Macromolecules **1992,** *25,* 4649–4651

Synthesis of a Model 3-Miktoarm[†] Star Terpolymer[‡]

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Received February 14, 1992; Revised Manuscript Received April 13, 1992

ABSTRACT: The synthesis of a well-defined, near monodisperse, star terpolymer with three different arms, i.e., polyisoprene, polystyrene, and polybutadiene, is described. The synthetic approach involves the reaction of polyisoprenyllithium with an excess of methyltrichlorosilane followed, after removal of the excess of methyltrichlorosilane, by a stoichiometric addition (titration) of polystyrillithium and finally by a small excess of polybutadienyllithium. The sequence of the addition of the different living polymers is very critical. After linking, the excess of the polybutadienyllithium was terminated with methanol and removed by fractionation. Characterization was carried out by size-exclusion chromatography, low-angle laser light scattering, laser differential refractometry, osmometry, and NMR and UV spectroscopy.

Introduction

Until now, the most rigorous way to prepare symmetrical star homopolymers and block copolymers is the coupling of narrow molecular weight distribution polymers with multifunctional chlorosilane compounds. By this method star polymers with $f \leq 18$ have been prepared.[1-4] Recently, this method has been extended to star polymers with 32 arms by using a starburst dendrimer carbosilane containing 32 Si–Cl bonds at the perimeter.[5] These model homopolymer and block copolymer stars are playing a critical role in the study of the relation between the architecture, the chain conformation, and the properties of the polymers.[6-10]

Pennisi and Fetters,[11] using the chlorosilane method, have prepared narrow molecular weight distribution three-arm polystyrene (PS) and polybutadiene (PBd) stars, where one of the three arms differs in molecular weight from the remaining two. Mays[12] employed that approach to prepare a near monodisperse mixed 3-arm star copolymer (simplest graft) of the A_2B type, where A was polyisoprene (PI) and B was PS. Teyssié and co-workers[13] by using naphtalene-terminated polymers have also prepared mixed star copolymers of the A_2B type, where A is polyoxirane and B poly(*p*-*tert*-butylstyrene), PS, or PI. Quirk and co-workers[14] using 1,1-diphenylethylenes[15] have prepared mixed stars of the A_2B_2 type, where A is PS and B is PI. Finally Rempp and co-workers[16] by using the divinylbenzene method[17] have prepared mixed stars of the A_nB_n type, where n = 3–12, A is PS, and B is poly(*n*-butyl methacrylate). These methods generally give polymers with a higher polydispersity than the chlorosilane route.

In this work the chlorosilane approach has been extended to prepare a new type of model polymer: the 3-miktoarm star terpolymer, an ABC type where A is PI, B is PS, and C is PBd.

Experimental Section

The purification of isoprene (Fluka), styrene (Merck), butadiene (Fluka), and benzene (Merck) to the standards required for anionic polymerization has been described elsewhere.[18,19] The linking agent, methyltrichlorosilane (Merck), was purified by fractional distillation on the vacuum line and subdivided into tubes without addition of solvent. *sec*-Butyllithium, prepared in vacuo from *sec*-butyl chloride and a lithium dispersion, was used as the initiator for all polymerizations. All manipulations were performed, under high vacuum, in glass reactors provided with break-seals for the addition of reagents and constrictions for removal of products. The reactors were previously washed with a benzene solution of *n*-butyllithium (*n*-BuLi) followed by rinsing with benzene, which was the solvent for all polymerization and linking reactions.

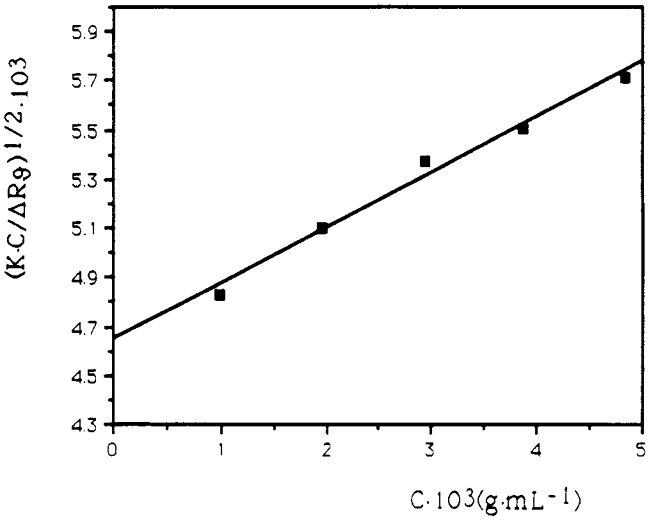

Figure 1. LALLS square-root plot for the 3-miktoarm terpolymer in THF at 25 °C (ΔR_ϑ, excess Rayleigh ratio; K, combination of known optical parameters; C, concentration).

The fractionation of the polymer was carried out by adding methanol to the polymer solution (1% w/v) in benzene at room temperature. It was performed in three steps. The efficiency of the fractionation was checked by size-exclusion chromatography (SEC).

SEC experiments were carried out at 30 °C using a Waters Model 510 pump and Waters Model 401 differential refractometer. Four μ-Styragel columns set with a continuous porosity range from 10^6 to 10^3 Å were used. Tetrahydrofuran (THF) was the carrier solvent at a flow rate of 1 mL/min.

The weight-average molecular weight (M_w) of the 3-miktoarm was measured with a Chromatix KMX-6 low-angle laser photometer. This instrument was equipped with a helium–neon laser and operates at a wavelength of 633 nm. THF, purified over sodium and distilled prior to use, was the solvent at 25 °C. The refractive index increments, dn/dc in THF at 25 °C, were measured with a Chromatix KMX-16 refractometer, operating at 633 nm and calibrated with NaCl solutions.

The number-average molecular weights (M_n) were determined with a Hewlett-Packard 503 membrane osmometer at 35 °C. Toluene, distilled over CaH_2 was the solvent. M_w and M_n were obtained from the corresponding square-root plots in order to minimize the curvature due to the third virial coefficient. In all cases the correlation coefficient was better than 0.99. The low-

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[†] From the greek word *μικτός* meaning mixed.

[‡] Part of this work was presented at the 2nd Greek Polymer Symposium, Athens, Dec 1991.

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0024-9297/92/2225-4649$03.00/0

Table I
Characteristics of the 3-Miktoarm Star Terpolymer

polymer	$M_w^a \times 10^{-4}$ (g·mol^{-1})	$A_2 \times 10^4$ (mL·mol·g^{-2})	$M_n^b \times 10^{-4}$ (g·mol^{-1})	$A_2 \times 10^4$ (mL·mol·g^{-2})	M_w/M_n^c	dn/dc^d (mL·g^{-1})
PI			1.56	18.6	1.03	0.129
PS			2.07	8.48	1.04	0.187
PBd			1.22	31.8	1.03	0.131
3-miktoarm^e	4.64	10.5	4.54	11.9	1.03	0.153

^{a} LALLS in THF at 25 °C. ^{b} Membrane osmometry in toluene at 35 °C. ^{c} SEC in THF at 30 °C. ^{d} Laser differential refractometry in THF at 25 °C. ^{e} 32/42/26 wt % PI/PS/PBd by ^{1}H NMR; 41% PS by UV.

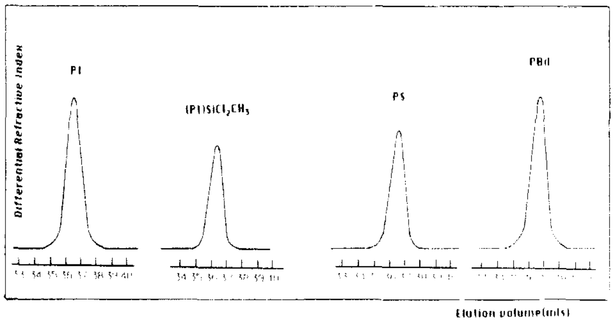

Figure 2. SEC chromatograms of the arm precursors and the methyldichlorosilane-capped polyisoprene (PI)Si(Cl$_2$)CH$_3$.

angle laser light scattering (LALLS) plot for the terpolymer is shown in Figure 1.

The microstructure of the dienic precursors was analyzed by ^{1}H- and ^{13}C-NMR (Bruker AC200) spectroscopy in CDCl$_3$ at 30 °C. The composition of the terpolymer was obtained from the ^{1}H-NMR spectra. The polystyrene content was also obtained by UV analysis at 269 and 262 nm.[20]

Results and Discussion

The synthesis of the 3-miktoarm star terpolymer was performed according to the following basic reactions:

$$\mathrm{PILi + excess\ CH_3SiCl_3 \rightarrow PISi(Cl_2)CH_3 + LiCl + CH_3SiCl_3\uparrow}$$

$$\mathrm{PISi(Cl_2)CH_3 + PSLi \rightarrow (PI)(PS)SiClCH_3 + LiCl}$$

$$\mathrm{(PI)(PS)SiClCH_3 + excess\ PBdLi \rightarrow (PI)(PS)(PBd)SiCH_3 + LiCl}$$

The polyisoprenyllithium (PILi) and polybutadienyllithium (PBdLi), after termination with CH$_3$OH, were found to have, via ^{1}H- and ^{13}C-NMR, the typical microstructures 10% 3,4, 70% cis-1,4, and 20% trans-1,4 for PI and 8% 1,2, 50% cis-1,4, and 42% trans-1,4 for PBd.

The initial step of the synthesis involved the reaction of a solution ~3% w/v of PILi in benzene with an excess of methyltrichlorisilane (Cl/Li ~ 60). The excess of methyltrichlorosilane and benzene were removed under vacuum-line conditions. After pumping for 1 day the product was redissolved in benzene and the solution pumped again for 1 day. Finally the product was redissolved one more time in benzene and pumped for 3 days at 50 °C.

The SEC chromatograph of the macromolecular difunctional linking agent—polyisoprene having the methyldichlorosilane unit at one end—is indistinguishable from the parent material (Figure 2). Thus, this procedure is effective in preparing the macromolecular difunctional linking agent, free from the coupled (linear) or linked (three-arm) polyisoprene.

Benzene was distilled into the reactor. A ~2.5% w/v solution of PSLi in benzene was then added dropwise to the PISi(Cl$_2$)CH$_3$ solution (~10% w/v). The progress of the linking reaction was monitored by removing samples from the reactor and analyzing them by SEC.

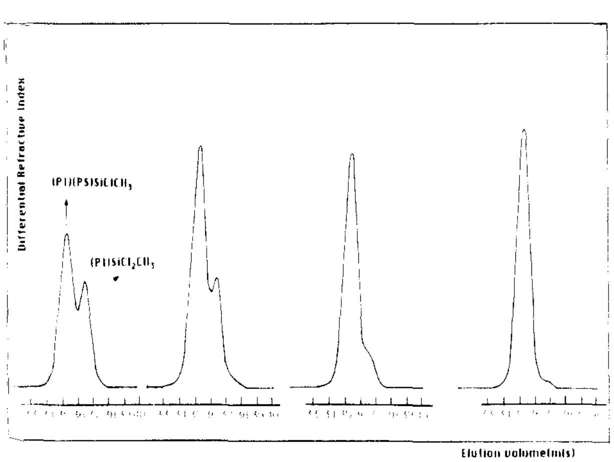

Figure 3. SEC chromatograms of samples taken during the linking reaction of PISi(Cl$_2$)CH$_3$ with PSLi.

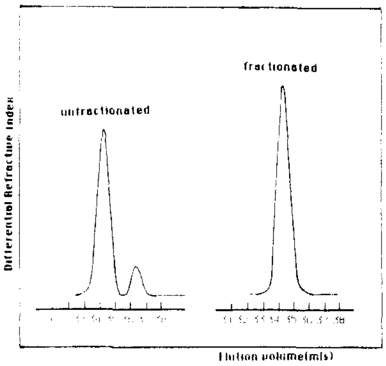

Figure 4. SEC chromatogram of the 3-miktoarm star terpolymer prior to and after three fractionations.

The peak corresponding to the macromolecular difunctional linking agent is decreasing while the (PI)(PS)SiClCH$_3$ peak is increasing (Figure 3). At the end point, the addition of PSLi stopped and a slight excess of a ~10% PBdLi solution in benzene was added.

The synthesis of the star terpolymer relies, on the one hand, on the inability of the sterically hindered, styryl anion[21,22] to undergo complete reaction with the macromolecular difunctional linking agent and, on the other hand, on the ability of the less sterically hindered butadienyl anion to react completely[23] with the monofunctional macromolecular linking agent. Thus, the sequence of the addition of the living polymers is very critical.

The SEC chromatogram of the raw product is shown in Figure 4 along with the chromatogram of the fractionated 3-miktoarm star terpolymer, where the excess of the PBd arm has been removed. The characteristics of the precursors and the fractionated terpolymer are given in Table I.

The good agreement between the apparent M_w determined by LALLS (Table I) and the M_w = 4.72 × 10^3

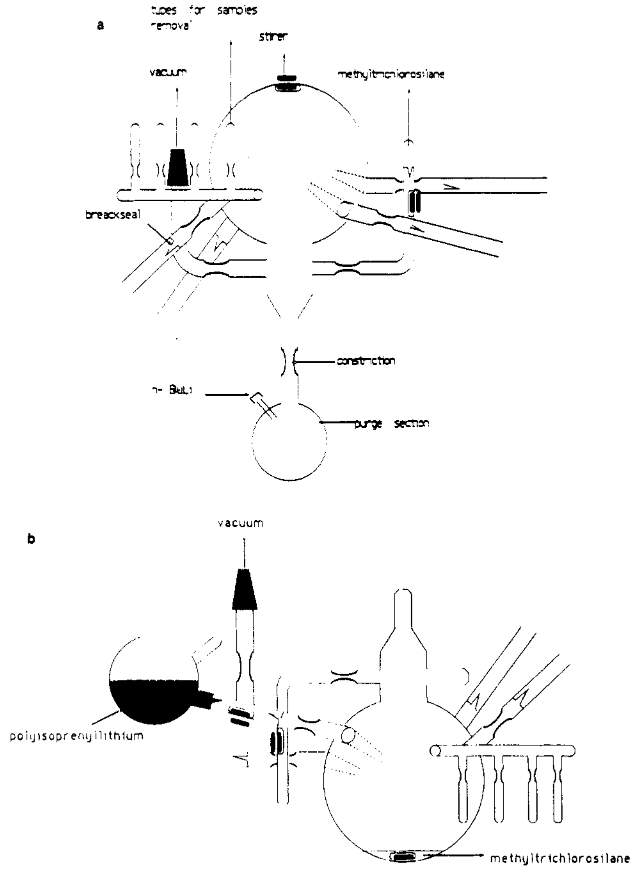

Figure 5. (a) Main reactor for the synthesis of the 3-miktoarm star terpolymer. (b) Sealing the secondary reactor of PILi to the main reactor.

calculated from the M_n and M_w/M_n of the terpolymer indicates the high degree of homogeneity in molecular weight and composition.[24]

This fact is also supported by (a) the good agreement between the composition of the terpolymer calculated from the M_n of the arms (PI, 32.2%; PS, 42.6%; PBd, 25.2%) and found by ^{1}H NMR and UV and (b) the excellent agreement between the dn/dc value found experimentally and calculated (0.154 mL·g^{-1}) from the following equation:

$$(\mathrm{d}n/\mathrm{d}c)_{\mathrm{ter}} = x(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PI}} + y(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PS}} + (1 - x - y)(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PBd}}$$

where x and y are the PI and PS contents, respectively, in % w/w. In conclusion, the combined characterization results indicate that the 3-miktoarm star terpolymer, having a high degree of molecular and compositional homogeneity, can be synthesized by using anionic polymerization techniques and methyltrichlorosilane as the linking agent.

Because of the incompatibility of PI, PS, and PBd, the morphologies of such "paranoic" macromolecules would be expected to be interesting.[25] This synthetic approach can also be used for the synthesis of star terpolymers having, for example, hydrophobic and hydrophilic, amorphous and crystalline (i.e., after hydrogenation of PBd 1,4), hydrogenated and deuterated arms.

Acknowledgment. We greatly appreciate the many fruitful discussions we have had with Dr. J. Roovers, Dr. L. Fetters, and Prof. J. W. Mays during their visit to our laboratory.

Appendix

The apparatus shown in Figure 5a was the main reactor for the synthesis of the 3-miktoarm star terpolymer. In this reactor all linking reactions were performed, while the living polymers PILi, PSLi, and PBdLi were prepared in secondary classic reactors in benzene at room temperature using *sec*-BuLi as the initiator. After removal of a sample for characterization, the secondary reactors were sealed to the main reactors via break-seals and by reattachment to the vacuum line as shown in Figure 5b.

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Registry No. (PI)(PS)(PBd) (copolymer), 110389-01-0.