyridine) (P2VP) (B) were successfully synthesized by this methodology [29, 39–42]. The number of arm segments in the star polymers thus synthesized is always widely distributed and even the molecular weight of the arms cannot be controlled. Thus, the third strategy is not suitable to synthesize well-defined star polymers, although it is synthetically straightforward and, therefore, technologically important.

2.2 Arm-First Termination Methodology Using Multifunctional Chlorosilane Reaction Site

In contrast to the above-mentioned terminating agents, chlorosilane compounds quantitatively react with highly reactive living anionic polymers, such as poly (styryl)lithium (PSLi), poly(1,3-butadienyl)lithium (PBLi), and poly(isoprenyl) lithium (PILi), without any side reactions. On the other hand, the incomplete reaction of PSLi with $SiCl_4$ was observed to occur, resulting in a mixture of star PSs having less than three arms, thus the target 4-arm star PS could not be obtained. This lack of reactivity is attributed to the steric hindrance between the core Si atom and the chain-end PS anion. In contrast, the reaction between a less bulky PBLi and $SiCl_4$ was found to be complete to afford the expected 4-arm star PB. It was feasible to synthesize the 4-arm star PS by converting the chain-end anion of PSLi to the butadienyl anion by end-capping a few 1,3-butadiene units and subsequently reacting with $SiCl_4$. Since PILi is situated between PSLi and PBLi in steric bulkiness, the careful choice of chlorosilane compounds and longer reaction times are usually required to complete the linking reaction. Thus, well-defined PSs, PBs, and PIs with arms ranging from 3 to even up to 18 were successfully synthesized [9]. However, the synthesis of multiarmed star polymers was still difficult due to the synthetic difficulty of multifunctional chlorosilane compounds.

Since the 1980s, there appeared a large breakthrough in the development of multiarmed star polymer synthesis. Roovers, Hadjichristidis, and their coworkers
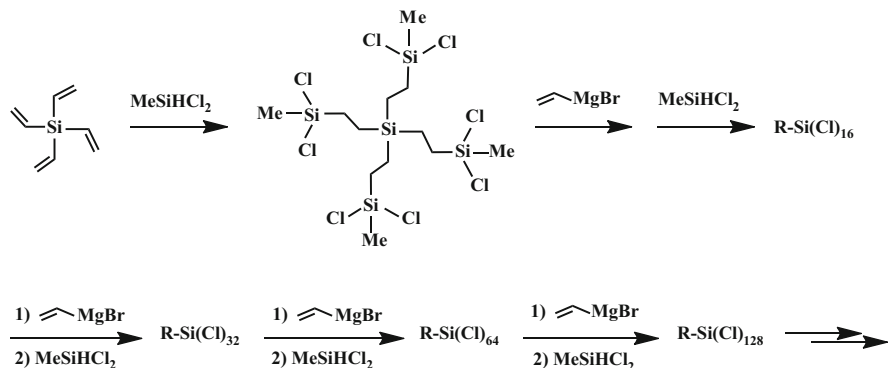
Scheme 6 Synthesis of carbosilane-based multifunctional chlorosilane compounds by iterative methodology

were the first to successfully synthesize a series of carbosilane-based multifunctional chlorosilane compounds having many Si-Cl reaction sites by employing a new iterative approach, as shown in Scheme 6 [43]. The carbosilane dendrimers were prepared starting with tetravinylsilane and using two reaction steps, that is, the hydrosilylation of the vinylsilane moieties with $MeSi(H)Cl_2$ and the reaction of the chlorosilane function with vinylmagnesium bromide to introduce a vinyl group to the silicon atom. The number of chlorosilane reaction sites were dramatically increased from 8 (4×2), 16 (4×2^2), 32 (4×2^3), 64 (4×2^4), even 128 (4×2^5) by repeating the two reaction steps. Thus, a series of multifunctional chlorosilane compounds having 8, 16, 32, 64, and even 128 chlorosilane reaction sites were successively prepared. Similarly, they also prepared another series of multifunctional chlorosilanes, in which 6, 12, and 18 chlorosilane reaction sites were introduced. These carbosilane-based multifunctional chlorosilane compounds are designed so as to separate the chlorosilane reaction site by the methylene chain and to possess only two chlorides on one silicon atom in order to facilitate the next linking reaction stage with living anionic polymers.

With the use of such multifunctional chlorosilane compounds in the linking reactions with living anionic polymers, the following multiarmed star polymers with well-defined structures were successfully synthesized for the first time: typically 6-, 12-, and 18-arm star PSs; 6-, 8-, 12-, and 18-arm star PIs; 8-, 16-, 32-, 64-; and 128-arm star PBs. Most of these star polymers were quite new and possessed remarkably high molecular weights up to 10^8 g/mol in some cases [44–48].

Later, reevaluation of the 32- and 64-arm star PBs by ^{1}H NMR and MALDI-TOF MASS analyses showed that the average number of introduced arms were 29 and 54, respectively, indicating the strict steric requirements in the synthesis of multiarmed star polymers [49, 50]. Nevertheless, the arm-first termination methodology using multifunctional chlorosilane compounds is still one of the most reliable and promising methodologies for the synthesis of well-defined multiarmed star polymers. The chlorosilane compounds also readily react with the living poly

(methyl methacrylate) PMMA and PEO. Unfortunately, the resulting star polymers are not stable due to the formation of hydrolysable Si-O-C linkages between the PMMA or PEO segments and their cores.

2.3 Arm-First Termination Methodology Using BnBr Reaction Site

It has long been believed that the linking reaction of highly reactive living anionic polymers, such as PSLi, PBLi, and PILi, with benzyl chloride (BnCl) or benzyl bromide (BnBr) proceeds along with several undesired side reactions such as the metal–halogen exchange, benzyl proton abstraction, and single-electron transfer reactions. Accordingly, fewer or extra-armed star polymers were by-produced in addition to target stars in the reaction of the living anionic polymer with multifunctional benzyl halides. However, it became feasible to dramatically reduce or almost eliminate such side reactions by end-capping the living anionic polymers with 1,1-diphenylethylene (DPE) prior to the reaction. Moreover, the choice of the reaction conditions is very important. The reaction efficiency could be further improved by carrying out the reaction under the conditions in THF at $-40\ ^{\circ}$C or lower temperature. It is also important to design in such a way that one halomethyl group is substituted on the phenyl ring to minimize the steric hindering and electronic effects. Among the benzyl halides, BnBr is superior to BnCl in the linking reaction, while benzyl iodide is too unstable for the practical use in the star polymer synthesis. Thus, the linking reaction between the BnBr reaction site and the DPE-end-capped living anionic polymer was observed to almost quantitatively proceed [51]. It should be noted that less reactive living polymers of 2VP, MMA, and ^{t}BMA cleanly and quantitatively linked with 1,2,4,5-tetrabromomethylbenzene in THF at $-78\ ^{\circ}$C to afford the corresponding 4-arm star polymers [52, 53].

Similar to the above-mentioned synthesis of multifunctional chlorosilanes by the iterative approach, Hirao et al. successfully synthesized a series of chain-end-(BnBr)$_{n}$-multifunctionalized polymers with different generations by employing a new iterative approach, which involves two reaction steps in each reaction sequence, that is, the iterative process as follows [51]: first, the reaction of the terminal BnBr reaction sites with a DPE anion prepared from sec-BuLi and 1,1-bis (3-tert-butyldimethylsilyloxymethylphenyl)ethylene (1); second, a transformation reaction of the introduced 3-tert-butyldimethylsilyloxymethylphenyl (TBDMSiOMP) groups into BnBr functions used as the reaction sites by treatment with a 1:1 mixture of Me$_3$SiCl and LiBr.

As shown in Scheme 7, a chain-end-(BnBr)$_2$-functionalized PS was initially prepared by reacting PSLi with 1 to introduce two TBDMSiOMP termini, followed by transformation into two BnBr reaction sites with Me$_3$SiCl/LiBr. In the first process, the DPE anion was prepared from sec-BuLi and 1 and reacted in situ
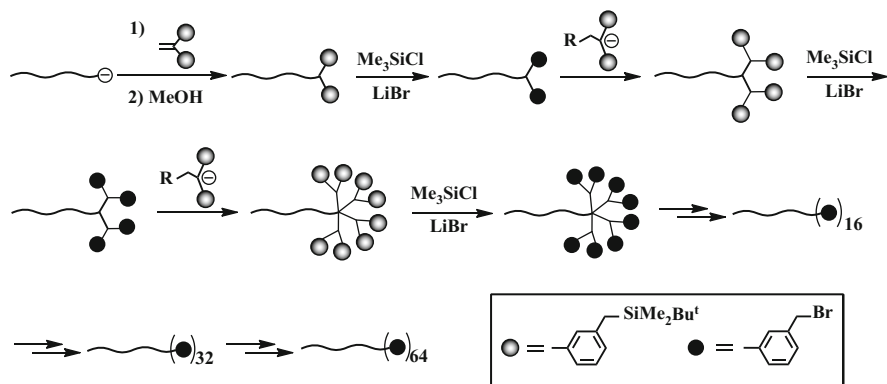
Scheme 7 Synthesis of chain-end-(BnBr)$_n$-multifunctionalized PSs by iterative methodology

with the resulting chain-end-(BnBr)$_2$-functionalized PS to introduce four TBDMOSiMP groups at the chain end. They were transformed into four BnBr reaction sites by the same treatment as that used above. These two reactions exactly correspond to the above-mentioned two reaction steps, respectively. Since the two reactions were observed to quantitatively proceed, the same process could be repeated. In fact, the number of BnBr reaction sites exponentially increased from 8 (2^3) to 16(2^4), 32(2^5), and 64 (2^6). The results are summarized in Table 1.

A star PS was synthesized by the linking reaction of PSLi (M_n = ca. 5,000 g/mol) with each of the chain-end-(BnBr)$_n$-multifunctionalized PSs (M_n values of PSs = ca. 5,000 g/mol) in THF at $-78\,^{\circ}$C. Prior to the linking reaction, PSLi was end-capped with DPE to avoid any side reaction. The reaction was very fast and actually completed within 1 h under such conditions to result in 3-, 5-, 9-, 17-, and 33-arm star PSs. Their structures were all well defined, as confirmed by the SEC and SLS analyses listed in Table 2.

Since living PMMA cannot react with *1* of the DPE derivative, the DPE anion is used as an initiator in the living anionic polymerization of MMA to introduce two TBDMOSiMP groups at the initiating chain end. As shown in Scheme 8, the same iterative reaction process was performed to increase the number of the BnBr reaction sites by repeating the process [54]. The reaction of the living PMMA (M_n = ca. 10,000 g/mol) with the chain-end-(BnBr)$_n$-multifunctionalized PMMAs (M_n values of PMMAs = ca. 10,000 g/mol) in THF at $-78\,^{\circ}$C quantitatively yielded well-defined 3-, 5-, 9-, and 17-arm star PMMAs (see also Table 3).

Next, several living anionic polymers with different reactivities were reacted with the chain-end-(BnBr)$_8$-multifunctionalized PS in order to investigate the reactivity of the BnBr reaction site. These polymer segments were all adjusted to be ca. 10,000 g/mol in M_n value. Both PBLi and PILi were end-capped with DPE and subsequently reacted in situ with the BnBr-functionalized PS in THF at $-78\,^{\circ}$C for 1 h. Under such conditions, 8 PB or 8 PI segments were readily and quantitatively coupled to afford well-defined 9-arm AB$_8$ μ-star polymers composed of PS (A) and PB (B) or PI(B) arms in virtually quantitative yields (see Scheme 9).

Table 1 Characterization results of chain-end-$(BnBr)_n$-multifunctionalized PSs

| Polymer	M_n (g/mol)		M_w/M_n	BnBr functionality	
	calcd	VPO	SEC	calcd	^{1}H NMR
PS(BnBr)$_2$	4,790	4,800	1.04	2	2.0$_0$
PS(BnBr)$_4$	5,470	5,420	1.04	4	3.9$_2$
PS(BnBr)$_8$	6,850	6,780	1.03	8	8.0$_8$
PS(BnBr)$_{16}$	9,590	9,640	1.04	16	15.9
PS(BnBr)$_{32}$	15,000	14,800	1.03	32	32.0
PS(BnBr)$_{64}$	25,600	24,700	1.03	64	64.2

Table 2 Synthesis of PS star polymers with 3, 5, 9, 17, and 33 arms by the linking reaction of PSLis with chain-end-$(BnBr)_n$-multifunctionalized PSs

Star polymer number of arms	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
3	17,900	17,800	1.03
5	26,800	26,600	1.04
9	44,000	44,700	1.03
17	88,100	87,600	1.05
33	190,000	196,000	1.02
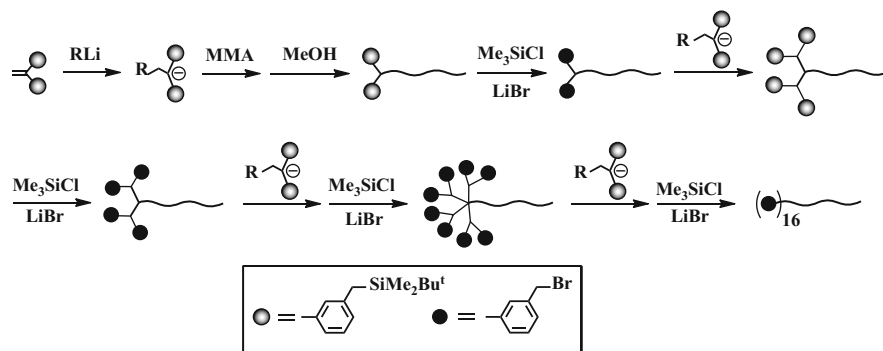
Scheme 8 Synthesis of chain-end-$(BnBr)_n$-multifunctionalized PMMAs by iterative methodology

Table 3 Synthesis of PMMA star polymers with 3, 5, 9, and 17 arms by the reaction of chain-end-$(BnBr)_n$-multifunctionalized PMMAs with living PMMAs

Star polymer number of arms	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
3	39,900	40,500	1.02
5	59,600	61,500	1.02
9	99,600	105,000	1.02
17	208,000	205,000	1.04

9 arm AB$_8$ μ-star polymer

B : PI, PB, P2VP, PMMA, PtBMA, PEO

$M_n = \sim 100\ 000$ g/mol, $M_w/M_n \sim 1.03$
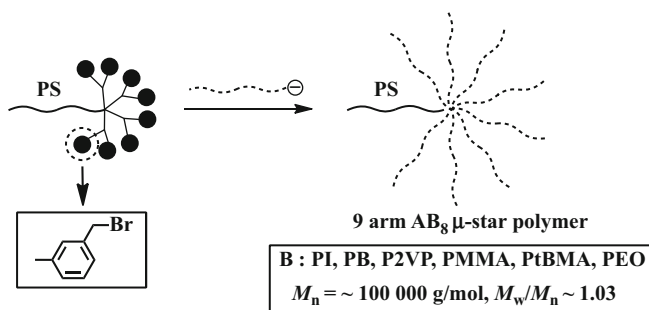
Scheme 9 Synthesis of 9-arm AB$_8$ μ-stars by the reaction of chain-end-(BnBr)$_8$-functionalized PS with various living anionic polymers

Similarly, the quantitative synthesis of a 9-arm AB$_8$ star polymer, whose B arm was P2VP or P^{t}BMA, was also achieved by reacting either the living P2VP or P^{t}BMA with the same BnBr-functionalized PS under identical conditions. The reaction of living PEO bearing K$^+$ with the BnBr-functionalized PS resulted in a 100 % linking of the eight PEO chains by adding DMF (ca. 20 vol %) as a cosolvent and gradually raising the temperature to 40 °C for 24 h. Thus, the eight BnBr reaction sites all were satisfactorily reacted with a variety of living anionic polymers to afford the corresponding star polymers. Based on these results, the methodology using the BnBr reaction sites demonstrated the possible synthesis of the multiarmed regular PS, PB, PI, P2VP, PMMA, P^{t}BMA, and PEO stars [55]. The latter three star polymers were observed to be practically stable, since PMMA, P^{t}BMA, or PEO arms were linked at the cores via stable C-C or C-O bonds.

It should be noted that the insufficient coupling reactions of chain-end-(BnBr)$_8$-multifunctionalized PSs ($M_n = 100$ kg/mol) were observed with very high-molecular-weight living anionic polymers having M_n values of more than 100 kg/mol even for longer reaction times of 48–168 h. This is at least partly due to the steric hindrance around the reaction sites at the core.

2.4 Arm-First Termination Methodology Using DPE Reaction Site

The final methodology is also based on the arm-first termination methodology involving the DPE reaction sites in conjunction with iterative approach. However, the iterative approach employed in this methodology is different in mechanism from those described in sections "Arm-first termination methodology using multifunctional chlorosilane reaction site" and "Arm-first termination methodology using BnBr reaction site." In the first two iterative approaches used above, the number of the reaction sites increased by repeating the iterative process and the arm segments were then introduced via the prepared reaction sites, resulting in
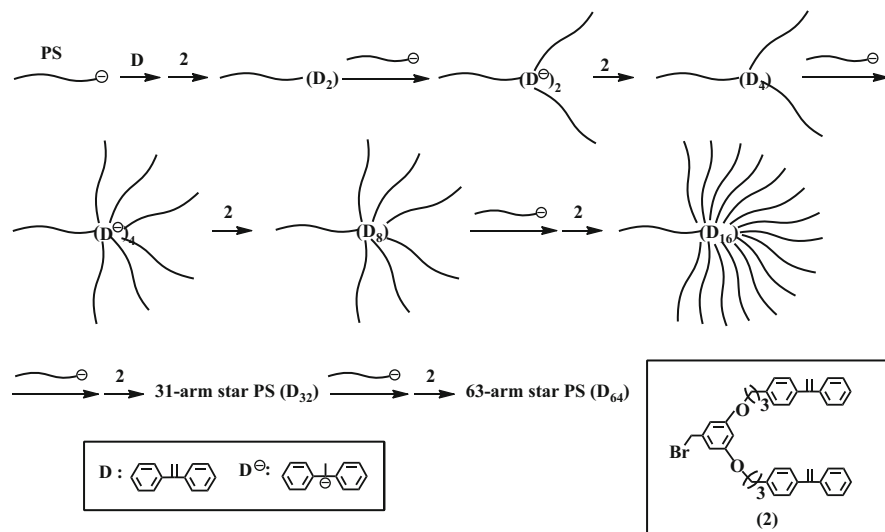
Scheme 10 Synthesis of multiarmed PS stars by iterative methodology using DPE reaction sites

multiarmed star polymers. On the other hand, the iterative approach herein proposed is designed so as to introduce both the reaction sites and arm segments at the same time in each iterative process. Accordingly, each process yields a star polymer and the resulting star polymer is always employed as the starting polymer in the next process. Since the synthetic significance of this methodology will be emphasized in the next section, a possible application to the synthesis of multiarmed star polymer is now described.

As shown in Scheme 10, a new DPE-functionalized agent, 3,5-bis (3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl bromide (2), is used as the key compound in each iterative process [56]. All the polymer segments were fixed at ca. 10,000 g/mol in M_n value throughout the synthesis. PSLi was initially end-capped with DPE and subsequently reacts with 2 to introduce two DPE reaction sites at the chain end. The addition reaction of two equivalents of PSLi to the two DPE reaction sites at the PS chain end was essentially quantitative, resulting in a 3-arm star PS having two DPE anions generated at the linking points. The four DPE reaction sites were introduced by in situ reacting 2 with the generated two DPE anions. Thus, the introduction of two PS arms and four DPE reaction sites was achieved in this process. Since the star PS had the same DPE reaction sites at the core and the two reaction steps were virtually quantitative, the same reaction process could be repeated four more times to successively afford the 7-, 15-, 31-, and 63-arm star PSs.

The yield of the 7-arm star PS was quantitative in THF at −78 °C within 1 h. However, the reaction was not complete in the next process under the same conditions. Accordingly, the reaction conditions were altered as follows: in *tert*-butylbenzene at 30 °C for 168 h (the second process) and in *tert*-butylbenzene with

Table 4 Synthesis of multiarmed star PSs by iterative methodology using DPE reaction sites via 2

Star PS arm number	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
3	32,200	33,700	1.03
7	79,400	79,000	1.04
15	163,000	166,000	1.05
31	330,000	330,000	1.05
63	625,000	623,000	1.03
127(113)	1,290,000	1,113,000	1.05

two equivalents of TMEDA at 40 °C for 72 h (the third and fourth processes). A further attempt for the synthesis of a 127-arm star PS by reacting PSLi with the core-(DPE)$_{64}$-functionalized 63-arm star PS was not successful even under the same conditions. The resulting polymer was found to possess on average 113 arms. The insufficient linking reaction may be attributed to the steric hindrance around the reaction sites as well as the ionic repulsions among the unreacted anionic sites and (PSLi)s.

As summarized in Table 4, a series of star PSs thus synthesized, except for the 113-arm star PS, was confirmed by ^{1}H NMR, SEC, and SLS to be well defined in star architecture and precisely controlled in arm segment. Even the 113-arm star PS possessed a narrow molecular weight distribution. Thus, this methodology demonstrates the high synthetic potential of the multiarmed star PSs. However, it should be mentioned that only highly reactive living anionic polymers capable of reacting with the DPE function, such as PSLi, PBLi, and PILi, are able to be used at the moment.

This iterative methodology can readily be changed to the original ones shown in sections "Arm-first termination methodology using multifunctional chlorosilane reaction site" and "Arm-first termination methodology using BnBr reaction site" as follows: The reaction of the chain-end-(DPE)$_2$-functionalized PS with two equivalents of sec-BuLi instead of PSLi, followed by in situ reacting the generated DPE anion with 2, yielded a chain-end-(DPE)$_4$-functionalized PS. By repeating the same reaction sequence, the DPE reaction sites increased 8, 16, followed by 32 in number. This indicates that the two original methodologies can also possibly be changed to the second alternative iterative one, with which arms as well as reaction sites are introduced at the same time.

In conclusion, the synthesis of regular star polymers has almost been established in cases using the arm-first termination methodologies with a variety of living anionic polymers with different reactivities. Indeed, regular star PS, PB, PI, P2VP, PMMA, P^{t}BMA, and PEO were successfully synthesized by carefully choosing the reaction site. The resulting stars all have well-defined architectures with controllable molecular weights, narrow molecular weight distributions, and many arms ranging from 6 to 63. A variety of functional star polymers can now be synthesized by applying the living anionic polymerization of new functional styrene derivatives to the above methodologies (see chapter Non-polar monomers:

styrene and 1,3-butadiene derivatives). Furthermore, a variety of recently developed living anionic polymers derived from cyclic monomers may also be usable in these methodologies, resulting in new well-defined multiarmed star polymers.

3   Asymmetric Star Polymers

As mentioned in the introduction, star polymers are usually categorized into regular and asymmetric star polymers. The asymmetric star polymer further subdivides into the following three types according to their architectures: (1) chemical structure asymmetry, (2) molecular-weight asymmetry, and (3) topological asymmetry, as illustrated in Fig. 1. Among them, we now focus on the chemical structure asymmetry-based miktoarm star polymers. These miktoarm arm star (abbreviated μ-star) polymers are classified as nonlinear branched block polymers and have recently attracted much attention because their morphological nanoscale suprastructures and supramolecular assemblies formed in bulk as well as selected solvents are new, characteristic, and, more importantly, quite different from those produced by linear block polymers. These structures and assemblies are expected to play important roles in the fields of nanoscience and nanotechnology with many potential applications. Accordingly, the μ-star polymers are currently recognized as a promising next-generation multiphase polymeric material.

In order to elucidate the formation of such structures and assemblies in detail, well-defined architectures and precisely controlled arm segments in μ-star polymers are strongly demanded. In general, such μ-star polymers are much more difficult in synthesis than regular star polymers due to the following requirements and still a challenging subject even now: (1) multistep reactions to introduce a number of different arms, (2) isolation of the intermediate polymers to obtain pure products, and, most importantly, (3) several different reaction sites selectively worked for the introduction of each arm. These requirements make the molecular design and practical synthesis of multiarmed and multicomponent μ-star polymers extremely difficult. Accordingly, the methodologies currently developed can mainly cover two-component A_xB_y types and several examples of three-component ABC type μ-star polymers. Only a few synthetic examples of the four-component ABCD μ-stars have been reported. Moreover, structural variation is considerably limited in the three- and four-component star polymer syntheses. There is no report about the synthesis of the five-component ABCDE or more-component μ-star polymers except for those to be introduced later. As emphasized in the introduction part, the living anionic polymerization is the most suitable system for the synthesis of well-defined μ-star polymers because of the excellent abilities to precisely control many structural variables.

In the first half of this section, the methodologies established so far for the synthesis of three- and/or four-component μ-star polymers will be introduced. The recently developed methodologies based on iterative strategy possible for the synthesis of multiarmed and multicomponent μ-star polymers will then be described in the latter half.
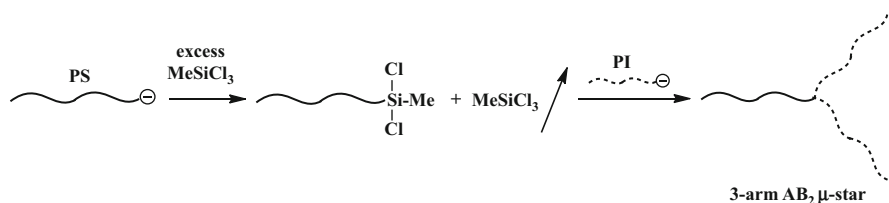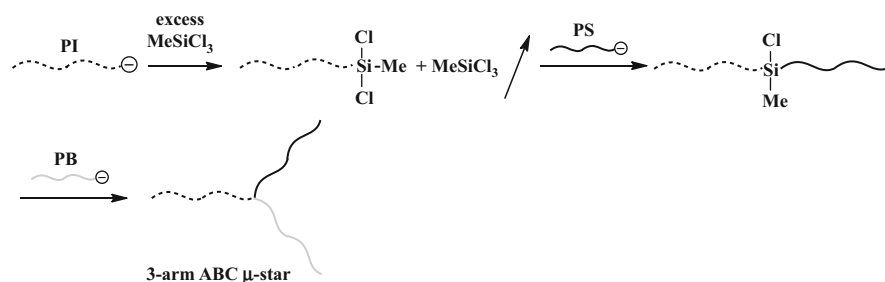
Scheme 11 Synthesis of 3-arm AB_2 µ-star polymer by the chlorosilane methodology

3.1 Methodology Using Chlorosilane Reaction Site

As mentioned in section "Arm-first termination methodology using multifunctional chlorosilane reaction site," multifunctional chlorosilane compounds are some of the most effective reaction sites to synthesize multiarmed regular star polymers as these compounds readily and quantitatively react with the living anionic polymers. In the synthesis of regular stars using multifunctional chlorosilane compounds, the reactivity of the living anionic polymer toward the Si-Cl bond was found to follow the sequence of PBLi > PILi > PSLi mainly due to the steric bulkiness of the chain-end anion. It was also found that the reactivity of the Si-Cl bond for the chain-end anion decreased as replacing the chlorine atom by the polymer chain by both the electron donating effect and steric hindrance. By utilizing such different reactivities, the methodology using multifunctional chlorosilane compounds was significantly developed to be an effective procedure for the synthesis of a variety of µ-star polymers.

Mays was the first to successfully synthesize a well-defined µ-star polymer of the 3-arm AB_2 type composed of PS (A) and PI (B) by the chlorosilane methodology, as illustrated in Scheme 11 [57]. The most sterically bulky and thereby less reactive PSLi first reacted with a large excess of MeSiCl$_3$ to prepare a chain-end-(SiCl$_2$)-functionalized PS and, after removal of the excess unreacted MeSiCl$_3$ in situ under high vacuum conditions, the more reactive PILi was reacted with the SiCl$_2$ terminus of PS, resulting in a 3-arm AB_2 µ-star polymer. The addition order of the living polymer is important in this case. For example, the reverse addition order makes it difficult to synthesize an in-chain-(SiCl)-functionalized (PI)$_2$ and finally introduce a PS chain into the core, due to the combination between the less reactive Si-Cl reaction site and sterically hindered PSLi. This methodology was developed by Hadjichristidis et al. to synthesize all possible combinations of the AB_2 star polymers, in which the A and B arms were PS, PB, or PI [58, 59]. Furthermore, an AB_3 µ-star polymer was synthesized in a similar manner using SiCl$_4$ instead of MeSiCl$_3$ [60–62].

The same group also successfully synthesized a 3-arm ABC µ-star composed of PS, PI, and PB arms for the first time by utilizing such different reactivities, as shown in Scheme 12 [63]. In the synthesis, PILi first reacted with a large excess of MeSiCl$_3$ to replace the chlorine atom by the PI chain to prepare a chain-end-(SiCl$_2$)-functionalized PI and the excess unreacted MeSiCl$_3$ was removed under

Scheme 12 Synthesis of 3-arm ABC μ-star by the chlorosilane methodology
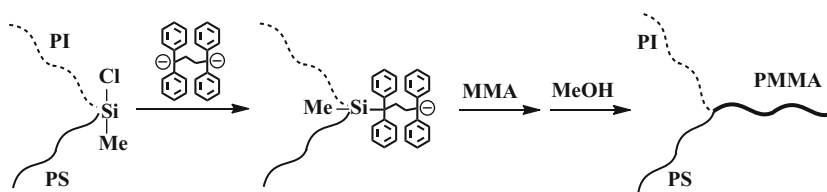
Scheme 13 Synthesis of 3-arm ABC μ-star polymer composed of PS, PI, and PMMA

high vacuum. The most bulky and least reactive PSLi was stoichiometrically reacted in situ with the Si-Cl terminus by a colorimetric titration changing from an orange-red to colorless. No more linking of the PSLi occurred by employing this technique in addition to the steric hindrance of PSLi. Finally, the most reactive PBLi was reacted with the least reactive in-chain-(SiCl)-functionalized PI-*b*-PS to afford a target 3-arm ABC μ-star with well-defined structures ($M_n = 45.4$ kg/mol, $M_w/M_n = 1.03$). Furthermore, a 4-arm ABCD μ-star polymer was synthesized by a similar procedure, in which PSLi, poly(4-methylstyryl)lithium (PMSLi), PILi, followed by PBLi, were sequentially added to SiCl$_4$ [64]. This polymer was the first successful four-component μ-star polymer ($M_n = 62.5$ kg/mol, $M_w/M_n = 1.05$). A very interesting ABC μ-star containing PDMS ($M_n = 58.9$ kg/mol, $M_w/M_n = 1.04$) could also be synthesized by reacting the above-prepared in-chain-(SiCl)-functionalized PS-*b*-PI with the living PDMS [65]. The methodology further demonstrated the effective synthesis of a variety of μ-star polymers, such as the AB$_3$, A$_2$B$_2$, AB$_5$, and A$_8$B$_8$ types, where A and B arms are PS, PI, PB, 2-methyl-1,3-pentadiene, 1,3-cyclohexadiene, and their block copolymer segments. The resulting polymers were all well defined in structure with narrow molecular weight distributions ($M_w/M_n \sim 1.05$) [66–73].

Unfortunately, the living PMMA and other related living polymers derived from alkyl methacrylate monomers cannot be directly applied in this effective methodology, because the silyl enol ether linkage formed between the PMMA arm and the core is readily hydrolyzed even with moisture in the air. In order to introduce the PMMA segment into the μ-star polymer, the reaction site was converted from the Si-Cl reaction site to a DPE anion, as illustrated in Scheme 13. After the in-chain-

(SiCl)-functionalized PS-*b*-PI was prepared in the same manner as that mentioned above, the Si-Cl reaction site was reacted with a dilithium compound, Li (CPh$_2$CH$_2$CH$_2$CPh$_2$)Li, to convert it to the DPE anion. This new anionic reaction site was used as an initiator for the polymerization of MMA, resulting in a 3-arm ABC μ-star polymer composed of PS, PI, and PMMA arms ($M_n = 77.0$ kg/mol, $M_w/M_n = 1.06$) [74]. This modification of the reaction site is advantageous in this respect that any monomer besides MMA that undergoes the living anionic polymerization with the DPE anion can be used.

Thus, a variety of well-defined three- and four-component μ-star polymers can be synthesized by utilizing the different reactivity of the living anionic polymer toward the Si-Cl reaction site as well as the reactivity difference of the Si-Cl bond by the number of chlorine atoms on the Si atom. On the other hand, the reaction order of the living polymers is very critical and limited by the above-mentioned reactivity differences. Moreover, the final linking reaction steps often take longer times even for a few months. Although the living polymers of MMA, other alkyl methacrylates, and ethylene oxide cannot be used in the original methodology, the development of the modified methodology with the anionic reaction site enables the introduction of these polymer segments into the stars.

3.2 Methodology Using Dual-Functionalized Reaction Sites

In 1992, Fujimoto et al. reported a general and versatile methodology for the synthesis of 3-arm ABC μ-star polymers by utilizing the dual-functionalized character of the DPE derivatives [75]. As illustrated in Scheme 14, a chain-end-DPE-functionalized PDMS was first prepared by the polymerization of hexamethylcyclotrisiloxane (D$_3$) with lithium alkoxide of the DPE derivative (see Scheme 14) and then reacted with PSLi to link the PDMS with the PS segment. Since a DPE anion was newly generated by this addition reaction, ^{t}BMA was subsequently added in situ to polymerize with the generated DPE anion, resulting in a 3-arm ABC μ-star polymer composed of PDMS, PS, and P^{t}BMA arms ($M_n = 59.0$ kg/mol and $M_w/M_n = 1.06$). The DPE function works as a dual-functionalized agent, which provides a linking site at first, followed by an initiation site. Consequently, the two different arm segments could be separately introduced. This means that the 3-arm ABC μ-star polymers can always be synthesized with the use of a chain-end-DPE-functionalized polymer as the starting material. Thus, this methodology combines the "arm-first" termination method to link two polymer chains with the "core-first" initiation method to grow the third arm segment. In the final step, any monomer undergoing the living anionic polymerization with the DPE anion can be used. Because of fewer operation steps and more choices of possible monomers including several cyclic monomers, the methodology has been further developed for the synthesis of various 3-arm μ-star polymers by Abetz et al. [1, 76] and recently Matsushita et al. [2, 77–81]. They used 1-(4-bromomethylphenyl)-1-phenylethylene or 1-(3-(3-chloropropyldimethylsilyl)phenyl)-1-phenylethylene in
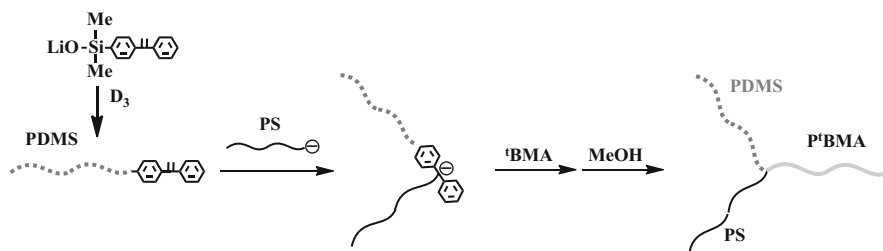
Scheme 14 Synthesis of 3-arm ABC μ-star polymer by the methodology using DPE dual-functionalized reaction site
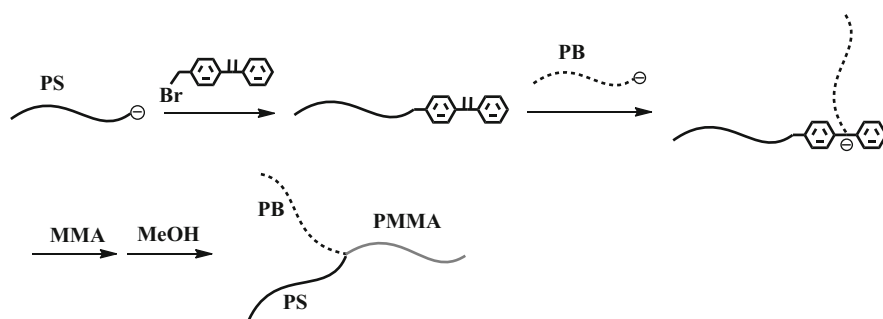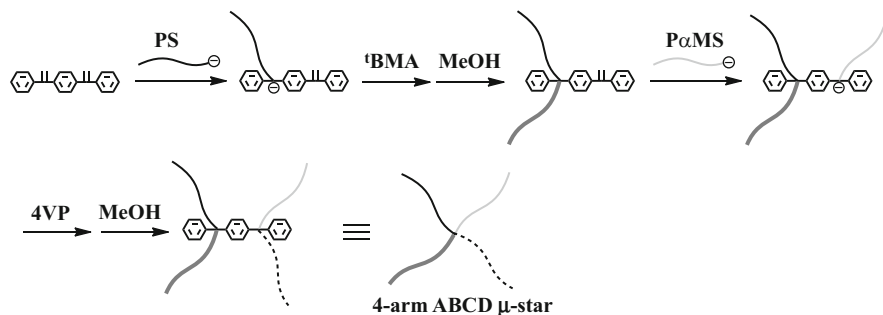

Scheme 15 Synthesis of 3-arm ABC μ-star polymer by the methodology using DPE reaction site

Table 5 Synthesis of 3-arm ABC μ-star polymers by the methodology using DPE reaction site

3-arm ABC μ-star					
A	B	C	M_n (g/mol)	M_w/M_n	lit.
PS	PB	PMMA	250,000	1.13	76
PS	PB	P2VP	96,000	1.01	1
PS	PB	P2VP	288,000	1.04	1
PS	PB	P2VP	134,000	1.04	77
PS	PB	P2VP	199,000	1.04	77
PS	PI	P2VP	154,700	1.02	2
PS	PI	P2VP	192,100	1.02	2
PS	PI	P2VP	241,000	1.03	79
PS	PI	P2VP	401,000	1.04	79

order to introduce the DPE functionality in the starting polymer. Scheme 15 shows the synthesis of the 3-arm ABC μ-star polymer composed of PS, PB, and PMMA arms. Representative μ-star polymers synthesized by this methodology are summarized in Table 5.

It was further reported that several functional DPE derivatives effectively work as the suitable nodules for the synthesis of the μ-star polymers. Quirk et al. synthesized a 4-arm A_2B_2 μ-star polymer by the addition reaction of two
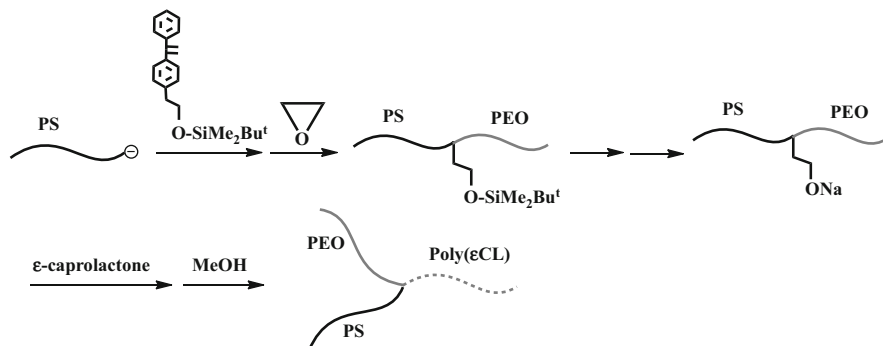
Scheme 16 Synthesis of 4-arm ABCD μ-star polymer by the methodology using two DPE reaction sites

equivalents of PSLi with 1,3-bis(1-phenylethenyl)benzene, which is regarded as a DPE derivative substituted with the DPE function, followed by the polymerization of 1,3-butadiene with the two generated DPE anions ($M_n = 23.4$ kg/mol and $M_w/M_n = 1.05$) [82]. Similarly, another 4-arm A_2B_2 star composed of PS and PMMA arms was synthesized by Young et al. ($M_n = 58.9$ kg/mol and $M_w/M_n = 1.03$) [83]. Quirk et al. also demonstrated the synthesis of a 3-arm AA′A″ star PS composed of three PS arms with different M_n values using 1,4-bis (1-phenylethenyl)benzene [84]. Unlike the reaction of PSLi with the above *meta*-isomer, the PSLi underwent the 1:1 addition reaction with this *para*-isomeric DPE derivative and no more addition occurred due to the delocalization of the generated anion. After quenching with methanol, another PSLi reacted with the resulting chain-end-DPE-functionalized PS, followed by polymerization of the styrene monomer, resulting in the above 3-arm star PS with molecular weight asymmetry. This synthetic success indicates the possible synthesis of 3-arm ABC μ-stars.

He et al. reported that the methodology using the above *para*-isomer allowed access to a 4-arm ABCD μ-star polymer synthesis [85]. The synthesis also takes advantage of the 1:1 addition reaction, as illustrated in Scheme 16. PSLi first reacted with 1,4-bis(1-phenylethenyl)benzene in the 1:1 addition manner, followed by the polymerization of ᵗBMA with the generated DPE anion. Poly (α-methylstyryl)lithium (PαMSLi) then reacted with the residual DPE moiety to link the PαMS chain, and 4-vinylpyridine (4VP) was subsequently in situ polymerized to grow the fourth arm, resulting in a 4-arm ABCD μ-star composed of PS, PᵗBMA, PαMS, and P4VP arms ($M_n = 30.0$ kg/mol and $M_w/M_n = 1.05$).

Dumas et al. developed the methodology using 1-(2-*tert*-butyldimethylsilyloxy-yethylplenyl)-1-phenylethylene for the synthesis of different types of 3-arm ABC star polymers [86, 87] (see Scheme 17). PSLi was first reacted with the above DPE derivative, followed by the polymerization of ethylene oxide, to afford the in-chain-functionalized PS-*b*-PEO. The 2-*tert*-butyldimethylsilyloxyethyl group between the two blocks was then deprotected to regenerate the hydroxyl group, which was converted to sodium alkoxide by treatment with Ph₂CHNa. The resulting sodium alkoxide function was used as the anionic initiator for the ring-opening
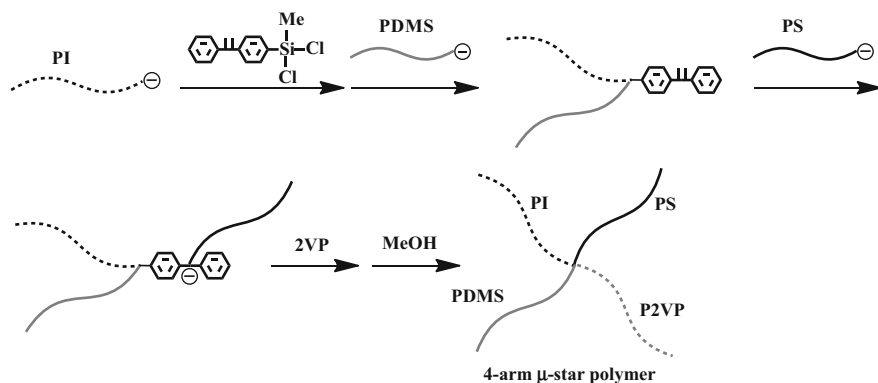
Scheme 17 Synthesis of 3-arm ABC μ-star polymer by the methodology using DPE reaction site
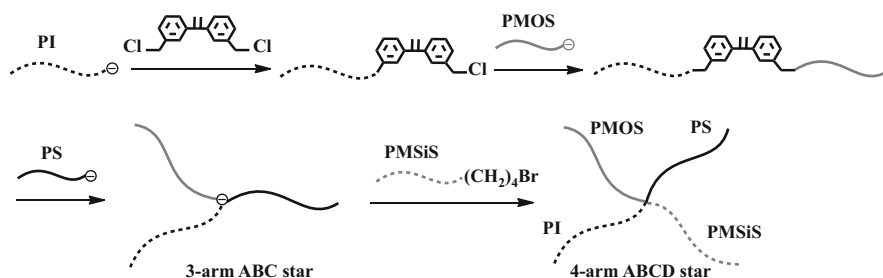
Scheme 18 Synthesis of 3-arm ABC and 4-arm ABCD μ-star polymers by the methodology using DPE reaction site

polymerization of ε-caprolactone, resulting in a 3-arm ABC star composed of PS, PEO, and poly(ε-caprolactone) arms ($M_n = 112$ kg/mol and $M_w/M_n = 1.29$). Similarly, another 3-arm ABC star composed of PS, PEO, and P^{t}BMA arms was synthesized.

Hirao et al. successfully synthesized a 3-arm ABC, followed by a 4-arm ABCD μ-star polymer, by the methodology with 1,1-bis(3-chloromethylphenyl)ethylene, as illustrated in Scheme 18 [88, 89]. A chain-end-(BnCl and DPE)-functionalized PI was first prepared by the reaction of the DPE-end-capped PILi with an excess of the above DPE derivative and subsequently reacted with the DPE-end-capped poly (4-methoxystyryl)lithium (PMOSLi) to prepare an in-chain-DPE-functionalized PI-*b*-PMOS. A 3-arm ($M_n = 31.8$ kg/mol and $M_w/M_n = 1.03$) was synthesized by reacting PSLi with the resulting DPE-functionalized PI-*b*-PMOS. The reaction of the intermediate 3-arm ABC star anion formed by the above reaction with a chain-end-(4-bromobutyl)-functionalized poly(4-trimethylsilylstyrene) (PMSiS) yielded a 4-arm ABCD μ-star polymer ($M_n = 43.0$ kg/mol and $M_w/M_n = 1.04$) composed of PI, PMOS, PS, and PMSiS arms. With the use of an in-chain-DPE-functionalized A$_2$ polymer in place of the in-chain-DPE-functionalized AB diblock copolymer in the above methodology, all possible 3- and 4-arm μ-star polymers including A$_2$B,
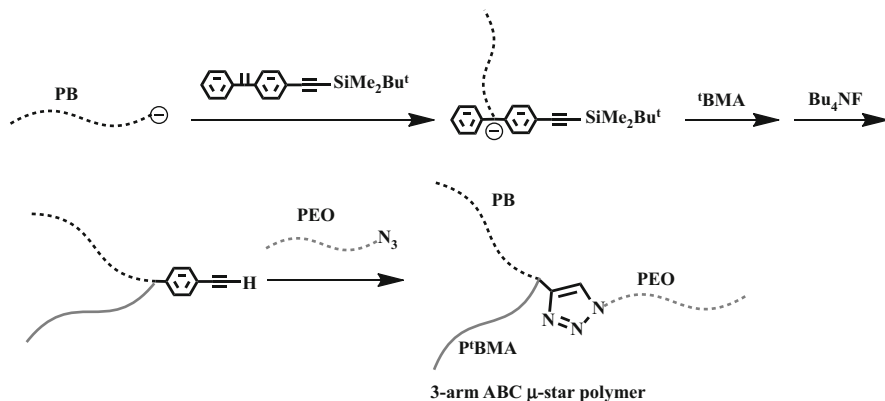
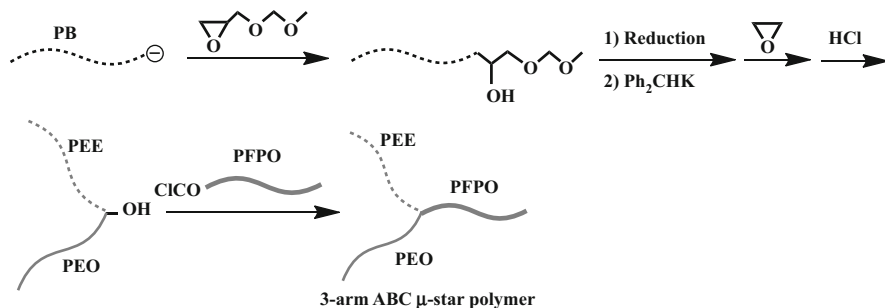**Scheme 19** Synthesis of 4-arm ABCD μ-star polymer by the methodology using chlorosilane and DPE reaction sites

AB_2, AB_3, A_2B_2, A_3B, A_2BC, AB_2C, and ABC_2 in addition to the ABC and ABCD types were successfully synthesized. The starting in-chain-DPE-functionalized A_2 was prepared by reacting two equivalents of a DPE-end-capped living polymer (A) with 1,1-bis(3-chloromethylphenyl)ethylene.

Hadjichristidis et al. successfully synthesized a 4-arm ABCD μ-star polymer by adding the dual functionality of DPE in the methodology with multifunctional chlorosilane compounds [90]. As shown in Scheme 19, 1-(4-dichloromethylsilylphenyl)-1-phenylethylene of a new DPE derivative was used as the key compound and PILi, followed by the living PDMS, was selectively replaced with the two chlorine atoms of this DPE to prepare an in-chain-DPE-functionalized PI-*b*-PDMS. The target 4-arm μ-star polymer was synthesized by the addition reaction of PSLi to the in-chain DPE function and the subsequent polymerization of 2VP with the generated DPE anion ($M_n = 75.9$ kg/mol and $M_w/M_n = 1.06$). A series of 4-arm A_2B_2, 4-arm A_2BC, and 5-arm A_2B_2C μ-star polymers were also synthesized by the similar methodologies ($M_n = 88.7$, 96.4, 109 kg/mol and $M_w/M_n = 1.05$, 1.02, 1.02). Their A, B, and C arms are PDMS, PS, and PI, respectively.

Recently, Müller et al. reported the methodology by combining a DPE derivative having a protected alkyne functionality with the azide–alkyne Huisgen cycloaddition reaction to synthesize the 3-arm ABC μ-star polymers [91]. As shown in Scheme 20, PBLi reacts with 1-((4-*tert*-butyldimethylsilyl)ethynyl)phenyl-1-phenylethylene, and ^{t}BMA was subsequently polymerized to prepare an in-chain-(ethynyl)-functionalized PB-*b*-P^{t}BMA. A chain-end-N_3-functionalized PEO was separately prepared by the anionic ring-opening polymerization, followed by terminating with azido acid chloride, and reacted with the in-chain ethynyl function of PB-*b*-P^{t}BMA to link the PEO chain, resulting in a 3-arm ABC μ-star composed of PB, P^{t}BMA, and PEO arms ($M_n = 32.7$ kg/mol and $M_w/M_n = 1.04$). Other 3-arm star polymers composed of PB, P^{t}BMA, PS and PB, P^{t}BMA, poly(2-*N*,*N*-dimethylaminoethyl methacrylate) arms were synthesized by the same procedure (M_ns = 20.8–32.5 kg/mol and M_w/M_ns = 1.03–1.11).

Scheme 20 Synthesis of 3-arm ABC μ-star polymer by the methodology using DPE reaction site in conjunction with Click reaction

Scheme 21 Synthesis of 3-arm ABC μ-star polymer by the methodology using EO reaction site

Hillmyer et al. developed a new, but basically similar methodology using the dual functionality of the EO derivative in place of the DPE function in order to synthesize two interesting 3-arm ABC star polymers, as illustrated in Scheme 21 [92–94]. The synthesis was started by the reaction of PBLi with methoxymethoxyoxirane to prepare a chain-end-functionalized PB with hydroxyl and acetal-protected hydroxyl functionalities. After catalytic hydrogenation of the PB main chain for conversion to poly(ethylethylene) (PEE), the hydroxyl group was changed to potassium alkoxide, followed by the polymerization of EO to afford an in-chain-OH-functionalized PEE-*b*-PEO after removal of the acetal protection. Two 3-arm ABC μ-star polymers composed of PEE, PEO, poly(γ-methyl-ε-caprolactone) arms ($M_n = 18.8$ kg/mol and $M_w/M_n = 1.22$) and PEE, PEO, poly(perfluoropropylene oxide) (PFPO) ($M_n = 17.9$ kg/mol and $M_w/M_n = 1.08$) were synthesized by the anionic ring-opening polymerization of γ-methyl-ε-caprolactone and the esterification reaction with a chain-end-(COCl)-functionalized PFPO, respectively.

As often mentioned, the dual-functionalized agent like the DPE and EO derivatives enables the sequential introduction of two of the same or different polymer chains into the core via the linking and initiation sites. Accordingly, if this agent is attached to a

polymer chain in advance, 3-arm ABC μ-star polymers can be synthesized by introducing two different polymer chains via the dual-functionalized reaction sites. If the agent is incorporated between two blocks in the block copolymer, the synthesis of 4-arm ABCD μ-star polymers may be feasible. Furthermore, 3-arm ABC and 4-arm ABCD stars can be synthesized in a similar manner using the DPE derivative having the function(s) capable of linking with other polymer chain(s). The methodologies herein introduced are all based on such mechanisms.

3.3 Methodologies Based on Iterative Strategy

The generality and versatility of the methodologies described above were demonstrated for the effective synthesis of three- and four-component μ-star polymers with well-defined structures. However, these methodologies cannot be used for the synthesis of more component and armed μ-star polymers, since the reaction site (s) always disappears after the introduction of arm(s) in the final stage and thereby the arm can be no longer introduced.

In order to overcome this difficulty, Hirao, Higashihara et al. have proposed a novel methodology, which is based on a new conceptual "*iterative strategy*," since 2001. In this methodology, the reaction system is designed in such a way that the same reaction site is regenerated after the introduction of an arm segment in each reaction sequence and this "arm introduction–regeneration of the same reaction site" sequence is repeatable. Accordingly, the same or different arm segment can be successively and, in principle, limitlessly introduced by repeating the reaction sequence, resulting in the synthesis of a series of many component and armed μ-star polymers. Since a new reaction site is always regenerated for the next reaction stage, several reaction sites selectively worked for the introduction of a number of arms are not needed and the above-mentioned complicated and practically difficult synthetic design can be avoided in this proposed iterative methodology. A variety of iterative methodologies using different reaction sites have been significantly developed based on the same concept and can allow access to a variety of synthetically difficult multiarmed and multicomponent μ-star polymers [10–13, 17, 95, 96].

3.3.1 Iterative Methodologies Using DPE Reaction Site

The first successful iterative methodology, in which a DPE function is used as the reaction site, is illustrated in Scheme 22. At first, a chain-end-DPE-functionalized A was prepared as the starting material by reacting a DPE-end-capped living polymer (A) with 1-(4-(3-bromopropylphenyl))-1-phenylethylene (*3*) [97]. In the first iterative process, the resulting chain-end-DPE-functionalized A was reacted with another living polymer (B) to link the B chain with the A segment, and a DPE anion was produced at the linking point by the linking reaction. The agent, *3*, was then in situ reacted with this DPE anion to reintroduce the DPE function. Thus, the linking
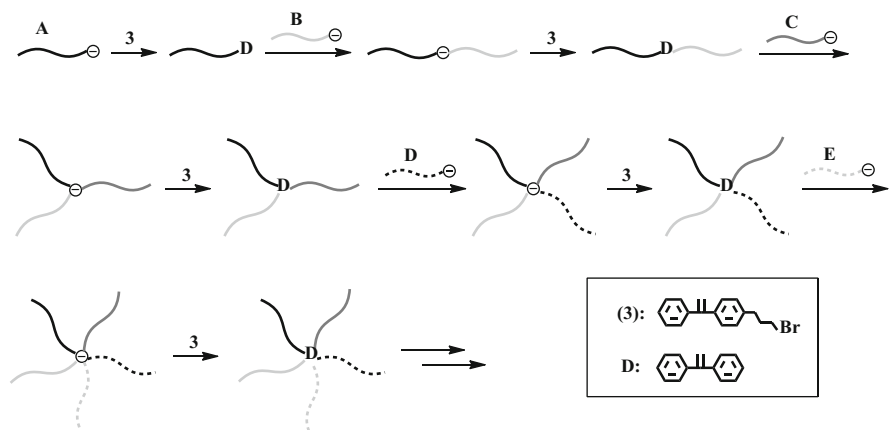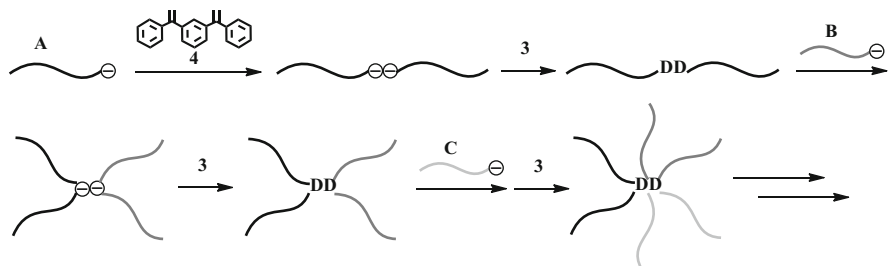
Scheme 22 Iterative methodology using DPE reaction site

Table 6 Synthesis of µ-star polymers by iterative methodology using DPE reaction site

Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
A	10,500	10,700	1.03
AB diblock	21,300	22,000	1.02
3-arm ABC	32,000	34,400	1.02
4-arm ABCD	42,800	43,000	1.02
5-arm ABCDE	59,300	57,000	1.02

reaction and the reaction of the DPE anion with *3* exactly correspond to "the arm introduction" and "the reaction site regeneration" steps, respectively. Since the resulting A-*b*-B possesses the DPE reaction site introduced between the two blocks, the same reaction process can be repeated. In fact, living polymer (C) reacted with the in-chain-DPE-functionalized A-*b*-B, followed by reacting with *3*, resulting in a 3-arm ABC µ-star polymer core functionalized with the DPE reaction site. By repeating the same process two more times with the sequential uses of living polymers (D) and (E), 4-arm four-component ABCD and 5-arm five-component ABCDE µ-star polymers were successfully synthesized. The DPE reaction site is capable of not only undergoing the linking reaction with a living anionic polymer, but also regenerating the DPE reaction site via the DPE anion produced by the linking reaction. Thus, the dual functionality of the DPE derivative is also utilized in each process of this methodology. Typically, the A, B, C, D, and E arms were the PMSiS, PMOS, PMS, PS, and poly(4-*tert*-butyldimethylsilyloxystyrene) (PTBDMSiOS) segments.

In each process, the two reactions were observed to virtually quantitatively proceed. The resulting µ-star polymers were confirmed by SEC, RALLS, and ^{1}H NMR analyses to be well defined and expected in structure, as listed in Table 6. The final 5-arm ABCDE µ-star polymer is the first successful example composed of five different arms. Hydrolysis of the E arm by treatment with $(C_4H_9)_4NF$ yielded a new 5-arm ABCDE µ-star including an acidic and ionic poly(4-vinylphenol) arm

Scheme 23 Synthesis of μ-star polymers by the iterative methodology with *3* and *4* using DPE reaction site
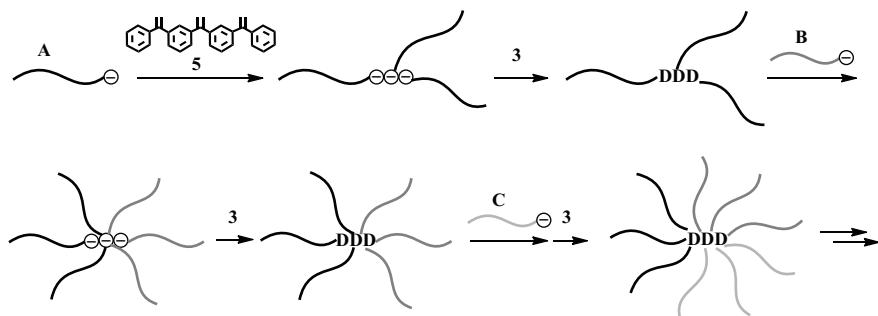
Scheme 24 Synthesis of μ-star polymers by the iterative methodology with *3* and *5* using DPE reaction site

segment. Since the final polymer possesses the DPE reaction site at the core, the synthesis of μ-stars with more arms and components is expected by further repeating the same process.

With the use of 1,3-bis(1-phenylethenyl)benzene (*4*) in place of DPE in the same iterative methodology, the arm number may increase by two in each iterative process, as illustrated in Scheme 23 [98, 99]. In the first process, two equivalents of a living polymer (A) reacted with *4* to link two A segments (the arm introduction step) and *3* was in situ reacted with the two produced DPE anions to reintroduce two DPE functions (the reaction site regeneration step). Next, the resulting in-chain-(DPE)$_2$-functionalized A$_2$ was reacted with a living polymer (B), followed by the in situ reaction with *3*, and produced a 4-arm A$_2$B$_2$ μ-star polymer core functionalized with two DPE reaction sites. One more repetition of the process using a living polymer (C) gave a 6-arm A$_2$B$_2$C$_2$ μ-star polymer. The A, B, and C arms used were PS, PαMS, PMOS and PS, PαMS, PI.

In the same sense, with the use of 1,1-bis(3-(1-phenylethenyl)phenyl)ethylene (*5*), composed of three DPE skeletons in the same methodology, the number of arms could increase by three in each process, resulting in the 3-arm A$_3$, 6-arm A$_3$B$_3$, and 9-arm A$_3$B$_3$C$_3$ μ-star polymers (see Scheme 24) [100]. Three 9-arm stars composed of PS, PMOS, PI arms, PS, PMOS, PMSiS arms, and PS, PMOS, PTBDMSiOS arms convertible to poly(4-vinylphenyl) segment. Each of these processes in both

Table 7 Synthesis of μ-star polymers by iterative methodology with 3 and 4 or 5 using DPE reaction sites

Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
4-arm A_2B_2	41,100	41,800	1.02
6-arm $A_2B_2C_2$[a]	61,700	62,400	1.02
6-arm $A_2B_2C_2$[b]	34,800	31,800	1.06
6-arm A_3B_3	67,800	66,700	1.03
9-arm $A_3B_3C_3$[c]	97,000	97,100	1.02
9-arm $A_3B_3C_3$[d]	101,000	103,000	1.04
9-arm $A_3B_3C_3$[e]	98,300	97,200	1.03

[a]PS/PαMS/PMOS
[b]PS/PαMS/PI
[c]PS/PMOS/PMSiS
[d]PS/PMOS/PI
[e]PS/PMOS/PTBDMSiOS
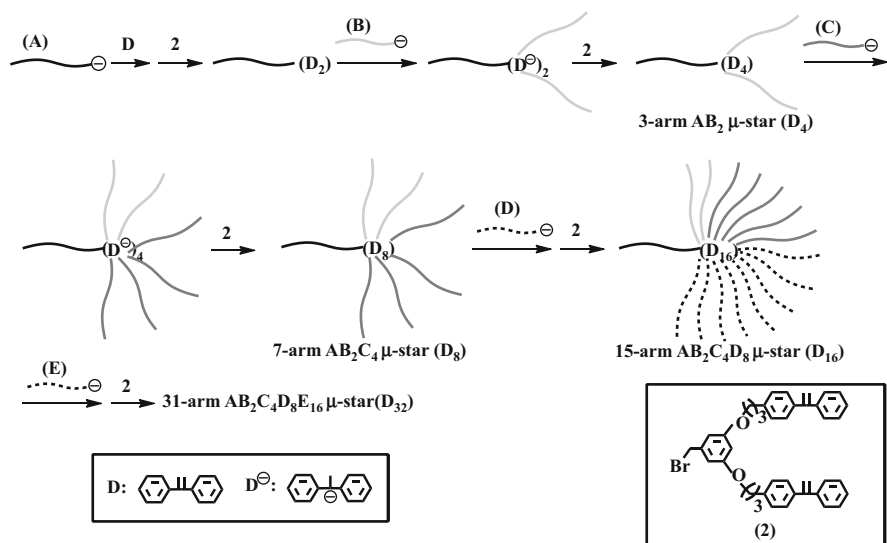
Scheme 25 Synthesis of multiarmed μ-star polymers with up to five components by the iterative methodology with *2* using DPE reaction sites

methodologies efficiently proceeded to afford well-defined μ-star polymers in almost 100 % yields. Their characterization results are listed in Table 7.

As mentioned in section "Arm-first termination methodology using DPE reaction site," it was possible to significantly increase the number of arm segments in each process using 3,5-bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl bromide (*2*) having two DPE and one BnBr functions [56]. This agent, *2*, is designed so as to regenerate the two DPE reaction sites via one DPE anion produced by the arm introduction step. As illustrated in Scheme 25 similar to Scheme 10, a DPE-end-capped living polymer (A) reacts with *2* to prepare a chain-end-(DPE)$_2$-functionalized A as the starting polymer. In the first process, two equivalents of a

Table 8 Synthesis of μ-star polymers by the iterative methodology with 2 using DPE reaction sites

Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
3-arm AB_2	32,100	35,700	1.02
7-arm AB_2C_4	77,000	79,200	1.02
15-arm $AB_2C_4D_8$	162,000	172,000	1.02
31-arm $AB_2C_4D_8E_{16}$[a]	339,000	363,000	1.02

[a]PS/PαMS/PMS/MOS/PMSiS

living polymer (B) reacted with the two DPE reaction sites of the starting polymer to link two B segments with the A chain and 2 was in situ reacted with two DPE anions produced by the linking reaction. As a consequence, a 3-arm AB_2 star was obtained and, importantly, four DPE reaction sites were regenerated at the core. Similarly, repetition of the same process three more times with the sequential uses of living polymers (C), (D), and (E) quantitatively yielded the 7-arm AB_2C_4, 15-arm $AB_2C_4D_8$, and even 31-arm $AB_2C_4D_8E_{16}$ μ-star polymers. The resulting polymers were all confirmed to be well-defined and expected structures, as listed in Table 8. The regeneration of 8, 16, and 32 DPE reaction sites was confirmed by ^{1}H NMR. Thus, the number of arms significantly increases by repeating the process according to the equation, $f = 2^{(n+1)} - 1$ (f and n are the arm and iterative process numbers, respectively).

Thus, the methodology using 2 allows readily, access to multiarmed μ-star polymers with up to 31 arms and possibly more arms. However, the synthetic variation of the μ-star polymers with more than 10 arms is limited only to 15 and 31 arms due to the rapid divergence of the number of arms. Recently, Higashihara et al. proposed to alternatively use 2 and 3 in each of the reaction site regeneration steps, with which the number of synthetically possible μ-star polymers can exponentially increase to 2, 4 (2^2), 8 (2^3), and 16 (2^4) by repeating the process four times, as illustrated in Scheme 26 [101]. After the completion of the fourth iterative process, a total of 30 ($2 + 4 + 8 + 16$) μ-star polymers can be synthesized, while the methodology using 2 yields only five polymers even after the fifth process.

The synthesis was initiated in order to prepare a chain-end-$(DPE)_2$-fuctionalized A by reacting the living polymer (A) with 2. During the first iteration, a linking reaction of the $(DPE)_2$-functionalized A with a living polymer (B) was followed by reacting either 3 or 2, affording two kinds of 3-arm AB_2 star polymers core functionalized two and four DPE reaction sites, which were abbreviated as 3-arm $AB_2(DPE)_2$ and 3-arm $AB_2(DPE)_4$, respectively. During the second iteration, a living polymer (C) reacted with either the 3-arm $AB_2(DPE)_2$ or 3-arm $AB_2(DPE)_4$ and 3 or 2 was in situ reacted to either of the resulting two polymer anions. The following four μ-star polymers were produced: 5-arm $AB_2C_2(DPE)_2$, 5-arm $AB_2C_2(DPE)_4$, 7-arm $AB_2C_4(DPE)_4$, and 7-arm $AB_2C_4(DPE)_8$. During the third iteration, the same process using a living polymer (D) was repeated to synthesize the eight stars as follows: 7-arm $AB_2C_2D_2(DPE)_2$, 7-arm $AB_2C_2D_2(DPE)_4$, 9-arm $AB_2C_2D_4(DPE)_4$, 9-arm $AB_2C_2D_4(DPE)_8$, 11-arm $AB_2C_4D_4(DPE)_4$, 11-arm $AB_2C_4D_4(DPE)_8$, 15-arm $AB_2C_4D_8(DPE)_8$, and 15-arm $AB_2C_4D_8(DPE)_{16}$. Furthermore, 16 five-component μ-stars could be synthesized by repeating the same
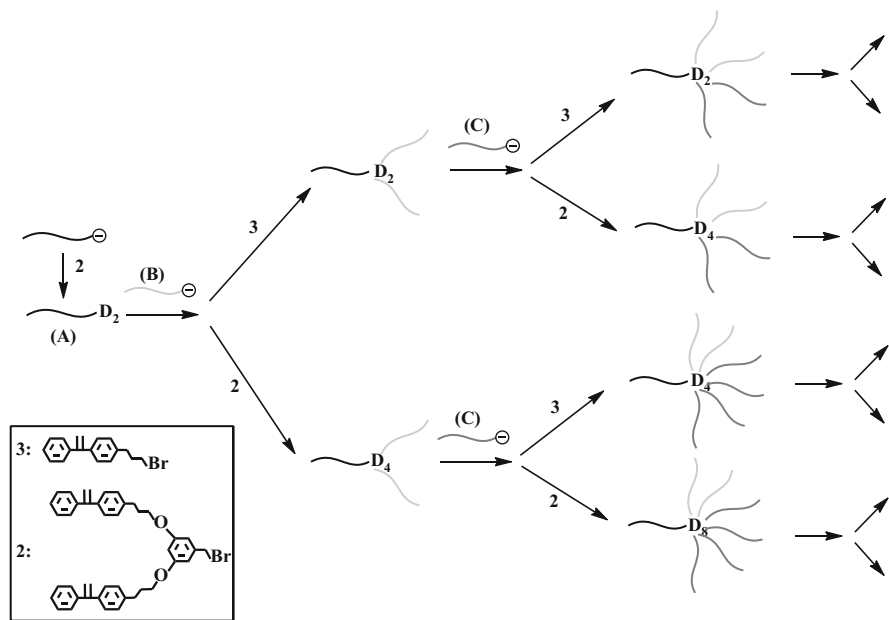
Scheme 26 Synthesis of μ-star polymers by the iterative methodology with an alternative choice of *2* and *3* using DPE reaction sites

process using a living polymer (E) as follows: 9-arm $AB_2C_2D_2E_2(DPE)_2$, 9-arm $AB_2C_2D_2E_2(DPE)_4$, 11-arm $AB_2C_2D_2E_4(DPE)_4$, 11-arm $AB_2C_2D_2E_4(DPE)_8$, 13-arm $AB_2C_2D_4E_4(DPE)_4$, 13-arm $AB_2C_2D_4E_4(DPE)_8$, 15-arm $AB_2C_4D_4E_4(DPE)_4$, 15-arm $AB_2C_4D_4E_4(DPE)_8$, 17-arm $AB_2C_2D_4E_8(DPE)_8$, 17-arm $AB_2C_2D_4E_8(DPE)_{16}$, 19-arm $AB_2C_4D_4E_8(DPE)_8$, 19-arm $AB_2C_4D_4E_8(DPE)_{16}$, 23-arm $AB_2C_4D_8E_8(DPE)_8$, 23-arm $AB_2C_4D_8E_8(DPE)_{16}$, 31-arm $AB_2C_4D_8E_{16}(DPE)_{16}$, and 31-arm $AB_2C_4D_8E_{16}(DPE)_{32}$.

Among them, 22 μ-star polymers were actually synthesized. The polymers obtained by this methodology were all well defined in structure and narrowly distributed in molecular weight distribution. The representative results of μ-star polymers with more than 9 arms are listed in Table 9. Thus, it is quite surprising that the alternative use of *3* and *2* in the reaction site regeneration step enables the synthetic range of μ-star polymers to be significantly broadened.

In all of the iterative methodologies herein developed, the living anionic polymers of styrene and its derivatives are used in order to react with the DPE reaction site(s) to continue the next process. The living anionic polymers of 1,3-butadiene, isoprene, and certain functional 1,3-diene monomers can also be used in these methodologies. Thus, almost all possible multiarmed and multicomponent μ-star polymers composed of such polymer segments are now available.

It is also possible to use 2- and 4-vinylpyridines, alkyl methacrylate monomers, and other vinyl and cyclic monomers that undergo the living anionic polymerization with the DPE anion(s) in the final step of each process. However, once these

Table 9 Synthesis of μ-star polymers by the iterative methodology with 2 and 3 using DPE reaction sites

| Polymer (DPE number)	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
9-arm $AB_2C_2D_4(4)$	98,400	100,000	1.05
9-arm $AB_2C_2D_4(8)$	98,200	106,000	1.02
9-arm $AB_2C_2D_2E_4(2)$	87,500	92,900	1.05
11-arm $AB_2C_4D_4(4)$	116,000	119,000	1.05
11-arm $AB_2C_4D_4(8)$	118,000	121,000	1.02
11-arm $AB_2C_2D_2E_4(4)$	116,000	109,000	1.04
13-arm $AB_2C_2D_2E_4(4)$	136,000	150,000	1.04
15-arm $AB_2C_4D_8(8)$	159,000	163,000	1.05
15-arm $AB_2C_4D_8(16)$	159,000	168,000	1.04
15-arm $AB_2C_4D_4E_4(4)$	158,000	154,000	1.02
17-arm $AB_2C_2D_4E_8(8)$	171,000	178,000	1.04
19-arm $AB_2C_4D_4E_8(8)$	188,000	181,000	1.04
23-arm $AB_2C_4D_8E_8(8)$	243,000	260,000	1.04
31-arm $AB_2C_4D_8E_{16}(32)$[a]	332,000	356,000	1.02

[a]PS/PαMS/PMS/PMOS/PMSiS

monomers are used, the iterative process can no longer be continued due to loss of the reaction site(s). Unfortunately, their living anionic polymers are not employed in each process due to the lack of reactivity toward the DPE reaction site(s).

3.3.2 Iterative Methodology Using 2-Alkyl-1,3-Butadiene Reaction Site

As mentioned in section "Iterative methodologies using DPE reaction site," the key in the iterative methodology is the dual-functional ability of the DPE reaction site which provides a linking site with a living anionic polymer as well as the same DPE reaction site via the DPE anion produced by the linking reaction. This ability of DPE reaction site makes it possible to carry out both steps (arm introduction and regeneration of reaction site) essential for the iterative methodology. Hirao et al. have found that a 1,3-butadiene (Bd) function attached to the PS chain-end via the 2-position shows the same dual-functionalized ability [102]. For example, PSLi reacted with the Bd terminus in PS in a 1:1 addition manner to link the two PS chains (the arm introduction step) and the PS chain-end anion was converted to a 1,3-butadienyl anion (Bd anion). The same Bd function was reintroduced by reacting in situ the produced Bd anion with 6-bromo-3-methylene-1-hexene (*6*) (the reaction site regeneration step). Somewhat surprisingly, neither polymerization nor even oligomerization of the Bd terminus occurred using a 1.5-fold excess of PSLi toward the Bd function in THF at −78 °C for 24 h. These experimental proofs strongly indicate the possible use of the Bd function in the iterative methodology.

As shown in Scheme 27, the methodology with the Bd reaction site is basically the same as that using the DPE reaction site [103]. The synthesis was started from the preparation of a chain-end-Bd-functionalized PS by reacting a DPE-end-capped
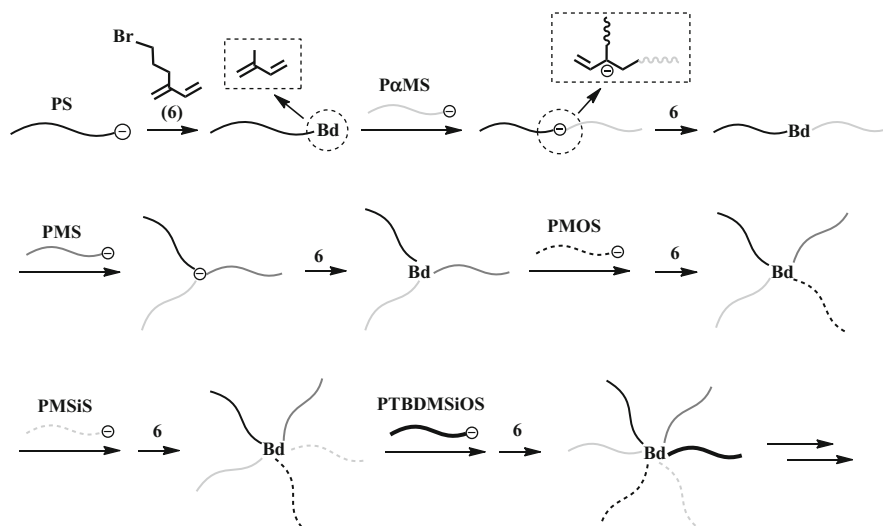
Scheme 27 Synthesis of μ-star polymers up to 6-arm ABCDEF type by the iterative methodology using Bd reaction site

PSLi with *6*. In the first iterative process, PαMSLi reacted with the Bd-functionalized PS, followed by reacting with *6*, to yield an in-chain-Bd-functionalized PS-*b*-PαMS. By conducting the next process using PMSLi, a 3-arm ABC μ-star polymer core functionalized with the Bd reaction site was synthesized. Since the Bd-functionalized AB diblock copolymer and the core-Bd-functionalized 3-arm ABC star were obtained in almost 100 % yields, it is obvious that both the arm introduction and reaction site regeneration steps satisfactorily work via the Bd reaction site. Furthermore, 4-arm ABCD, 5-arm ABCDE, and even 6-arm ABCDEF μ-star polymers were successively synthesized by repetition of the same process three more times. The A, B, C, D, E, and F arms correspond to the PS, PαMS, PMS, PMOS, PMSiS, and PTBDMSiOS (convertible to poly (4-vinylphenol)) segments. As evidenced in Table 10, all of the resulting polymers were confirmed by SEC, RALLS, and ¹H NMR analyses to be well defined and expected in structure. The successful use of Bd reaction site is thus obvious in the iterative methodology.

An additional advantage of the Bd reaction site is the quantitative conversion to highly reactive and synthetically useful anhydride and two epoxide functions by the Diels-Alder and oxidation reactions, as shown in Scheme 28 [102, 104].

3.3.3 Iterative Methodologies Using α-Phenylacrylate Reaction Site

The two iterative methodologies using the DPE and Bd reaction sites demonstrate the successful synthesis of a variety of new μ-star polymers. This is undoubtedly attributed to the quantitative linking reactions of such reaction sites with highly

Table 10 Synthesis of μ-star polymers by the iterative methodology using Bd reaction site

Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
A homopolymer	11,200	11,500	1.03
AB diblock copolymer	24,200	25,300	1.04
3-arm ABC	34,800	35,900	1.01
4-arm ABCD	47,100	47,200	1.01
5-arm ABCDE	58,800	58,500	1.02
6-arm ABCDEF[a]	71,800	71,500	1.03

[a]PS/PαMS/PMS/PMOS/PMSiS/PTBDMSiOS

Scheme 28 Preparation of chain-end-anhydride-functionalized or chain-end-two epoxides-functionalized PS by the Diels-Alder or oxidation reaction of chain-end-Bd-functionalized PS
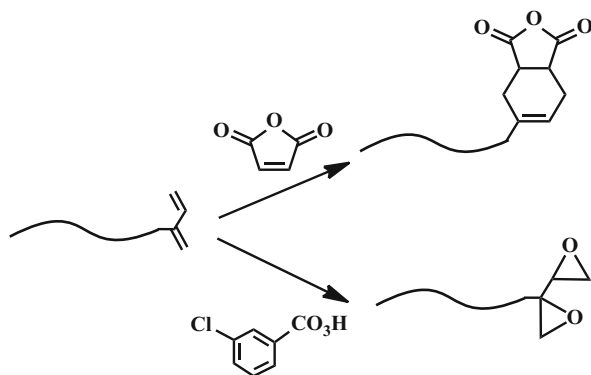
reactive living anionic polymers of styrene, 1,3-butadiene, isoprene, and their derivatives. On the other hand, the living anionic polymers of 2VP and alkyl methacrylates (RMAs) cannot be applied to these iterative methodologies because their chain-end anions are too low in nucleophilicity to react with the DPE and Bd reaction sites.

In order to overcome this difficulty, we have newly developed an α-phenylacrylate (PA) function as the reaction site in the iterative methodology [13, 17, 95, 96, 105]. Since the C = C bond of PA is activated by the ester carbonyl electron-withdrawing character, the PA function is considered to show a higher reactivity toward anionic species than the DPE and Bd functions. Furthermore, a sterically bulky α-phenyl substituent may prevent further addition reactions of the PA function leading to oligomerization and polymerization. In practice, it was observed that the PA reaction site at the polymer chain-end undergoes a 1:1 addition reaction with either the living P2VP or PRMA to link the two polymer chains in THF at low temperatures in the range from −20 to −78 °C. No more addition reactions occurred at all under such conditions. Unfortunately, however, several attempts were unsuccessful to find a suitable reaction to regenerate the PA function, because the enolate anion produced from the PA function was neither stable nor reactive. Accordingly, another route via a hydroxyl group for the regeneration of the PA reaction site is proposed, as illustrated in Scheme 29 [106].

Scheme 29 Synthesis of μ-star polymers by the iterative methodology using PA reaction site

In the proposed methodology, a new DPE derivative substituted with trimethylsilyl (TMS), and *tert*-butyldimethylsilyl (TBDMS) ethers, *7*, is used as the key agent. The two silyl ethers are converted to the PA reaction sites in turn for the arm introduction and reaction site regeneration in each process. A chain-end-(TMS and TBDMS ethers)-functionalized polymer (A) was first prepared as the starting polymer by the polymerization of a certain methacrylate monomer with a DPE anion having TMS and TBDMS ethers prepared from *7* and *sec*-BuLi. The TMS ether was then converted to the first PA reaction site by treatment with methanol containing K_2CO_3 and the subsequent Mitsunobu esterification reaction with α-phenylacrylic acid. Under such conditions, the TBDMS ether remained completely intact. The PA reaction site was reacted with the living polymer (B) to link the B chain to the A segment, resulting in an in-chain-(TBDMS ether)-functionalized A-*b*-B. Next, the TBDMS ether was deprotected with $(C_4H_9)_4NF$, followed by the same esterification with α-phenylacrylic acid to convert to the second PA reaction site. The PA reaction site was then reacted with the DPE anion having TMS and TBDMS ethers to reintroduce both the TMS and TBDMS ethers.

Since the two silyl ethers are the same as those introduced in the starting polymer (A), the above process can be repeated. In fact, it could be repeated three more times by progressively reacting living polymers (C), (D), and (E) to successively synthesize the μ-star polymers with up to five arms. Thus, the TMS ether was converted to the first PA reaction site, which was used for the arm introduction, while the second PA was prepared from TBDMS ether in the same manner for the reintroduction of both the TMS and TBDMS ethers to repeat the same process. Typically, the A, B, C, D, and E arms are PMMA, poly(ethyl methacrylate) (PEMA), P^{t}BMA, poly(benzyl methacrylate) (PBnMA), and poly(2-methoxyethyl methacrylate) (PMOEMA), respectively. The results are summarized in Table 11.

Table 11 Synthesis of μ-star polymers by the iterative methodology using PA reaction site

Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
3-arm ABC	32,200	33,800	1.03
4-arm ABCD	43,400	43,000	1.03
5-arm ABCDE[a]	52,000	51,500	1.03
5-arm ABCDE[b]	52,700	50,200	1.04

[a]PMMA/PEMA/P^{t}BMA/PBnMA/PMOEMA
[b]PS/PMMA/P^{t}BMA/PMS/PBnMA

2-*tert*-Butyldimethylsilyloxyethyl methacrylate (Si-HEMA), (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (acetal-DHPMA), and ferrocenylmethyl methacrylate (PFMMA) were also introduced as the arm segments. The first two polymers are readily converted to hydrophilic poly(2-hydroxyethyl methacrylate) (PHEMA) and water-soluble poly(2,3-dihydroxypropyl methacrylate) (PDHPMA) segments by deprotection of the silyl and acetal groups. The resulting 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE stars were the first successful μ-star polymers composed of all different poly(methacrylate)-based arm segments. The living anionic polymers of styrene, 1,3-butadiene, isoprene, and 2VP can also be used in this methodology because the PA reaction site could be quantitatively reacted with these more reactive living anionic polymers. Thus, a wide variety of living anionic polymers with different reactivities can advantageously be employed for the PA reaction site during the iterative methodology, which makes it more general and versatile.

A more efficient iterative methodology using a new trifunctional DPE anion as the key agent was also proposed, as illustrated in Scheme 30 [107]. The trifunctional DPE anion having TMS, TBDMS, and THP ethers is prepared by reacting 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium (TBDMS-PLi) with a DPE derivative substituted with TMS and THP ethers. These three ethers are designed so as to be selectively deprotected in turn to regenerate hydroxyl groups under carefully selected conditions. The hydroxyl groups are then converted step by step to three PA reaction sites by different reaction stages. The two PA reaction sites among them were used for the introduction of two different arms, while the third one was used to reintroduce the three different ethers by reacting the trifunctional DPE anion to continue the methodology.

The trifunctional DPE anion was prepared by reacting TBDMS-PLi with the DPE derivative substituted with TMS and THP ethers and used as an initiator in the polymerization of a certain methacrylate monomer to introduce the three ethers at the initiating chain end of polymer (A). The TMS ether was selectively removed, followed by conversion to the first PA reaction site. The living polymer (B) reacted with the PA reaction site to link the B chain to the A segment, resulting in an in-chain-(TBDMS and THP ethers)-functionalized A-*b*-B. The TBDMS ether was then selectively deprotected and converted to the second PA reaction site. A 3-arm ABC μ-star was obtained by reacting living polymer (C) with the PA reaction site. The THP ether that remained at the core was then converted to the third PA reaction site, followed by reacting the trifunctional DPE anion with the PA reaction site. Thus, the three different ethers were reintroduced into the core.
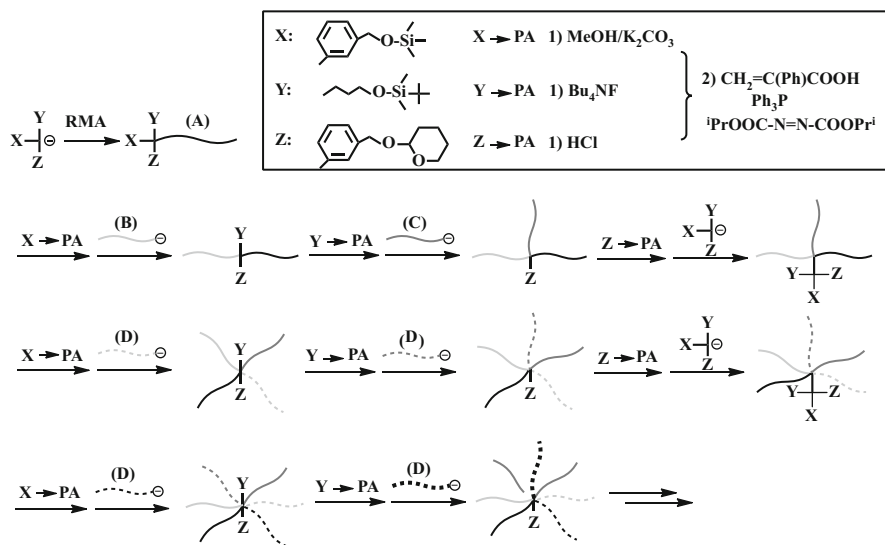
Scheme 30 Synthesis of μ-star polymers by the iterative methodology with trifunctional Li reagent using PA reaction site

Since the three ether functions were exactly the same as those in the starting polymer (A), the same process using two living polymers, (D) and (E), could be repeated. As a consequence, a core-(TMS, TBDMS, and THP ethers)-functionalized 5-arm ABCDE μ-star polymer could be synthesized. One more repetition yielded a 7-arm ABCDEFG μ-star polymer. Since the three ether functions are reintroduced at the core, μ-stars with more arms and components may possibly be synthesized by repeating the process.

The synthetic key in this methodology is the selective and progressive deprotection of TMS, TBDMS, and THP ethers at each reaction stage. The TMS ether was removed in methanol containing a small amount of K_2CO_3. Both the TBDMS and THP ethers were completely stable under such conditions. The TBDMS ether was selectively deprotected by $(C_4H_9)_4NF$ in the presence of the THP ether. In the μ-star polymer consisting of the PBnMA arm, the addition of phenol equal to $(C_4H_9)_4NF$ in amount is needed to prevent the hydrolysis of the benzyl ester function. Finally, the THP ether was readily and quantitatively cleaved by treatment with 0.2 N HCl. Thus, the selective deprotection of TMS, TBDMS, and THP ethers in this order was successfully carried out in each of all three processes by the above careful treatments. The resulting polymers are all observed to be well defined in structure and architecture, as summarized in Table 12. In addition to the less reactive living PRMAs and P2VP, highly reactive living polymers of styrene, 1,3-diene monomers, and their derivatives are usable in this methodology using the PA reaction site similar to the first methodology shown in Scheme 29.

Table 12 Synthesis of μ-star polymers having up to 7-arm ABCDEFG type by the iterative methodology with a trifunctional reagent using PA reaction site

Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
4-arm ABCD[a]	43,200	43,200	1.03
4-arm ABCD[b]	80,900	80,000	1.04
3-arm ABC	35,000	34,900	1.03
4-arm ABCD	45,900	47,100	1.03
5-arm ABCDE	56,600	53,500	1.04
6-arm ABCDEF	62,800	64,900	1.05
7-arm ABCDEFG[c]	73,800	74,200	1.04

[a]Poly(cyclohexyl methacrylate)/PMMA/PBnMA/PMOEMA
[b]Poly(allyl methacrylate)/PS/PMOEMA/P2VP
[c]Poly(cyclohexyll methacrylate)/PS/PMOS/PMS/PMMA/PEMA/PMOEMA
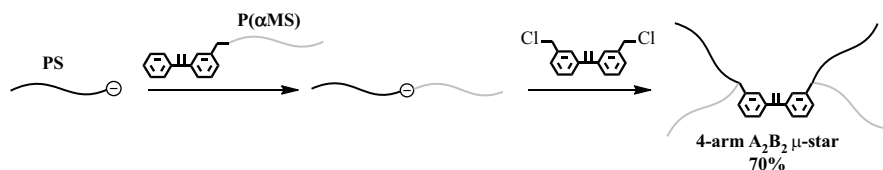
Scheme 31 Synthesis of 4-arm A_2B_2 μ-star polymer by the reaction of in-chain-(DPE anion)-functionalized AB diblock copolymer with *8*

A series of μ-star polymers with up to 7 arms and 7 components were successfully synthesized by repeating the process three times. On the other hand, the six iterative processes are required to synthesize the same 7-arm μ-star polymer by the first methodology. Accordingly, the success of the proposed second methodology makes it possible to synthesize multiarmed and multicomponent μ-star polymers by fewer processes. The universality of the PA reaction site is thus obvious as compared to the DPE reaction site.

3.3.4 Iterative Methodologies Using Intermediate Polymer Anions

In this section, a new iterative methodology based on a different molecular design illustrated in Scheme 31 is proposed [108]. In the methodology, the star polymer synthesis was started from an in-chain-(DPE anion)-functionalized AB diblock copolymer, which was prepared by the reaction of PSLi with a chain-end-DPE-functionalized PαMS. The in situ reaction of the diblock copolymer anion thus prepared with 1,1-bis(3-chloromethylphenyl)ethylene (*8*) yielded a 4-arm A_2B_2 μ-star polymer ($M_n = 45,000$ g/mol) in one pot in THF at −78 °C for 1 h. Since the resulting star possessed a DPE reaction site convertible to the DPE anion, both the arm introduction and the reaction site regeneration steps essential in the iterative methodology were achieved at the same time in this first iterative process. However, the polymer yield was 70 % and could not be improved by taking a longer
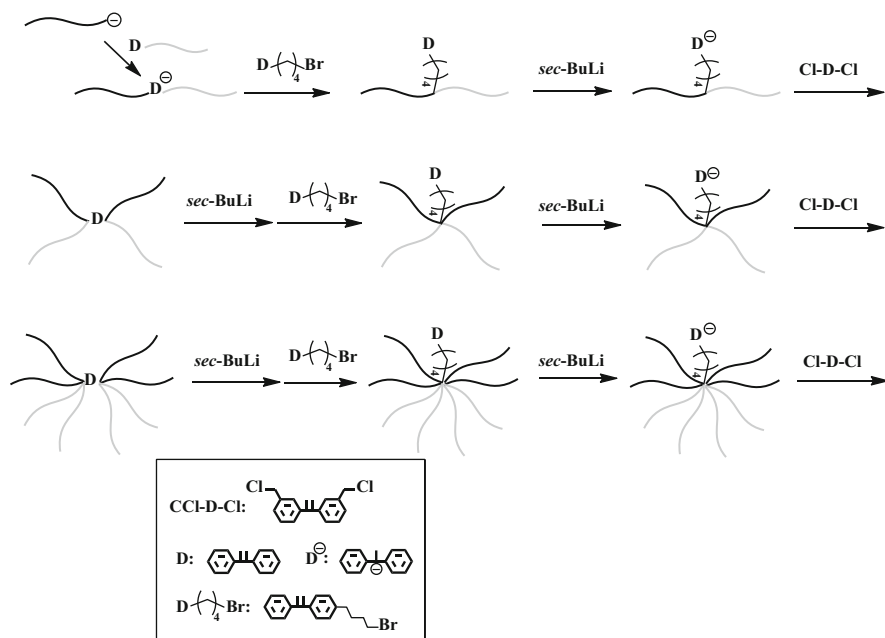
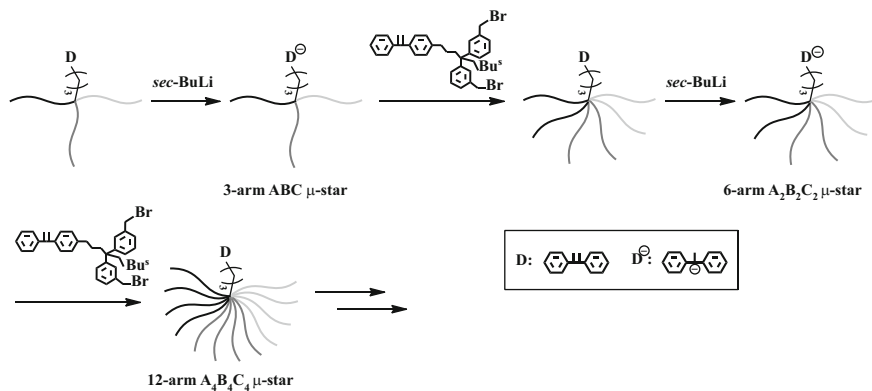**Scheme 32** Synthesis of μ-star polymers by the improved iterative methodology

Table 13 Synthesis of μ-star polymers by the improved iterative methodology using intermediate polymer anion

	M_n (g/mol)		M_w/M_n
Polymer	calcd	SLS	SEC
AB diblock copolymer	22,100	23,200	1.03
4-arm A_2B_2	46,600	48,300	1.03
8-arm A_4B_4	99,000	108,000	1.04
16-arm $A_8B_8{}^a$	208,000	199,000	1.02

[a]PS/PαMS

reaction time of 24 h. The insufficient coupling efficiency is undoubtedly attributed to the steric hindrance around the DPE anions.

In order to reduce the steric hindering effect and improve the polymer yield, one more reaction step was added in each process as shown in Scheme 32. The DPE anion once produced was in situ reacted with 1-(4-(4-bromobutylphenyl))-1-phenylethylene (*9*) to reintroduce the DPE reaction site, which was separated by four methylene chains from the core. The reintroduced DPE was again converted to the DPE anion by treatment with *sec*-BuLi and in situ used in the coupling reaction with *8*. This treatment was effective in improving the polymer yield. Almost quantitative yields of the 4-arm A_2B_2 and 8-arm A_4B_4 stars were realized in THF at −78 °C within 1 h. A 16-arm A_8B_8 μ-star polymer could also be efficiently synthesized, but the yield was 70 % even after 24 h (Table 13). As expected, the coupling reaction during the fourth iterative process was difficult, resulting in a 32-arm $A_{16}B_{16}$ μ-star polymer in less than 5 % yield.

Scheme 33 Synthesis of μ-star polymers by the iterative methodology using intermediate μ-star polymer anion and *10*

The similar iterative methodology was next carried out using a core-DPE-functionalized 3-arm ABC μ-star polymer in order to synthesize multiarmed three-component μ-star polymers [109]. As illustrated in Scheme 33, the DPE reaction site was always separated by three methylene chains from the core to reduce the steric hindrance similar to the case using in-chain-DPE-functionalized AB diblock copolymer mentioned above. Furthermore, a new agent, 1-(4-(5,5-bis (3-bromomethylphenyl)-7-methylnonyl)phenyl-1-phenylethylene (*10*) having two more reactive BnBr functions, was used as the coupling agent in place of *8*. The starting core-DPE-functionalized 3-arm ABC μ-star polymer was prepared by the reaction of an in-chain-DPE-functionalized PS-*b*-PαMS with PMSLi, followed by in situ reacting with *3*. A target 6-arm $A_2B_2C_2$ μ-star polymer was successfully obtained in 100 % yield in the first process. By repeating the reaction sequence in the second process, a 12-arm $A_4B_4C_4$ μ-star polymer could also be obtained. However, the yield was reduced to 70 %. As expected, the coupling reaction for the synthesis of the 24-arm $A_8B_8C_8$ star in the next process was observed to take place only to a very small extent. By changing the component from PS, PαMS, and PMS to PS, PαMS, and PI in the μ-star polymer, the same iterative methodology was performed under the same conditions. Again, a 6-arm $A_2B_2C_2$ star was quantitatively synthesized, but a 12-arm $A_4B_4C_4$ was obtained in 65 % yield. With the use of a 3-arm A_2B μ-star polymer, a 6-arm A_4B_2 m-star (100 %) and a 12-arm A_8B_4 m-star (75 %) were synthesized by the same methodology. The results are listed in Table 14.

The iterative methodology herein shown is of great value to obtain the synthetically difficult μ-star polymers, such as 6-arm A_4B_2, 6-arm $A_2B_2C_2$, 12-arm A_8B_4, and 12-arm $A_4B_4C_4$ types. The occurrence of the coupling reaction between high-molecular-weight polymers ($M_n \sim 70{,}000$ g/mol) at a very low temperature of $-78\,°C$ is somewhat surprising. However, the increase in both the steric hindrance and molecular weight by repeating the process renders the coupling reactions yielding more armed stars significantly difficult.
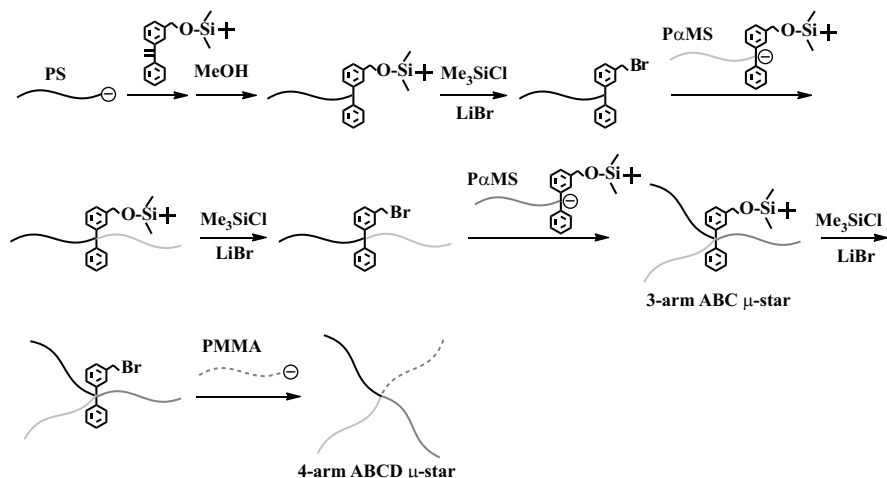
Table 14 Synthesis of μ-star polymers by the iterative methodology using intermediate 3-arm μ-star polymer anion and 10

Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
3-arm ABC	32,000	33,400	1.02
6-arm $A_2B_2C_2$	67,100	66,600	1.02
12-arm $A_4B_4C_4$[a]	134,000	134,000	1.02
3-arm A_2B	36,300	35,300	1.03
6-arm A_4B_2	72,600	73,500	1.03
12-arm A_8B_4[b]	145,000	148,000	1.03

[a]PS/PαMS/PMS
[b]PS/PI

3.3.5 Iterative Methodologies Using BnBr Reaction Site

As already mentioned, the BnBr function was observed to quantitatively react with a variety of living anionic polymers with different reactivities under carefully selected conditions. For example, a highly reactive living polymer of styrene, 1,3-butadiene or isoprene is first end-capped with DPE, followed by a coupling reaction with the BnBr function in THF at $-78\,^{\circ}$C. Under the same conditions, less reactive living polymers of 2VP and RMA are able to directly react with the BnBr function. The use of a 1.2-fold excess of these living polymers for the BnBr function was sufficient to go to completion in the reaction. An iterative methodology using the BnBr function as a reaction site was also developed, as illustrated in Scheme 34 [110]. The reaction design is somewhat different from those of the methodologies using the DPE, Bd, and PA reaction sites, since the transformation reaction of the 3-*tert*-butyldimethylsilyloxymethylphenyl (TBDMSOMP) group into the BnBr function is employed as the reaction site regeneration step. At first PSLi reacted with 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-phenylethylene (*11*) to introduce the TBDMSOMP group at the chain end, which was quantitatively transformed into the BnBr reaction site by treatment with a 1:1 mixture of Me$_3$SiCl and LiBr. Next, PαMSLi reacted with *11* to introduce the TBDMSOMP group at the chain end and the resulting polymer anion was coupled in situ with the above chain-end-BnBr-functionalized PS to afford an in-chain-TBDMSOMP-functionalized PS-*b*-PαMS. Again, the TBDMSOMP group introduced between the two blocks was transformed into the BnBr reaction site. Thus, the coupling and transformation reactions exactly correspond to the arm introduction and the BnBr reaction site regeneration steps, respectively. The same reaction process involving the two steps were repeated with the use of PMSLi and *11*, resulting in a 3-arm ABC μ-star polymer consisting of the PS, PαMS, and PMS arms. The TBDMSOMP group introduced at the core was transformed into the BnBr reaction site in the same manner with Me$_3$SiCl/LiBr. In the next process, a less reactive living PMMA was coupled with the 3-arm ABC μ-star core-functionalized with the BnBr reaction site. The coupling reaction was quantitative to afford a 4-arm ABCD star polymer composed of the PS, PαMS, PMS, and PMMA arms. Thus, both steps in each process satisfactorily work to successively synthesize the AB diblock, 3-arm ABC,

Scheme 34 Synthesis of μ-star polymers by the iterative methodology with *11* using BnBr reaction site

Table 15 Synthesis of μ-star polymers by iterative methodology with 11 using BnBr reaction site

Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
A polymer	10,600	11,200	1.02
AB diblock copolymer	20,200	21,200	1.02
3-arm ABC	32,300	35,700	1.02
4-arm ABCD[a]	46,700	48,800	1.02
A$_2$ polymer	24,100	25,200	1.02
4-arm A$_2$B$_2$	44,300	43,700	1.03
6-arm A$_2$B$_2$C$_2$[b]	65,700	67,000	1.02

[a]PS/PαMS/PMS/PMMA. [b]PS/PαMS/P^{t}BMA

and 4-arm ABCDμ-star polymers (Table 15). In the final reaction stage for the introduction of the PMMA arm, the TBDMSOMP group was not introduced into the 4-arm ABCD μ-star polymer, because the living PMMA could not react with *11*.

Therefore, the same reaction sequence was no longer repeated. On the other hand, since PBLi, PILi, PSLi, or other living polystyrene derivatives react with *11*, the reaction process can be further continued by using such living polymers, leading to the synthesis of more armed and component μ-star polymers.

With the use of an in-chain-(BnBr)$_2$-functionalized A$_2$ as the starting polymer in the same methodology, a 4-arm A$_2$B$_2$, followed by a 6-arm A$_2$B$_2$C$_2$ μ-star polymer, were synthesized. Thus, the number of arms can increase by two in each process, as shown in Scheme 35. The resulting polymers were all well defined in structure as listed also in Table 15. In order to continue the process in this methodology, a living anionic polymer is always required to react with *11* of the DPE derivative in each process for the regeneration of the reaction site(s). Accordingly, the use of highly reactive living polymers of styrene, 1,3-butadiene, isoprene, and their derivatives
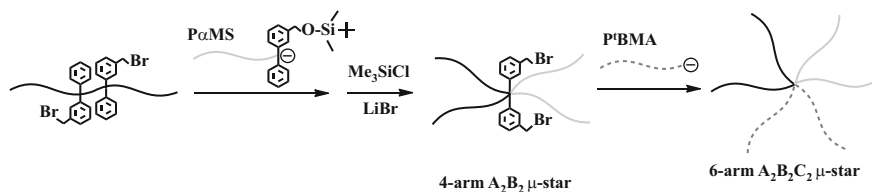
Scheme 35 Synthesis of 4-arm A_2B_2 and 6-arm $A_2B_2C_2$ μ-star polymers by the iterative methodology using two BnBr reaction sites

are required, while the less reactive living P2VP and PRMAs cannot be used except for the final linking step, as mentioned above.

As also shown in Scheme 7, the number of BnBr functions can be exponentially increased by developing an iterative methodology. By repeating the same reaction sequence from chain-end-$(BnBr)_2$-functionalized PS, the number of BnBr reaction sites could indeed increase from 2 to 4 (2^2), 8 (2^3), 16 (2^4), 32 (2^5), and even 64 (2^6). By reacting another living polymer (B) with the chain-end-$(BnBr)_n$-functionalized polymers (A)s at each reaction stage, it was possible to synthesize a series of (n + 1) arm AB_n μ-star polymers, in which the A and B arms were PS (A) and PI (B), PB (B), P2VP (B), PMMA (B), or PEO (B) segments as mentioned in section "Arm-first termination methodology using BnBr reaction site."

Although the living PMMA cannot directly react with *1*, the DPE anion prepared from *1* and *sec*-BuLi initiates the polymerization of MMA to introduce two TBDMSOMP groups at the initiating chain end. The same iterative treatment enabled a series of chain-end-$(BnBr)_n$-functionalized PMMAs, in which the "n" number readily increased from 2 (2^1) to 4 (2^2), 8 (2^3), and 16 (2^4) in the same manner as that described above. The coupling reaction of the chain-end-$(BnBr)_n$-functionalized PMMA with other living anionic polymers also gave various (n + 1) arm AB_n μ-star polymers. Typically, the A and B arms were PMMA and P^{t}BMA, PS, PI, or P2VP segments. In practice, a variety of 3-arm AB_2, 5-arm AB_4, 9-arm AB_8 μ-star polymers, etc., were successfully synthesized, also as described in section "Arm-first termination methodology using BnBr reaction site" [54, 55].

In the iterative methodologies described in the preceding sections and the methodology using BnBr reaction site(s) described in the first part of this section, the μ-star polymer synthesized in each process always became the starting polymer in the next process. On the other hand, although the number of BnBr reaction sites increased by basically the same iterative approach in the above-mentioned methodology, the μ-star polymer synthesized in each process did not correspond to the next starting material. Accordingly, the above-mentioned methodology deviated from the definition of an iterative methodology introduced in the beginning of this section "Methodologies based on iterative strategy," but considered to be one of the iterative methodologies.

In addition to the chain-end-$(BnBr)_n$-functionalized polymers, in-chain-$(BnBr)_2$-functionalized A_2 as well as A-*b*-B could also be used. These polymers were prepared as shown in Scheme 36. The living chain-end-$(TBDMSOMP)_2$-
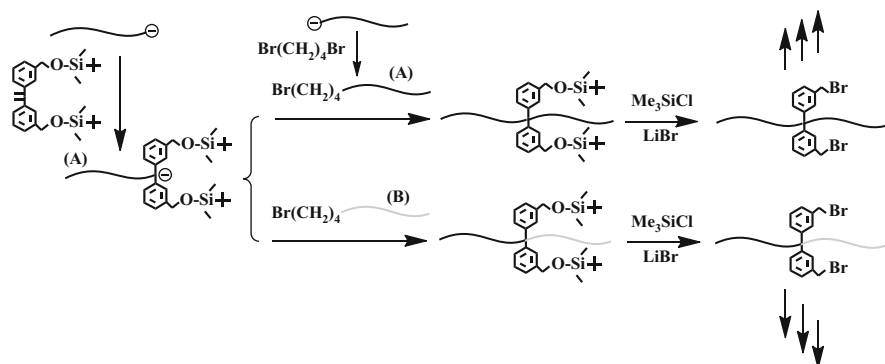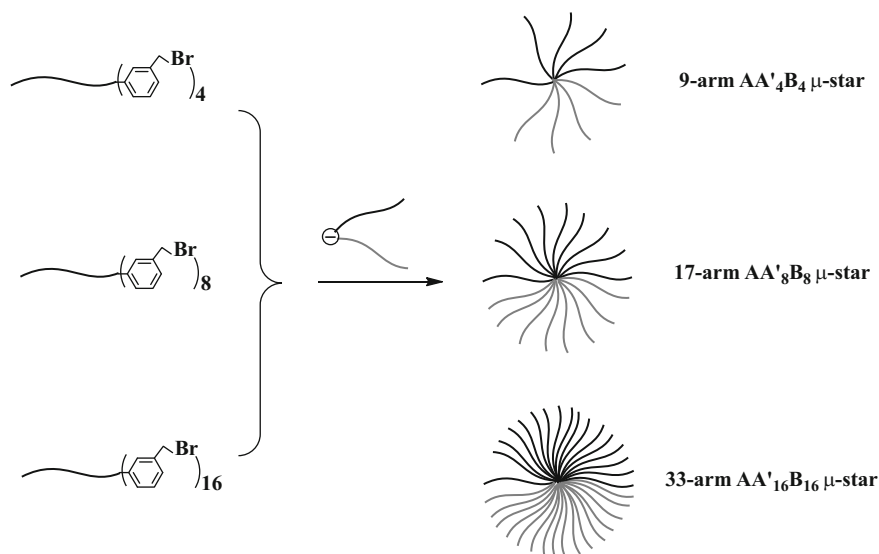
Scheme 36 Synthesis of in-chain-functionalized A_2 or A-*b*-B

functionalized polymer (A) was first prepared by reacting living polymer (A) with *1* and subsequently in situ reacted with a chain-end-(4-bromobutyl)-functionalized polymer (A) or (B). The two introduced TBDMSOMP groups were transformed into two BnBr functions. In these polymers, the number of BnBr functions can readily increase to 4 (2^2), 8 (2^3), 16 (2^4), etc., by the same iterative methodology as that used above. With these in-chain-$(BnBr)_n$-functionalized polymers, the synthesis of two series of $(2+n)$ arm A_2B_n and $(2+n)$ arm ABC_n μ-star polymers were possible by the coupling reaction of either the living polymer (B) or living polymer (C). Furthermore, the synthesis of the $(2+n)$ arm $A_{1+n}B$ as well as $(2+n)$ arm AB_{1+n} μ-star polymers was also possible using either the living polymer (A) or living polymer (B) in the reaction with the in-chain-$(BnBr)_2$-functionalized A-*b*-B [111, 112].

The methodology was extended to the synthesis of multiarmed μ-star polymers by reacting an off-centered A-*b*-B anion with either of a series of the chain-end-$(BnBr)_n$-As, in which the A and B arms were the PS and PMSiS segments, as shown in Scheme 37 [113–115]. The term "off-centered A-*b*-B anion" is defined as a polymer consisting of A and B blocks having an anionic site present at the junction of such blocks. This polymer anion was prepared by reacting PMSiSLi with the chain-end-DPE-functionalized PS and used in situ in the coupling reaction with the chain-end-$(BnBr)_n$-functionalized PS. In order to examine the possibility of the coupling reaction, the off-centered A-*b*-B anions and BnBr-functionalized PSs were adjusted to be ca. 10,000 g/mol (5,000 g/mol/5,000 g/mol) and ca. 10,000 g/mol in M_n value.

Surprisingly, the coupling reaction was complete in THF within 10 min even at −78 °C. 9-Arm AA'_4B_4, 17-arm AA'_8B_8, and even 33-arm $AA'_{16}B_{16}$ μ-star polymers were successfully synthesized (A, A', and B are PS ($M_n = 10,000$ g/mol), PS ($M_n = 5,000$ g/mol), and PMSiS ($M_n = 5,000$ g/mol)). However, the quantitative coupling reaction between the chain-end-$(BnBr)_{32}$-functionalized PS and the polymer anion was not achieved. The coupling efficiency was observed to be 75 %, but not improved by allowing the reaction mixture to react for the longer reaction time of 168 h. A 49-arm (on average) $AA'_{24}B_{24}$ star polymer was obtained. Thus, the steric hindrance appeared at this stage using the $(BnBr)_{32}$-functionalized PS (Table 16).

Scheme 37 Synthesis of μ-star polymers by the reaction of chain-end-(BnBr)$_n$-multifunctionalized PSs with the off-centered PS-*b*-PMSiM anions
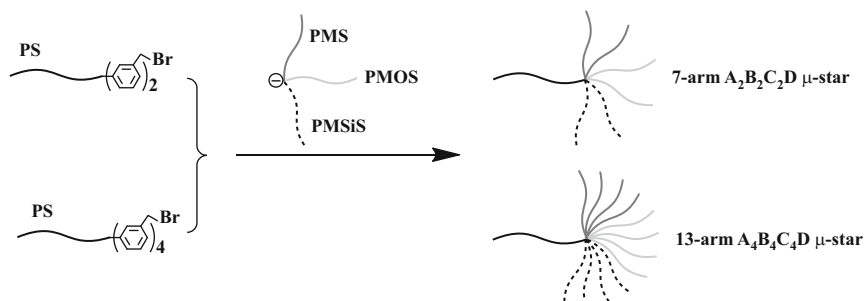
Table 16 Synthesis of μ-star polymers by the reaction of chain-end-(BnBr)$_n$-multifunctionalized PSs with the off-centered PS-*b*-PMSiS anions

Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
9-arm AA′$_4$B$_4$	50,500	51,200	1.03
17-arm AA′$_8$B$_8$	93,900	96,800	1.03
33-arm AA′$_{16}$B$_{16}$	188,000	190,000	1.02
65-arm AA′$_{33}$B$_{33}$	358,000	270,000[a]	1.02

[a]48 arms were introduced based on the observed molecular weight. Efficiency = 75 %

The above success of the coupling reactions using the off-centered AB diblock anion motivated us to use a bulkier 3-arm ABC μ-star polymer having an anionic site at the core in the same reaction. According to the procedure shown in Scheme 38, a 3-arm ABC μ-star polymer anion (M_n = 30,000 (10,000/10,000/10,000) g/mol) composed of P(MSiS), P(MOS), and P(MS) arms was prepared by the procedure shown in Scheme 22 and in situ reacted with either the chain-end-(BnBr)$_2$-, or (BnBr)$_4$-functionalized PS (M_n = 10,000 g/mol) in THF at −78 °C for 24 h [116, 117]. The coupling reaction smoothly proceeded to afford the 7-arm A$_2$B$_2$C$_2$D and 17-arm A$_4$B$_4$C$_4$D μ-star polymers in virtually a 100 % yield. The results are listed in Table 17.

All of the μ-star polymers were observed to possess predictable M_n values and narrow molecular weight distributions. Their compositions were very close to the

Scheme 38 Synthesis of μ-star polymers by the reaction of chain-end-(BnBr)$_n$-multifunctionalized PSs with 3-arm ABC μ-star polymer anions

Table 17 Synthesis of μ-star polymers by the reaction of chain-end-(BnBr)$_n$-multifunctionalized PSs with 3-arm ABC μ-star polymer anions
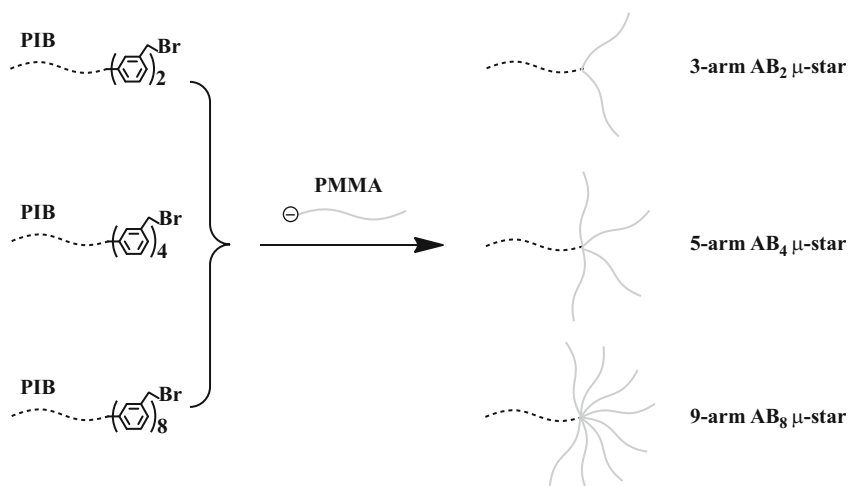
Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
7-arm A$_2$B$_2$C$_2$D[a]	73,600	77,900	1.03
13-arm A$_4$B$_4$C$_4$D	134,000	133,000	1.02

[a]PMSiS/PMS/PMOS/PS

theoretical values. Thus, it was demonstrated that the iterative methodology based on the coupling reaction of the chain-end-(BnBr)$_n$-functionalized polymers with off-centered block copolymer anions or 3-arm μ-star terpolymer anions well worked for synthetic access to a series of characteristic multiarmed μ-star polymers, which are synthetically difficult by any other methods.

As mentioned above, the synthesis of a 65-arm AA′$_{32}$B$_{32}$ μ-star polymer was not successful possibly due to the steric hindrance around the core by reacting the chain-end-(BnBr)$_{32}$-multifunctionalized A with an off-centered A′-*b*-B. Similarly, several attempts failed to synthesize a 49-arm A$_{16}$B$_{16}$C$_{16}$D μ-star polymer composed of the PMSiS (A), PMOS (B), PMS (C), and PS(D) arms by coupling of the 3-arm ABC star polymer anion with the chain-end-(BnBr)$_{16}$-multifunctionalized PS. Insufficient coupling efficiencies are also possibly due to the steric hindering effect. However, high efficiencies of 80–90 % could be achieved by changing the reaction time (168 h) and temperature (−40 °C).

Faust and Higashihara et al. synthesized a series of multiarmed AB$_n$ μ-star polymers composed of poly(isobutylene) (PIB) (A) and PMMA (B) arms by developing a similar iterative approach [118]. As shown in Scheme 39, a PIB having an allyl chloride terminus was first prepared by the living cationic polymerization of IB, followed by terminating with 1,3-butadiene. The resulting chain-end-(allyl chloride)-functionalized PIB was reacted with the DPE anion prepared from *1* and *sec*-BuLi to introduce two TBDMSOMP groups at the chain end. The two TBDMSOMP groups were then transformed into BnBr reaction sites by the

Scheme 39 Synthesis of μ-star polymers composed of PIB and PMMA by the reaction of chain-end-(BnBr)$_n$-multifunctionalized PIBs with living PMMAs

Table 18 Synthesis of μ-star and pom-pom polymers composed of PIB and PMMA

| Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
3-arm AB$_2$[a]	26,600	27,200	1.06
5-arm AB$_4$	47,600	45,800	1.03
9-arm AB$_8$	119,000	124,000	1.02
pom-pom B$_2$AB$_2$	50,100	51,000	1.02
pom-pom B$_4$AB$_4$	56,600	55,600	1.02
pom-pom B$_8$AB$_8$	52,200	54,500	1.03

[a]PIB/PMMA

treatment with Me$_3$SiCl/LiBr in the same manner as that already described. By repeating the reaction sequence involving the reaction of the BnBr reaction sites with the DPE anion and the transformation reaction to the BnBr reaction site, the number of terminal BnBr functions increased to $2(2^1)$, $4(2^2)$, and $8(2^3)$. The living PMMA reacted with each of the prepared chain-end-(BnBr)$_n$-multifunctionalized PIBs, resulting in the successful formation of well-defined 3-arm AB$_2$, 5-arm AB$_4$, and 9-arm AB$_8$ μ-star polymers. A new B$_2$AB$_2$, B$_4$AB$_4$, or B$_8$AB$_8$ pom-pom polymer was also synthesized in a similar manner by reacting the living PMMA with an end-functionalized PIB with BnBr functions at both chain ends. The results are summarized in Table 18. Thus, in this procedure for the synthesis of μ-star polymers, the chain-end-functionalized polymers obtained by the living cationic polymerization could also be employed.

# 4 μ-Star Polymers Composed of Random Coil and Rigid Segments

Block polymers composed of random coil and rigid segments have recently received much attention because such molecular conjugates combine the characteristics of random coils such as flexibility, elasticity, solubility, and processability with mechanically tough rigid segments. It is now recognized that very unique and unconventional morphologies at the molecular level, previously unknown for fully amorphous block polymers, are often produced. Furthermore, the individual characteristic features of the rigid segments are also advantageous to provide additional functionalities to the polymers. For these reasons, a variety of such block polymers have been already synthesized and their potential applications have been widely investigated especially in the fields of nanomaterial and nanoscience. In contrast, only a few μ-star polymers including rigid segments have been synthesized, although such polymers could also be of significant interest for the same reasons. In this section, three recently synthesized μ-star polymers composed of vinyl polymers and rigid segments will be introduced.

The first example is the μ-star polymers including rigid rodlike π-conjugated poly(acetylene) (PA) segments, which show high conductivities and nonlinear optical activities. However, the PA generally prepared by the transition-metal-mediated polymerization of acetylene is not suitable for the star polymer synthesis because the polymerization is not well controlled. In 1990, Hogen-Esch et al. developed an efficient two-step methodology for the synthesis of a well-defined PA via the living anionic polymerization of phenyl vinyl sulfoxide (PVS), followed by thermal elimination of the resulting polymer, converting to the PA segment, as shown in Scheme 40 [119, 120]. With this methodology, linear PAs with known molecular weights and relatively narrow molecular weight distributions ($M_w/M_n = 1.2$–1.5) were first synthesized. Later, the polymerization was improved with respect to the control using 4-methylphenyl vinyl sulfoxide (4MPVS) and by adding a tenfold or more excess of LiCl to the initiator [121, 122]. The molecular weight distributions of the resulting polymers became narrower ($M_w/M_n < 1.2$).

By applying this improved polymerization system to the iterative methodology (see Scheme 22) described in section "Iterative methodologies using DPE reaction site," a series of μ-star polymers containing the PA segments were synthesized as illustrated in Scheme 41 [123, 124].
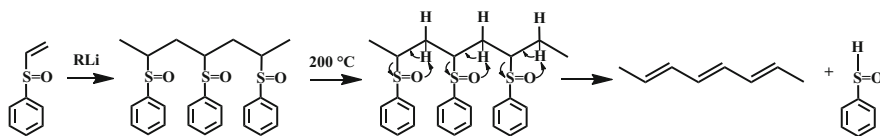
Scheme 40 Preparation of well-defined PA by the anionic polymerization of phenyl vinyl sulfoxide, followed by thermal elimination of the resulting polymer
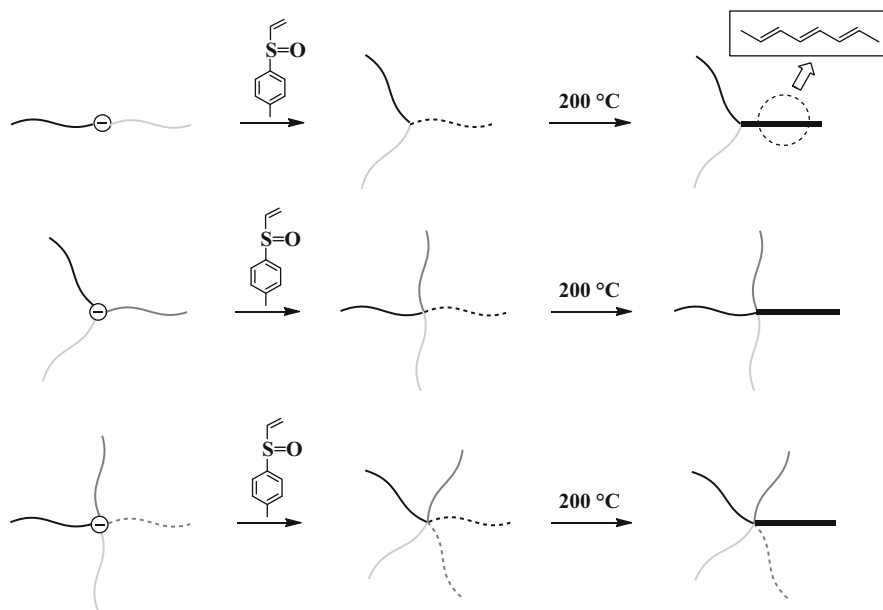
**Scheme 41** Synthesis of coil-rod μ-star polymers using iterative methodology

Table 19 Characterization results of μ-star polymers including (P4MPVS)s convertible to PA segments

Polymer	M_n (g/mol)		M_w/M_n
	calcd	SLS	SEC
3-arm ABE	31,800	32,700	1.02
3-arm ACE	31,800	34,600	1.03
4-arm ABCE	42,700	44,600	1.02
4-arm ABDE	43,300	43,600	1.03
5-arm ABCDE[c]	51,600	53,600	1.03

[a]PS/PaMS/PMOS/PMSiS/poly(4MVS)

In the synthesis, the intermediate polymer anion was used as a macroinitiator in the living anionic polymerization of 4MPVS, and the resulting P4MPVS was converted to the PA segment by thermal treatment. In practice, 4MPVS was quantitatively polymerized with either an AB diblock copolymer anion, a 3-arm ABC μ-star polymer anion, or a 4-arm ABCD μ-star polymer anion, yielding the corresponding 3-arm ABE, 4-arm ABCE, or 5-arm ABCDE μ-star polymer with well-defined and expected structures (Table 19). The A, B, C, D, and E segments were PS, PαMS, PMOS, PMSiS, and P4MPVS segments, respectively.

Similarly, two 3-arm AB$_2$ μ-star polymers (M_n = 22,000–54,000 g/mol and $M_w/M_n < 1.1$) were synthesized via the ion-bond by the stoichiometric reaction either between chain-end-$(NMe_2)_2$-functionalized PPVS and chain-end-(COOH)-functionalized PS or chain-end-(NMe_2)-functionalized PPVS and in-chain-(COOH)-functionalized PS, followed by thermal treatment, as shown in Scheme 42
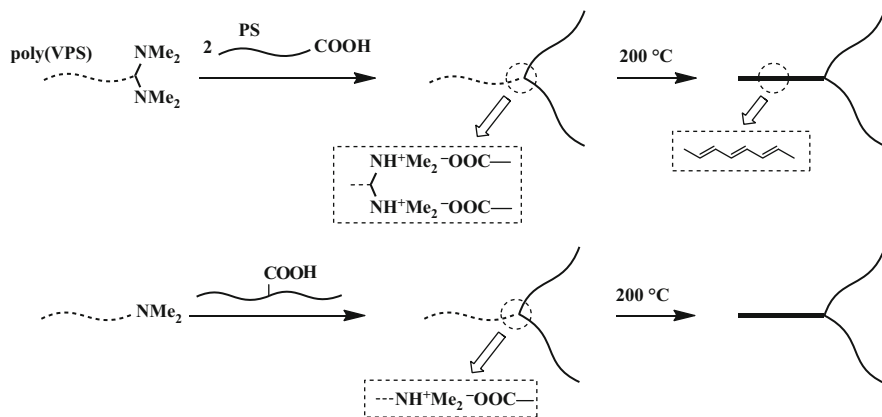
Scheme 42 Synthesis of ion-bonded 3-arm AB$_2$ μ-star polymers having one PA segment

[122]. Periodic lamellar morphologies were observed in the cast films of such polymers by TEM measurement.

The resulting polymers are of special interest in that the PA arms are phase-separated, followed by self-organizing to arrange the conductive PA segments inside the microdomains or self-assemblies in selected solvents. In addition, their mechanical properties and behavior are also of interest because of rigid rodlike characters of the PA segment. Thus, various μ-star polymers having the PA segment (s) are now available by developing the methodology via the living anionic polymerization, followed by thermal treatment.

The second example is the μ-star polymers having poly(alkyl isocyanate) segment(s), which adopt an extended helical conformation with unique optical activities and liquid crystallinities. Lee et al. were the first to succeed in achieving the living anionic polymerization of hexyl isocyanate (HIC) and the related isocyanate monomers under rather specific conditions in THF at -98 °C with the use of initiators bearing Na$^+$ [125–127]. Certain suitable additives, such as NaBPh$_4$ and 15-crown-5, were needed to prevent the unwanted trimer formation by the back-biting that occurred after the polymerization. Under such conditions, PHICs with controlled molecular weights ($M_n \sim 50,000$ g/mol) and narrow molecular weight distributions ($M_w/M_n < 1.1$) were quantitatively obtained. Well-defined block copolymers of PHIC-b-PS-b-PHIC, PHIC-b-PI-b-PHIC, and PHIC-b-P2VP-b-PHIC could also be synthesized by the sequential polymerization of styrene, isoprene, or 2VP, followed by HIC, to sodium naphthalene [128].

The synthesis of μ-star polymers with PHIC arms by Lee et al. are shown in Scheme 43 [129]. A PHIC-COCH$_2$CO-PHIC with an active methylene reaction site between the two blocks was first prepared by coupling of the living PHIC with malonyl chloride.

Subsequently, the Michael reaction of the PHIC-COCH$_2$CO-PHIC with the α-methacryloyl-functionalized polyethylene glycol (PEG) macromonomer in the
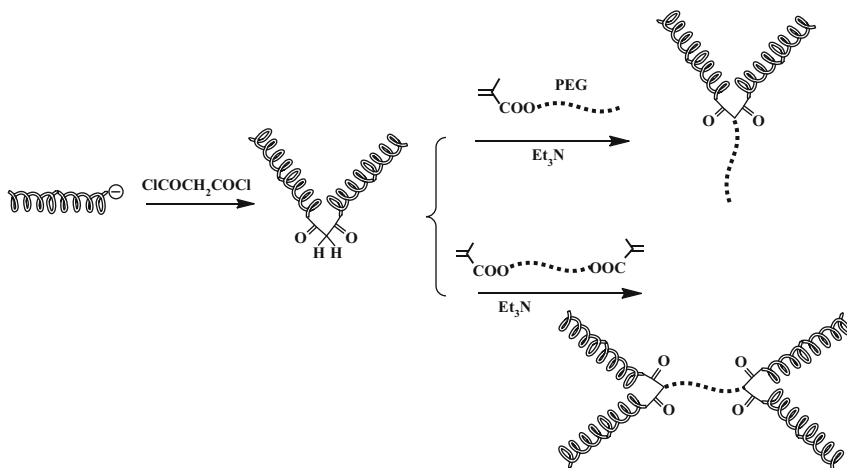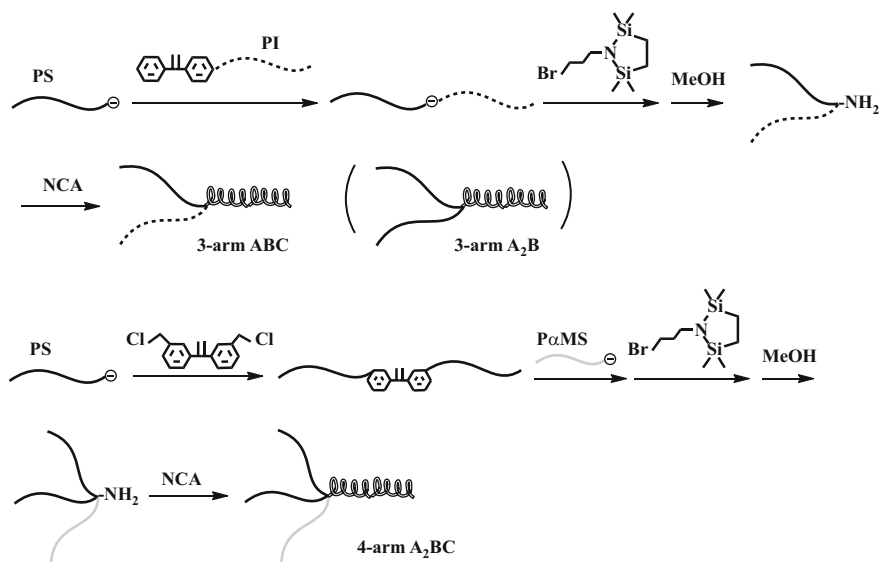
Scheme 43 Synthesis of coil–helix 3-arm AB$_2$ μ-star and B$_2$AB$_2$ pom-pom polymer

presence of triethylamine yielded a 3-arm AB$_2$ μ-star polymer composed of PEG (A) and PHIC (B). Two polymer chains of PHIC-COCH$_2$CO-PHIC could be linked with an α,ω-dimethacryloyl-functionalized PEG macromonomer leading to an B$_2$AB$_2$ pom-pom type of (PHIC)$_2$(PEG)(PHIC)$_2$. The resulting μ-star polymers were composed of helical PHIC and biocompatible PEG arms and possessed controlled M_n values ($M_n = 9,600–12,400$ g/mol) and narrow molecular weight distributions ($M_w/M_n = 1.08–1.14$). It was observed that the 3-arm AB$_2$ μ-star polymers form solid core-shell or hollow spherical micelles simply by changing the solvent from THF to a mixed solvent of THF and ethanol (1/9, v/v).

A variety of block polymers combining polypeptide sequences with synthetic polymers have already been synthesized, since rigid ordered conformations, such as α-helices or β-strands, can be incorporated, with which unusual nanostructures are produced and control over the nanoscale structures is significantly enhanced through intramolecular hydrogen bonding. It is also interesting that the resulting polypeptide–vinyl polymer conjugates behave as potentially biocompatible and new smart materials, whose conformation and association properties can reversibly respond by changing the pH and temperature [130–132]. These polymers were generally prepared by the anionic ring-opening polymerization of α-amino acid N-carboxyanhydrides (NCAs) with chain-end-amine-functionalized vinyl polymers, but the polymerization control was somewhat difficult until recently. This difficulty has been overcome by the use of an organonickel complex, ammonium chloride, hexamethyldisilazane, and several primary amines as the initiators. Thus, the molecular weights could be controlled up to a 10^5 g/mol order with narrow molecular weight distributions ($M_w/M_n = 1.04–1.18$) [133–140].

With these improved polymerization systems, Hadjichristidis et al. first synthesized new μ-star polymers including polypeptide segments by anionic polymerization [141]. These polymers involved 3-arm A$_2$B, 3-arm ABC, and 4-arm A$_2$BC

Scheme 44 Synthesis of coil–helix μ-star polymers

Table 20 Synthesis of coil–helix μ-star polymers with polypeptide arms

Polymer	M_n (g/mol)		M_w/M_n
	calcd	SEC-TALLS	SEC
3-arm (PS)(PI)(PBLG)	35,000	33,300	1.09
3-arm (PS)(PI)(PBocLL)	35,000	34,200	1.07
3-arm (PS)₂(PBLG)	32,000	32,600	1.05
3-arm (PS)₂(PBocLL)	32,000	31,500	1.02
4-arm (PS)₂(PαMS)(PBLG)	40,000	38,900	1.08
4-arm (PS)₂(PαMS)(PBocLL)	40,000	38,500	1.07

PBLG poly(γ-benzyl-L-glutamate), *PBocLL* poly(ε-*tert*-butoxycarbonyl-L-lysine)

μ-stars, where the A, B, and C arms are polypeptide, PI, PS, or PαMS, respectively. The reaction sequences for the synthesis of such μ-star polymers are given in Scheme 44. In-chain-NH₂-functionalized (PS)₂, PS-*b*-PI diblock copolymer, or 3-arm core-NH₂-functionalized (PS)₂(PαMS) μ-star are first synthesized by reacting 1-(3-bromopropyl)-2,2,5,5-tetramethyl-aza-2,5-disilacyclopentane with the corresponding polymer anions, followed by deprotection. These amine-functionalized polymers were used as the macroinitiators in the living anionic polymerization of the NCAs.

All the macroinitiators were completely consumed, as evidenced by the absence of the corresponding peaks in the SEC charts of the final products. From the characterization results in Table 20, it can be seen that the final μ-star polymers have low polydispersities and their stoichiometric molecular weights are in good

agreement with those determined by SEC-TALLS. Consequently, the resulting μ-star polymers having polypeptide arms are well defined in structure. Among these synthesized μ-star polymers, 3-arm $(PS)_2PBocLL$ and 4-arm $(PS)_2(PBocLL)_2$ stars (PBocLL: poly(ε-*tert*-butoxycarbonyl-L-lysine)) were first deprotected and then complexed with sodium dodecyl sulfonate of an anionic surfactant to give the supramolecular complexes [142]. They are lamellar polypeptide–surfactant self-assemblies with a β-sheet conformation. The ionic complexation leads to a particularly pronounced small-scale ordering of the polypeptide–surfactant complex arms that dominate over the formation of block copolymer scale structures.

5 Conclusions

At the present time, well-defined regular star polymers having multiarms can be synthesized by the linking reaction using multifunctional chlorosilane compounds, followed by the development of the linking reaction using BnBr reaction sites. Both the methodologies are based on "arm-first termination" procedure. The usable arms of such star polymers are PS, PαMS, PI, PB, P2VP, PMMA, P^tBMA, and PEO. Any monomer including cyclic monomers that undergoes living anionic polymerization can be used to result in the synthesis of the corresponding multiarmed regular star polymers. It should be emphasized that the chlorosilane methodology is excellent with respect to the synthesis of very high-molecular-weight star polymers with M_n values of over 10^7 g/mol.

Regarding the μ-star polymer synthesis, only one example concerning the synthesis of a four-component 4-arm ABCD μ-star polymer appeared before 2000. Even in the 3-arm ABC stars, a few examples were synthesized by the methodologies using multifunctional chlorosilanes or dual-functionalized DPE reaction sites. Since 2001, Hirao, Higashihara et al. have proposed the iterative strategy using repeatable reaction sequences capable of simultaneous introduction of arm(s) and reaction site(s). With the use of the methodologies based on this iterative strategy, the limit for the synthesis of μ-star polymers is readily surpassed and the almost all types of multiarmed and multicomponent μ-star polymers have been successfully synthesized, as introduced in section "Methodologies based on iterative strategy." With the development of various reaction sites, any monomer that undergoes living anionic polymerization can be used. Furthermore, since the iterative strategy may possibly be applied to other living polymerization systems in conjunction with several click reactions, the range of available star polymers will be greatly expanded in the near future. The development of living anionic polymerization of phenyl vinyl sulfoxide, alkyl isocyanate monomers, and NCAs has allowed access to various well-defined coil–rod and coil–helix μ-star polymers with interesting functionalities. Thus, a wide variety of multiphase polymers with star-branched architectures having more structural variables than linear block polymers are now available. Their applications to both material science and nanoscience will be expected.

Abbreviations

4-DVB	4-Divinylbenzene
4MPVS	4-Methylphenyl vinyl sulfoxide
acetal-DHPMA	(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl methacrylate
Bd	1,3-Butadiene
BnBr	Benzyl bromide
BnCl	Benzyl chloride (BnCl)
DPE	1,1-Diphenylethylene
HIC	Hexyl isocyanate
NCAs	*N*-carboxyanhydrides
P2VP	Poly(2-vinylpyridine)
P4VP	Poly(4-vinylpyridine)
PA	Poly(acetylene)
PA	α-Phenylacrylate
PB	Poly(1,3-butadiene)
PBLG	Poly(γ-benzyl-L-glutamate)
PBLi	Poly(1,3-butadienyl)lithium
PBnMA	Poly(benzyl methacrylate)
PBocLL	Poly(ε-*tert*-butoxycarbonyl-L-lysine)
PDHPMA	Poly(2,3-dihydroxypropyl methacrylate)
PDMS	Poly(dimethylsiloxane)
PEE	Poly(ethylethylene)
PEG	Polyethylene glycol
PEMA	Poly(ethyl methacrylate)
PEO	Poly(ethylene oxide)
PFMMA	Poly(ferrocenylmethyl methacrylate)
PFPO	Poly(perfluoropropylene oxide)
PHEMA	Poly(2-hydroxyethyl methacrylate)
PHIC	Poly(hexyl isocyanate)
PI	Polyisoprene
PILi	Poly(isoprenyl)lithium)
PMMA	Poly(methyl methacrylate)
PMOEMA	Poly(2-methoxyethyl methacrylate)
PMOSLi	Poly(4-methoxystyryl)lithium
PMSiS	Poly(4-trimethylsilylstyrene)
PS	Polystyrene
PSLi	Poly(styryl)lithium
P^{t}BA	Poly(*tert*-butyl acrylate)
PTBDMSiOS	Poly(4-*tert*-butyldimethylsilyloxystyrene)
P^{t}BMA	Poly(*tert*-butyl methacrylate)
PVS	Phenyl vinyl sulfoxide
PαMSLi	Poly(α-methylstyryl)lithium
RMAs	Alkyl methacrylates

sec-BuLi	*sec*-Butyllithium
Si-HEMA	2-*tert*-Butyldimethylsilyloxyethyl methacrylate
TBDMS	*tert*-Butyldimethylsilyl
TBDMSiOMP	3-*tert*-Butyldimethylsilyloxymethylphenyl
TBDMSOMP	3-*tert*-Butyldimethylsilyloxymethylphenyl
TBDMS-PLi	3-(*tert*-butyldimethylsilyloxy)-1-Propyllithium
TMS	Trimethylsilyl

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