Macromolecules 1993, *26*, 2479–2484

Synthesis and Characterization of Model 4-Miktoarm Star Co- and Quaterpolymers[†]

Hermis Iatrou and Nikos Hadjichristidis*

Department of Chemistry, University of Athens, 157 71 Athens, Greece,
and Institute of Electronic Structure and Laser Research, 71 110 Heraklion, Crete, Greece

Received November 30, 1992; Revised Manuscript Received February 4, 1993

ABSTRACT: The synthesis of well-defined, nearly monodisperse, 4-miktoarm (from the Greek word μικτός meaning mixed) star co- and quaterpolymers of the A_2B_2 and ABCD types, is described. A is polystyrene, B polybutadiene, C polyisoprene, and D poly(4-methylstyrene). The synthetic approach involves the reaction of tetrachlorosilane with the active chain end centers of the first arm under conditions unfavorable to chain coupling or linking, followed by a stoichiometric addition (titration) of the living polymer of the second or the third arm, and finally by an excess of the living polymer of the last arm. The sequence of addition of the different living polymers and the monitoring of the progress of the linking reaction by size-exclusion chromatography (SEC) are the key for successful synthesis. Characterization was carried out by SEC, low-angle laser light scattering, laser differential refractometry, membrane and vapor pressure osmometry, and NMR spectroscopy.

Introduction

The design and synthesis of new well-defined and nearly monodisperse, homopolymers and block copolymers, represent a molecular level architecture with monomeric building blocks. These model materials have facilitated many studies on polymers, including dynamics,[1] adsorption,[2] morphology,[3] diffusion,[4] rheology,[5] unperturbed dimensions,[6] etc.

Star copolymers with different arms of the A_2B,[7,8] A_2B_2,[9] and A_nB_n[10] type, have been prepared previously. For this class of materials the name miktoarm (from the greek word μικτός meaning mixed) star copolymers has been proposed.[11]

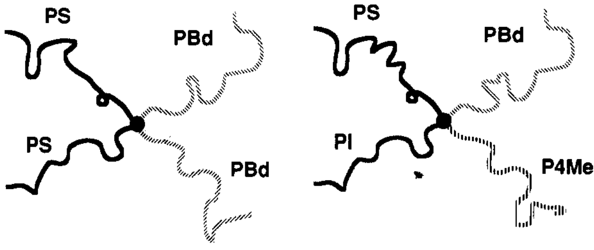
More recently, Sawamoto et al.,[12] using living cationic polymerization techniques and an appropriate divinyl compound as linking agent, have prepared a miktoarm star copolymer of the A_nB_n type, where $n = 10$, A is poly(isobutyl vinyl ether), and B is poly(2-acetoxyethyl vinyl ether). Alkaline hydrolysis of the pendant acetoxyethyl groups to hydroxyl groups led to an amphiphilic miktoarm star copolymer. Unfortunately, no characterization data were given in this communication.

Khan et al.,[13] using anionic polymerization techniques and the hydrosilylation addition of Si–H to the double bond, have prepared 3-miktoarm star copolymers of the A_2B type, where A is polystyrene and B is poly(2-vinylpyridine). This method generally gives polymers with polydispersity (M_w/M_n) as high as 1.5.

Takano et al.,[14] using anionic polymerization techniques and a block copolymer having a multifunctional linking agent at one end, have prepared a miktoarm star copolymer of the A_nB type where $n = 13$, A is polystyrene, and B is poly(vinyl-β-naphthalene). This method suffers the disadvantages that the number of arms is difficult to control precisely and that a large amount of unreacted double bonds remains.

Fujimoto et al.[15] have prepared a 3-miktoarm star terpolymer with three different arms, i.e. poly(dimethylsiloxane), polystyrene, and poly(*tert*-butyl methacrylate). The synthetic approach involves the reaction of PSLi with a diphenylethylene-terminated poly(dimethylsiloxane), followed by polymerization of *tert*-butyl methacrylate with the formed $-CH_2C(Ph_2)Li$ group. The weak point of this method is that fractionation is needed after each step.

Chart I



4-miktoarm star copolymer of the A_2B_2 type

4-miktoarm star quaterpolymer of the ABCD type

Finally, Naka,[16] using complexation of bipyridyl-terminated polymers with an Ru(II) ion, was able to prepare 3-miktoarm star copolymers of the A_2B type, where A is poly(oxyethylene) and B is polyoxazoline. Unfortunately, only limited characterization results were given in this communication.

In a previous paper,[11] we described the synthesis of a model 3-miktoarm star terpolymer with three different arms, i.e. polyisoprene (PI), polystyrene (PS), and polybutadiene (PBd). Our synthetic approach involves the reaction of poly(isoprenyllithium) (PILi) with an excess of methyltrichlorosilane, followed, after removal of the excess of methyltrichlorosilane, by a stoichiometric addition (titration) of poly(styryllithium) (PSLi), and finally by the addition of a small excess of poly(butadienyllithium) (PBdLi).

In the present work the chlorosilane approach has been applied to prepare (a) a new type of model polymer, i.e. the 4-miktoarm star quaterpolymer of the ABCD type where A is PS, B is PBd, C is PI, and D is poly(4-methylstyrene) (P4MeS), and (b) a 4-miktoarm star copolymer of the A_2B_2 type which had already been prepared using 1,3-bis(1-phenylethenyl)benzene[9] as the linking agent (see Chart I).

Experimental Section

The purification procedures for monomers, linking agents, and benzene to the standards required for anionic

---

[†] Part of this work was presented at the 5th International Symposium on Polymer Analysis and Characterization, Inuyama, Japan, June 1992.

0024-9297/93/2226-2479$04.00/0 © 1993 American Chemical Society

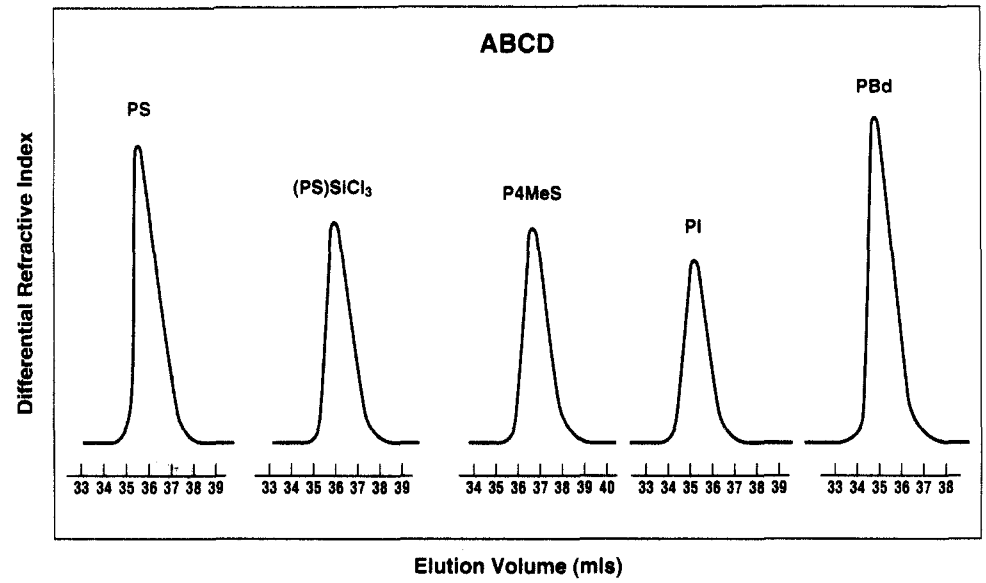


Figure 1. SEC chromatograms of the arm precursors and the trichlorosilane-capped polystyrene (PS)SiCl$_3$.

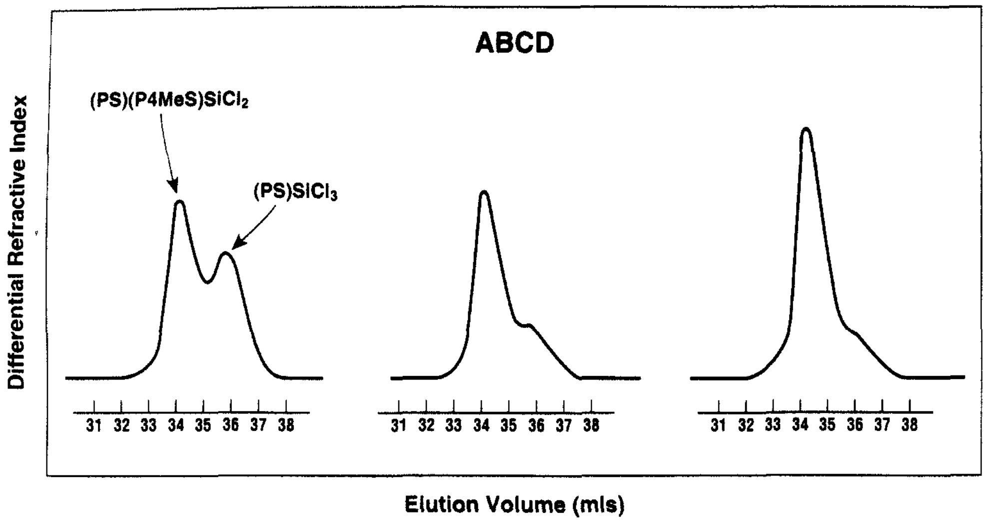


Figure 2. SEC chromatograms of samples taken during the linking reaction of (PC)SiCl$_3$ with P4MeSLi.

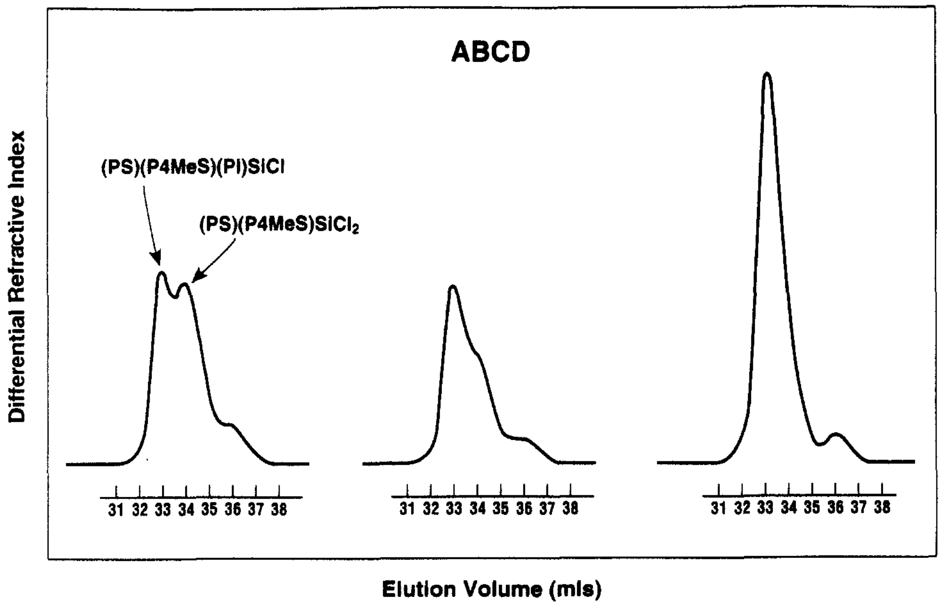


Figure 3. SEC chromatograms of samples taken during the linking reaction of (PS)(P4MeSLi)SiCl$_2$ with PISLi.

polymerization have been described in detail elsewhere.[17] *sec*-Butyllithium, prepared in vacuo from *sec*-butyl chloride and a lithium dispersion, was used as initiator for all polymerizations. All manipulations were performed in evacuated, *n*-BuLi-washed, and benzene-rinsed glass reactors provided with breakseals and constrictions.[11,18] In

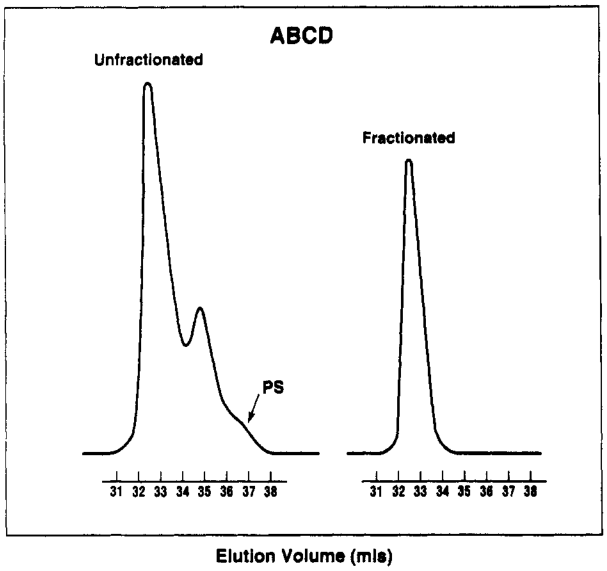


Figure 4. SEC chromatograms of the 4-miktoarm star quaterpolymer prior to and after four fractionations.

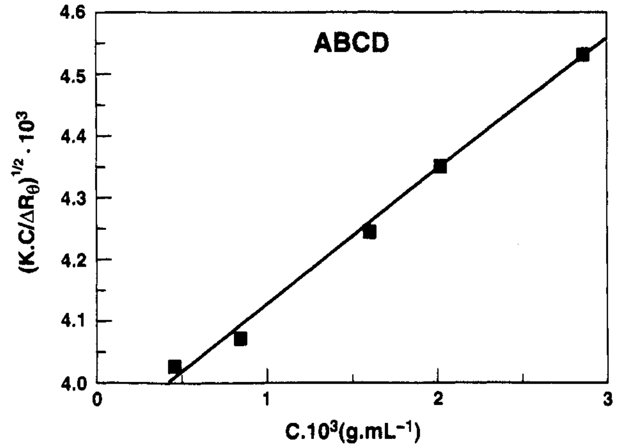


Figure 5. LALLS square-root plot for the 4-miktoarm quaterpolymer in THF at 25 °C.

the case of tetrachlorosilane the reactor was washed with trimethylchlorosilane. The excess of $(CH_3)_3SiCl$ was removed in the vacuum line.

The fractionation of the A_2B_2 and ABCD type miktoarm stars was performed in two steps. In the first step the low molecular weight homopolystyrene, originating from the reaction of PSLi with the trimethylchlorosilane (see below), was eliminated using benzene and methanol as the solvent/nonsolvent pair. In the second step the excess of polybutadiene was removed using a 50/50 mixture of benzene/hexane as solvent and methanol as nonsolvent.

SEC experiments were carried out at 30 °C using a Waters Model 510 pump and Waters Model 401 differential refractometer. Four μ-Styragel columns 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.

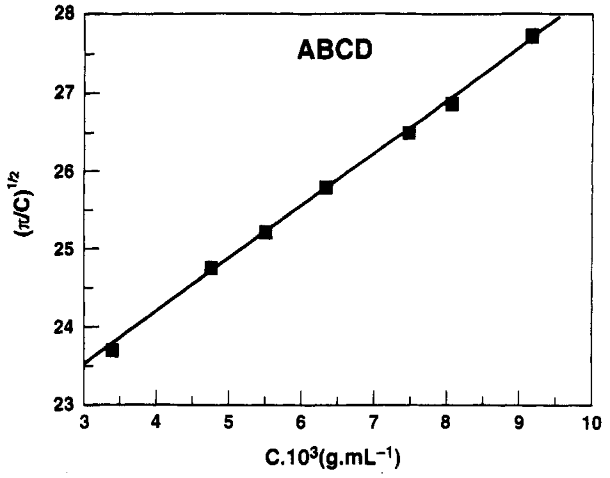


Figure 6. Osmometry square-root plot for the 4-miktoarm quaterpolymer in toluene at 37 °C.

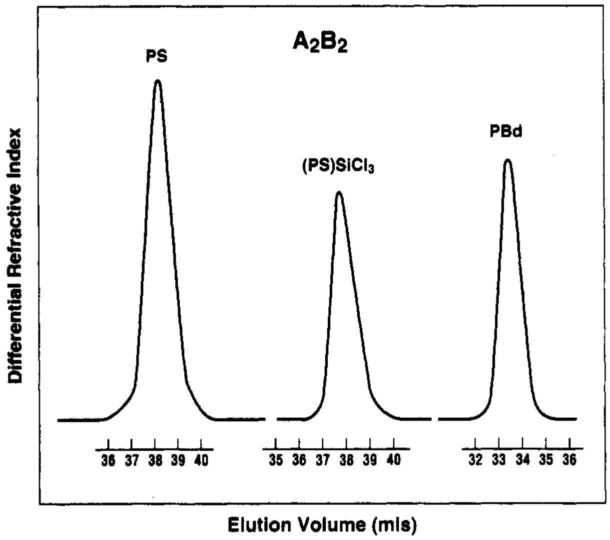


Figure 7. SEC chromatograms of the arm precursors and the trichloro-capped polystyrene $(PS)SiCl_3$.

The weight-average molecular weight (M_w) of the precursors and the miktoarm stars was measured with Chromatix KMX-6 low-angle laser photometer. This instrument is 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 M_w values were obtained from the corresponding $(KC/\Delta R\theta)^{1/2}$ vs C plots ($\Delta R\theta$, excess Rayleigh ratio; K, combination of known optical constants; C, concentration) in order to minimize the curvature due to the third virial coefficient. In all cases the correlation coefficient was better than 0.98.

The number-average molecular weights (M_n) were determined with a Wescan Model 230 membrane osmom-

Table I. Characteristics of the 4-Miktoarm Star Quaterpolymer

polymer	$10^{-4}M_w$[a]	10^4A_2 (mL mol g⁻²)	$10^{-4}M_n$[b]	10^4A_2 (mL mol g⁻²)	M_w/M_n[c]	M_z/M_w[c]	dn/dc[d] (mL g⁻¹)
PS	1.67	7.6	1.59	7.1	1.06	1.05	0.189
P4MeS	1.67	12.1	1.54	16.2	1.06	1.06	0.170
PI	1.65	17.2	1.62	20.1	1.05	1.04	0.132
PBd	1.54	17.4	1.45	20.4	1.04	1.04	0.134
4-miktoarm[e]	6.55	8.2	6.25	10.1	1.06	1.05	0.154

[a] LALLS in THF at 25 °C. [b] Membrane osmometry in toluene at 37 °C. [c] SEC in THF at 30 °C. [d] Laser differential refractometry in THF at 25 °C. [e] 25/25/27/23 wt % PS/P4MeS/PI/BPd by ¹H NMR.

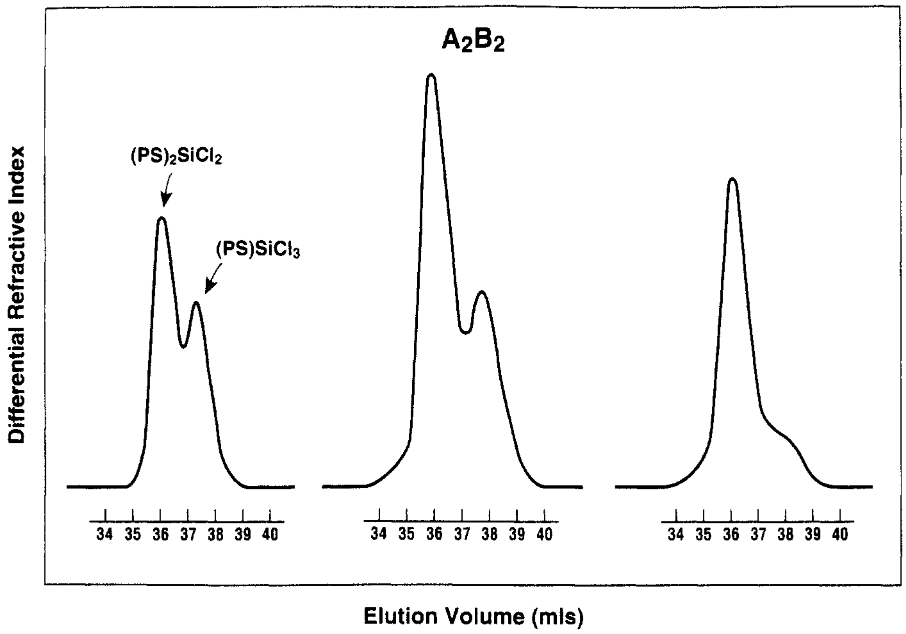


Figure 8. SEC chromatograms of samples taken during the linking reaction of (PS)SiCl$_3$ with PSLi.

eter (MO) at 37 °C and in a few cases (M_n < 13 000) with a Wescan Model 233 vapor pressure osmometer (VPO) at 50 °C. Toluene, distilled over CaH$_2$, was the solvent. The M_n values from MO were obtained from the corresponding $(\pi/C)^{1/2}$ vs C plots, where π is the osmotic pressure. In the case of VPO the M_n values were obtained from the $(\Delta R/C)$ vs C plots (ΔR is the change in the resistance of the thermistors), using the relation $(\Delta R/C)_{C\to 0} = k_v/M_n$ where k_v is the calibration constant. In all cases the correlation coefficient was better than 0.98.

The dienic precursors analyzed by ^{1}H and ^{13}C NMR (Bruker AC200) spectroscopy in CDCl$_3$ at 30 °C were found to have the following typical microstructures: for PI, 10 wt % 3,4, 70 wt % cis-1,4, and 20 wt % trans-1,4; for PBd 8 wt % 1,2, 50 wt % cis-1,4, and 42 wt % trans-1,4. The composition of the miktoarm stars was obtained from the ^{1}H NMR spectra.

Results and Discussion

4-Miktoarm Star Quaterpolymer. The basic reactions used for the synthesis of the 4-miktoarm star quaterpolymer are schematically the following:

$$\mathrm{PSLi + excess\ SiCl_4 \rightarrow PSSiCl_3 + LiCl + SiCl_4}\uparrow$$

$$\mathrm{PSSiCl_3 + P4MeSLi \xrightarrow{titration} (PS)(P4MeS)SiCl_2 + LiCl}$$

$$\mathrm{(PS)(P4MeS)SiCl_2 + PILi \xrightarrow{titration} (PS)(P4MeS)(PI)SiCl + LiCl}$$

$$\mathrm{(PS)(P4MeS)(PI)SiCl + excessPBdLi \rightarrow (PS)(P4MeS)(PI)SiPBd + LiCl}$$

ABCD type
4-miktoarm
star

A ~2% w/v solution of PSLi in benzene was added slowly into a large excess of tetrachlorosilane (Cl/Li ~ 100). The excess of SiCl$_4$ and the benzene were removed in the vacuum line. After pumping for at least 1 day, benzene was distilled into the reactor to redissolve the polymer and pumped for 3 days at 50 °C to dryness. This procedure was repeated at least two times. The SEC chromatogram of the macromolecular trifunctional linking agent is indistinguishable from the parent material (Figure 1).

Benzene was distilled into the reactor until a ~10% w/v solution was obtained and then a ~2% w/v solution of P4MeSLi in benzene was added dropwise. The progress of the linking reaction was monitored by removing samples from the reactor and analyzing them by SEC. The peak corresponding to the (PS)(P4MeS)SiCl$_2$ increases while the (PS)SiCl$_3$ peak decreases without, however, disappearing even by adding a slight excess of P4MeSLi (Figure 2). This means that a small amount of PSLi was terminated probably by traces of (CH$_3$)$_3$SiCl, the compound used during the purification and subdivision into ampules of SiCl$_4$.

Benzene was removed from the reactor in order to obtain a ~10% solution, after which a ~2% w/v solution of PILi in benzene was added dropwise. The progress of the linking reaction was monitored by SEC (Figure 3). At the end point, the addition of PILi was stopped and an excess (Li/Cl ~ 2) of a ~10% PBdLi solution in benzene was added. The peak corresponding to PS (~36 mL) remains constant during this procedure, implying that some unreacted PS is present, probably in the form of (PS)-Si(CH$_3$)$_3$ (see Figure 4).

The synthesis of the star quaterpolymer relies on (a) the inability of the sterically hindered 4-methylstyryl anions[19-21] to undergo complete reaction with the macromolecular trifunctional linking agent, (b) the ability of the moderately hindered isoprenyl anion to react with the difunctional but not with the monofunctional macromolecular linking agent as supported by the fact that even the PBdLi took ~2 months to react with this last chlorine, and (c) the ability of the less sterically hindered butadienyl anion to react completely[22] with the monofunctional macromolecular linking agent. Thus the sequence of the addition of the living polymers is critical to the success of the synthesis.

The SEC chromatogram of the raw product is shown in Figure 4 along with the chromatogram of the fractionated 4-miktoarm star quaterpolymer, where the excess of PBd and the unreactive (PS)Si(CH$_3$)$_3$ have been removed. The

Table II. Characteristics of the 4-Miktoarm Star Copolymer

polymer	$10^{-4}M_w$[a]	10^4A_2 (mL mol g^{-2})	$10^{-4}M_n$	10^4A_2 (mL mol g^{-2})	M_w/M_n[d]	M_z/M_w[d]	dn/dc[e] (mL g^{-1})
PS			1.22[b]		1.04	1.04	0.181
PBd	3.08	19.4	2.93[c]	18.2	1.04	1.04	0.134
4-miktoarm[f]	8.97	9.8	8.40[c]	11.1	1.06	1.04	0.149

[a] LALLS in THF at 25 °C. [b] Vapor pressure osmometry in toluene at 50 °C. [c] Membrane osmometry in toluene at 37 °C. [d] SEC in THF at 30 °C. [e] Laser differential refractometry in THF at 25 °C. [f] 28/72 wt % PS/PBd by ^{1}H NMR.

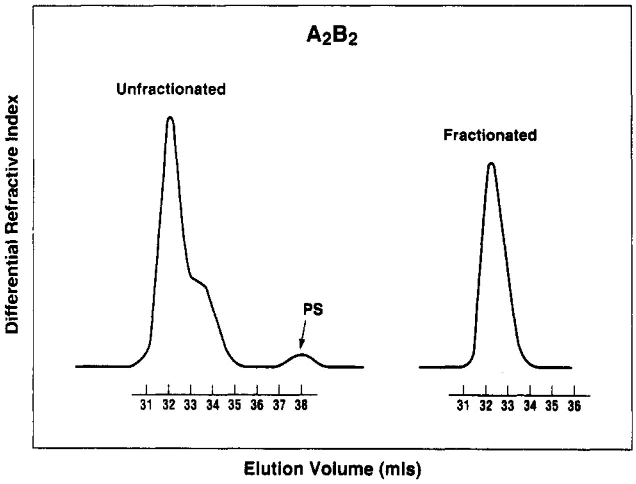


Figure 9. SEC chromatograms of the 4-miktoarm star copolymer prior to and after three fractionations.

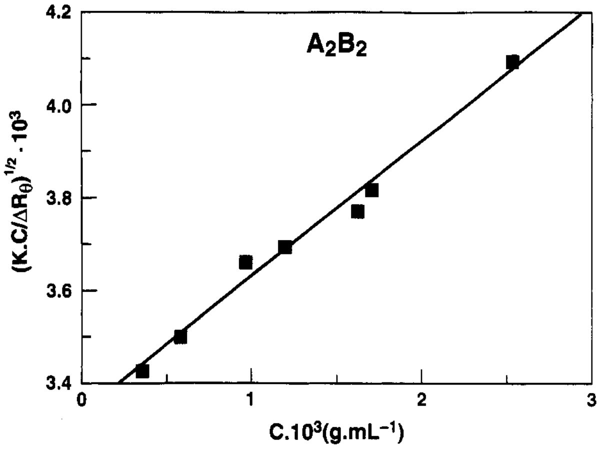


Figure 10. LALLS square-root plot for the 4-miktoarm copolymer in THF at 25 °C.

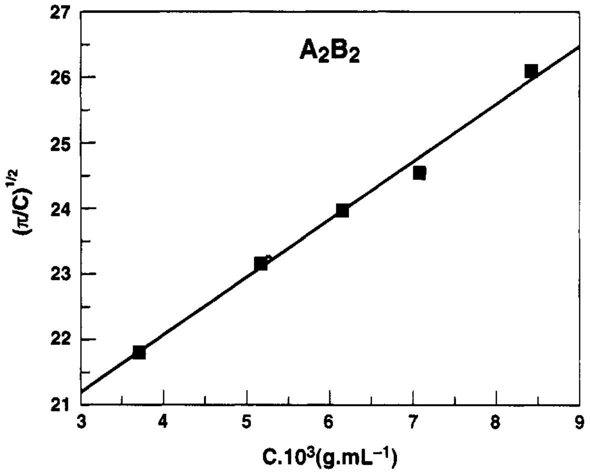


Figure 11. Osmometry square-root plot for the 4-miktoarm copolymer in toluene at 37 °C.

characteristics of the precursors and of the fractionated quaterpolymer are given in Table I.

The low polydispersity and good agreement of the calculated values of M_w (6.53 × 10^4) and M_n (6.20 × 10^4) with the M_w and M_n found by LALLS (apparent) and osmometry (Figures 5 and 6 and Table I) indicates a high degree of homogeneity in molecular weight and composition. This fact is also supported by (a) the very good agreement between the composition of the quaterpolymer calculated from the M_n of the arms (PS, 25.6 wt %; P4MeS 24.8 wt %; PI, 26.1 wt %; PBd, 23.5 wt %) and found by ^{1}H NMR and (b) the very good agreement between the overall dn/dc value found experimentally and that calculated (0.155) from the M_n of the arms and of the corresponding dn/dc values.

4-Miktoarm Star Copolymer. The synthesis of the 4-miktoarm star copolymer was performed according to the following basic reactions:

$$\mathrm{PSLi + excess\ SiCl_4 \rightarrow PSSiCl_3 + LiCl + SiCl_4\uparrow}$$

$$\mathrm{PSSiCl_3 + PSLi \xrightarrow{titration} (PS)_2SiCl_2 + LiCl}$$

$$\mathrm{(PS)_2SiCl_2 + excess\ PBdLi \rightarrow (PS)_2Si(PBd)_2 + 2LiCl}$$

A_2B_2 type
4-miktoarm
star

With a few modifications this procedure is similar to that for the ABCD polymer. In order to have better control of the incorporation of the first and second arm, the PSLi was added in two separate steps. The progress of the linking reactions was monitored by removing samples from the reactor and analyzing them by SEC (Figure 7 and 8).

The same peak (~38 mL) corresponding to the reaction product of PSLi with the $(CH_3)_3SiCl$ impurity of $SiCl_4$ is also present. The fractionation was performed in two steps, as was the case with the ABCD miktoarm. The SEC chromatogram of the raw product is shown in Figure 9 along with that of the fractionated 4-miktoarm star copolymer, where the excess of the PBd and PS arms has been removed. The characteristics of the precursors and of the fractionated copolymer are given in Table II.

The good agreement (a) between the apparent M_w determined by LALLS (Figure 10 and Table II) and the M_w (=8.90 × 10^4) calculated from the M_n and M_w/M_n of the copolymer and (b) between the M_n determined by osmometry (Figure 11 and Table II) and the M_n (=8.3 × 10^4) of the copolymer calculated from the M_n of the precursors indicates the high degree of homogeneity in molecular weight and composition.

This fact is also supported by (a) the low polydispersity of the copolymer and the very good agreement between the composition of the copolymer calculated from the M_n of the arms (PS, 29.4 wt %; PBd, 70.6 wt %) and found by ^{1}H NMR and (b) the agreement between the dn/dc value found experimentally and calculated (0.149) from the precursors.

It seems that the chlorosilane method gives better results than the method using 1,3-bis(1-phenylethenyl)benzene[9] as linking agent. The main disadvantage of the latter method is the difference in the reactivity of the active centers created after the addition of the living polymer and the reactivity of the remaining double bonds.

In conclusion, the combined characterization results indicate that miktoarm stars of the ABCD and A_2B_2 types having a high degree of molecular and compositional homogeneity can be synthesized by anionic polymerization techniques and with tetrachlorosilane as the linking agent.

This synthetic approach can also be used for the synthesis of other miktoarm stars, for example: $(A_1)(A_2)(A_3)$, $(A_1)_2(A_2)$, $(AB)_2A$, $(AB)_2B$, AB_3, A_3B, $(AB)_2A_2$, $(AB)_2B_2$, $(AB)_2BC$, etc. The properties of all these model miktoarms are expected to be interesting. A forthcoming paper[23] describes the microphase separation of the A_2B, A_2B_2, and ABC type miktoarm stars by TEM, SAXS, and DSC.

Acknowledgment. We are grateful to Drs. J. Roovers, L. Fetters, and J. Mays for their assistance and advice and to Exxon Chemical Co. and Exxon Research and Engineering Co. for partial support of this work.

References and Notes

(1) Huang, J.; Fetters, L.; Richter, D.; Farago, B.; Ewen, B. *Mater. Res. Soc. Symp. Proc.* **1990**, *166*, 457.

(2) Granick, S.; Patel, S.; Tirell, M. *J. Chem. Phys.* **1986**, *85*, 5370.

(3) Kinning, D.; Thomas, E.; Fetters, L. *J. Chem. Phys.* **1989**, *90*, 5806.

(4) Shull, K.; Kramer, E.; Fetters, L. *Nature* **1990**, *345*, 790.

(5) McKenna, G.; Hostetter, B.; Hadjichristidis, N.; Fetters, L.; Plazek, D. *Macromolecules* **1989**, *22*, 1834.

(6) Zirkel, A.; Richter, D.; Pyckhout-Hintzen, W.; Fetters, L. *Macromolecules* **1992**, *25*, 954.

(7) Mays, J. W. *Polym. Bull.* **1990**, *23*, 247.

(8) Huynh-Ba-Gia; Jérome, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3483.

(9) Quirk, R.; Ignatz-Hoover, F. In *Recent advances in anionic polymerization*; Hogen-Esch, T. E., Smid, J., Ed.; Elsevier Science Publishing Co.: New York, 1987.

(10) Tsitsilianis, C.; Ghaumont, Ph.; Rempp, P. *Makromol. Chem.* **1990**, *191*, 2319.

(11) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 4649.

(12) Sawamoto, M.; Kanaoka, S.; Omura, T.; Higashimura, T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 148 (ACS San Francisco Meeting).

(13) Khan, I.; Gai, Z.; Khougaz, K.; Eisenberg, A. *Macromolecules* **1992**, *25*, 3002.

(14) Takano, A.; Okada, M.; Nose, T.; Fujimoto, T. *Macromolecules* **1992**, *25*, 3596.

(15) Fujimoto, T.; Zhang, H.; Kazama, T.; Isomo, Y.; Hasegawa, H.; Hashimoto, T. *Polymer* **1992**, *33*, 2208.

(16) Naka, A.; Sada, K.; Chujo, Y.; Saegusa, T. *Polym. Prepr. Jpn.* **1991**, *40* (2), E116 (SPSJ Okayama Meeting).

(17) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.

(18) Roovers, J.; Toporowski, P. *Macromolecules* **1983**, *16*, 843.

(19) Morton, M.; Halminiak, T. E.; Gadkary, S. D.; Bueche, F. *J. Polym. Sci.* **1962**, *57*, 471.

(20) Roovers, J. E. L.; Bywater, S. *Macromolecules* **1972**, *5*, 385.

(21) Pitsikalis, M.; Hadjichristidis, N. Unpublished data.

(22) Fetters, L. J.; Morton, M. *Macromolecules* **1974**, *7*, 552.

(23) Hadjichristidis, N.; Iatrou, H.; Behal, S. K.; Chludzinski, J. J.; Disko, M. M.; Garner, T. R.; Liang, K.; Lohse, J. D.; Milner, S. T. *Macromolecules*, in press.