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Synthesis and characterization of polystyrene-block-poly(methylphenylsilylene) and polyisoprene-block-poly(methylphenylsilylene) ☆

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Abstract

Polystyrene/poly(methylphenylsilylene) and polyisoprene/poly(methylphenylsilylene) block copolymers were prepared by two independent methods. Subsequent additions of solutions of cyclotetrasilanes in benzene to the living ends of polystyrene and polyisoprene resulted in the formation of well-defined block copolymers with narrow molecular weight distributions ($M_w/M_n < 1.3$). Condensation of the living ends of polyisoprene and polystyrene with bromide end-terminated polysilanes also resulted in the formation of block copolymers. The materials were characterized by ^{1}H and ^{29}Si NMR, GPC, DSC and elemental analysis.

Keywords: Silicon; Polysilanes; Living polymerization; Polysilylene; Block copolymers; Cyclotetrasilane

1. Introduction

Very few reports have described the synthesis of block copolymers in which one of the blocks is a polysilylene (polysilane), consisting of a linear chain of silicon atoms carrying two substituents, generally either alkyl or aryl [1–3]. The polysilylenes possess sigma delocalization which gives rise to intense UV absorptions in the range 300–400 nm [4,5]. The polysilylenes, in general, do not possess exceptionally good mechanical properties [1]. Two ways to improve mechanical properties are by blending and the synthesis of block copolymers [1,6]. Block copolymers may microphase separate and possibly lead to interesting morphologies which may also improve the mechanical properties.

The most common synthetic method employed to prepare polysilylenes, Wurtz coupling of dichlorosilanes, limits the potential routes leading to block copolymers to condensation reactions of halide end-terminated polysilylenes with anionic living polymers. However, the polymerizations of masked disilenes and cyclotetrasilanes provide more versatile synthetic pathways to block copolymers [2,7]. For example, Sakurai et al. have prepared well-defined block copolymers by subsequent additions of methyl methacrylate to masked disilene polymerizations [2]. This paper will describe the synthesis and preliminary characterization of polysilane block copolymers prepared by the subsequent addition of cyclotetrasilane monomers to solutions of polystyryl lithium and polyisopropenyl lithium, and also by condensation reactions with bromide end-terminated polysilylenes.

2. Results and discussion

2.1. *Polystyrene-block-poly(methylphenylsilylene)*

Two different block copolymers were prepared using the living ends of polystyrene and polyisoprene to initiate the ring-opening polymerization (ROP) of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane (Scheme 1). Styrene and isoprene were polymerized in benzene using sec-BuLi as the initiator. After complete consumption of the first monomer a solution of cyclotetrasilane, benzene and 12-crown-4 was added and initiation of the second monomer was evidenced by a color change to the dark gold of silyl lithium.

☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

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Polystyryl lithium and polyisopropenyl lithium were of insufficient reactivity to initiate ROP without the presence of 12-crown-4. The reactions were followed by size exclusion chromatography (SEC) to provide evidence for the synthesis of truly block copolymers and not simply a mixture of the two homo-polymers. For comparison, block copolymers were also prepared by coupling the living ends of both polystyrene and polyisoprene chains with bromine-capped polysilylene chains, prepared by cleaving higher molecular weight polysilylenes with bromine in benzene solution.

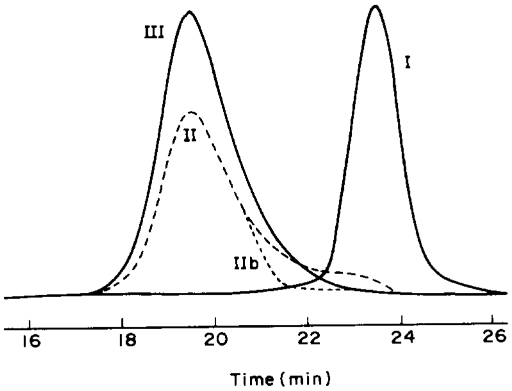
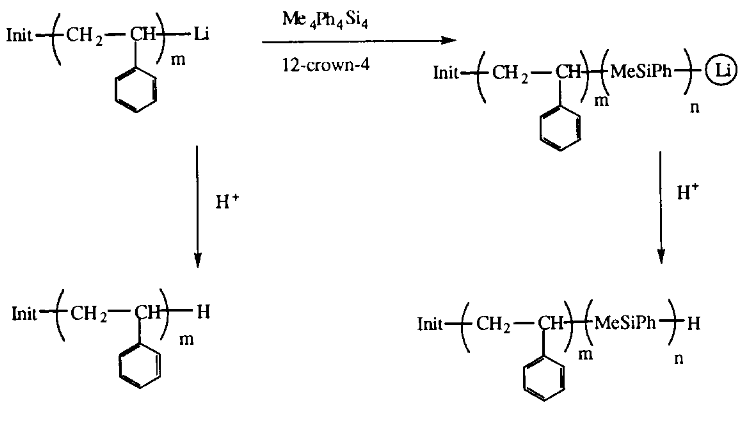


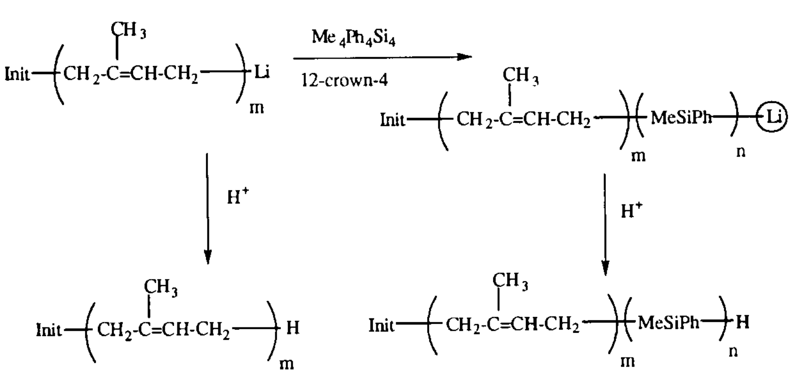
Fig. 1. GPC traces (at 254 nm) for (I) homo-polystyrene; (II) the crude block copolymer after addition of the cyclotetrasilane; (IIb) trace at 338 nm (unique to polysilylene); and (III) copolymer purified by precipitation into acetone.

Fig. 1 displays SEC traces for the products from a representative polystyrene block copolymer reaction. Trace I is from a sample of polystyrene terminated before the addition of the cyclotetrasilane; trace II is from the crude reaction product after addition of the cyclotetrasilane monomer; and trace III is from the product isolated by precipitation into acetone. As can be seen, the molecular weight for the crude reaction product is shifted to higher values than for the original polystyrene indicating the formation of block copolymers. Overlaying of two traces obtained for the crude block product (trace IIb) at 254 and 338 nm, a wavelength specific to the polysilylene block, showed the presence of some uncoupled polystyrene chains, as the two traces do not overlap exactly and the trace at 254 nm possesses a small shoulder of lower molecular weight material. The uncoupled polystyrene chains could be separated by precipitation into acetone, yielding only

polystyrene-*block*-poly(methylphenylsilylene)



polyisoprene-*block*-poly(methylphenylsilylene)



Scheme 1.

Table 1
Molecular weight data for polystyrene and polystyrene-block-PMPS copolymers determined by GPC analysis at 254 nm. $[\mathrm{St}]_0$, $[\mathrm{I}]_0$, $[\mathrm{Si_4}]_0$, and adjusted $[\mathrm{I'}]_0$ are in mol $\mathrm{l^{-1}}$

$[\mathrm{St}]^0$	$[\mathrm{I}]_0$	$\mathrm{DP_t^1/DP_e^1}$ [a]	M_w/M_n	$[\mathrm{Si_4}]_0$	$[\mathrm{I'}]_0$	$M_{n(\mathrm{total})}$	M_w/M_n	$\mathrm{DP_t^2/DP_e^2}$ [b]
0.91	0.04	23/23	1.06	0.23	0.015	13900	1.34	15/24
1.80	0.04	46/45	1.05	0.23	0.015	16300	1.31	15/24
2.10	0.04	53/52	1.05	0.30	0.015	26400	1.24	20/44
3.60	0.04	92/88	1.08	0.23	0.015	26500	1.40	15/36
7.20	0.04	184/180	1.08	0.23	0.015	38900	1.37	15/42

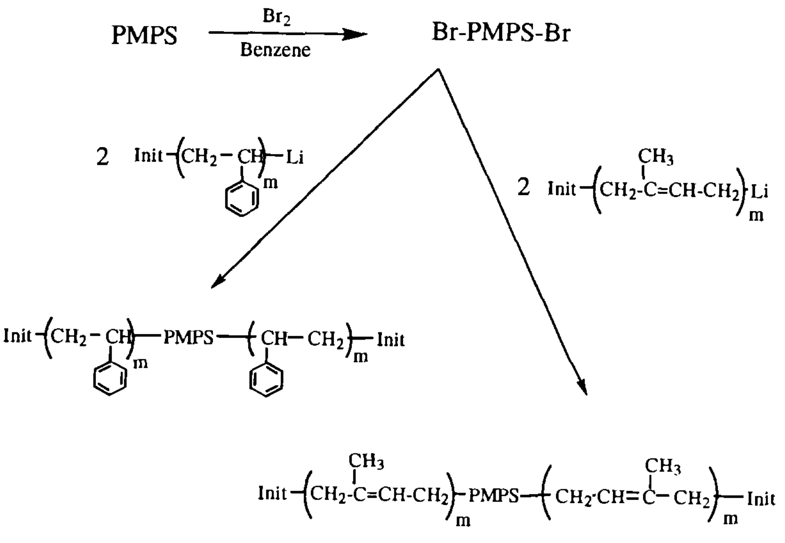
[a] $\mathrm{DP_t^1}$ and $\mathrm{DP_e^1}$ are theoretically predicted for quantitative initiation and experimentally observed by GPC molecular weights of polystyrene.
[b] $\mathrm{DP_t^2}$ and $\mathrm{DP_e^2}$ are theoretically predicted for quantitative initiation and experimentally observed by GPC molecular weights of polysilane block.

the block copolymer as an insoluble white powder. This separation method was confirmed by separating a mixture of the two homo-polymers in the same manner. It is possible that homo-polysilylene, which may be formed by initiation through a transfer mechanism, is present in the precipitate as well. However, the monomodal SEC trace at 338 nm indicates only one polysilylene containing component is present.

Table 1 contains the pertinent molecular weight data for a series of polystyrene/PMPS block copolymers in which the polystyrene block lengths were varied. In all cases the molecular weights determined experimentally for the polystyrene homo-polymer corresponded reasonably well with the expected value. The molecular weight distributions for the block copolymers are also quite low in comparison with previously reported blocks of the same two components [1]. However, the molecular weights determined for the polysilylene segments are nearly doubled from that of the expected value. This can be explained in one of two ways. Either initiation of the cyclotetrasilane polymerization using polystyryl lithium is inefficient, which would result in unreacted polystyrene chains and higher than expected molecular weights for the PMPS segments, or the molecular weights determined by SEC do not accurately reflect the actual molecular weights of the system.

Assuming that the molecular weights determined for the original polystyrene homo-polymers are accurate (the calibration was done using polystyrene standards), another way to determine the molecular weight of the second block is by integration of the ^{1}H NMR spectra of the purified block copolymers. A representative spectrum of a block copolymer, after precipitation into acetone, is shown in Fig. 2.

Table 2 contains the molecular weight data determined for the polysilane block by SEC and also by ^{1}H NMR spectroscopy. As can be seen, the molecular weights determined by the two methods differ considerably. Those determined by integration should be more accurate leading to the conclusion that initiation of cyclotetrasilane polymerization using polystyryl lithium has the efficiency approximately 70%, resulting in the presence of polystyrene homo-polymers. Low efficiency of coupling may be due to small amount of electrophilic impurities in the cyclotetrasilane. The block copolymers do not act as an ideal random coil in solution, which leads to enhanced values of molecular weights determined by SEC.



Scheme 2.

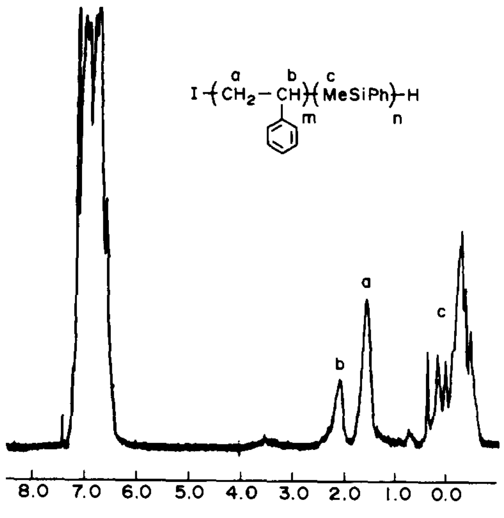


Fig. 2. 300 MHz ^1H NMR spectrum (C_6D_6) of a sample of purified polystyrene-block-poly(methylphenylsilylene) showing the presence of both polymers.

2.2. PS-PMPS-PS by condensation

Synthesis of polystyrene-PMPS-polystyrene triblock copolymers has been achieved by the coupling of polystyryl lithium with halide end-terminated polysilylene chains (Scheme 2). Preparation of bromide end-terminated PMPS was afforded by the reaction of PMPS with bromine in benzene solution under an argon atmosphere, which effectively cleaves the polysilane chain into smaller fragments and results in the desired bromide functionalities. The molecular weight decreases linearly with an increased percentage of added bromine. However, because the cleavage is a random process and a statistical distribution results, not all chains possess two bromide endgroups which precludes the clean synthesis of triblock copolymers.

The bromide end-terminated polymers were protected from air and moisture to preserve the functionalities. A stoichiometric amount, based on the total number of silyl bromides in solution, of polystyryl lithium was added dropwise to the stirred solution of Br-PMPS-Br. SEC traces of the original PMPS, cleaved PMPS, polystyrene homopolymer, and the product of the reaction of polystyryl lithium with Br-PMPS-Br are given in Fig. 3. The molecular weight of the pristine polysilylene (trace I) decreased after the reaction with bromine, indicating that cleavage of the chains had taken place and bromide end groups were present (trace II). The molecular weight increased again after reaction with polystyryl lithium (trace III), which is evidence for the formation of coupled products between the two chains (trace IV). The molecular weight determined was between the values expected for diblocks and triblocks, indicating the presence of a mixture of the two different types of blocks.

Table 2
Comparison of molecular weights for PMPS block in the PS-PMPS block copolymers determined by GPC and ^1H NMR spectroscopy

Sample	GPC (254 nm)	^1H NMR
1	11500	8700
2	11500	9700
3	21200	—
4	17300	10800
5	20200	[a]

[a] Polystyrene had too high a molecular weight to be removed by precipitation into acetone.

2.3. Polyisoprene-block-PMPS

Combination of PMPS with a flexible block, such as polyisoprene, may lead to polysilanes with elastomeric properties. Synthesis of block copolymers of this type was afforded in the same manner as for the polystyrene blocks.

Isoprene was polymerized in benzene using sec-BuLi as the initiator. Samples were taken to determine the molecular weight of the isoprene homo-polymers; solutions of $Me_4Ph_4Si_4$ in benzene with 12-crown-4 were then added to the stirred solutions of polyisoprenyl lithium, at which time the colorless solution turned to the dark gold-brown color of silyl lithium. The color change indicated initiation of polymerization of the second monomer.

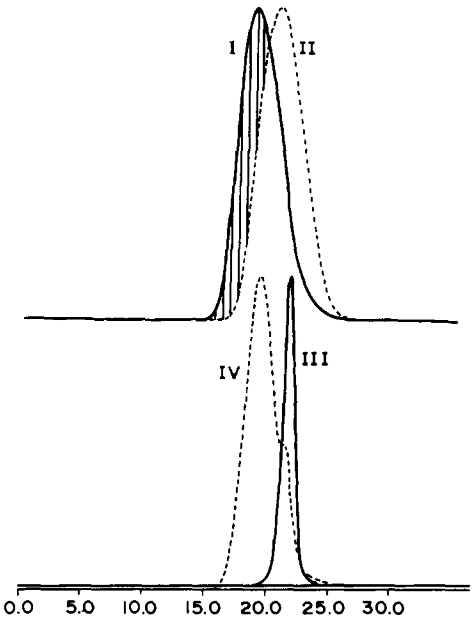


Fig. 3. GPC traces (at 254 nm) of the products from a condensation block copolymer forming reaction where (I) is the original polysilylene; (II) is the polysilylene after reaction with bromine; (III) is the homo-polystyrene; and (IV) is the trace of the crude product after the reaction of polystyryl lithium with bromide capped polysilylene.

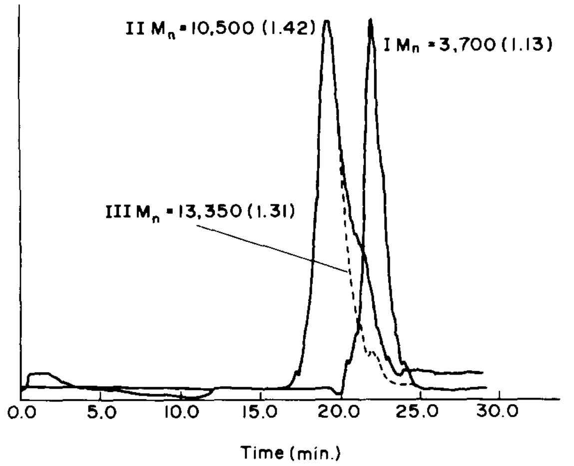


Fig. 4. GPC traces (refractive index detector) for (I) homo-polyisoprene; (II) the crude product after addition of the cyclotetrasilane; and (III) the purified block copolymer after precipitation into pentane to remove homo polyisoprene.

SEC traces obtained, using a refractive index detector, for polyisoprene homopolymer (trace I), crude polyisoprene-block-PMPS (trace II), and purified polyisoprene-block-PMPS (trace III) are given in Fig. 4. Trace II is shifted to higher molecular weights indicating the formation of a block copolymer; there is also a small, lower molecular weight shoulder, which corresponds to uncoupled polyisoprene chains. Homo-polyisoprene was removed by precipitation into pentane, a good solvent for polyisoprene, but a nonsolvent for both PMPS and the block copolymer. The resulting precipitate was too fine to be filtered and formed a fine suspension. Separation was effected by centrifugation to provide the block copolymer free from homo-polyisoprene, as evidenced by trace III. This trace shows no lower molecular weight shoulder as seen with the crude product. The molecular weight is slightly higher and the molecular weight distribution is narrower.

Molecular weight data for the original homo-polyisoprene and the block copolymers are given in Table 3. The molecular weights of the homo-polyisoprene correlate well with the expected values based on the monomer-to-initiator ratio. In this system also, the molecular weights determined for the blocks, and thus the PMPS segments, are different to the theoretical values. The discrepancy in molecular weights is not as simple to explain in this case as the molecular weights of the polyisoprene homopolymers are relative to polystyrene standards and cannot be used as absolute values for determination of the molecular weights of the PMPS segments by integration of the ^{1}H NMR spectra.

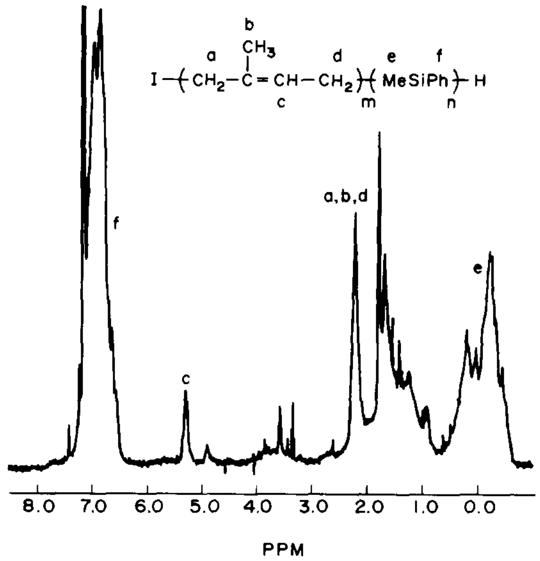


Fig. 5. 300 MHz ^{1}H NMR spectrum (C_6D_6) of a sample of purified polyisoprene-block-poly(methylphenylsilylene) showing the presence of both polymers.

A comparison of molecular weights determined by GPC and ^{1}H NMR integration is given in Table 4. A representative ^{1}H NMR spectrum of a polyisoprene/PMPS block, after purification, is given in Fig. 5. The molecular weights determined by the two methods are similar at lower molecular weight values, but deviate considerably in the higher molecular weight range. Since the molecular weights determined by GPC and ^{1}H NMR integration did not correlate well for the polystyrene/PMPS blocks, it is difficult to come to any firm conclusions about the efficiency of initiation of ROP by polyisopropenyl lithium. Nevertheless, the efficiency appears to be much higher in the lower polyisoprene molecular weight range.

A–B–A triblock copolymers were also prepared with polyisoprene and PMPS, using the same route as that described for PS–PMPS–PS triblock copolymers. GPC traces for the condensation experiments are shown in Fig. 6. The molecular weight of the original PMPS

Table 3
Molecular weight data determined by GPC using a refractive index detector for homo-polyisoprene and polyisoprene-block-poly(methylphenylsilylene). $[I_{SO}]_0$, $[I]_0$, $[Si_4]_0$, and adjusted $[I']_0$ are in mol l^{-1}

$[I_{SO}]_0$	$[I]_0$	DP_t^1/DP_e^1 [a]	M_w/M_n	$[Si_4]_0$	$[I']_0$	$M_{n(total)}$	M_w/M_n	DP_t^2/DP_e^2 [b]
2.2	0.036	61/54	1.13	0.342	0.015	13360	1.32	21/20
2.0	0.036	55/45	1.10	0.350	0.015	23000	1.40	23/40
2.0	0.073	27/22	1.11	0.350	0.030	5600	1.40	12/9

[a] DP_t^1 and DP_e^1 are theoretically predicted for quantitative initiation and experimentally observed by GPC molecular weights of polyisoprene.
[b] DP_t^2 and DP_e^2 are theoretically predicted for quantitative initiation and experimentally observed by GPC molecular weights of polysilane block.

Table 4
Comparison of molecular weights for PMPS block in the polyisoprene-block-PMPS copolymers determined by GPC and ^{1}H NMR spectroscopy

Sample	GPC (RI)	^{1}H NMR
1	9700	11700
2	19200	25000
3	4100	4200

decreased after reaction with bromine, and an increase was observed after reaction with polyisoprenyl lithium. However, the coupling process is not as clean as with polystyryl lithium, as evidenced by the presence of uncoupled PMPS chains and also homo-polyisoprene. Three maxima were observed in the trace at 338 nm, indicating the presence of both di- and tri-block copolymers along with homo-PMPS. The position of peaks on GPC traces may correspond to diblock ($M_p = 17000$) and triblock copolymers ($M_p = 30000$).

Elemental analyses were performed on samples of both polyisoprene-block-PMPS and polystyrene-block-PMPS and the results were in good agreement with the percentages of respective monomer units determined by ^{1}H NMR spectroscopy. This also justified the application of ^{1}H NMR integration for molecular weight determinations of these particular polysilane block copolymers.

2.4. Thermal analysis

Both types of block copolymers were analyzed by differential scanning calorimetry (DSC). Homo-PMPS shows very weak and broad glass transition and is usually very difficult to observe by DSC. However, both the polyisoprene and polystyrene segments display clear glass transition. Thermal scans of the two different blocks are shown in Fig. 7 for representative samples. The scans were taken from the second heating cycle to eliminate any thermal history of the samples.

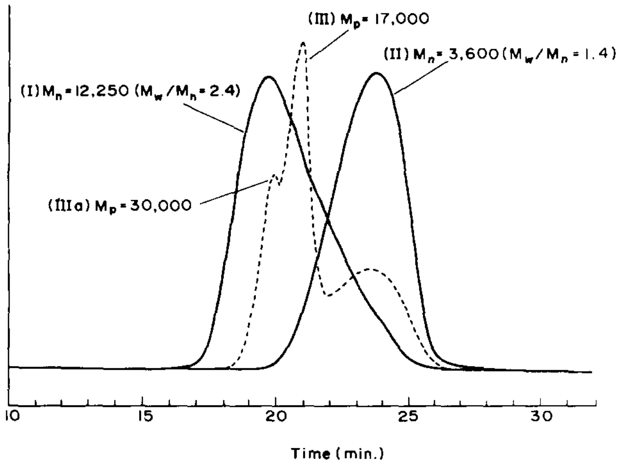


Fig. 6. GPC traces (at 338 nm) of the products from a condensation block copolymer forming reaction where (I) is the original polysilylene; (II) is the polysilylene after reaction with bromine; and (III) is the trace of the crude product after the reaction of polyisoprenyl lithium with bromide capped polysilylene. The molecular weight of the homo-polyisoprene was $M_n = 10000$ with $M_w/M_n = 1.06$.

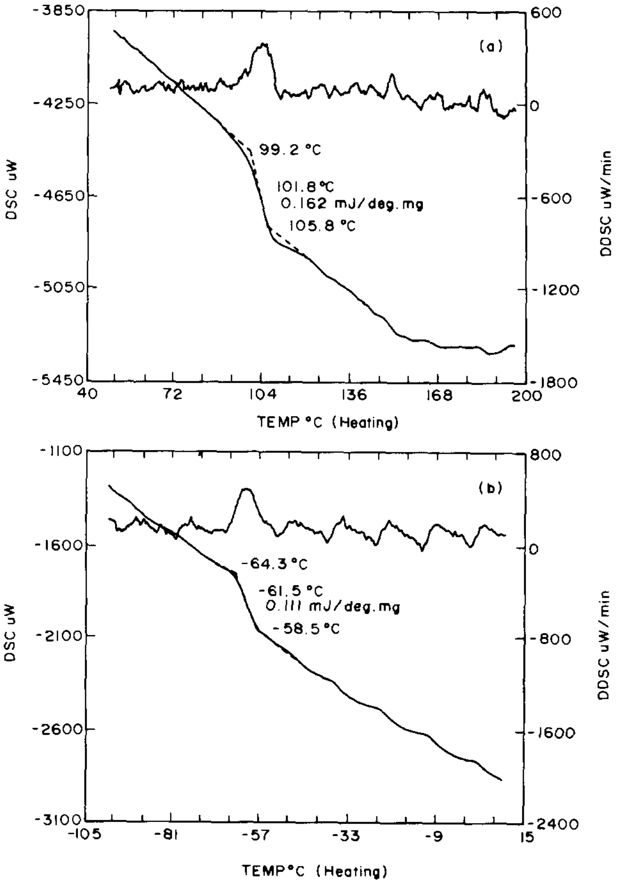


Fig. 7. Differential scanning calorimetry traces (second heating scan) of (a) polystyrene-block-PMPS; and (b) polyisoprene-block-PMPS.

Both the polyisoprene and polystyrene blocks exhibit glass transitions for these segments in the range for the respective homopolymers, 102 ± 1 and −61.5 ± 1°C for polystyrene and polyisoprene, respectively. The enthalpy of the transitions increases with increased content of the respective units, as would be expected, but the transition temperature remains constant. No thermal transitions other than glass transitions were observed and transitions for the PMPS segments were too weak to be detected.

2.5. ^{29}Si NMR analysis

The block copolymers were also characterized using ^{29}Si NMR spectroscopy. The microstructures for all of the block copolymers appeared to be similar to that of PMPS prepared by polymerization of $Me_4Ph_4Si_4$ using BuLi/cryptand [2.1.1] in benzene. The microstructure

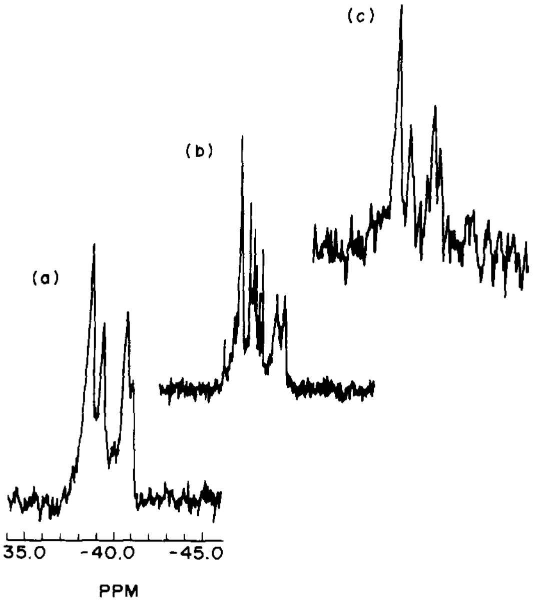


Fig. 8. 59.6 MHz ^{29}Si NMR spectra (C_6D_6) of (a) PMPS prepared by the ^{n}BuLi/12-crown-4 initiated ROP of the all-*trans*-isomer of $Me_4Ph_4Si_4$, (b) polystyrene-block-PMPS, (c) polyisoprene-block-PMPS. Chemical shifts are referenced externally to tetramethylsilane.

consists of 50% heterotactic, 15% syndiotactic and 35% isotactic triads [8]. The samples exhibited three broad resonances present between −37.5 and −41.0 ppm (Fig. 8). However, the polystyrene-block-PMPS samples prepared by the subsequent addition of $Me_4Ph_4Si_4$ to living polystyrene displayed somewhat unique spectra. Some of the resonances are considerably sharper than those in the previous cases and more lines are present. These peaks may be due to crossover points, suggesting that more than just one connecting unit is effected by neighboring polystyrene chain.

3. Conclusions

Both di-and tri-block copolymers consisting of either polystyrene or polyisoprene, in conjunction with poly(methylphenylsilylene) have been prepared by two routes. The coupling of polystyryl lithium or polyisopropenyl lithium with bromide-capped PMPS affords the respective triblock copolymers. Subsequent addition of $Me_4Ph_4Si_4$ to polystyryl lithium or polyisopropenyl lithium provides access to the respective diblock copolymers. The existence of block copolymers was confirmed by GPC analysis, ^{1}H NMR studies and fractionation experiments. The materials exhibit glass transitions for the organic block consistent with literature values; no thermal transitions were observed for the PMPS blocks. Further studies to characterize the morphologies of the block copolymers are in progress.

4. Experimental details

All experiments were performed in a Vacuum Atmospheres HE-30 dry box under a dinitrogen atmosphere with < 1 ppm of oxygen and moisture. Molecular weights and molecular weight distributions were determined by GPC using a Waters 510 HPLC equipped with a 410 differential refractometer and a Waters 991 Photo Diode Array detector with THF as an eluent and a flow rate of 1.0 ml min^{-1}. Three ULTRASTYRAGEL columns (100 Å, 500 Å, and linear) were used in series. The molecular weights are reported relative to a calibration curve obtained using polystyrene standards.

NMR measurements were performed using an IBM NR-300 spectrometer. ^{1}H NMR spectra were recorded at 300 MHz, ^{13}C NMR spectra at 75.4 MHz and ^{29}Si NMR spectra at 59.6 MHz, using a standard Bruker DEPT micro program. All spectra were obtained using C_6D_6 as the solvent and C_6H_6 as an internal reference for ^{1}H and ^{13}C, TMS was used as an external standard for ^{29}Si.

Differential Scanning Calorimetry measurements were performed on a Seiko 5200 system using scan rates of 10 K min^{-1}. All samples were run through two heating and cooling cycles to eliminate thermal histories. Reported data are for the second heating scan. Polymer samples, from 5 to 10 mg, were sealed in aluminum pans prior to thermal analysis.

4.1. Materials

Benzene was refluxed over potassium metal and distilled under argon prior to use. 12-crown-4 (Aldrich) was dried under high vacuum for several days. Isoprene (Aldrich) was dried over CaH_2 and distilled under argon prior to use. Styrene (Aldrich) was purified by washing with 5% NaOH solution, washing with water, drying over CaH_2, degassing and transferred on a vacuum line prior to use. sec-BuLi in hexanes (Aldrich) was used as received. $Me_4Ph_4Si_4$ was prepared by previously reported procedures [9].

4.2. Poly(methylphenylsilylene)

Poly(methylphenylsilylene) was prepared by either the previously reported Wurtz coupling route or by ROP of $Me_4Ph_4Si_4$. The PMPS samples were dried in a vacuum over for 24 h prior to being used for bromine reactions.

4.3. Br–PMPS–Br

Br–PMPS–Br was prepared by the reaction of PMPS with bromine in benzene solution. 0.402 g of PMPS with $M_n = 12250$ ($M_w/M_n = 2.4$) was placed in a 25 ml round-bottom flask equipped with a stir bar and septum. The flask was purged with argon and the polymer then dissolved in 10 ml of benzene. 5 μl of bromine was then added dropwise to the stirred solution resulting in a brown color that faded almost immediately. The solution was stirred overnight and a small sample was taken for GPC analysis. The sample was precipitated in MeOH, filtered and dried. GPC analysis (338 nm): $M_n = 3600$ ($M_w/M_n = 1.4$). The rest of the solution was taken to the glovebox for coupling reactions. Under such conditions approximately equimolar amounts of mono- and di-functional polymers should be obtained.

4.4. Polystyryl lithium

To a solution of 150 μl 1.3 M sec-BuLi (hexanes) in 5 ml of benzene was added, dropwise, 1.4 ml of styrene; a dark orange color appeared and persisted. The solution was stirred for ca. 40 min. Longer reaction times were used for higher $[M]_0/[I]_0$ concentrations. Samples of the homo-polystyrene were terminated with either protonic acids or with trimethylsilyl chloride and precipitated into MeOH, filtered and dried prior to GPC analysis.

4.5. PS–PMPS–PS

To the stirred solution of Br–PMPS–Br was added, dropwise, a solution of polystyryl lithium. Each drop resulted in an orange color which faded almost immediately. Upon complete addition, the mixture was stirred for 1.5 h and then precipitated into MeOH yielding a white powder which was filtered and dried in a vacuum oven prior to analysis.

4.6. PS–PMPS

In a typical experiment, 14 μl of 1.3 M sec-BuLi was dissolved in 0.5 ml of benzene. To this was added 0.120 ml of styrene. The dark orange solution was stirred for ca. 10 min, at which point a 0.15 ml sample was taken for GPC analysis. To the stirred orange solution was added 0.121 g of $Me_4Ph_4Si_4$, 0.5 ml of benzene and 5 μl of 12-crown-4. The solution changed from dark orange to dark yellow and the color persisted for the reaction time of 10 min. The solution was then removed from the glovebox and exposed to moisture for termination. Precipitation into methanol yielded a white powdery polymer with Mn = 23 000 (1.35) at 254 nm and Mn = 26 400 (1.24) at 338 nm. Uncoupled polystyrene was removed by redissolving the polymer in THF and precipitating into acetone. The white powder was filtered off and dried in a vacuum oven prior to subsequent analysis.

4.7. Polyisopropenyl lithium

In a 10 ml round bottom flask equipped with a stir bar, 14 μl of 1.3 M (in hexanes) sec-BuLi was dissolved in 0.5 ml of benzene. To this was added 0.110 ml of freshly distilled isoprene. The reaction mixture was stirred for 1.5 h prior to subsequent experiments and samples were taken for GPC analysis. Reactions times were adjusted depending the concentration of isoprene.

4.8. PI–PMPS–PI

Triblock copolymers of PI–PMPS–PI were prepared in a similar fashion to PS–PMPS–PS triblock copolymers. Purifications were performed by precipitation into MeOH, followed by redissolution in THF and precipitation into pentane to remove unreacted polyisoprene. Block copolymers were then separated by centrifugation yielding very fine white powders.

4.9. PI–PMPS

Diblock copolymers were prepared in a similar fashion to PS–PMPS diblock copolymers. Purification was achieved as noted for PI–PMPS–PI triblocks.

Acknowledgments

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