Synthesis of Model Nonlinear Block Copolymers of $A(BA)_2$, $A(BA)_3$, and $(AB)_3A(BA)_3$ Type

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INTRODUCTION

Due to the academic and industrial significance of block copolymers, the design and synthesis of new such materials is of great interest. For this reason nonlinear block copolymers have recently received much attention. A family of nonlinear block copolymers are the so-called miktoarm (mikto comes from the Greek word *μικτος* meaning mixed) star copolymers, which are star-shaped molecules having chemically different arms.[1–12] In this study, anionic polymerization and chlorosilane chemistry were used to prepare new model miktoarm stars of the $A(AB)_2$ and $A(AB)_3$ type, as well as, model bridged miktoarm stars of the $(AB)_3A(BA)_3$ (or Super H-shaped) type (see Scheme 1). In all cases A is polystyrene (PS) and B polyisoprene (PI). The intermediate and final products were characterized by size exclusion chromatography, low-angle laser light scattering, laser differential refractometry, membrane osmometry, ^{1}H-NMR, and UV spectroscopy.

EXPERIMENTAL

The purification of styrene (Merck), isoprene (Fluka), and benzene (Merck) to the standard required for anionic polymerization has been described elsewhere.[13] Tetrahydrofuran (THF, Merck) was stirred overnight over CaH_2, distilled on the vacuum line to a sodium mirror and was left for 24 h to react. This procedure was repeated until no degradation of the sodium mirror was observed. Then it was distilled into a flask containing a sodium mirror and traces of styrene. The appearance of red color due to the formation of PSNa is an indication of the THF high purity. A middle fraction of THF was always used. Methyltrichlorosilane and tetrachlorosilane were fractionally distilled on the vacuum line and were subdivided into ampules. *sec*-Butyllithium, prepared from *sec*-butyl chloride and a lithium dispersion, was the initiator and benzene the solvent for the polymerizations leading to ω-monofunctional living polymers. Sodium napthalenide[14] prepared from napthalene (purified by triple sublimation) and sodium was the initiator and a mixture of tetrahydrofuran and benzene the solvent for the synthesis of α, ω-difunctional living polymers.

Fractionation was carried out by adding methanol to the polymer solution (ca. ~ 0.5% w/v) in toluene at room temperature with stirring until turbidity was established. The mixture was then heated gently with stirring until clear, transferred to a warm separatory funnel and allowed to equilibrate at room temperature overnight. This procedure was repeated until no precursors or undesirable products were shown to be present by size exclusion chromatography (SEC).

SEC experiments were carried out at 30°C using a Waters model 510 pump, Waters Model 410 differential refractometer and Waters model 486 tunable absorbance detector. Three Phenomenex (type: phenogel 5 linear, pore size: $50-10^{-6}$ Å) columns were used. THF distilled over CaH_2 and sodium was the carrier solvent at a flow rate of 1 mL/min.

The weight-average molecular weight (M_w) of the final polymers was determined with a Chromatix KMX-6 low-angle laser photometer (LALLS). This instrument, equiped with a helium–neon laser was operating at a wavelength of 633 nm. THF, purified over CaH_2 and sodium-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 weight (M_n) was determined with a Wescan Model 230 membrane osmometer at 35°C. Toluene, distilled over CaH_2, was the solvent.

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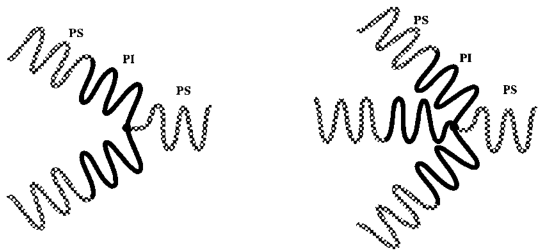
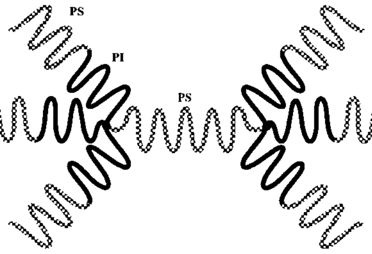


3-miktoarm star block copolymer of the A(BA)$_2$ type

4-miktoarm star block copolymer of the A(BA)$_3$ type



Super H-shaped block copolymer of the (AB)$_3$A(BA)$_3$ type

Scheme 1.

The M_w values were obtained from the $(KC/\Delta R_\theta)^{1/2}$ vs. C plots (ΔR_θ, excess Rayleigh ratio; K, combination of known optical constants; C, concentration) and the M_n values from the $(\Pi/C)^{1/2}$ vs. C plots (Π is the osmotic pressure). In all cases the correlation coefficient was better than 0.99. The LALLS and MO graphs of the final copolymers are given in Figures 1 and 2.

The composition of the linear diblock precursors and the final nonlinear block copolymers was determined from the ^{1}H-NMR spectra and by the SEC–UV chromatograms at 260 nm.[15]

RESULTS AND DISCUSSION

3-Miktoarm Star Block Copolymer

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

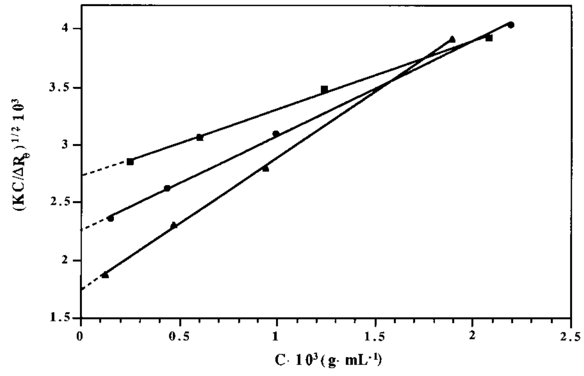


Figure 1. LALLS square root plots for the nonlinear copolymers (extrapolated to infinite dilution): (■) A(BA)$_2$, (●) A(BA)$_3$, (▲) (AB)$_3$A(BA)$_3$.

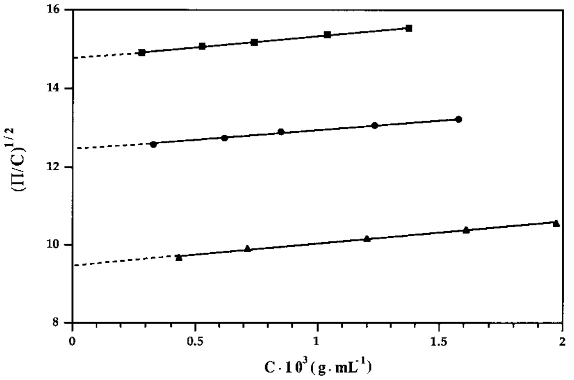


Figure 2. MO square root plots for the nonlinear copolymers (extrapolated to infinite dilution): (■) A(BA)$_2$, (●) A(BA)$_3$, (▲) (AB)$_3$A(BA)$_3$.

$$\text{St} + sec\text{-BuLi} \rightarrow \text{PSLi (A)}$$

$$\text{(A)} + \text{Is} \rightarrow \text{PSPILi}$$

$$\text{(A)} + \text{(excess) } CH_3SiCl_3 \rightarrow PSSi(Cl)_2(CH_3) + LiCl + CH_3SiCl_3 \uparrow$$

$$PSSi(Cl)_2(CH_3) + \text{(excess) PSPILi} \rightarrow (PS)(PIPS)_2SiCH_3 + 2\ LiCl$$

3-miktoarm star
block copolymer
of the A(BA)$_2$ type

The initial step of the synthesis involved the reaction of a solution ca. ~ 3% w/v of PSLi in C_6H_6 with an excess of CH_3SiCl_3 (Cl/Li ~ 200). The excess of CH_3SiCl_3 and C_6H_6 were removed under vacuum line conditions. After pumping for 1 day, the product was redissolved in benzene and the solution pumped again for 2 days. Finally the product was redissolved once more and pumped for 5–6 days at 50°C. The SEC chromatograms of the macromolecular difunctional linking agent is indistinguishable from the parent material (Fig. 3).

Benzene was distilled into the reactor until a ca. ~ 5% w/v solution was obtained and then a ca. ~ 5% w/v solution of the PSPILi (20% excess) in benzene was added. The progress of the linking reaction was monitored by removing samples from the reactor and analyzing them by SEC.

The SEC chromatogram of the raw product is shown in Figure 3 along with the chromatogram of the fractionated 3-miktoarm star block copolymer where the excess of PSPI has been removed. The characteristics of the precursors and the fractionated polymers are given in Table I.

4-Miktoarm Star Block Copolymer

The reactions used for the synthesis of the 4-miktoarm star copolymer are schematically the following:

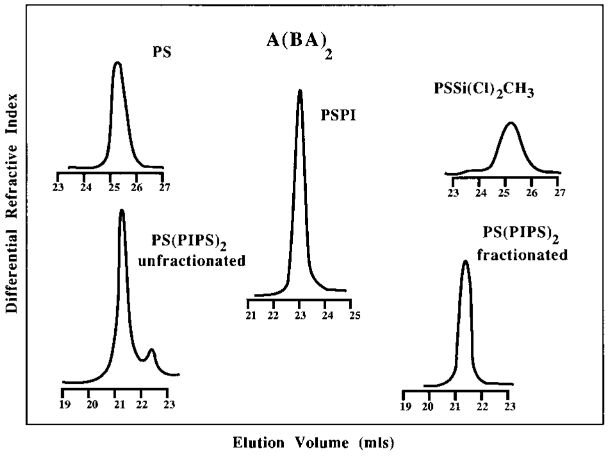


Figure 3. SEC chromatograms of the arm precursors, the methyldichlorosilane capped polystyrene PSSi$(Cl)_2CH_3$, the unfractionated, and the fractionated PS$(PIPS)_2$.

St + *sec* − BuLi → PSLi (A)

(A) + Is → PSPILi

(A) + (excess) $SiCl_4$ → $PSSiCl_3$ + LiCl + $SiCl_4$ ↑

$PSSiCl_3$ + (excess) PSPILi → (PS)$(PIPS)_3$Si + 3 LiCl

4-miktoarm star
block copolymer
of the A$(BA)_3$ type

The procedure followed was the same as in the case of the 3-miktoarm star block copolymer except that $SiCl_4$ was used instead of CH_3SiCl_3. The progress of the linking reaction was also monitored by removing samples from the reactor and analyzing them by SEC. (Fig. 4). The SEC chromatogram of the raw product is shown in Figure 4 with that of the fractionated polymer where the excess of the PSPI arms has been removed. The characteristics of the precursors and the fractionated polymers are shown in Table I.

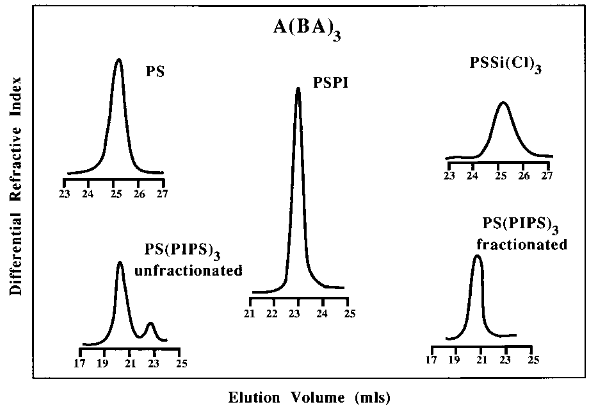


Figure 4. SEC chromatograms of the arm precursors, the trichlorosilane capped polystyrene $PSSiCl_3$, the unfractionated, and the fractionated PS$(PIPS)_3$.

Super H-Shaped Block Copolymer

The basic reactions used for the synthesis of the super H-shaped copolymers of the $(AB)_3A(BA)_3$ type are given below:

Napthalene + Na → Sodium Napthalenide (I)

St + (I) → NaPSNa (II)

(II) + (excess) $SiCl_4$ → $Cl_3SiPSSiCl_3$ (III) + $SiCl_4$ ↑

St + *sec* − BuLi → PSLi (A)

(A) + Is → PSPILi

(III) + (excess) PSPILi → $(PSPI)_3PS(PIPS)_3$ + 6 LiCl

Super H-shaped block
copolymer of the
$(AB)_3A(BA)_3$ type

The difunctional initiator[16] and the connector were prepared in a mixture of solvents C_6H_6/THF = 1.2/1. The final concentration of the disodium initiator never

Table I. Molecular Characteristics of the Precursors and the Final Polymers

Sample	$M_n{}^a \times 10^{-3}$ (g/mol^{-1})	$M_w{}^b \times 10^{-3}$ (g/mol^{-1})	$M_w/M_n{}^c$	PS (^{1}H-NMR) (wt %)	PS (UV/SEC) (wt %)	PS (Calculated) (wt %)
PS-20K	21.5	22.4	1.03	—	—	—
PSI-20K/30K	51.4	54.0	1.05	42	40	40
Difunctional PS	46.0	47.8	1.03	—	—	—
3-Miktoarm star	129.0	133.5	1.05	50	51	52
4-Miktoarm star	185.0	193.2	1.05	48	50	49
Super H-shaped	315.2	337.3	1.09	48	49	49

[a] Membane osmometry in toluene at 35°C.
[b] LALLS in THF at 25°C.
[c] SEC in THF at 30°C.

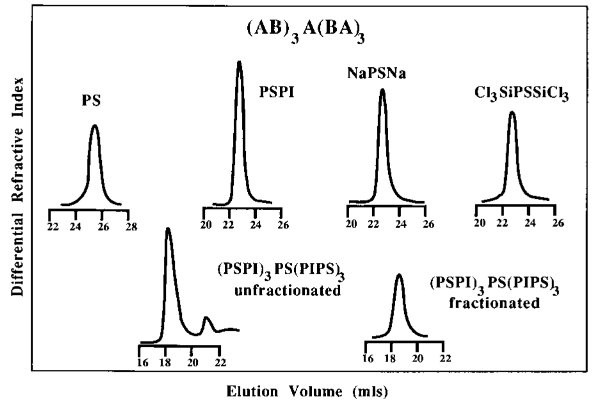


Figure 5. SEC chromatograms of the arm precursors, the hexachlorosilane capped polystyrene $Cl_3SiPSSiCl_3$, the unfractionated, and the fractionated $(PSPI)_3PS(PIPS)_3$.

exceeded 0.03 g/mL due to solubility reasons. The living difunctional polystyrene (connector) was maintained for 1 h at −20°C and then left to react with the linking agent. The preparation of initiator and connector along with the addition of the $SiCl_4$ were performed within a period of 10–12 h to avoid side reactions. The ratio of Cl/Na was very high (ca. ~ 2000) to avoid the reaction of more than one chlorine atom/chlorosilane molecule with the difunctional PS. The excess of the $SiCl_4$ was removed under vacuum line conditions following the same procedure as in the case of the 3- and 4-miktoarm star block copolymers. The progress of the linking reactions was also monitored by removing samples from the reactor and analyzing them by SEC (Fig. 5). In both cases the SEC chromatogram of the hexafunctional macromolecular linking agent was indistinguishable from the parent material (Fig. 5). The characteristics of the precursors and the final fractionated products are given in Table I.

CONCLUSIONS

In all cases the final nonlinear block copolymer has low polydispersity and there is a good agreement between the calculated values of M_w and M_n, from the precursors, and those obtained by LALLS and MO. On the other hand there is a good agreement between the composition of the final products calculated from the M_n of the precursors and those found by ^{1}H-NMR and UV–SEC. The above results indicate that miktoarm stars of the $A(BA)_2$, $A(BA)_3$ type and the bridged miktoarm star of $(AB)_3A(BA)_3$ type, having high molecular and compositional homogeneity, can be synthesized by anionic polymerization techniques and chlorosilane chemistry.

A complete morphological characterization of these novel materials using transmission electron microscopy (TEM) and small-angle x-ray Scattering (SAXS) will be presented in a forthcoming paper.[17]

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REFERENCES AND NOTES

1. H. Iatrou and N. Hadjichristidis, *Macromolecules,* **25,** 4649 (1992).
2. H. Iatrou and N. Hadjichristidis, *Macromolecules,* **26,** 2479 (1993).
3. N. Hadjichristidis, H. Iatrou, S. K. Behal, S. J. Chludzinski, M. M. Disko, T. R. Garner, K. Liang, J. D. Lohse, and S. T. Milner, *Macromolecules,* **26,** 5812 (1993).
4. G. Floudas, N. Hadjichristidis, H. Iatrou, T. Pakula, and E. W. Fischer, *Macromolecules,* **27,** 7735 (1994).
5. H. Iatrou, E. Siakali-Kioulafa, N. Hadjichristidis, J. Roovers, and J. Mays, *J. Polym. Sci. Part B: Polym. Phys.,* **33,** 1925 (1995).
6. C. Vlahos, A. Horta, N. Hadjichristidis, and J. Freire, *Macromolecules,* **28,** 1500 (1995).
7. C. Tsitsillianis, P. Chaumont, and P. Rempp, *Makromol. Chem.,* **191,** 2319 (1990).
8. C. Tsitsillianis, S. Graff, and P. Rempp, *Eur. Polym. J.,* **27,** 243 (1991).
9. G. Floudas, N. Hadjichristidis, H. Iatrou, A. Avgeropoulos, and T. Pakula, submitted to *Macromolecules.*
10. G. Floudas, N. Hadjichristidis, H. Iatrou, and T. Pakula, *Macromolecules,* **29,** 3139 (1996).
11. Y. Tselikas, N. Hadjichristidis, R. L. Lescanec, C. C. Honeker, M. Wohlgemuth, and E. L. Thomas, *Macromolecules,* **29,** 3390 (1996).
12. H. Iatrou, A. Avgeropoulos, and N. Hadjichristidis, *Macromolecules,* **27,** 6232 (1994).
13. M. Morton and L. J. Fetters, *Rubber Chem. Technol.,* **48,** 359 (1975).
14. J. Roovers and P. Toporowski, *Macromolecules,* **16,** 843 (1983).
15. E. J. Meehan, *J. Polym. Sci.,* **1,** 175 (1946).
16. J. Roovers and P. Toporowski, *Macromolecules,* **14,** 1174 (1981).
17. A. Avgeropoulos, N. Hadjichristidis, and E. L. Thomas, to appear.