Anionic Polymerization of Styrenic Macromonomers

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Introduction. Polymacromonomers[1−3] are comblike polymers with an extremely high-density branching, since each monomeric unit bears a polymeric chain. Depending on the degree of polymerization of the side and the main chain, they can form either starlike or brushlike (molecular brushes) structures. The most popular polymerization of macromonomers[4−6] is by using radical initiators.[7−10] Ring-opening (ROMP),[11,12] atom transfer radical (ATRP),[13−17] and Ziegler−Natta[18] polymerization of macromonomers[19] have also been reported in the literature. A few attempts have been undertaken for the anionic polymerization of macromonomers without complete success.[20] It seems that during the polymerization the growing macroanions are terminated by impurities accompanying the macromonomers. These impurities are introduced during the isolation step of macromonomer by pouring the macromonomer solution into the nonsolvent. Since macromonomers are solid materials, their purification to the standards required for anionic polymerization is extremely difficult.

In this communication, we are proposing a new methodology to overcome this problem by synthesizing and polymerizing the macromonomer in the same reactor and by using high-vacuum techniques.

Experimental Section. Purification of all monomers (isoprene, butadiene, styrene), solvents (benzene and tetrahydrofuran), and terminating agent (methanol) were performed using standard high-vacuum techniques, described in detail elsewhere.[21] *sec*-Butyllithium (*sec*-BuLi), prepared from *sec*-butyl chloride and lithium dispersion, was the initiator for all polymerizations. Magnesium turnings (Aldrich) were washed with THF and dried in the vacuum line. *p*-Chlorostyrene was distilled under vacuum, over calcium hydride, to ampules equipped with break-seals. 4-(Chlorodimethylsilyl)styrene (CDMSS) was prepared from the Grignard reagent of *p*-chlorostyrene and dichlorodimethylsilane, using high-vacuum techniques, as reported in detail recently.[22]

Polymerizations and linking reactions were carried out in evacuated, *n*-BuLi-washed, and solvent-rinsed glass reactors. Reagents were introduced via break-seals, and aliquots for characterization were removed by heat-sealing of constrictions. Full details of the high-vacuum techniques are given elsewhere.[21] The apparatus of Figure 1 was used for the synthesis and polymerization of macromonomers.

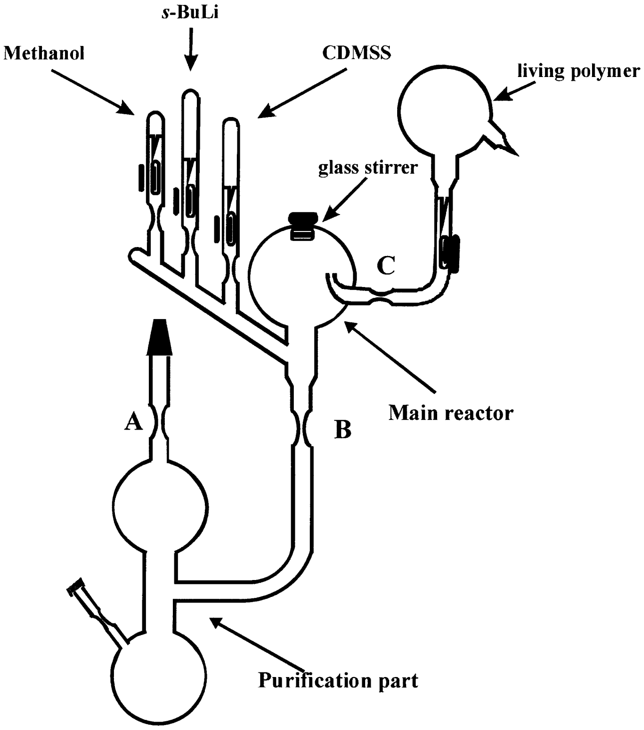

Figure 1. Apparatus for the synthesis and polymerization of macromonomers.

The apparatus (Figure 1) was attached to the vacuum line and evacuated. A few milliliters of *n*-BuLi solution in *n*-hexane was introduced through the septum. After distilling benzene through the vacuum line, the apparatus was again evacuated and sealed off at constriction A. The apparatus was purged with the *n*-BuLi benzene solution, and the purified part was removed by heat-sealing at constriction B. The 4-(chlorodimethylsilyl)styrene solution was then introduced to the main reactor by breaking the corresponding break-seal, and the living polymer was added dropwise to the solution of CDMSS, until a permanent weak orange color (end point) appeared. The ampule containing the excess of the living polymer solution was removed by heat-sealing, and the *sec*-BuLi solution was immediately added to the main reactor by breaking the corresponding break-seal. The characteristic deep orange color of polystyryllithium anion immediately appeared, indicating that the polymerization of macromonomer started. The polymerization was monitored by taking samples and analyzing them by SEC. After the complete consumption of the macromonomer, the polymacromonomer was terminated with methanol, precipitated into an excess of methanol, and dried under vacuum, until constant weight.

Size exclusion chromatography with differential refractive index detector (SEC, THF, 30 °C), low-angle laser light scattering (LALLS, THF, 25 °C), and ^{1}H NMR ($CDCl_3$, 30 °C) measurements were performed following procedures described in detail elsewhere.[23,24]

Results and Discussion. The general synthetic route followed for the anionic polymerization of macromonomers is given in Scheme 1.

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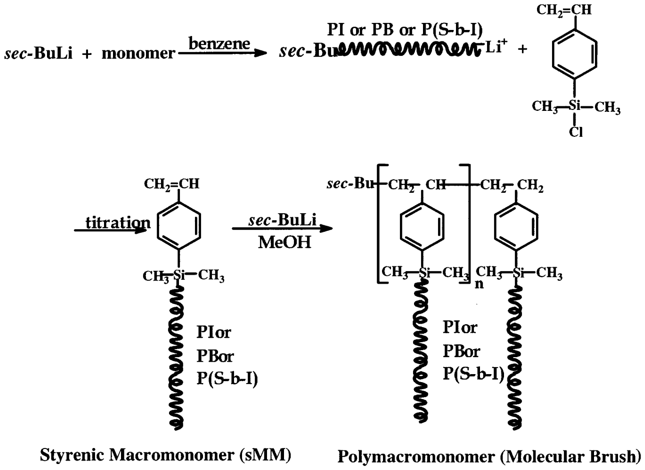
Scheme 1. General Reaction Scheme for the Synthesis of Styrenic Macromonomers and Polymacromonomers of Polyisoprene (PI), Polybutadiene (PB), and Poly(styrene-*b*-isoprene) [P(S-*b*-I)]



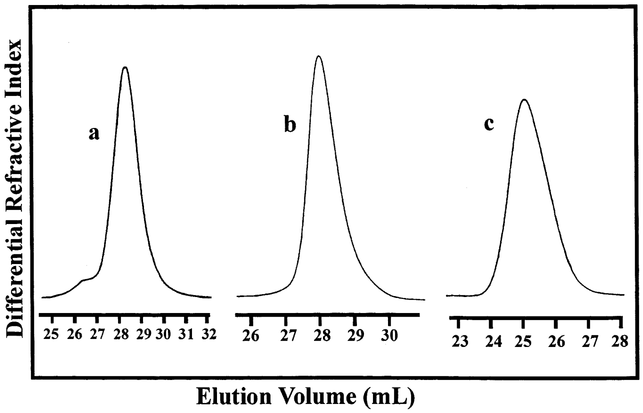


Figure 2. Size exclusion chromatograms of styrenic polyisoprene macromonomer sMMI1 (a) and the corresponding polymacromonomer PsMMI1 (b).

The key factor for the synthesis of the macromonomers is the faster reaction of the living polymer with the chlorosilane group than with the double bond of CDMSS.[25,26] The orange color of the styrenic anion produced, from the reaction of the living chain with the double bond of CDMSS, allows the visual monitoring of the reaction titration. When a permanent weak orange color appears, the addition of the living chain is stopped and *sec*-BuLi is added. The color turns immediately to the characteristic deep orange color of the polystyryllithium anion, indicating the initiation of the polymerization of macromonomers. The produced LiCl does not inhibit the polymerization and in a few cases (methacrylic macromonomers) is beneficial. As an example, Figure 2 gives the chromatograms of the polyisoprene macromonomer sMMI1 and the corresponding polymacromonomer PsMMI1. A small amount (less than 5%) of in-chain living PI is shown in the chromatogram of the macromonomer. This percentage, almost the same for all macromonomers prepared, indicates that the end point was only slightly over passed. Two days after the addition of the initiator, the macromonomer peak disappeared and a new peak, at smaller elution volume, appeared, indicating the success of the polymerization.

Table 1. Molecular Characteristics of Styrenic Polyisoprene (PsMMI) and Polybutadiene (PsMMB) Polymacromonomers

sample	macromonomer $M_n{}^a \times 10^{-3}$	$M_w/M_n{}^a$	polymacromonomer $M_w{}^b \times 10^{-3}$	$M_w/M_n{}^a$
PsMMI1	1.3	1.10	30.8	1.04
PsMMI2	3.2	1.06	35.3[c]	1.04
PsMMI3	3.2	1.06	68.5[d]	1.02
PsMMI4	6.0	1.05	103.9	1.07
PsMMI5	15.0	1.03	125.5	1.11
PsMMB1	4.1	1.06	32.5	1.04

[a] Size exclusion chromatography (SEC) in THF at 25 °C, using PS and PI standards. [b] Low-angle laser light scattering (LALLS) in THF at 25 °C. [c] Calculated $M_n = 35.4 \times 10^3$ (1.9 g of sMMI2 and 5.36×10^{-5} mol of *sec*-BuLi). [d] Calculated $M_n = 70.9 \times 10^3$(1.9 g sMMI3 and $2.68 \times 10-5$ mol *sec*-BuLi).

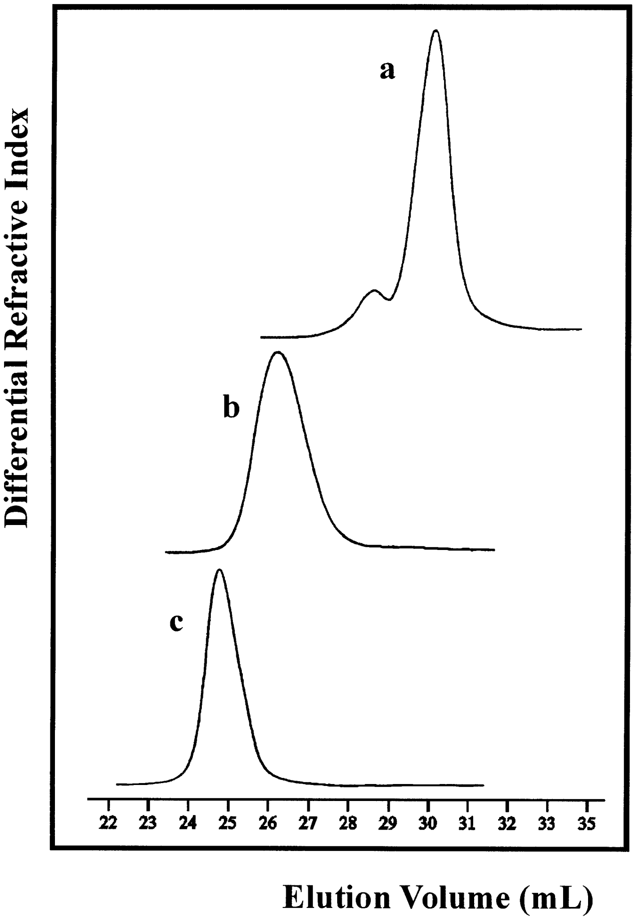


Figure 3. Size exclusion chromatograms of polymacromonomers obtained from the polymerization of 1.9 g of styrenic polyisoprene macromonomer (a), with 5.36×10^{-5} mol of *sec*-BuLi, PsMMI2 (b), and with 2.68×10^{-5} mol of *sec*-BuLi, PsMMI3 (c).

To investigate whether the consumption of the initiator was complete and thus the number-average molecular weight, M_n, is given by the well-known equation [M_n = (g of monomer)/(mol of initiator)], the following experiment was carried out. A solution containing 3.8 g of polyisoprene macromonomer was prepared and divided into two equal parts (1.9 g each) under high-vacuum conditions. The first part was polymerized by using 5.36×10^{-5} mol and the second 2.68×10^{-5} mol of *sec*-BuLi. The polymacromonomer obtained from the polymerization of the second part (PsMMI3) had double the molecular weight than that of the first part (PsMMI2), as determined from LALLS measurements (Table

Table 2. Molecular Characteristics of Styrenic Poly(styrene-*b*-isoprene) Polymacromonomer (PsMMSI)

	PS block		P(S-*b*-I) macromonomer		polymacromonomer		wt % PS
sample	$M_n{}^a \times 10^{-3}$	$M_w/M_n{}^a$	$M_n{}^a \times 10^{-3}$	$M_w/M_n{}^a$	$M_w{}^b \times 10^{-3}$	$M_w/M_n{}^a$	^{1}H NMR
PsMMSI	7.2	1.06	9.8	1.08	58.6	1.07	71

^{a} Size exclusion chromatography (SEC) in THF at 25 °C, using PS and PI standards. ^{b} Low-angle laser light scattering (LALLS) in THF at 25 °C.

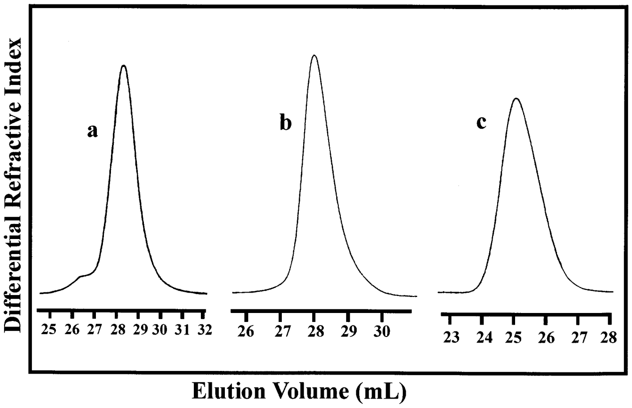


Figure 4. Size exclusion chromatograms of PS block (a), PS-*b*-PI macromonomer sMMSI (b), and the corresponding polymacromonomer, PsMMSI (c).

1), meaning that the consumption of macromonomer was complete. The corresponding chromatograms are given in Figure 3.

Similar results were obtained in the case of polybutadiene macromonomer polymerization. The whole amount of the macromonomer had been consumed in 2 days after the addition of the initiator. The molecular characteristics of polyisoprene and polybutadiene macromonomers and the corresponding polymacromonomers are summarized in Table 1.

A diblock macromonomer of styrene and isoprene, with the PI block attached to CDMSS, was also prepared and polymerized anionically, using the same synthetic route. The chromatograms are given in Figure 4 and the molecular characteristics in Table 2.

Conclusions. It can be concluded that the anionic polymerization of styrenic macromonomers is very well controlled, giving well-defined polymacromonomers and in polymerization rates comparable to that of conventional monomers. It seems that the failure of previous attempts was due to the impurities accompanying the macromonomer. This problem can be overcome by synthesizing and polymerizing the macromonomer in the same reactor, without isolating it.

By using this methodology, a new family of well-defined complex macromolecular architectures, having macromonomers as building blocks, can be synthesized. A few examples are PsMMI-*b*-PsMMB, PsMMI-*co*-PsMMB, PsMMI-*b*-PS-*b*-PsMMI, $(\text{PsMMI})_3$, PsMMSIM, etc. Further research concerning the influence of chemical nature and molecular weight on the anionic polymerization of the macromonomer is in progress.

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