Communications to the Editor

Synthesis of Model 3-Miktoarm Star Terpolymers of Styrene, Isoprene, and Methyl Methacrylate

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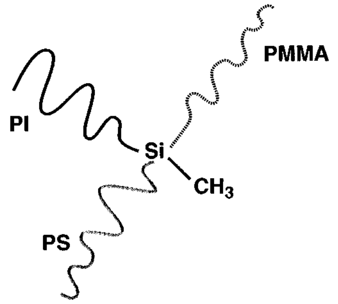
Introduction. Substitution of chlorine atoms of chlorosilanes by macroanions of an identical nature produces regular star polymers with equivalent arms, whereas controlled substitution by different (in molecular weight or chemical nature) macroanions leads to miktoarm stars (mikto from the greek word *μικτός*, meaning mixed). By using the chlorosilane method, we have synthesized homostars with up to 128 arms,[1] block star copolymers with up to 18 arms,[2] and miktoarm star block co-, ter- and quaterpolymers of the following structures: A_2B,[3] $(AB)_2A$,[4] A_2B_2,[5] A_3B,[6] $(AB)_3A$,[4] $(AB)_2(BA)_2$,[7] ABC,[8] and ABCD,[5] as well as more complex architectures such as A_2BA_2,[9] (A,B)B(B,A),[9] A_3BA_3,[10] and $(AB)_3A(BA)_3$[4] where A, B, and C are polystyrene (PS), polyisoprene-1,4 (PI), or polybutadiene-1,4 (PBd) and D is poly(4-methylstyrene).

The chlorosilane approach is a powerful tool for manipulating macromolecular architecture and until today unique in synthesizing such a wide variety of materials with high degrees of molecular and compositional homogeneity. High-vacuum techniques have to be used and time consuming reactions (i.e. incorporation of the third and fourth arm usually takes 1−4 weeks), which drew critisism,[11,12] have to be applied in order to achieve the desired products. Also, an excess of the last arm is intentionally added to force the final linking step to completion. The remaining living arm, which has been misinterpreted by others,[11] is subsequently removed by fractionation. Nevertheless, these “limitations” are a small price to pay given the potential of these techniques for generating true macromolecular model compounds. Other techniques lead to compromised homogeneity or difficulties in rigorously characterizing the products.

Incorporation of polymethacrylate branches by the chlorosilane method has not been possible simply because the reaction of SiCl with the living polymethacrylate fails to give the linked product.[13] We overcame this difficulty by transforming the SiCl group to $SiC(Ph_2)(CH_2)_2C^{-}(Ph_2)Li^{(+)}$ (Ph is phenyl) and polymerizing in situ the methacrylate monomer with the sterically hindered anionic center. In this paper we present the synthesis and characterization of model 3-miktoarm star terpolymers of PS, PI, and poly(methyl methacrylate) (PMMA) (Chart 1). Fujimoto et al.[14] have prepared 3-miktoarm stars of PS, poly(dimethylsiloxane) and poly(*tert*-butyl methacrylate) by using a macromonomer approach while Hückstädt et al.[12] have prepared the 3-miktoarm star of PS, PBd-1,2, and PMMA by using a slightly different macromonomer method. The synthetic approach presented here is a general method which does not require the isolation of intermediate products (i.e. macromonomers) prior to the anionic polymerization of the methacrylate monomers. The importance of these nonlinear terpolymers is obvious due to their ability to form multiphase morphologies.[15,16]

Chart 1. 3-Miktoarm Star Terpolymer of Styrene, Isoprene, and Methyl Methacrylate



Experimental Section. High-vacuum techniques, described in detail elsewhere,[8] were used for the synthesis of the 3-miktoarm star terpolymers. The separation of the terpolymer from the reaction product (traces of homo PI and unreacted diblock PS-*b*-PI) was performed in two steps. First the final material was heated with cyclohexane at 70 °C followed by fractional precipitation of the star by using the solvent (toluene: cyclohexane, 1:1 by volume)−nonsolvent (hexane) system. The fractionation was monitored by size exclusion chromatography. SEC experiments were carried out in THF at 30 °C using a Waters 510 pump, Waters 401 differential refractometer, Waters 486 UV detector, and four styragel columns with a continuous porosity from 10^6 to 10^3 Å.

The number-average molecular weight, M_n, was determined in toluene either by membrane osmometry (MO) at 35 °C with a Wescan 230 membrane osmometer or by a Jupiter model 833 vapor pressure osmometer (VPO) at 50 °C. The M_n values (MO) were obtained from the $(\pi/c)^{1/2}$ vs c plots, where π is the osmotic pressure and c is the concentration. The M_n value for the PI arm (VPO) was determined by plotting $\Delta R/c$ vs c, where ΔR is the change in the resistance of the thermistors. In all cases the correlation coefficient was better than 0.99.

The weight-average molecular weight M_w of the 3-miktoarm stars was measured with a Chromatix KMX-6, operating at $\lambda = 633$ nm, in THF purified over sodium at 25 °C. The refractive index increment (dn/dc) in THF at 25 °C was determined with a Chromatix KMX-16, operating at 633 nm and calibrated with aqueous NaCl solutions. The M_w values were obtained from the corresponding $(Kc/\Delta R_\theta)^{1/2}$ vs c plots (ΔR_θ is the excess Rayleigh ratio, and K is a combination of known

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Table 1. Characteristics of the 3-Miktoarm Star Terpolymers

polymer	$M_w \times 10^{-3}$ [a]	$M_n \times 10^{-3}$ [b]	M_w/M_n [d]	dn/dc (mL/g)	PS/PI/PMMA[f] (% wt)	PS[g] (% wt)
PS(arm)[h]		18	1.03	0.198		
PI(arm)[h]		7.5[c]	1.04	0.146		
SIM-1	83	77	1.06	0.123 (0.117)[e]	24/8/68	23
SIM-2	201	172	1.12	0.096 (0.098)[e]	9/3/88	10

[a] LALLS in THF at 25 °C. [b] MO in toluene at 35 °C. [c] VPO in toluene at 50 °C. [d] SEC in THF at 30 °C. [e] Calculated (see text). [f] ^{1}H-NMR in CDCl$_3$ at 35 °C. [g] SEC−UV at 260 nm. [h] Same for the two star terpolymers.

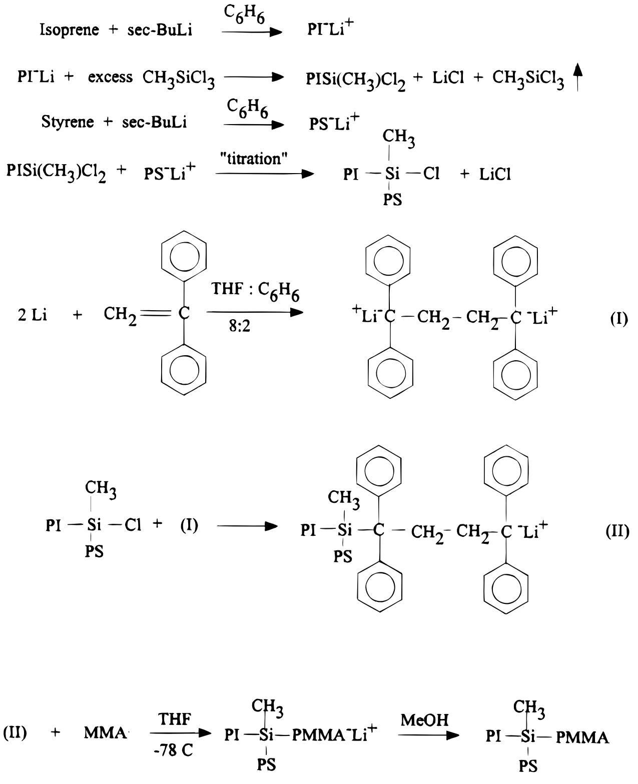
optical parameters). In all cases the correlation coefficient was better than 0.99.

The PI arm analyzed by ^{1}H and ^{13}C NMR (Varian 540 Unity Plus) spectroscopy in CDCl$_3$ at 35 °C was found to have the following microstructure: 71 wt % cis-1,4; 21 wt % trans-1,4; 8 wt % 3,4. The composition of the fractionated terpolymers was analyzed by ^{1}H-NMR, and the PS content was also determined by SEC−UV at 260 nm. The dn/dc values of SIM determined experimentally and those found by applying the well-known equation

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

where x and y are the weight fractions, determined by NMR, of PS and PI, respectively, are almost identical (Table 1). Thus the composition results found by NMR and UV are further supported. The dn/dc values of the linear precursors PS and PI and of a PMMA prepared by the same anionic center have been determined experimentally.

Results and Discussion. The synthesis of the 3-miktoarm star terpolymers of polystyrene (PS), polyisoprene (PI), and poly(methyl methacrylate) (PMMA) was performed according to the following basic reactions:



$$\text{Isoprene} + \text{sec-BuLi} \xrightarrow{C_6H_6} \text{PI}^-\text{Li}^+$$

$$\text{PI}^-\text{Li} + \text{excess } CH_3SiCl_3 \longrightarrow \text{PISi}(CH_3)Cl_2 + \text{LiCl} + CH_3SiCl_3\uparrow$$

$$\text{Styrene} + \text{sec-BuLi} \xrightarrow{C_6H_6} \text{PS}^-\text{Li}^+$$

$$\text{PISi}(CH_3)Cl_2 + \text{PS}^-\text{Li}^+ \xrightarrow{\text{"titration"}} \text{PI}-\overset{\displaystyle CH_3}{\underset{\displaystyle \text{PS}}{\text{Si}}}-\text{Cl} + \text{LiCl}$$

$$2\,\text{Li} + CH_2{=}C(C_6H_5)_2 \xrightarrow[8:2]{\text{THF}:C_6H_6} {}^+\text{Li}^-C(C_6H_5)_2-CH_2-CH_2-C(C_6H_5)_2{}^-\text{Li}^+ \quad \text{(I)}$$

$$\text{PI}-\overset{\displaystyle CH_3}{\underset{\displaystyle \text{PS}}{\text{Si}}}-\text{Cl} + \text{(I)} \longrightarrow \text{PI}-\overset{\displaystyle CH_3}{\underset{\displaystyle \text{PS}}{\text{Si}}}-C(C_6H_5)_2-CH_2-CH_2-C(C_6H_5)_2{}^-\text{Li}^+ \quad \text{(II)}$$

$$\text{(II)} + \text{MMA} \xrightarrow[-78\,C]{\text{THF}} \text{PI}-\overset{\displaystyle CH_3}{\underset{\displaystyle \text{PS}}{\text{Si}}}-\text{PMMA}^-\text{Li}^+ \xrightarrow{\text{MeOH}} \text{PI}-\overset{\displaystyle CH_3}{\underset{\displaystyle \text{PS}}{\text{Si}}}-\text{PMMA}$$

The synthetic procedure involves the controlled substitution of two chlorines of trichloromethylsilane (TCMS) by PS and PI, using methods developed by our group[8] and of the third chlorine by C(Ph$_2$)(CH$_2$)$_2$C$^-$(Ph$_2$)Li$^{(+)}$ (Ph is phenyl), followed by polymerization in situ of methyl methacrylate.

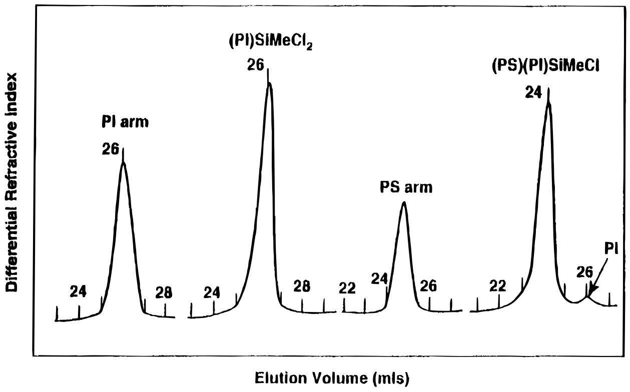


Figure 1. Size exclusion chromatograms for monitoring the synthesis of (PS)(PI)SiMeCl.

Polyisoprenyllithium, prepared in benzene with s-BuLi as initiator, was reacted with a large excess of TCMS. Only one of the three chlorines has been replaced by a PI chain, as can be seen in Figure 1. After careful removal of the excess of TCMS the dichloro-capped polyisoprene (PI)SiMeCl$_2$ was dissolved in benzene and titrated with polystyryllithium, prepared in benzene with s-BuLi. The titration was monitored by SEC and the end point, where the incorporation of the PS chain was completed, was determined accurately (Figure 1). Subsequently, the resulting monofunctional macromolecular chlorosilane (PS)(PI)SiMeCl solution (∼8 wt %) was slowly added to a dilute solution (∼0.5 wt %) containing a stoichiometric amount of the α,ω-dilithium initiator. This procedure was followed in order to ensure complete reaction with one active center of the initiator. The initiator was prepared from 1,1-diphenylethylene (DPE) and lithium dispersion. DPE was purified by distillation over n-BuLi, twice. The purified DPE was distilled in THF/benzene (8:2 by volume) mixture and allowed to react with a large excess of lithium dispersion for 3 days. A bright red color, indicating the formation of tertiary carbon anion was immediately formed. The concentration and the quality of the difunctional initiator (∼3 × 10^{-5} mol/mL) were determined by polymerizing styrene in benzene (∼10 wt %) at room temperature for 1 day and analyzing the product by SEC. The deep red color of the initiator changed immediately to the orange of polystyryllithium upon its addition to the styrene solution. This fast initiation step, which is due to the presence of THF, leads to two species with narrow molecular weight distribution (M_w/M_n < 1.1). The one has double the molecular weight of the other, meaning that the initiator is a mixture of mono- and difunctional compounds. The presence of the monofunctional initiator (∼30 wt %) does not influence the synthesis of the star because it gives, with (PS)(PI)SiMeCl, the unreactive diblock, which has a composition and molecular weight different from that

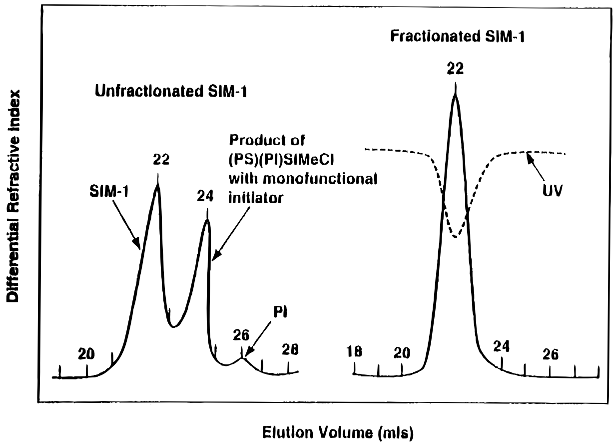


Figure 2. Size exclusion chromatograms of 3-miktoarm star terpolymer SIM-1 before and after fractionation.

of the star terpolymer and can be separated by appropriate fractionation. In a forthcoming paper[17] the origin of the monofunctional species and the influence of the reaction conditions will be studied in order to increase the yield of the star terpolymer.

The macromolecular initiator so created was used to polymerize MMA at −78 °C in THF. The PMMA arm was grown on the living diblock. This last step differentiates this strategy from the one used in synthesizing miktoarm stars having only diene and styrene arms, since the living PMMA does not give the desired linking product with chlorosilane. The reaction product was first treated with hot cyclohexane ($\sim$70 °C) in order to eliminate the diblock copolymer PS-*b*-PI, coming from the monofunctional initiator, and the small amount of PI homopolymer produced by undesirable termination of PILi. Cyclohexane is a good solvent for PI and PS at 70 °C (at 34.5 °C is a θ-solvent for PS) and a nonsolvent for PMMA. The product treated by cyclohexane (fractionation by composition) was fractionated with the toluene/cyclohexane (solvent)−hexane (nonsolvent) system (fractionation according molecular weight).

The SEC chromatograms (DRI, UV) of SIM-1 before and after fractionation are given in Figure 2. We note here that no $(PI)_2(PS)_2$ star copolymer was observed in the SEC chromatograms, due to the high steric hindrance of the dilithium initiator which is accentuated by the presence of the (PS) and (PI) chains already incorporated. SIM-2 behaves the same way. The molecular characteristics of the fractionated star terpolymers are given in Table 1. The above results indicate a high degree of molecular and compositional homogeneity.

In conclusion, we presented here a general method for incorporating methacrylate branches in chlorosilane-functionalized polymers. This approach opens new horizons for the synthesis of new multicomponent polymeric materials like star molecules having a hydrophobic crystalline branch (i.e. hydrogenated PBd-1,4), a hydrophobic amorphous branch (i.e. PS), and a hydrophilic branch (if.e. poly(methacrylic acid) coming after the hydrolysis of poly(*tert*-butylmethacrylate)). Furthermore, this method can be used for the synthesis of $(PS)(PI)_2$-(PMMA), (PS)(PI)(PBd)(PMMA), etc.

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