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PREPARATION OF WELL DEFINED POLYSTYRENE-BLOCK-POLY (METHYLPHENYLSILYLENE) COPOLYMERS

by

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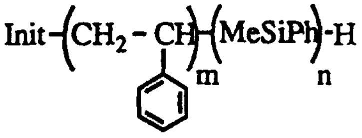
Combination of the living anionic polymerization of styrene with the ring opening polymerization of cyclotetrasilanes affords the preparation of well-defined polystyrene-*block*-poly(methylphenylsilylene). Block copolymers with ratios of polystyrene to polysilylene, PS:PMPS ranging from 1:4 to 2:1 have been prepared. The molecular weight distributions are narrow, $M_w/M_n = 1.3$. Removal of any homo polystyrene can be accomplished by precipitation into acetone yielding pure block copolymers with known compositions. The materials have been characterized by ^1H and ^{29}Si NMR spectroscopy, Gel Permeation Chromatography, and Differential Scanning Calorimetry.



$Init-(CH_2-CH)_m-(MeSiPh)_n-H$

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Preparation of Well-Defined Polystyrene-*block*-Poly(methylphenylsilylene) Copolymers

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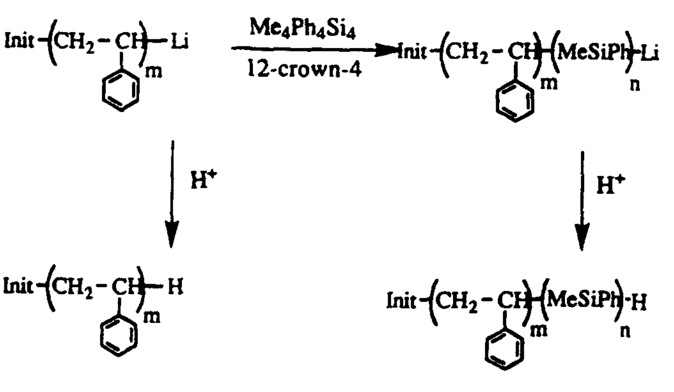
Polysilylenes (polysilanes) consist of a linear chain of silicon atoms with two organic substituents, generally, either alkyl or aryl groups.[1,2,3] These polymers possess interesting properties, such as sigma catenation and thermochromism. These properties lead to potential applications including non-linear and photo-optical materials, initiators for radical polymerizations, and precursors to silicon carbide.

However, the mechanical properties of polysilylenes are insufficient for many applications.[4] Therefore, it is interesting to combine the mechanical properties of other polymers with the polysilylenes by either blending or preparing block copolymers. Several groups have reported the synthesis of block copolymers of polystyrene and polysilylenes. West et al. reported the radical polymerization of styrene initiated by photochemical reaction of poly(methylphenylsilylene), PMPS.[5] Demoustier-Champagne et al. synthesized polystyrene-block-PMPS by the reaction of living polystyryl anions with chloro endcapped PMPS.[4] Sakamoto et al. have prepared block copolymers of poly(methyl methacrylate) and -[SiMe(n-Bu)SiMe$_2$]$_n$ by subsequent addition of MMA to the still active end groups of the polysilylene chains.[6].

Ring opening polymerization of cyclotetrasilanes provides a new and promising route to linear polysilylenes.[7,8,9] It is possible to combine ROP with other anionic living systems to prepare new block copolymers. The synthesis of well-defined polystyrene-block-PMPS and polyisoprene-block-PMPS copolymers will be presented.

Experimental. Benzene was dried over K and then distilled prior to use. Me$_4$Ph$_4$Si$_4$ was prepared as reported previously and recrystallized prior to polymerizations.[7,8,9] *Sec*-BuLi (Aldrich) was used as received. 12-crown-4 was dried prior to use. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC), using a Waters 510 pump equipped with a 410 differential refractometer and photodiode array UV detector, using THF as eluent with a flow rate of 1.0 mL·min^{-1} and with three ULTRASTYRAGEL columns (100 Å, 500 Å, and Linear) in series. The molecular weight calibration curve was obtained using polystyrene standards. NMR spectra were recorded on an IBM NR-300 spectrometer. All experiments were performed in a VAC Atmospheres HE-30 dry box under a nitrogen atmosphere with water and O$_2$ concentrations below 1 ppm. In a typical experiment sec-BuLi was added to 0.5 mL of benzene and stirred vigorously. 110 µL of styrene (freshly distilled) was added via syringe. After complete conversion of the styrene to polymer, ca. 20 min., a 0.15 mL sample was taken for GPC analysis. A solution of 120 mg of Me$_4$Ph$_4$Si$_4$, 5.0 µL 12-crown-4, and 0.5 mL of benzene was added via syringe, the color turned from dark orange to a yellow/brown in color. After a further 20 min. the solution was exposed to air to terminate the polymerization. Precipitation into methanol yielded the crude product which contained some homo polystyrene. Homo polystyrene was removed by precipitation into acetone to yield pure block copolymer.

Scheme I



Results and Discussion.

Initiation of the ROP of cyclotetrasilanes using living polystyryl anions in benzene in the presence of 12-crown-4 results in the formation of block copolymers (Scheme I). The crossover reaction to cyclosilane polymerization is not 100% efficient as can be shown by the presence of unreacted living polystyrene chains. The reactions were followed by both ^{1}H NMR and GPC analysis.

The ^{1}H NMR spectrum in Figure 1 confirms the formation of block copolymers as it contains peaks for both polystyrene and poly(methylphenylsilylene). This spectrum was taken after precipitation of the reaction mixture into acetone; PMPS is not soluble in acetone, but lower molecular weight polystyrene is soluble. This effectively removes any homo polystyrene impurities leaving only the block copolymer. GPC traces of the purified block copolymers are shown in Figure 2. The traces are monomodal indicating complete removal of the polystyrene and have low polydispersities, $\overline{M}_w/\overline{M}_n = 1.3$.

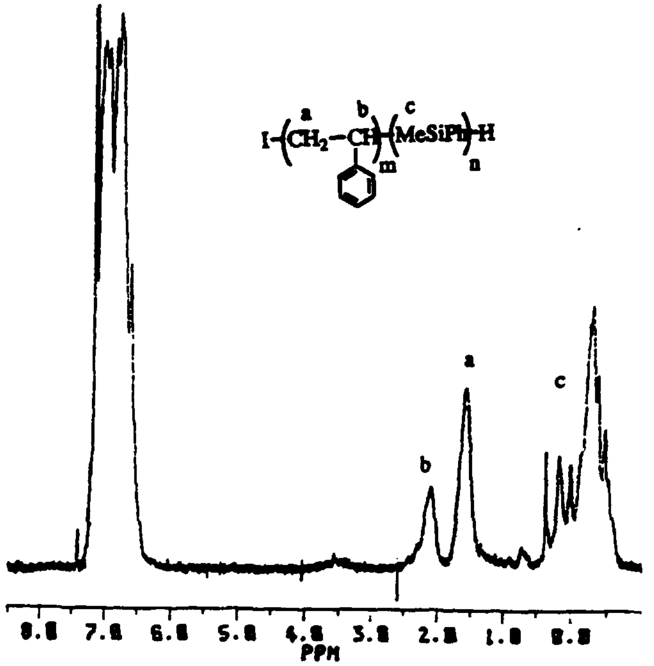


Figure 1. 300 MHz ^{1}H NMR spectrum (C$_6$D$_6$) of PS/PMPS block precipitated from acetone to remove homo polystyrene.

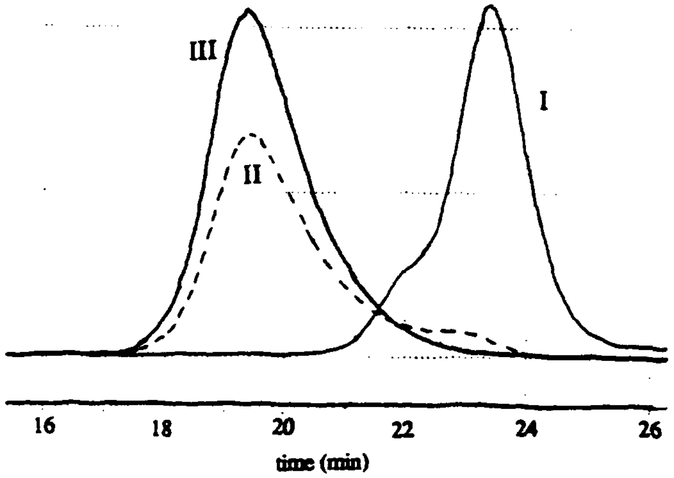


Figure 2. GPC traces of I) homo polystyrene ($\overline{M}_n$=5,300, $\overline{M}_w/\overline{M}_n$=1.15), II) crude PS/PMPS block ($\overline{M}_n$=12,900, $\overline{M}_w/\overline{M}_n$=1.37), and III) purified PS/PMPS ($\overline{M}_n$=16,300, $\overline{M}_w/\overline{M}_n$=1.31) acquired at 254 nm.

Evidence for the formation of blocks rather than two homopolymers also comes from the GPC traces shown in Figure 2. The trace for the crude block product is shifted to much higher molecular weights than that for the original polystyrene. At 254 nm unreacted polystyrene is present evidenced by the small lower molecular weight shoulder. However, this lower molecular weight shoulder is absent at 338 nm, a wavelength unique to polysilylenes. This indicates the formation of block copolymers and the presence of homo polystyrene.

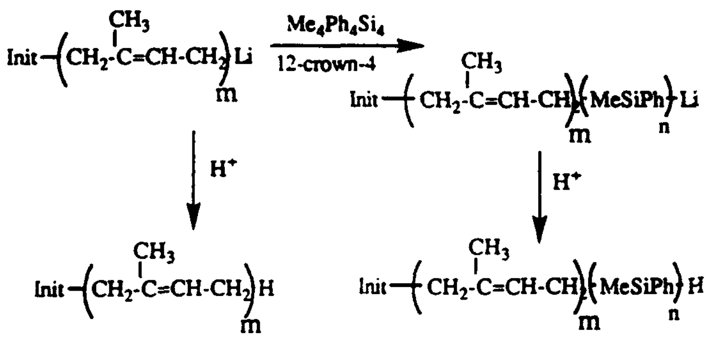
The relevant molecular weight data for homo polystyrene, crude reaction products, and purified block copolymers is shown in Table 1. As the percentage of polystyrene increased it became increasingly difficult to precipitate the block copolymers into acetone because of increased solubility, therefore, it was necessary to remain on the lower end of styrene composition.

Table 1. Molecular weight data for homo polystyrene, purifed PS-*block*-PMPS, and the calculated theoretical molecular weight values.

$[S]_0/[I]_0$	DP^1_t/DP^1_e	$\overline{M}_n$ $(\overline{M}_w/\overline{M}_n)$	$[Si_4]_0/[I]_0$	DP^2_t/DP^2_e	$\overline{M}_n$ total $(\overline{M}_w/\overline{M}_n)$
0.907/0.04	23/23	2,400 (1.16)	0.23/0.015	15/24	13,900 (1.34)
1.80/0.04	46/51	5,300 (1.15)	0.23/0.015	15/23	16,300 (1.31)
3.60/0.04	92/116	12,100 (1.13)	0.23/0.015	15/30	26,500 (1.34)
7.20/0.04	184/245	25,500 (1.18)	0.23/0.015	15/28	38,900 (1.37)

The molecular weights of the polysilylene blocks do not correlate well with $[M]_0/[I]_0$ and are nearly twice as high as the expected values. The higher values for the polysilylene block can be explained by an inefficient cross-over reaction and also the presence of a small amount of impurity in the cyclotetrasilane solution which may terminate some polystyrene chains leading to actual concentrations of initiator lower than the calculated values. Also, the molecular weights determined for the blocks are based on polystyrene standards and may not give absolute values for the polysilylene block. Regardless, the molecular weight distributions are relatively low for block copolymers of this type, which indicates that transfer reactions are not likely. Thermal transitions, such as glass transition temperatures for the styrene blocks, are consistent with known values. The possibility of phase separation in these systems is currently under study.

Scheme II



It is also interesting to prepare block copolymers of polysilylenes with elastomeric polymers, such as polyisoprene. The living anionic polymerization of isoprene in benzene initiated by sec-BuLi allows for the synthesis of polyisoprene-block-PMPS starting from the polymerization of isoprene (Scheme II). The appearance of a dark yellow to brown color after addition of the cyclotetrasilane indicated the switch-over to cyclosilane polymerization and the presence of silyl anions. The reaction was followed by both ^1H NMR and GPC.

The ^1H NMR spectrum of the copolymer precipitated from pentane is shown in Figure 3. Peaks for both polyisoprene and polysilylene are present indicating formation of the desired product.

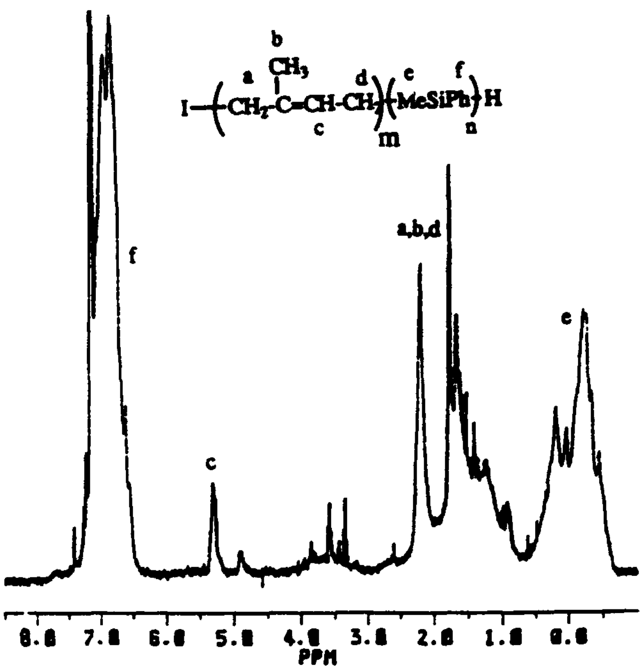


Figure 3. 300 MHz ^1H NMR spectrum of the copolymer of polyisoprene and PMPS precipitated from pentane to remove homo polyisoprene.

The GPC trace of the crude block copolymer is shifted to higher molecular weights than the parent polyisoprene, but the large, lower molecular weight shoulder indicates inefficient initiation of the second monomer. The homo polyisoprene can be removed by precipitation into hexane yielding only the block copolymer as the precipitate. This material could have a higher potential for microphase separation than the PS/PMPS blocks due to the greater differences in chemical nature of the individual components. Studies involving the effects of composition in this system are currently being carried out.

Conclusions.

Block copolymers of polystyrene and poly(methylphenylsilylene), PS/PMPS, and polyisoprene and PMPS, PI/PMPS have been prepared by the subsequent addition of cyclotetrasilane monomer to the living anionic polymerizations of the respective monomers. Evidence for the formation of block copolymers as opposed to mixtures of homopolymers resulting from transfer reactions comes from GPC analysis and also solubility differences of the two homopolymers. The efficiencies of initiation of the second monomer are relatively high allowing for the synthesis of block copolymers in reasonably good yields. The phase behavior for the copolymers is currently under study.

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