Linear and Star Block Copolymers of Styrenic Macromonomers by Anionic Polymerization

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ABSTRACT: We describe the synthesis of a number of linear and star block copolymers where at least one block consists of a polymacromonomer (molecular brush). The key to this general technique is the use of styrene-tipped macromonomers, which polymerize in a manner similar to styrene monomer. By this means well-defined styrenic macromonomers of polyisoprene, PI (sMMI), polybutadiene, PB (sMMB), and poly(styrene-*b*-isoprene), PSI (sMMSI), have been prepared by selective reaction of PILi, PBLi, and PSILi with the chlorine of 4-(chlorodimethylsilyl)styrene. These macromonomers and conventional monomers (styrene, isoprene, and butadiene) were homopolymerized or block copolymerized, by anionic polymerization high-vacuum techniques, to synthesize the following structures: PsMM-*b*-PM, PS-*b*-PsMM-*b*-PM, and PsMM1-*b*-PsMM2 where PsMM is PsMMI or PsMMB and PM is PS, PI, or PB. Furthermore, by utilizing the chlorosilane method, star polymers of the $(PS)_2(PsMMB)$ and $(PsMMI\text{-}b\text{-}PI)_3$ type were synthesized. Attempts to prepare A_3 and A_4 star polymers with polymacromonomer arms were not entirely successful. All materials were characterized by size exclusion chromatography (SEC) with DRI and UV detectors, SEC with two-angle-laser-light-scattering detector (SEC/TALLS), and NMR spectroscopy. It was concluded that macromonomers can be used much like the conventional monomers under appropriate experimental conditions.

Introduction

Polymacromonomers (molecular brushes) can be synthesized by “grafting from”, “grafting onto”, and “grafting through” (macromonomer) methods.[1] Matyjaszewski’s group, using the “grafting from” method, has successfully synthesized linear[2,3] and star[4] molecular brushes with extremely high degrees of polymerization and narrow molecular weight distribution. The “grafting onto” method is less suitable for molecular brushes, as it involves polymer−polymer reactions. However, a number of recent publications show that this technique can also be used to provide well-defined linear[5,6] and cyclic[7] molecular brushes. Very recently, Hirao’s group used this method to prepare molecular brushes carrying two branch chains on each monomeric unit.[8,9]

The macromonomer method involves the synthesis and subsequent polymerization of macromonomers. Most known polymerization methods have been used to produce homopolymacromonomers.[10] The macromonomer technique is the only method that ensures one side chain per repeating unit. The main disadvantages of this method are the steric hindrance of the growing polymacromonomer−macromonomer reaction and the extremely low concentration of active centers (high molecular weight monomers). Therefore, in most cases the polymerization degrees and yield were low. High degrees of polymerization are usually attained by free radical polymerization, but the materials obtained are not well-defined.[11,12]

Although anionic polymerization is the most powerful and established method leading to living polymer chains, it has rarely been used for the polymerization of macromonomers, much less for the preparation of complex macromolecular architectures involving polymacromonomers. The main reason for this is the high degree of monomer purity required for anionic polymerization combined with the low active center concentration. A few attempts have been undertaken for the anionic polymerization of PS macromonomers, after isolation of the macromonomers by precipitation in a nonsolvent, without full success.[13,14]

In two previous papers[15,16] we have shown that styrenic macromonomers of poly(isoprene), poly(butadiene), and poly(styrene) could be polymerized with *sec*-BuLi, in benzene, in rates comparable to styrene polymerization, at least when the chain molecular weight was not very high ($M_w < \sim 7$ kg/mol). The key for the successful polymerization is the elimination of the isolation step of macromonomers, a step which introduces impurities in the polymerization system. In addition, all reagents and apparatuses should be thoroughly purified because of the very low concentration of the living species.

By using these principles, we were able to prepare block copolymer architectures PMM-*b*-PM, PS-*b*-PsMM-*b*-PM, PsMM1-*b*-PsMMI2, and PsMMI-*b*-PsMMSI using the sequential monomer addition technique and star-shaped polymers $(PS)_2(PsMM)$ and $(PsMM\text{-}PM)_3$ using the chlorosilane method (where PMM is PsMMI or PsMMB and PM is PS, PI, or PB). Furthermore, a few attempts were undertaken to prepare 3- and 4-arm star polymacromonomers with limited success. All macromolecular architectures synthesized and attempted are given in Scheme 1.

Experimental Section

All monomers [isoprene (Acros, 99%+), butadiene (Aldrich, 99%+), and styrene (Acros, 99%+)], solvents [tetrahydrofuran (THF), benzene, and hexane, all reagent grade], terminating

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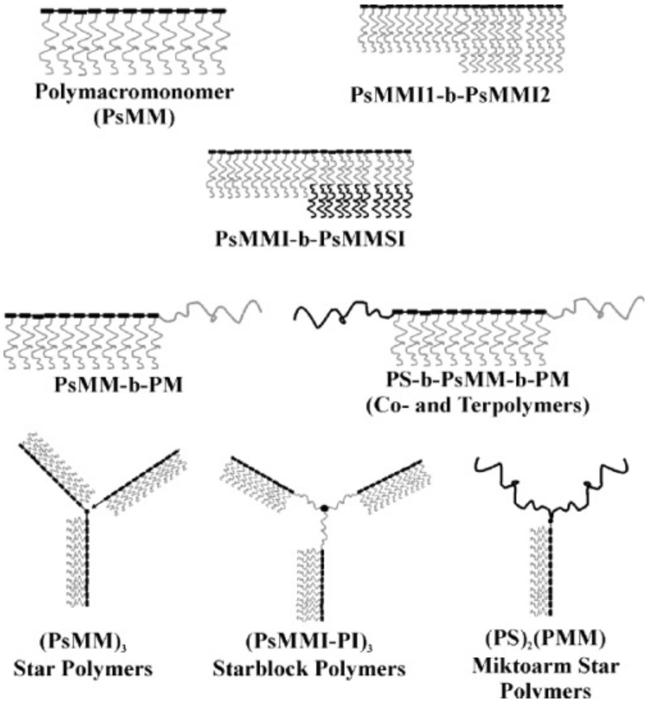
Scheme 1



agent [methanol], and coupling agents [dichlorodimethylsilane (Me_2SiCl_2, Aldrich, 99%+), trichloromethylsilane ($MeSiCl_3$, Aldrich, 97%+), and 1,2-bis(dichloromethylsilyl)ethane (BDCSE)] were purified using high-vacuum techniques and standard procedures described in detail elsewhere.[17] The initiator *sec*-BuLi was prepared from *sec*-BuCl and lithium,[17] and the dual functionality compound 4-(chlorodimethylsilyl)-styrene (CDMSS) was from the Grignard reagent of 4-chlorostyrene and Me_2SiCl_2.[16,18] Details for the synthesis of sMMI, sMMB, and sMMSI are given in our previous papers.[15,16] The quantities of the final polymers ranged between 5 and 7 g. For all samples prepared (precursors, final products) the difference between experimentally determined and stoichiometric molecular weights were within 5−10%.

Synthesis of Diblock Copolymers (PsMM-*b*-PM) and Triblock Terpolymers (PS-*b*-PsMM-*b*-PM). Diblock copolymers of PB or PI macromonomers with styrene, isoprene, or butadiene were prepared by sequential addition of macromonomers and the conventional monomers to *sec*-BuLi. The macromonomers were produced by slow addition of the living chain into the CDMSS solution, followed by the addition of *sec*-BuLi or the macroinitiator (PSLi).

After complete polymerization of the macromonomer (about 12 h), an aliquot was removed for characterization, and the purified second monomer (styrene, isoprene, or butadiene) was added into the reactor. The polymerization was terminated by methanol; the copolymer was precipitated into excess of methanol, redissolved in toluene, precipitated/washed again with methanol, and dried.

The reverse procedure, i.e., the addition first of styrene and then of the macromonomers to *sec*-BuLi, was also used with success. Living PS-*b*-PsMM$^-$Li$^+$ was used for the preparation of PS−PMM−PM triblock co- or terpolymers of isoprene and butadiene, by adding the appropriate monomer to the reaction solution. The polymerization was terminated by methanol; the triblock copolymer was precipitated into excess of methanol, redissolved in toluene, precipitated/washed again with methanol, and dried.

Synthesis of Diblock Copolymacromonomers (PsMM1-*b*-PsMM2). These materials are composed of two different polymacromonomer blocks. The first polymacromonomer block PsMM1$^-$Li$^+$ was prepared and collected into an ampule having a break-seal. This ampule is then connected to the apparatus that will be used to prepare the second macromonomer. The synthesis of the second macromonomer was also performed according to the given procedure[16] and was then polymerized using the living PsMM1$^-$Li$^+$ as initiator. The diblock copoly(macromonomer) polymer was terminated, washed and precipitated in methanol twice, and then dried.

Synthesis of 3-Miktoarm Star Copolymers of PS and Polymacromonomer, (PsMMB)(PS)$_2$. Polymerization of styrene was carried out as described above. After complete consumption of the monomer, $MeSiCl_3$ was added in a ratio [PS$^-$Li$^+$]:[$MeSiCl_3$] = 2.2: 1. One week later $(PS)_2(Me)SiCl$ was obtained as was concluded by molecular weight characterization. The steric hindrance caused by the first two PS blocks does not allow a third PS arm to react with the last chlorine.[19]

The living polymacromonomer PsMMB$^-$Li$^+$ was prepared in a secondary reactor and end-capped with ∼5 units of butadiene, by adding butadiene and allowing the reaction to proceed for 24 h. The PsMMB$^-$Li$^+$ was added to $(PS)_2(Me)SiCl$, in a 1:2 ratio. The progress of the linking reactions was monitored by taking samples and analyzing them by SEC. The reaction was completed after 1 month.

Synthesis of 3- and 4-Arm Star Polymacromonomers, (PsMMB)$_3$ and (PsMMB)$_4$. The living polymacromonomers (PsMMB$^-$Li$^+$) were synthesized as described before. After complete polymerization of the macromonomer, an aliquot was removed for characterization, and a small quantity of purified butadiene diluted in benzene was added into the reactor. The butadiene is used for end-capping of the bulky polymacromonomer to allow easy access to the linking reagent. Approximately ∼8 butadiene monomeric units were used for end-capping. After 24 h the break-seal of the ampule containing the linking reagent, namely ($MeSiCl_3$) for the 3-arm star and 1,2-bis(dichloromethylsilyl)ethane (BDCSE) for the 4-arm star polymers, was ruptured, and the linking agent was introduced to the reactor. The ratio used was [PsMMB$^-$Li$^+$]:[$MeSiCl_3$] = 6:1 and [PsMMB$^-$Li$^+$]:[BDCSE] = 6:1. The progress of the linking reactions was monitored by SEC.

Synthesis of 3-Arm Star Block Copolymacromonomers, (PMMI-*b*-PI)$_3$. Synthesis of the “living” PMMI-*b*-PI$^-$Li$^+$ was carried out as described above, and then $MeSiCl_3$ was added in the reactor in a [PMMI-*b*-PI$^-$Li$^+$]:[$MeSiCl_3$] = 6:1 ratio. The progress of the linking reactions was monitored with SEC and was completed after 3 weeks.

Molecular Characterization. SEC analysis was performed using a Waters HPLC system equipped with a Waters 501 high-pressure liquid chromatographic pump, four Waters Styragel columns having a porosity range of 10^2−10^6 Å, and a Waters 410 differential refractometer detector and a UV detector. The linear range of the calibration curve was between 3.0×10^3 and 6.0×10^5, covering the molecular weight range of the measured samples. Tetrahydrofuran was the eluent at a rate of 1 mL/min at 30 °C. Linear PS, PI, and PB standards were used for the calibration of the instrument.

Multidetector SEC analysis (SEC-RI and SEC-TALLS) was performed using a Waters system equipped with a Waters 1525 high-pressure liquid chromatographic pump and Waters Ultrastyragel columns (HR-2, HR-4, HR-5E, and HR-6E) with THF eluent at a rate of 1 mL/min at 30 °C. A Waters 2410 differential refractometer detector and a Precision PD 2020 two angles (15°, 90°) light scattering detector at 35 °C were used.

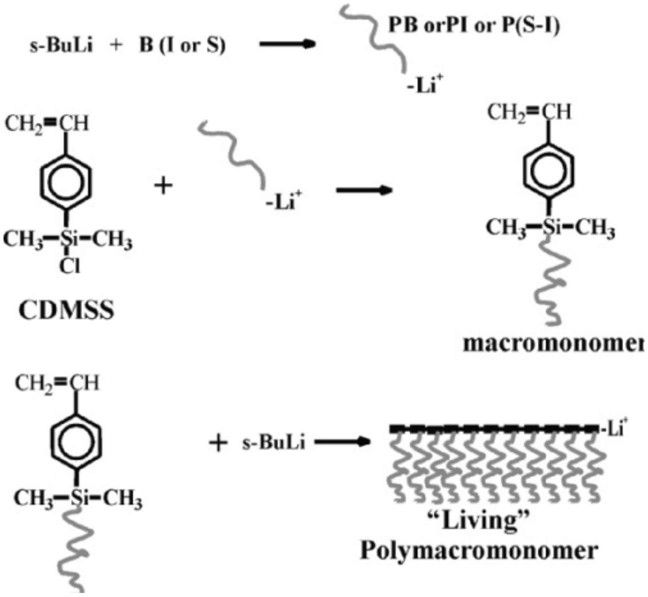
The composition of the copolymers was obtained by ^{1}H NMR spectroscopy (Varian Unity Plus 300/54 instrument) in $CDCl_3$.

Results and Discussion

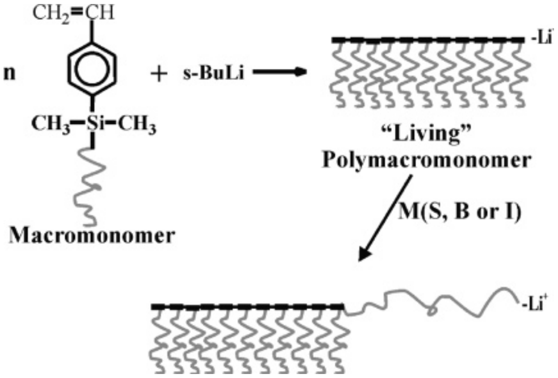
Synthesis of Diblock Copolymers (PsMM-*b*-PM) and Triblock Co- and Terpolymers (PS-*b*-PsMM-*b*-PM).

The key for the synthesis of the styrenic macromonomer is the relatively faster reaction of the living chain with the SiCl group than with the vinyl group (Scheme 2), whereas for the synthesis of the polymacromonomer the key is the in-situ polymerization without

Scheme 2



Scheme 3



isolation.[15,16] The general reactions for the synthesis of diblock copolymers are given in Scheme 3.

The problem encountered in this procedure was that part of the "living" polymacromonomer (10%−40%) was deactivated when the second monomer was added. SEC chromatographs of a typical example (PsMMI1−PI) are given in Figure 1.

This phenomenon is often observed in anionic polymerization in preparation of high molecular weight diblocks, where extremely low concentrations of initiator are used, as in our case (5×10^{-6}−5×10^{-7} mol/mL). When using such low initiator quantities, termination reactions can be observed even when using conventional monomers. The higher the degree of polymerization of the macromonomer (i.e., the smaller the amount of *sec*-BuLi used), the higher the percentage of deactivated polymacromonomer that was observed. The pure diblock was isolated by fractionation, using a toluene/methanol solvent/nonsolvent system (Figure 1f). By adding a nonsolvent into a solution of the polymer (0.5−2% w/v), the species with the higher molecular weight precipitate first due to lower solubility. The molecular characterization results are included in Table 1. NMR analysis of these materials gave % w/w of monomers matching those calculated from M_w.

It is also possible to prepare coil-*block*-polymacromonomer using the reverse procedure (Scheme 4). Styrene is polymerized, and the resulting PS^-Li^+ is used to initiate the macromonomer polymerization. This synthetic sequence proceeded much better than the reverse. Only 5−7% of deactivated PS was observed in the SEC chromatographs of these polymers. Typical SEC chromatograms of macromonomer PI, PS first block, and PS-*b*-polymacromonomer (PS-*b*-PsMMI) are shown in Figure 2.

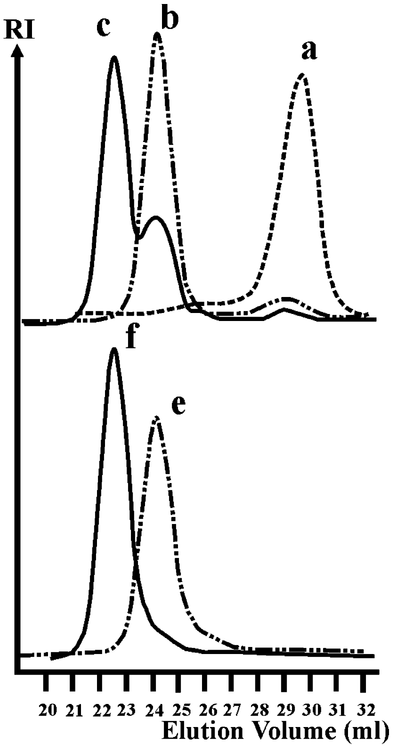


Figure 1. SEC traces of the synthesis of PsMMI 2-*b*-PI: (a) PI macromonomer; (b) polymacromonomer PsMMI 2 (as taken from the reactor); (c) PsMMI 2-*b*-PI diblock polymer (as taken from the reactor); the smaller peak corresponds to deactivated PsMMI 2; (e) polymacromonomer PsMMI 2 (fractionated); (f) PsMMI 2-*b*-PI (fractionated).

Living (PS-*b*-PMM)Li was used for the preparation of triblock co- and terpolymers (Scheme 4). The SEC chromatogram of a coil-*block*-polymacromonomer-*block*-coil triblock terpolymer (PS-*b*-PsMMI-*b*-PI), a typical example, is shown in Figure 2. The molecular characteristics of the final triblock co- and terpolymers as well as of the precursors are given in Table 2.

As concluded from molecular characterization the polymers have very narrow molecular weight distributions. The second route presented for the preparation of coil-*b*-polymacromonomer diblocks can only be used with PS first block. PS^-Li^+ will efficiently initiate polymerization of the styrenic macromonomers, while polyisoprenyllithium or butadienyllithium will not unless a polar additive is used (e.g., THF).[17]

Synthesis of Diblock Copolymacromonomers (PsMM1-*b*-PsMM2). If the living polymacromonomer is used to initiate the polymerization of a second macromonomer, then a diblock polymer with blocks of two different macromonomers can be obtained. Two molecules of this type were synthesized: PMMIa-*b*-PMMIb and PMMIa-*b*-PMM(S-I). The general reactions of this synthesis are given in Scheme 5, and the SEC chromatographs of the synthesis of PMMIa-*b*-PMMIb, as an example, are given in Figure 3.

Molecular characterization results are given in Table 3.

Table 1. Polymacromonomer-*block*-Coil Diblock Copolymers (PsMM-*b*-PM)

sample	macromonomer (M_w/(g/mol), M_w/M_n)^a	M_w polymacromonomer^a (M_w/M_n)	2nd block	$M_w{}^a$ diblock (M_w/M_n)
PsMMI 1-PS	PI (6200, 1.05)	96 000 (1.07)	PS	302 000 (1.10)
PsMMI 2-PI	PI (3500, 1.06)	58 000 (1.05)	PI	91 000 (1.05)
PsMMB 1-PS	PB (2000, 1.06)	36 000 (1.08)	PS	132 000 (1.07)
PsMMB 1-PI	PB (2000, 1.06)	36 000 (1.08)	PI	60 000 (1.07)
PsMMB 2-PB1	PB (3500, 1.05)	119 000 (1.06)	PB	129 000 (1.04)
PsMMB 2-PB2	PB (3500, 1.05)	119 000 (1.06)	PB	143 000 (1.03)

[a] Results from SEC-TALLS in THF.

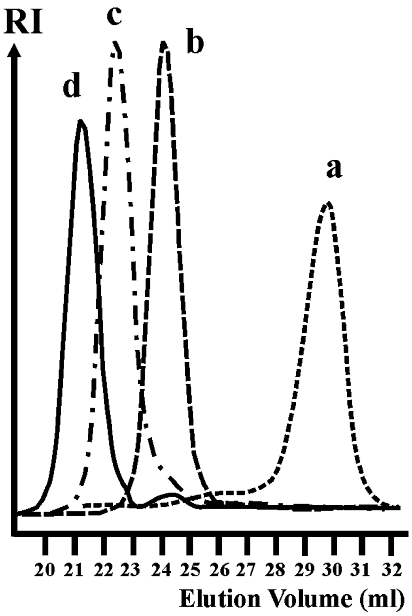


Figure 2. SEC traces of the synthesis of PS-PsMMIa-*b*-PS: (a) PI macromonomer; (b) PS first block; (c) PS-*b*-PsMMI block polymer (as taken from the reactor); (d) PS-*b*-PsMMI-*b*-PS triblock copolymer (as taken from the reactor).

Table 2. Characterization Results of PS−PMM-PM Triblock Co- and Terpolymers and of PS−PMM Diblock Precursors

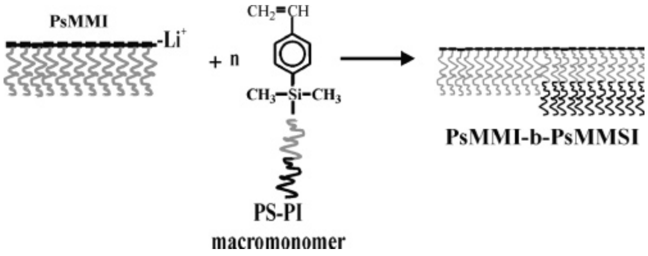
sample	macromonomer (M_w/(g/mol), M_w/M_n)^a	3rd block	$M_w{}^a$	$M_w/M_n{}^a$
PS (1st block)			47 000	1.01
PS−PsMMI	PI (3700, 1.07)		105 000	1.04
PS−PsMMI−PI	PI (3700, 1.07)	PI	142 000	1.05
PS−PsMMI−PS	PI (3700, 1.07)	PS	140 000	1.07
PS−PsMMB	PB (3500, 1.05)		131 000	1.07
PS−PsMMB−PB	PB (3500, 1.05)	PB	195 000	1.05
PS−PsMMB−PS	PB (3500, 1.05)	PS	189 000	1.07

[a] Results from SEC-TALLS and SEC-UV/RI in THF.

Scheme 4

Synthesis of Miktoarm Star Copolymers of PS and Polymacromonomer, (PsMMB)(PS)$_2$. Even more complex macromolecular architectures can be prepared via the living polymacromonomer method. Miktoarm stars having two coil blocks (PS) and one polymacromonomer block were prepared using chlorosilane chemistry. The synthesis of these molecules is outlined in Scheme 6.

Scheme 5



The preparation of the macromolecular linking agent having one chlorosilyl group and two PS arms (PS)$_2$(Me)SiCl was achieved by addition of MeSiCl$_3$ directly to living PS in a [PS$^-$Li$^+$]:[MeSiCl$_3$] = 2.2:1 ratio. After 1 week the desired product was obtained, which was verified by molecular characterization (Figure 4). This simple procedure is based on the steric crowding caused by the first two PS blocks that are incorporated to the silicon molecule. A third PS arm that is very bulky cannot react with the last chlorine, unless a large excess is used and even then very slowly.[19]

The living polymacromonomer PsMMB$^-$Li$^+$ was end-capped with a few units of butadiene. The styrenic end unit of the living polymacromonomer was transformed to butadienyllithium to allow easier access to the chlorosilyl group of (PS)$_2$(Me)SiCl, as is standard procedure in these reactions.[1] The (PS)$_2$(Me)SiCl was used in 2:1 excess compared with the living polymacromonomer. Usually in star copolymer synthesis using the chlorosilane method, the last living polymer to be added is used in excess.[1] Here we used the (PS)$_2$(Me)SiCl in excess since we considered that the less reactive molecule in this reaction is PsMMB$^-$Li$^+$ (see below). The progress of the linking reactions was monitored by taking samples and analyzing with SEC. SEC chromatographs of the synthesis of (PSb)$_2$(PsMMB3) are given in Figure 4.

The reaction was completed after 1 month. The star polymer was fractionated using the toluene:DMF(4:1)/methanol solvent/nonsolvent system. 10% of deactivated polymacromonomer was also present in the byproducts of the reaction. Extensive molecular characterization of the fractionated product proved that it is the desired miktoarm star polymer. Molecular characteristics of the two miktoarm stars prepared in this fashion are presented in Table 4.

Synthesis of Star Block Polymers (PMMI2-PI)$_3$ and Attempts for the Synthesis of (Polymacromonomer)$_3$ and (Polymacromonomer)$_4$ Stars. Several attempts were made to prepare A$_3$-type star with polymacromonomer arms by using MeSiCl$_3$ as coupling agent (Scheme 7B).

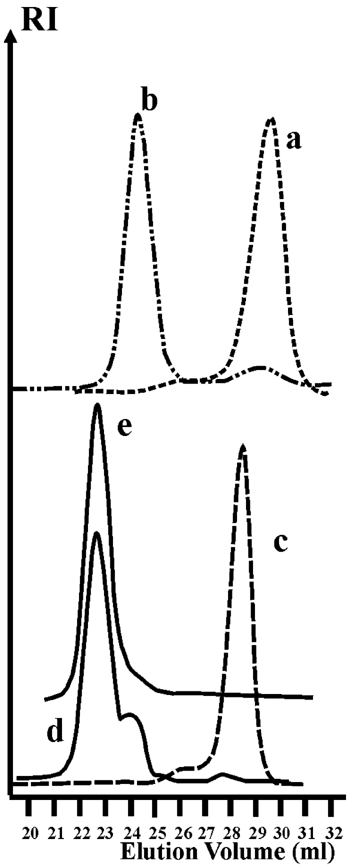


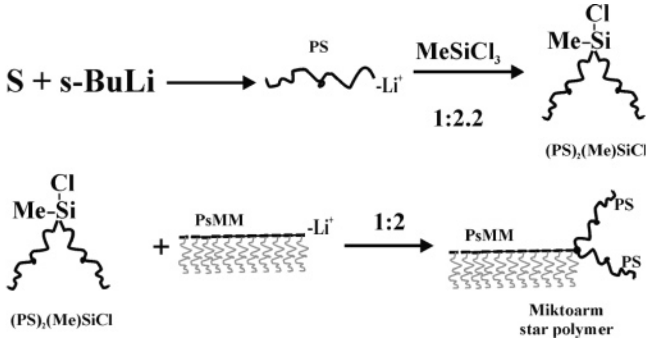
Figure 3. SEC traces of the synthesis of PsMMIa-*b*-PsMMIb: (a) PIa macromonomer; (b) PsMMIa polymacromonomer; (c) PIb macromonomer; (d) diblock polymacromonomer PsMMIa-*b*-PsMMIb (as taken from the reactor); (e) diblock polymacromonomer PsMMIa-*b*-PsMMIb (fractionated).

Table 3. Characterization Results of PsMMIb-*b*-PsMMIc and PsMMIb-*b*-PsMM(S-I) Diblock Polymacromonomers

sample	$M_{\mathrm{w}}{}^{a}$ (g/mol)	$M_{\mathrm{w}}/M_{\mathrm{n}}{}^{a}$
PIa macromonomer	3 500	1.05
PsMMIa	58 000	1.04
PIb macromonomer	7 500	1.04
PsMMIa-*b*-PsMMIb	176 000	1.11
PS−PI macromonomer (PS:50%)	6 800	1.05
PsMMIa-*b*-PsMM(S-I)	392 000	1.12

[a] Results from SEC-TALLS and SEC-UV/RI in THF.

Scheme 6



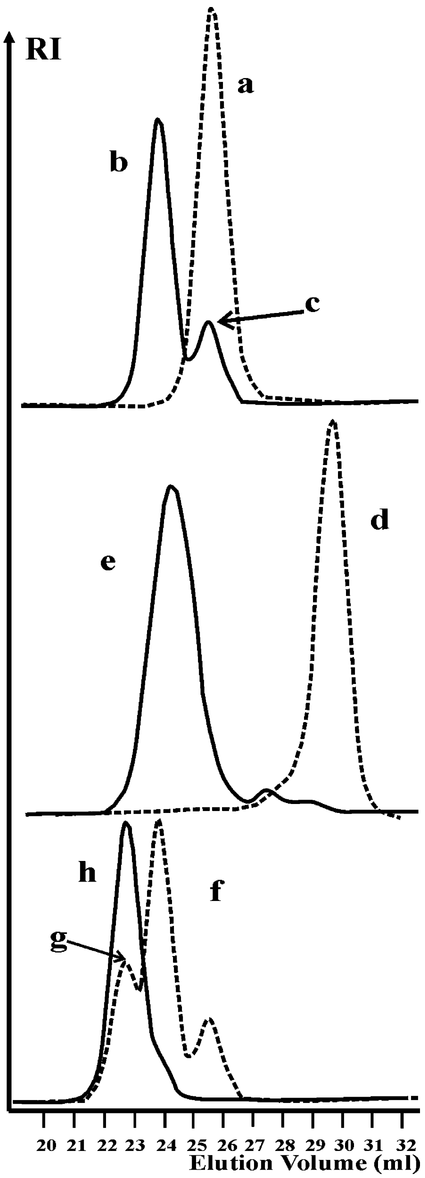


Figure 4. SEC traces of the synthesis of PsMMB4(PS)$_2$ mikto arm star block polymer: (a) PS precursor; (b) (PS)$_2$(Me)SiCl; (c) PS precursor excess; (d) PB macromonomer; (e) PsMMB 3 polymacromonomer; (e) final product as taken from the reactor (dotted line); (f) star polymer peak; (g) fractionated (PsMMB 3)(PS)$_2$ miktoarm star polymer (solid line).

Table 4. Molecular Characteristics of Miktoarm Star Polymers PsMMB(PS)$_2$

sample	$M_{\mathrm{w}}{}^{a}$ (g/mol)	$M_{\mathrm{w}}/M_{\mathrm{n}}{}^{a}$
PSa branch	29 000	1.02
PsMMB 3	45 000	1.05
(PSa)$_2$(PsMMB3)	106 000	1.04
PSb branch	69 000	1.01
PsMMB 4	94 000	1.05
(PSb)$_2$(PsMMB4)	218 000	1.06

[a] Results from SEC-TALLS in THF.

The macromonomer was end-capped with 6−8 units of butadiene to avoid steric hindrance at the active site of the chlorosilane. The "living" polymacromonomer was used in large excess (100%) in comparison with the chlorines to make certain that the reaction will take place. One week after the reaction a sample was taken from the reactor, and the SEC chromatograms (Figure 5) showed that 30% of the "living" polymacromonomer had reacted to form the product.

Samples were taken regularly, but the reaction did not proceed any further. After 1 month the reaction was stopped, and the product was separated from the remaining polymacromonomer by fractional precipitation. SEC-TALLS analysis showed that the molecular weight of the product was 2.3 times larger than the corresponding polymacromonomer (PsMMB 4: $M_{\mathrm{w}} = 94$

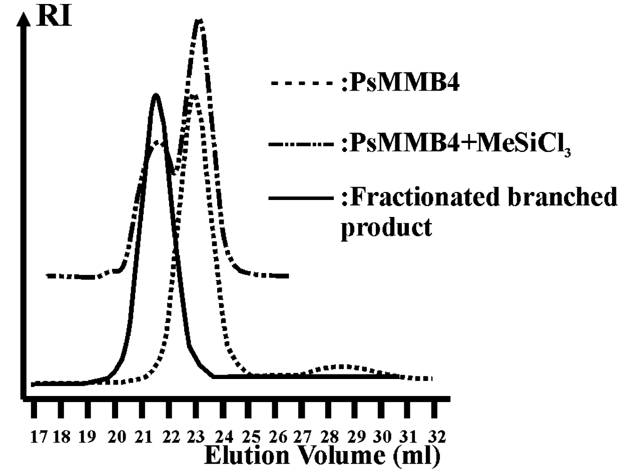
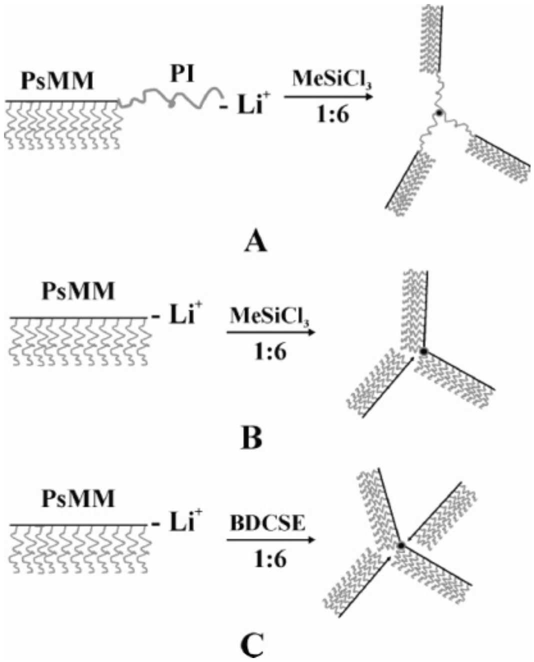


Figure 5. SEC traces of attempted synthesis of A_3 star $(PsMMB5)_3$.

Scheme 7



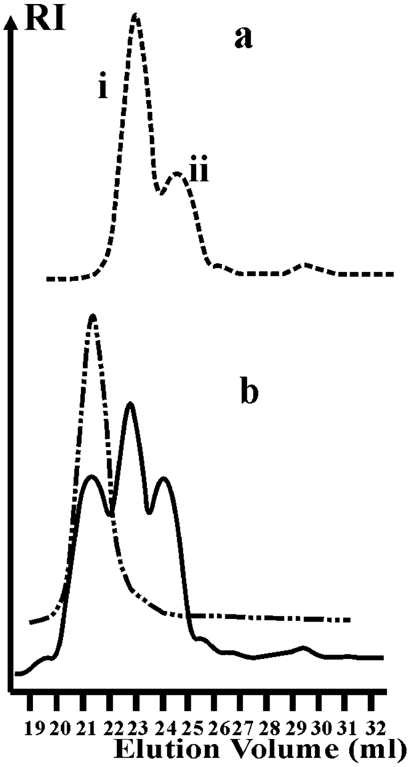


Figure 6. SEC traces of the synthesis of (PsMMI 2-*b*-PI) star block polymer. (a) PsMMI 2-*b*-PI: (i) living polymer; (ii) deactivated polymacromonomer. (b) Star block polymer $(\text{PsMMI 2-}b\text{-PI})_3$: solid line, product as taken from the reactor; dashed line, fractionated star polymer.

kg/mol, product M_w = 210 kg/mol) (see Table 4 for PsMMB 4 molecular characteristics). We can conclude that the product of the reaction is a mixture of dimers and trimers. Further fractionation of the product was impossible as polymacromonomer dimers and A_3 star eluted in the same time in SEC. We were led to the conclusion that the active center of the polymacromonomer was too sterically overcrowded by neighboring side branches to effectively react with the chlorosilane. To verify this 1,2-bis(dichloromethylsilyl)ethane (BDCSE), in which the two pairs of chlorine are far apart, thus rendering the silane atoms less crowded, was used as coupling agent. The same procedure as above was used with the same "living" polymacromonomer (PsMMB 4) (Scheme 7C). In this case the reaction proceeded to 35% of product, still less than the expected amount. After 1.5 months the reaction was stopped, and the product was fractionated and characterized. SEC-TALLS analysis showed that the molecular weight ratio of the product to the polymacromonomer precursor was 2.4:1 (PsMMB 4, M_w = 94 kg/mol, product M_w = 218 kg/mol) (Table 4), rather than the expected 4:1 molecular weight ratio. Repeated experiments showed more or less the same results, demonstrating the inability to quantitatively incorporate three (or four) polymacromonomers in the same star molecule. We can further comment that this is not due to active center steric hindrance, as the aforementioned reaction of PSLi with $MeSiCl_3$, but is probably connected with the overall bulkiness and dense structure of the polymacromonomers. This is in agreement with Roovers et al. results,[20] where, when the molecular weight of the arm was increasing, the linking reaction of PSLi with BDCSE was not quantitative due to the bulkiness of the PS arms.

The next step was to use a polymacromonomer-*b*-coil diblock to investigate whether these complex molecules can form stars (Scheme 7A). The diblock was synthesized as described above (PsMMI 2-PI: PI macromonomer M_w = 3.5K; PPsMMI 2 M_w = 58 kg/mol; PsMMI 2-PI total M_w = 91 kg/mol) (Table 1). Upon completion of the polymerization, we found, as reported above, that an amount of the living polymacromonomer was terminated (26%). Using this new concentration of living centers (i.e., calculating deactivated active centers) and using 100% excess compared to the chlorines, we repeated the coupling reaction with $MeSiCl_3$. The idea was to further remove the active center from the bulky polymacromonomer (about 500 monomeric units instead of 6−8). This time SEC analysis showed a 45% product. The reaction was left for 1 month, and samples were taken frequently for SEC analysis (Figure 6). The product was subsequently fractionated, and the M_w was found to be 279 000, which gives an exactly 3:1 ratio with the branches we used (PsMMI 2-PI). Taking into consideration that the two molecules we used for the experiments (PsMMB 4 and PsMMI 2-*b*-PI) have about the same molecular weight, we can see how significant was the role of the highly compact structure of the polymacromonomer in preventing the coupling reaction (Scheme 7).

Conclusions

Sequential anionic polymerization of conventional monomers and styrenic macromonomers was used to prepare a variety of novel complex macromolecular architectures based on polymacromonomers. Our results indicate that if the styrenic macromonomers are used without the isolation step, they behave much like styrene. "Living" polymacromonomers were used to synthesize star polymers. It was demonstrated that no more than two polymacromonomer molecules can be quantitatively coupled due to their bulky and dense structure. However, miktoarm star polymers having one polymacromonomer branch as well as star block polymers with polymacromonomer outer blocks were successfully prepared, demonstrating the synthetic capabilities of the anionic "living" polymacromonomer.

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References and Notes

(1) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747.

(2) Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. *Macromolecules* **1998**, *31*, 9413.

(3) Borner, H. G.; Beers, K. L.; Matyjaszewski, K.; Sheiko, S. S. *Macromolecules* **2001**, *34*, 4375.

(4) Matyjaszewski, K.; Qin, S.; Broyce, J. R.; Shirvanyants, D.; Sheiko, S. S. *Macromolecules* **2003**, *36*, 1843.

(5) Schappacher, M.; Deffieux, A. *Macromol. Chem. Phys.* **1997**, *198*, 3953.

(6) Ryu, S. W.; Hirao, A. *Macromolecules* **2000**, *33*, 4765.

(7) Schappacher, M.; Billaud, C.; Paulo, C.; Deffieux, A. *Macromol. Chem. Phys.* **1999**, *200*, 2386.

(8) Hirao, A.; Ryu, S. W. *Macromol. Symp.* **2003**, *192*, 31.

(9) Ryu, S. W.; Asada, H.; Watanabe, T.; Hirao, A. *Macromolecules* **2004**, *37*, 6291.

(10) Hadjichristidis, N.; Pitsikalis, M.; Iatrou, H.; Pispas, S. *Macromol. Rapid Commun.* **2003**, *24*, 979.

(11) Tsukahara, Y.; Mizuno, K.; Segawa, A.; Yamashita, Y. *Macromolecules* **1989**, *22*, 1546.

(12) Tsukahara, Y.; Tsutsumi, K.; Yamashita, Y.; Shimada, S. *Macromolecules* **1990**, *23*, 5201.

(13) Rempp, P.; Lutz, P. J.; Masson, P.; Chaumont, P.; Franta, E. *Macromol. Chem., Suppl.* **1985**, *13*, 47.

(14) Ederle, Y.; Isel, F.; Grutke, S.; Lutz, P. J. *Macromol. Symp.* **1998**, *132*, 197.

(15) Pantazis, D.; Chalari, I.; Hadjichristidis, N. *Macromolecules* **2003**, *36*, 3783.

(16) Vazaios, A.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.*, in press.

(17) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211.

(18) Chalari, I.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1519.

(19) Wright, S. J.; Young, P. N.; Croucher, T. G. *Polym. Int.* **1994**, *33*, 123.

(20) Roovers, J.; Bywater, S. *Macromolecules* **1972**, *5*, 384.

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