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Controlled Anionic Polymerization of Hexamethylcyclotrisiloxane. Model Linear and Miktoarm Star Co- and Terpolymers of Dimethylsiloxane with Styrene and Isoprene

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ABSTRACT: Controlled polymerization of hexamethylcyclotrisiloxane was achieved by carrying out the polymerization first at room temperature to about 50% conversion and then at −20 °C until complete conversion in order to avoid side reactions. The poly(dimethylsiloxane)s produced show narrow molecular weight distributions ($M_w/M_n \leq 1.1$). Using this approach, a model linear triblock copolymer PS-*b*-PDMS-*b*-PS, as well as 3-miktoarm star co- and terpolymers of the (PDMS)(PS)$_2$ and (PDMS)(PS)(PI) type, where PS is polystyrene, PI is polyisoprene, and PDMS is poly(dimethylsiloxane), have been prepared.

Introduction

Polysiloxanes are materials that combine unique properties of wide scientific and technological interest. The most popular member of this class of polymers is poly(dimethylsiloxane) (PDMS). As a result of its excellent thermal and oxidative stability, low absorption in deep UV, and good oxygen reactive ion etch resistance, PDMS is used in lithographic applications for microelectronics.[1] In addition, PDMS has high chain flexibility, low glass transition temperature, low surface energy, and low solubility parameter. These properties render PDMS-based materials very attractive in a variety of industrial areas. Consequently, the synthesis of well-defined homo- and copolymers of dimethylsiloxane with different architectures is of capital importance for designing new materials.

Until now, anionic polymerization combined with appropriate linking chemistry is the most powerful tool for synthesizing PDMS with controlled macromolecular architecture.[2] Unfortunately, anionic polymerization of hexamethylcyclotrisiloxane (D_3), the usual monomer for PDMS, suffers from backbiting reactions[3−5] (mostly equilibration). At room temperature and up to 50−75% conversion, depending on the molecular weight, the polymerization of D_3 proceeds without any problem, because at high monomer concentration side reactions are slow relative to propagation.[4] At higher conversion or low monomer concentration, the backbiting reactions compete with propagation to the polymerization and thus broaden the molecular weight distribution. To avoid side reactions, Zilliox et al.[4] neutralized the living PDMS before complete conversion (50−75%) and were able to synthesize model linear diblock copolymers of dimethylsiloxane (D) and styrene. Hogen-Esch et al.[6] end-capped dilithium polystyrene (PS) with 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane before adding D_3 and initiated the polymerization of D_3 at −20 °C to synthesize model cyclic block copolymers by reaction of the dilithium PDMS with dichlorodimethylsilane. Finally, Almdal et al.[7] lowered the temperature to −20 °C and added hexamethylphosphoric triamide and D_3 in a hexane solution of polyisoprenyllithium to prepare well-defined block copolymers of dimethylsiloxane and isoprene.

In the above methodologies, the living PDMS is contamined by either D_3 or polar additives, thus rendering the synthesis of polymers with complex macromolecular architecture difficult or impossible. As a consequence, only a limited number of PDMS copolymers with simple macromolecular architectures have been presented so far (di- and triblocks, star-block copolymers).[4,8−23]

This paper presents a two-step methodology for the complete polymerization of D_3 without side reactions. Using the two-step methodology and well-established chlorosilane linking chemistry, we were able to prepare a linear triblock copolymer PS-*b*-PDMS-*b*-PS, as well as 3-miktoarm star co- and terpolymers of the (PDMS)(PS)$_2$ and (PDMS)(PI)(PS) type.

Experimental Section

The purification of hexamethylcyclotrisiloxane, D_3 (Aldrich, 98%), is performed as follows: The appropriate amount of D_3 is melted, put in a flask, diluted by an equal volume of purified benzene, and stirred over CaH_2 overnight. Then the solvent along with the monomer is sublimed into a flask containing PSLi. The monomer is allowed to stand in contact with PSLi for about 2 h at room temperature and then is distilled along with the solvent into a cylinder and split down in precalibrated ampules.

The purification of isoprene (Aldrich, 99%) was performed by drying an appropriate amount of monomer over finely grounded CaH_2 overnight, followed by distillation over *n*-BuLi where it remained with continuous stirring for 30 min at 0 °C. This step is repeated as many times needed until a light yellow color remains before the pure monomer is distilled in precalibrated ampules.

Styrene (Aldrich, 99%) was dried overnight, on the vacuum line over CaH_2, followed by distillation over dibutylmagnesium (1 M solution in heptane) until a pale green color developed, and finally was distilled in precalibrated ampules.

sec-BuLi was prepared in vacuo from *sec*-butyl chloride and lithium dispersion. THF (Merck) was purified by fractional distillation, first over CaH_2 and then over Na−K alloy. The linking agents—trichloromethylsilane, trimethylchlorosilane, and bis(dimethylchlorosilyl)ethane (Aldrich)—were purified by fractional distillation on the vacuum line. It was then diluted with benzene and subdivided into ampules equipped with break-seals. All manipulations were performed under high

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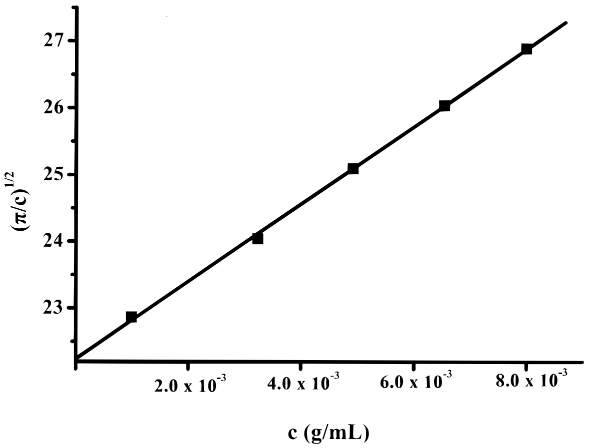


Figure 1. Membrane osmometry plot of the 3-miktoarm star terpolymer of the (PS)(PI)(PDMS) type. π is the osmotic pressure and c the concentration.

vacuum in glass reactors equipped with break-seals for the addition of the reagents and constrictions for removal of products.

Because of the high difference in solubility parameter and surface tension of PDMS from the other polymeric chains and fractionation solvents, the purification of the final product was very difficult. For example, if toluene/methanol was used as solvent/nonsolvent pair, the two phases had almost the same composition in the different polymeric species. After examining many pairs of solvents and nonsolvents the mixture of hexane/toluene 80/20 as the solvent and methanol as the nonsolvent was chosen.

Size exclusion chromatography (SEC) experiments were carried out at 25 °C with two different setups. In the first a Waters model 510 pump and a Waters model 410 differential refractometer and three styragel columns with a porosity range from 10^3 to 10^6 Å were used. Chloroform was the carrier solvent at a flow rate of 1.0 mL/min. In the second setup a Waters 610 pump, a Waters model 410 differential refractometer, a 996 diode-array UV detector, and six columns with a porosity range of 10^2-10^6 Å and a flow rate of 1 mL/min were used. THF was the carrier solvent. In both SEC setups the $\log(M_w)$ vs elution time plot was fitted with a third-order polynomial equation. The differential refractive index increment dn/dc in mL/g of PS, PI, and PDMS in chloroform at 25 °C is 0.159, 0.091, and −0.044, respectively. The dn/dc values in mL/g of PS, PI, and PDMS in THF at 25 °C is 0.185, 0.132, and 0.005 (almost zero), respectively. The differential refractive index increments in chloroform and THF at 25 °C were measured with a Chromatix KMX-16 refractometer, operating at 633 nm and calibrated with aqueous NaCl solutions.

The weight-average molecular weight of the final polymers was not measured by light scattering because it was difficult to find a solvent in which the dn/dc values for the different chains are high (>0.1 mL g^{-1}), a condition necessary for obtaining the true and not apparent molecular weight.

The number-average molecular weights (M_n) of the precursors and the final products were measured with a Jupiter model 231 recording membrane osmometer (MO) at 35 °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 and c is the concentration in g/mL. In all cases the correlation coefficient was better than 0.99. An example is given in Figure 1.

Nuclear magnetic resonance (NMR) spectra were generated using a Bruker 400 MHz instrument with $CDCl_3$ as solvent.

Results and Discussion

Controlled Polymerization of D_3. The initiation of D_3 was performed in benzene. First initiation takes place at room temperature with *sec*-butyllithium (*sec*-BuLi) in benzene. The propagation was carried out in two steps after adding an equal volume of THF. In the first step the polymerization allow to proceed until 50% conversion at room temperature. In the second step the temperature is lowered to −20 °C, and the polymerization is allowed to proceed until completion. THF was chosen to promote the polymerization of D_3 due to its weak donor character (soft donor), which permits the polymerization of D_3 with minimum side reactions.[3]

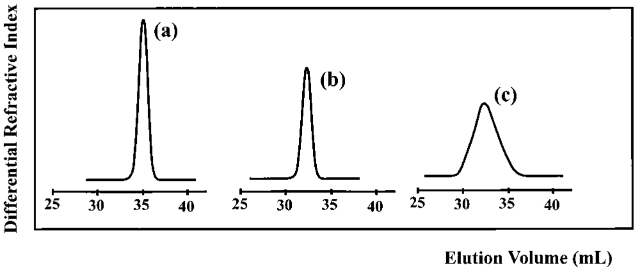


Figure 2. SEC chromatograms, of PDMS in THF, using different polymerization conditions: (a) 25 °C until 50% conversion, $M_n = 5 \times 10^4$, $M_w/M_n = 1.06$; (b) continuation of (a) at −20 °C for 8 days, $M_n = 10^5$, $M_w/M_n = 1.07$; (c) 25 °C until 100% conversion, $M_w/M_n = 1.3$. The M_n and M_w/M_n values are relative to linear PS.

To find the time needed for 50% conversion at room temperature and for 100% conversion at −20 °C, a few preliminary experiments have been carried out. In all experiments the concentration of D_3 was 10% (w/v) whereas the concentration of initiator was changing. The results are as follows: at room temperature [*sec*-BuLi] = 10^{-3} mol/L, $t_{1/2} = 2$ h; [*sec*-BuLi] = 2.5×10^{-4}, $t_{1/2} = 3$ h; [*sec*-BuLi] = 10^{-4}, $t_{1/2} = 4$ h. At −20 °C and [*sec*-BuLi] = 10^{-3} mol/L the half-life-time was 1 day. The influence of the different polymerization conditions to the molecular weight distribution is obvious in Figure 2.

The synthesis of co- and terpolymers is achieved by reacting the living chains with the appropriate chlorosilane. Unfortunately, the linking reaction of living PDMS with dichloro or trichlorosilyl linking agents occurs at room temperature but not at −20 °C. A few preliminary experiments were therefore performed in order to find the conditions where minimum side reactions and maximum linking occur. In the case of bis(dimethylchlorosilyl)ethane, the linking reaction was fast and 20% excess of living ends during 24 h was sufficient. When trichloromethylsilane was used, the optimum conditions were [SiOLi]/[SiCl] = 3:1 at room temperature and 3 days reaction time. Although the linear triblock or the 3-arm star is always contaminated by precursors or coupled product, the reaction needed to be stopped at this stage in order to avoid backbiting reactions.

PS−PDMS−PS Triblock Copolymers. A schematic representation of the sequence of reactions used to prepare the PS−PDMS−PS linear triblock copolymer is shown in Scheme 1.

The polymerization of styrene was initiated with *sec*-BuLi in benzene at room temperature. When all styrene was polymerized, D_3 was added and was left to react for 18 h. After the color of living PSLi had completely disappeared, the appropriate amount of THF was added in order to make a 50% (v/v) mixture with benzene and then was left to react for 2 h at 25 °C (~50% conversion). Then the temperature was adjusted at −20 °C, and the

Table 1. Molecular Characteristics of the Polymers Prepared Containing PDMS

sample	M_n(PS) $\times 10^{-3}$ [a]	M_n(PI) $\times 10^{-3}$ [a]	M_n(PDMS) $\times 10^{-3}$ [a]	M_n total calcd $\times 10^{-3}$	M_n total $\times 10^{-3}$ [a]	M_w/M_n [b]	$A_2 \times 10^{-3}$ [a] (mL s mol g^{-2})	% PS (w/w) (NMR)[c]	% PS (w/w) (UV)[b]
(PS−PDMS) (half of the triblock)	34.0				48.7	1.03	8.35	68	67
PS−PDMS−PS	34.0			97.4	96.1	1.04	5.64	69	67
(PS)$_2$PDMS	15.9		16.1	47.9	47.7	1.03	0.80	66	64
(PS)(PI)(PDMS)	19.5	20.7	19.0	59.2	58.9	1.04	0.89	33	33

[a] Membrane osmometry in toluene at 35 °C. [b] Size exclusion chromatography in THF at 30 °C. [c] ^{1}H NMR in CDCl$_3$ at 20 °C.

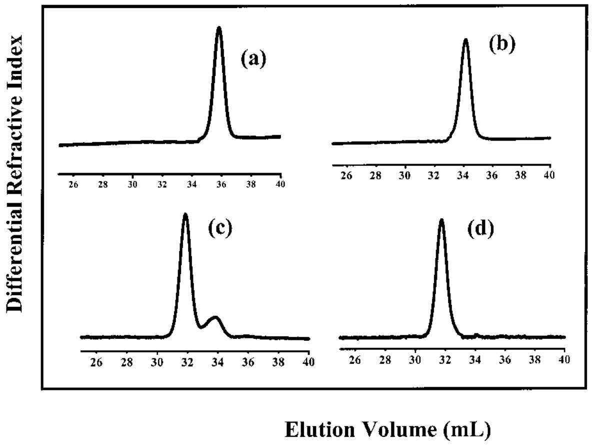
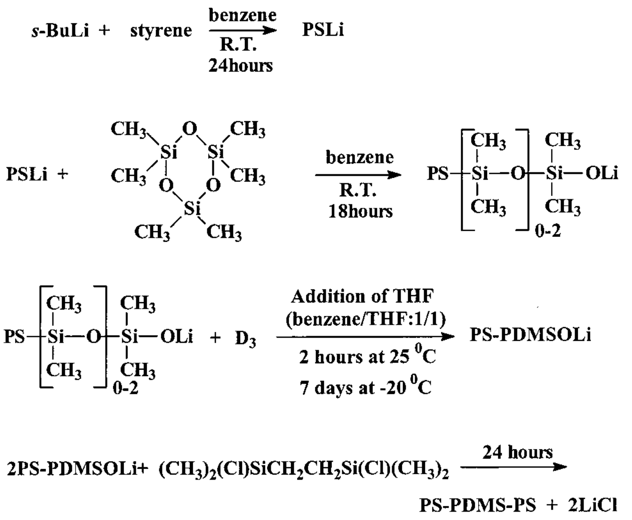


Figure 3. SEC chromatograms, in THF, monitring the synthesis of PS−PDMS−PS triblock copolymer: (a) PS, (b) PS−PDMS precursor, (c) unfractionated product, (d) fractionated PS−PDMS−PS.

Scheme 1



polymerization was allowed to proceed for one more week followed by addition of bis(dimethylchlorosilyl)ethane in a C−Li/Si−Cl ratio of 1.2. After 24 h the reaction was terminated by adding trimethylchlorosilane. The triblock PS−PDMS−PS was separated from the diblock PS−PDMS by fractional precipitation. The crude product along with the fractionated triblock copolymer is shown in Figure 3. The molecular characteristics of the triblocks are shown in Table 1. The low polydispersity index of the final product along with the good agreement between the composition found by ^{1}H NMR spectroscopy and UV analysis reveals the high degree of molecular and compositional homogeneity of the triblock copolymer.

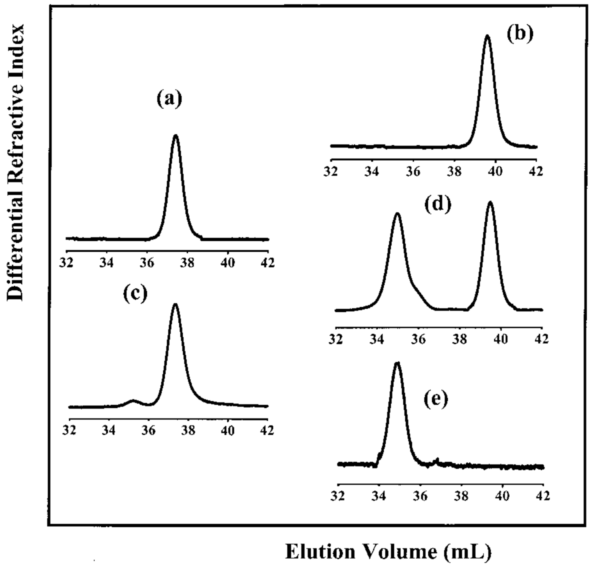
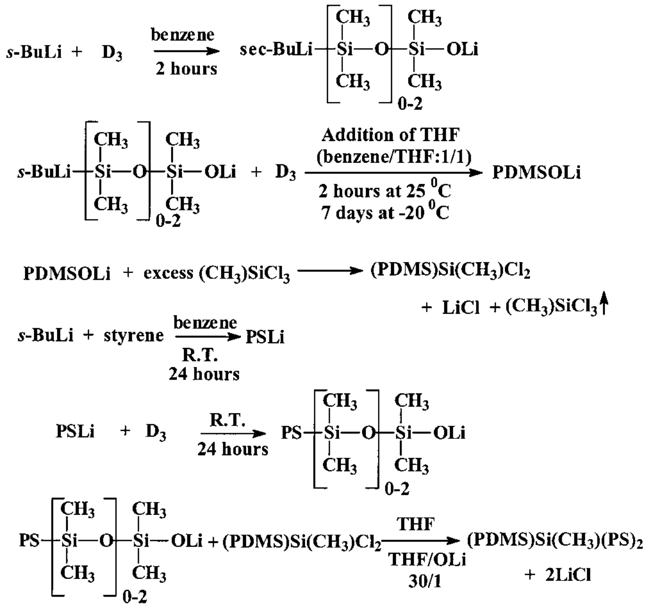


Figure 4. SEC chromatograms, in THF, monitoring the synthesis of 3-miktoarm star copolymer of the (PS)$_2$PDMS type: (a) PDMS arm, (b) PS arm, (c) PDMS−SiCl$_2$, (d) unfractionated product, (e) fractionated miktoarm copolymer.

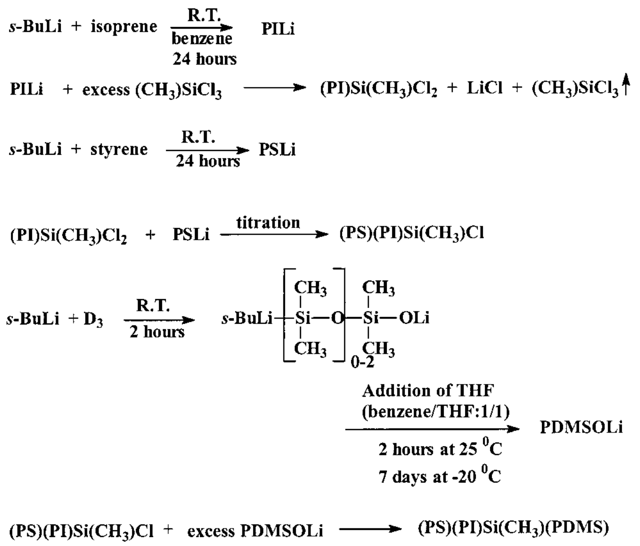
Scheme 2



3-Miktoarm Star Copolymer of the PDMS(PS)$_2$ Type. The basic reactions used for the preparation of the 3-miktoarm star copolymer of the PDMS(PS)$_2$ type are shown in Scheme 2.

In the first step a benzene−THF (50/50 v/v) solution of the living PDMS (~5% w/v) was slowly added into a large excess of trichloromethylsilane (Si−Cl to SiO−Li ratio approximately 100) and was allowed to react for 4 h at room temperature. The resulting macromolecular linking agent (PDMS)SiCl$_2$ was analyzed by SEC and found to be almost identical to the parent material

Scheme 3



(Figure 4). Excess linking agent was removed by extended pumping on the vacuum line and by repeatedly redissolving the polymer in benzene and removing the solvent.

In the second step of the synthesis of the 3-miktoarm copolymer, the linking reaction was again performed using a 3-fold excess of living PS chains end-capped with D_3. Without THF no linking reaction occurred. After the addition of traces amount of THF, the linking reaction was fast. The addition of THF disrupts the aggregation and leads to a fast reaction with the Si−Cl bonds. After 3 days the reaction was terminated by addition of a slight excess of trimethylchlorosilane. The C−Li living ends of the PS were transformed to the less reactive Si−OLi, to minimize backbiting reactions in the PDMS block during the linking reaction. The SEC chromatograms of the crude products along with the fractionated $(PDMS)(PS)_2$ are given in Figure 4. The experimental number-average molecular weights are compared with the calculated molecular weight (Table 1):

$$(M_n)_{calc} = 2(M_n)_{PS} + (M_n)_{PDMS} \quad \text{for the (PDMS)(PS)}_2$$

$$(M_n)_{calc} = (M_n)_{PS} + (M_n)_{PDMS} + (M_n)_{PI} \quad \text{for the (PS)(PI)(PDMS)}$$

Table 1 shows that the experimental and calculated values agree satisfactorily.

3-Miktoarm Star Terpolymer. The basic reactions used for the synthesis of the 3-miktoarm star terpolymer are shown in Scheme 3. A ~5% solution of PILi was added slowly into a large excess of methyltrichlorosilane (Cl/Li ~ 100). The excess of the linking agent was removed from the macromolecular linking agent $(PI)SiMeCl_2$, by using the same procedures discussed in section C for the separation of the same linking agent from $PDMSSiCl_2$. A ~5% w/v solution of PSLi in benzene was added dropwise, and the progress of the linking reaction was monitored by SEC. At the end point the addition of PSLi was stopped, and a 3-fold excess of living PDMSLi was added. The linking reaction was monitored by SEC (Figure 5) and after 3 days was terminated by addition of trimethylchlorosilane (Figure 6). The raw product along with the fractionated terpolymer is shown in Figure 6.

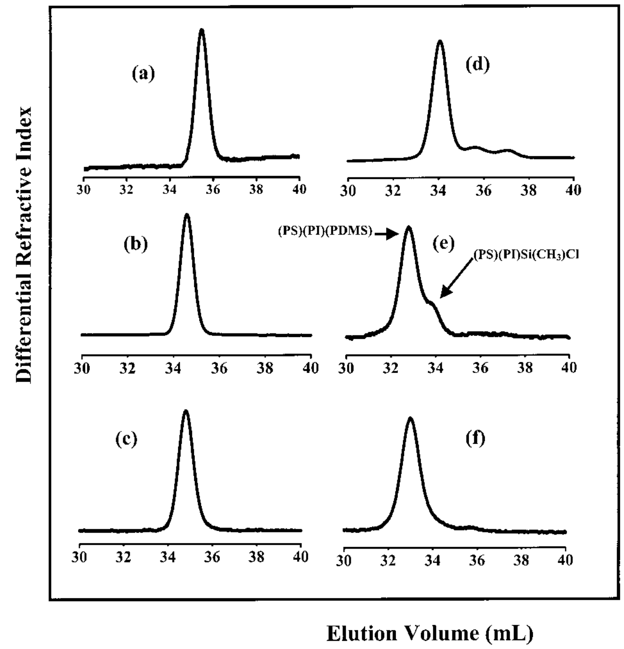


Figure 5. SEC chromatograms, in THF, monitoring the synthesis of the 3-miktoarm star terpolymer: (a) PS arm, (b) PI arm, (c) PDMS arm, (d) (PS)(PI)SiCl macromolecular linking agent, (e) unfractionated product, (f) fractionated (PS)(PI)(PDMS) star terpolymer.

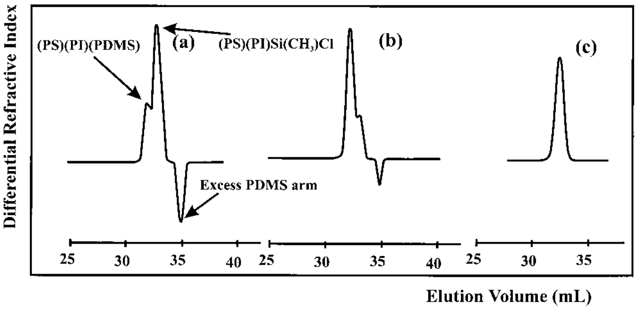


Figure 6. SEC chromatograms, in chloroform, monitoring the linking reaction of (PS)(PI)SiCl with PDMSOLi: (a) after 1 day, (b) after 3 days, (c) fractionated.

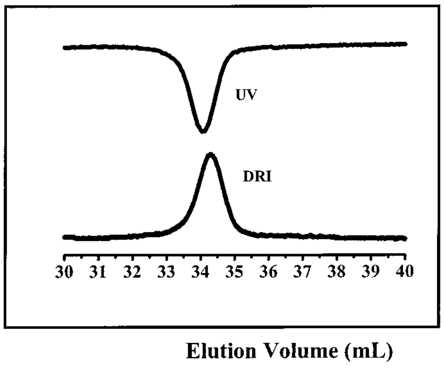


Figure 7. SEC-UV-DRI analysis of the 3-miktoarm star copolymer $(PS)_2PDMS$ in THF. UV detector at 260 nm.

The good agreement between the measured PS, PI, and PDMS content by ^1H NMR (and UV in the case of PS) and the composition calculated on the basis of the molecular weights of the arms and the total molecular weight of the final products indicates high degrees of molecular and compositional homogeneity. This is also supported by the narrow molecular weight and compo-

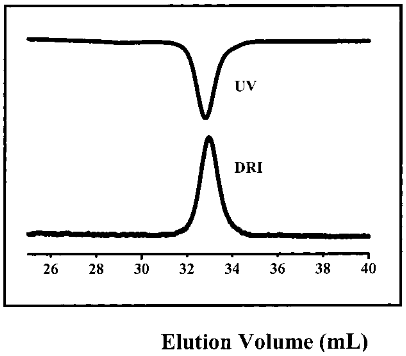


Figure 8. SEC-UV-DRI analysis of the 3-miktoarm star terpolymer (PS)(PI)(PDMS) in THF. UV detector at 260 nm.

sitional distribution obtained by SEC (DRI and UV) (Figures 7 and 8).

In conclusion, controlled and complete polymerization of D_3 was achieved using a two-step methodology. The first step involved initiation with *sec*-BuLi in benzene at room temperature, and propagation in a mixture of benzene/THF = 1/1, up to 50% conversion. In the second step, the polymerization was continued at −20 °C until completion. The PDMS macroanions can react with an appropriate chlorosilane linking agent under conditions where the linking reaction is faster than the side reactions. By using this strategy, model copolymers with complex macromolecular architectures were synthesized.

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