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Regular Comb Polystyrenes and Graft Polyisoprene/Polystyrene Copolymers with Double Branches ("Centipedes"). Quality of (1,3-Phenylene)bis(3-methyl-1-phenylpentylidene)dilithium Initiator in the Presence of Polar Additives

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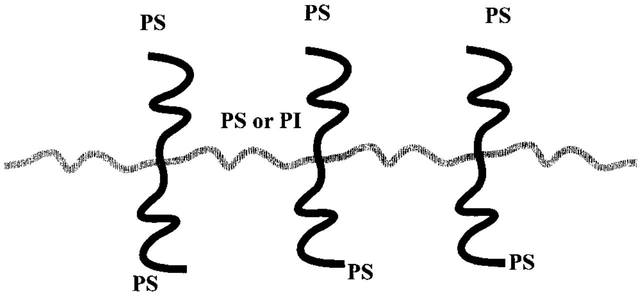
ABSTRACT: The synthesis of regularly spaced comb polystyrenes and graft polyisoprene/polystyrene copolymers with two branches at each junction point (centipedes) is presented. The synthetic approach involves the selective replacement of two chlorines of $SiCl_4$ by polystyrene (PS) followed by step−growth polymerization of the produced $(PS)_2SiCl_2$ with α,*ω*-dilithium PS or 1,4 polyisoprene (PI). The polydispersity indices of the reaction products, PS-*g*-PS_2 (homocentipedes) and PI-*g*-PS_2 (cocentipedes), varied between 2.0 and 3.0 but was reduced to 1.2−1.3 by fractionation. The quality of (1,3-phenylene)-bis(3-methyl-1-phenylpentylidene)dilithium initiator (DLI), used for the synthesis of the dianion, in the presence of polar additives (THF, Et_3N, and *s*-BuOLi), was evaluated.

Introduction

Comb homopolymers and graft copolymers with one or two branches in a well-defined position along the main chain have been prepared by anionic polymerization and controlled chlorosilane chemistry.[1−4] Synthetic routes leading to comb polymers with more than two branches suffer from random placement of the branches along the backbone.[5] Therefore, the structure−property relationships determined for these materials reflect a variation not only in the number of branches but in their placement also. Strazielle and Herz[6] synthesized "comb-like" PS with regular distribution of branches along the backbone by reacting dipotassium PS with two allyloxy groups of tris(allyloxy)-*s*-triazine (step-growth polymerization) followed by reaction of the remaining allyloxy group with living PS. Rempp and collaborators[7] observed an increase in molecular weight of dicarbanionic PS when it was reacted with difunctional deactivating reagents (dibromobutane or -hexane) due to the step-growth polymerization. Along the same lines, but by using the macrocoupling agent $(PS)_2SiCl_2$ instead of low molecular weight coupling agents, we have prepared PS-*g*-PS_2 (homocentipedes) and PI-*g*-PS_2 (cocentipedes) graft copolymers (Scheme 1). At each grafting point two PS chains are linked and the spacing between the grafting points is constant and controllable. The degree of polymerization can be predicted by using a known excess of the α,*ω*-dianionic species which were produced by polymerization of isoprene and styrene with DLI. The use of polar additives was studied in order to find the optimum conditions for polymerization and the linking reaction.

Scheme 1



PS(PI)-g-St
homo- and cocentipede

Experimental Section

The purification of isoprene (Aldrich), styrene (Aldrich), butadiene (Aldrich), and benzene to the standards required for anionic polymerization has been described elsewhere.[8] The linking agent, tetrachlorosilane (Aldrich), was purified by fractional distillation on the vacuum line. It was then diluted with benzene and subdivided into tubes equipped with break-seals. Methyllithium (Aldrich), triphenylmethylphosphonium iodide (98% Alpha) and 1,3-bis(1-phenone)benzene (PBOP) (98%, Aldrich) were used for the preparation of 1,3-bis(1-phenylethenyl)benzene (PEB) according to the method of Ignatz−Hoover.[9] *s*-Butyllithium (*s*-BuLi), prepared in vacuo from *s*-butyl chloride and lithium dispersion, was used as the activator of PEB and as the initiator of the monofunctional PS arms. DLI along with *s*-BuOLi or tetrahydrofuran (THF) was used for the synthesis of the difunctional PI or PS connectors, respectively. THF (Aldrich) was purified by fractional distillation, first over CaH_2 and then over Na−K alloy. A pale blue color formed, indicating the high purity of the THF. All manipulations (except the preparation of PEB) were performed, under high vacuum, in glass reactors with break-seals for the addition of the reagents and constrictions for removal of products.

The fractionation of the graft homo- and copolymers was performed by using toluene and methanol as a solvent/nonsolvent pair.

Size exclusion chromatography (SEC) experiments were carried out at 30 °C using a Waters Model 510 pump, a LDC Milton Roy UV detector, and a Waters Model 410 differential refractometer. Two ultrastyragel columns with a continuous porosity range from 10^6 to 10^3 Å were used. THF was the carrier solvent at a flow rate of 1.0 mL/min.

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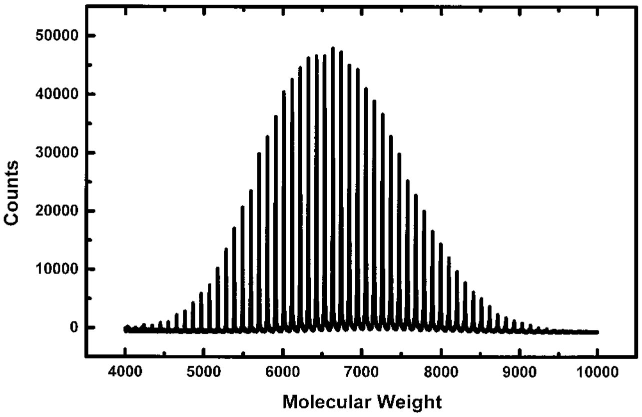


Figure 1. Matrix-assisted laser desorption/ionization time-of-flight mass spectrum of the PS arm with $M_n = 6700$.

The number average molecular weights (M_n) of the precursors were measured with a Jupiter Model 231 Recording Membrane Osmometer (MO) at 37 °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 all cases the correlation coefficient was better than 0.99. In a few cases ($M_n < 2 \times 10^4$) the molecular weight was determined by using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI/TOF/MS); an example is given in Figure 1, where the high quality of the polymerization technique used can be seen. The instrument (Perseptive Biosystems Voyager Elite DE) was calibrated with monodisperse proteins. *trans*-Retinoic acid was used as the matrix with silver trifluoroacetate as the cationization agent for the analysis of PS.

The weight-average molecular weight (M_w) of the graft polymers was measured with a Chromatix KMX-6 low-angle laser light scattering 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, d*n*/d*c*, 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 $(KC/R_\theta)^{1/2}$ vs C plots (ΔR_θ, excess Rayleigh ratio; *K*, combination of known optical constants) in order to minimize the curvature due to the third virial coefficient. In all cases the correlation coefficient was better than 0.99. Nuclear magnetic resonance (NMR) spectra were generated using a Bruker 400 MHz instrument with $CDCl_3$ as solvent. Long relaxation times were used in ^{13}C NMR experiments to obtain quantitive spectra.

Results and Discussion

Quality of (1,3-Phenylene)bis(3-methyl-1-phenylpentylidene)dilithium Initiator (DLI) in the Presence of Polar Additives. The DLI was prepared from PEB and *s*-BuLi according to procedures given elsewhere.[9] The concentration of the C−Li bonds was determined by titration of LiOH, produced after reaction with water, with aqueous HCl solution.

Tung and Lo[10] monitored the polymerization of isoprene with the DLI for different duration times in hydrocarbon solvents. They found that two different kinds of living ends were participating in the polymerization resulting in a bimodal PI. By adding a variety of polar additives e.g. alkoxides, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine in a variety of [polar additive]/[C−Li] ratios, i.e., 0.1−0.9, monomodal PI could be obtained.

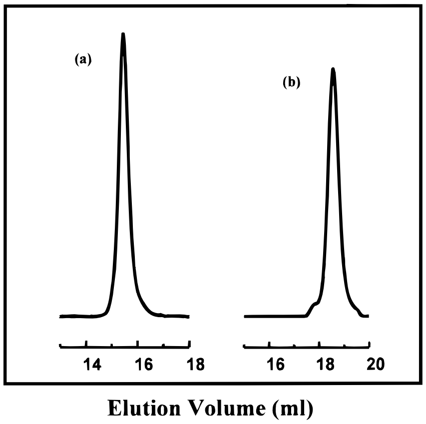


Figure 2. SEC chromatograms of difunctional PS: (a) $M_n = 9 \times 10^4$; (b) $M_n = 2 \times 10^4$.

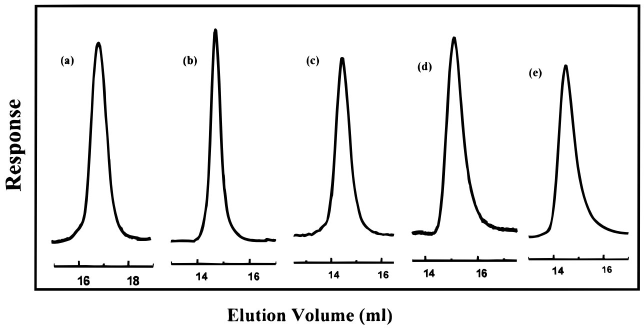


Figure 3. SEC chromatograms of difunctional polyisoprenes prepared with different [*s*-BuOLi]/[C−Li]: (a) [*s*-BuOLi]/[C−Li] = 14, *I* = 1.1, polymerization time = 24 h; (b) [*s*-BuOLi]/[C−Li] = 14, polymerization time = 8 days; (c) [*s*-BuOLi]/[C−Li] = 7; (d) [*s*-BuOLi]/[C−Li] = 4; (e) [*s*-BuOLi]/[C−Li] = 1.

Quirk and Ma[11] investigated the influence of polar additives on the polydispersity (PS, PBd) and microstructure of PBd and PS produced by DLI polymerization in hydrocarbon solvents in the presence of THF and *s*-BuOLi. In the case of PS they found that addition of THF in a ratio THF/C−Li ~ 30 gave narrow molecular weight distributions (polydispersity index $I = M_w/M_n \leq 1.1$). For butadiene they found that addition of *s*-BuOLi to the polymerization system in a ratio [*s*-BuOLi]/[C−Li] = 0.5−0.6 reduced the polydispersity of the difunctional PBd ($I \sim 1.1$) without altering the microstructure significantly (% w/w of 1,2 = 13). Further addition of *s*-BuOLi did not influence the polydispersity according to these authors.

We undertook similar experiments for styrene and isoprene in order to find the optimum conditions for the synthesis of our comb and graft copolymers. Four different polymerizations of styrene in benzene in the presence of THF (in a ratio THF/C−Li ~ 30) were performed at room temperature. In all cases monomodal polymers with narrow molecular weight distributions were obtained in accordance with the findings of Quirk and Ma. In Figure 2 size exclusion chromatograms of the lower and higher molecular weight PS are given. The values of M_n calculated from the stoichiometric values of M_n agree very well with the ones determined by SEC using PS standards.

In the case of isoprene, a series of polymerizations was performed by using a variety of [*s*-BuOLi]/[C−Li] ratios at room temperature. It was found that by increasing the [*s*-BuOLi]/[C−Li] ratio the polydispersity of PI was reduced from 1.20 to 1.03 (Figure 3, Table 1). With [*s*-BuOLi]/[C−Li] ≤ 8, a pale red color always remained throughout the reaction. This implies that a

Table 1. Dependence of Polydispersity on the [*s*-BuOLi]/[C−Li] Ratio

sample	[*s*-BuOLi]/[C−Li]	$M_n \times 10^{-4\,b}$	$I^a(M_w/M_n)$
PI 4	1	10	1.20
PI 3	4	6.0	1.14
PI 2	8	12.5	1.07
PI 1	14	7.5	1.03

[a] Polydispersity index obtained by SEC in THF at 25 °C. [b] Obtained by SEC in THF at 25 °C.

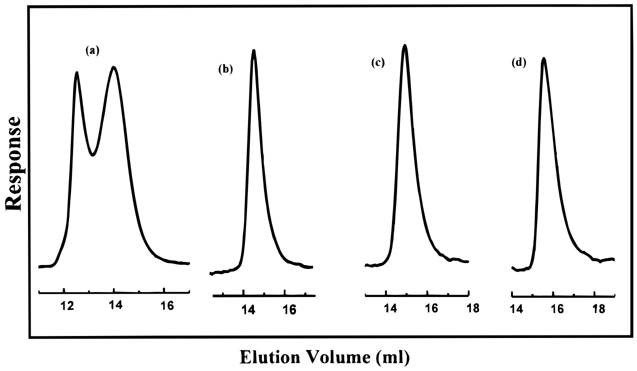


Figure 4. (a) Polymerization of isoprene with DLI in the presence of TEA in a [TEA]/[C−Li] ratio of 1. (b) Difunctional polyisoprene with $M_n = 8.3 \times 10^4$, [*s*-BuOLi]/[C−Li] = 1, and I = 1.17. (c) Difunctional polyisoprene with $M_n = 6.3 \times 10^4$, [*s*-BuOLi]/[C−Li]=1, and I = 1.24. (d) Difunctional polyisoprene with $M_n = 2.6 \times 10^4$, [*s*-BuOLi]/[C−Li] = 1, and I = 1.35.

small amount of initiator remains aggregated and does not participate in the polymerization, in agreement with the observations of Tung.[10] In addition, the living polymer solutions were highly viscous indicating the strong association of the living ends. When the [*s*-BuOLi]/[C−Li] ratio was 14, the red color disappeared, the living anions had the typical pale yellow color of PILi, and the viscosity was reduced.

In the case of polymerization with [*s*-BuOLi]/[C−Li] = 14 small aliquots were removed after 24 h and one week and analyzed by SEC (Figure 3a,b). The molecular weight of the PI after 24 h was 1.0×10^4 and the polydispersity was lower than 1.1. The polymer obtained after 1 week had a molecular weight of 7.5×10^4 and exhibited a very low polydispersity ($I \leq 1.1$). Although in this case the initiation time was comparable to that for [*s*-BuOLi]/[C−Li] < 14, the polymerization required 1 week for completion instead of 2 days required when the ratio was lower than 14. This implies that the propagation rate is decreased. This increase in the time required for complete polymerization is probably due to complexation of the chain ends and *s*-BuOLi, which prevents the access of the monomer. Similar results for polymerization of isoprene with *s*-BuLi in the presence of *t*-BuOLi were reported by Roovers et al.[12,13] The experiment was repeated by using a [*s*-BuOLi]/[C−Li] ratio of 18. In this case a shoulder (≈3%) corresponding to half the molecular weight of the main peak was observed. This is probably due to the small amount of *s*-BuOH remaining in the *s*-BuOLi solution which can deactivate one of the two active centers, leading to the low molecular weight peak.

Table 2. Dependence of Polydispersity on the M_n of the PI Chain When [*s*-BuOLi]/[C−Li] = 1

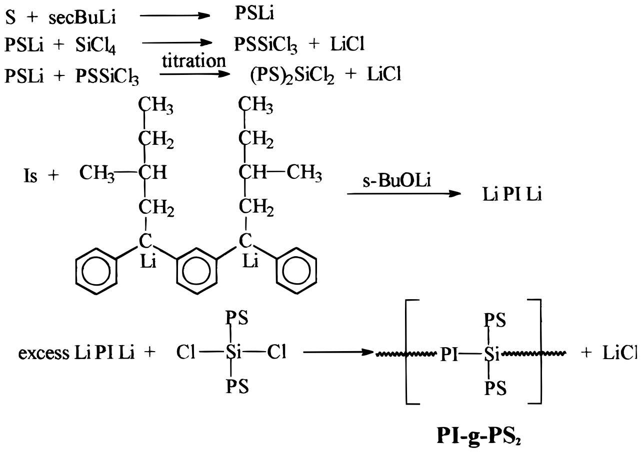
sample	$M_n \times 10^{-4\,b}$	$I^a(M_w/M_n)$
PI 5	8.3	1.17
PI 6	6.3	1.24
PI 7	2.6	1.35

[a] Polydispersity index obtained by SEC in THF at 25 °C. [b] Obtained by SEC in THF at 25 °C.

Figure 4 shows the SEC chromatograms of PI prepared with the same amount of initiator and a [*s*-BuOLi]/[C−Li] ratio of 2. The only difference was the amount of monomer added, which was increasing with molecular weight (Figure 4b−d). By increasing the molecular weight, the polydispersity decreased from 1.35 to 1.17 (Table 2). This implies that the increased polydispersity in the DLI system is due to initiating species with different aggregation numbers, which have different initiation rates. In the case of Figure 4a, triethylamine (TEA) was used as a polar additive in a ratio of [TEA]/[C−Li] = 1. The SEC chromatogram was bimodal and similar to the one obtained by Tung[10] and Quirk[11] for polymerizations with incomplete disruption of the aggregates of DLI. Therefore we conclude that TEA at this ratio does not break the aggregates of DLI, although the vinyl content of PI is increased.

The ^{13}C NMR of the PI obtained with [sec-BuOLi]/[C−Li] = 14 revealed that the 3,4 content was 15%. This value is a little higher than the vinyl content obtained from the polymerization of isoprene (high ratios of butoxide to chain end) with *s*-BuLi in hydrocarbon solvents (7−8%). However, it is one of the lowest obtained for a difunctional initiation system with a very low polydispersity and very high amount of difunctional species. The latter conditions were not used for the preparation of the cocentipede polymers because of concern about the reaction of butoxides with chlorosilanes (discussed below).

PI-*g*-PS2 Graft Copolymers (Cocentipedes). The reactions used for the synthesis of the graft copolymers are the following:



The progress of the linking reaction was monitored by SEC (Figure 5a−d). In Figure 5, the SEC results for the raw product are also given along with those for the fractionated copolymer.

A 3% w/v solution of PSLi in benzene was added into a solution of $SiCl_4$, in a ratio of $[C{-}Li]/[SiCl_4] = 1.3$. The resulting mixture of $(PS)_2SiCl_2$ and $PSSiCl_3$ was titrated with PSLi, until nearly all the $PSSiCl_3$ was transformed into $(PS)_2SiCl_2$. More details of the procedure are given elsewhere.[14,15] The solution of $(PS)_2SiCl_2$ was split in two parts. One part was used for the preparation of the copolymers and the other part was used for the preparation of homopolymers. An excess of difunctional

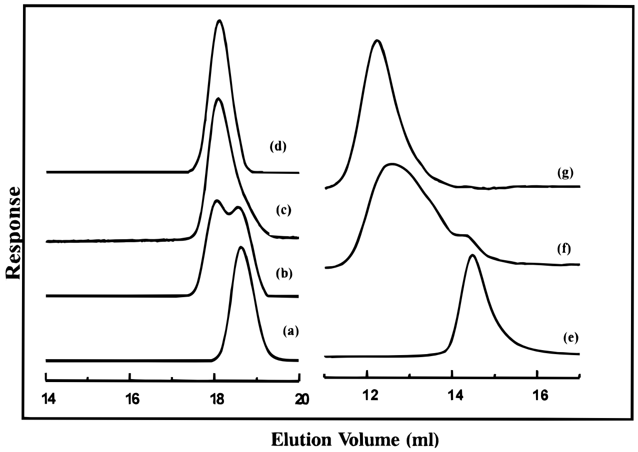


Figure 5. (a) PS arm. (b and c) Titration of $PSSiCl_3$ with living PSLi arm. In this step the higher molecular weight peak corresponds to the $(PS)_2SiCl_2$ and the lower molecular weight peak to the $PSSiCl_3$. (d) The product at the end point. (e) PI connector. (f) Unfractionated graft copolymer. (g) Fractionated copolymer (sample GSI 60−25).

PI solution (Li/Cl = 1.2) in benzene was added in order to control the degree of polymerization. *s*-BuOLi in a ratio of [*s*-BuOLi]/[C−Li] = 4 was used for the polymerization of the connector. This was necessary since *s*-BuOLi disrupts the aggregates of DLI and PI chains, and the resulting product has a low polydispersity index. However, *s*-BuOLi reacts with Si−Cl bonds. The resulting C−O−Si group is not stable and will be transformed to the more stable C-Si bond by further reaction with the living connector.[16] This should, however, slow the linking reaction. If the ratio 4 is chosen, a low polydispersity along with a fast linking reaction can be achieved.

The progress of the step polymerization was monitored by SEC analysis of small aliquots of the polymer solution. In the first 2 weeks, the SEC chromatograms showed a significant increase in the molecular weight of the graft copolymer. After this period of time, the linking reaction was much slower. Finally, the linking reaction was considered complete after 5 weeks.

According to the Carothers equation for monodisperse low molecular weight monomers $I = 1 + p$, where p is the extent of polymerization. The polydispersity of the raw product was between 2.1 and 2.5 although according to the above relation the $I_{max} = 2$ ($p = 1$). This is due to the unreacted amount of connector and $(PS)_2SiCl_2$ and to the polydispersity of the connector. Part of the amount of the connector remaining in the raw products may be due to the formation of cyclic polymer.

The number average degree of polymerization (DP_N) is given by the following equation:

$$DP_N = [1 + r]/[1 + r - 2rp]$$

Here $r = N_A/N_B$, and N_A and N_B are the number of Si−Cl and C−Li bonds, respectively. In most cases the amounts of unreacted species were less than 5% ($p \sim 0.95$), and for a 20% excess of connector $r = 1.83$. By using these values the degree of polymerization of the raw product were calculated to be around 7. The DP of the final polymers was calculated by using the equation:

$$DP = [M_{wgraft} - M_{ncon}]/[2M_{narm} + M_{ncon}]$$

Table 3. Molecular Characteristics of the Graft Copolymers PI-*g*-PS₂

sample	M_n(PS arm)[a] $\times 10^{-4}$	M_n(PI con)[a] $\times 10^{-4}$	$I^b(M_w/M_n)$	$M_w \times 10^{-6}$ [c]
GSI 25-35	3.44	2.74	1.30	1.22
GSI 60-25	2.88	6.18	1.29	1.26
GSI 70-15	1.35[d]	7.27	1.30	1.17
GSI 90-7	0.67[d]	9.16	1.32	1.02

[a] Membrane osmometry in toluene at 37 °C. [b] Polydispersity index obtained by SEC in THF at 25 °C. [c] LALLS in THF at 25 °C. [d] Obtained by MALDI/TOF/MS measurements.

Table 4. Composition of the Graft Copolymers, PI-*g*-PS₂

sample	% PS (from M_n)	% PS (NMR)	d*n*/d*c* (mL g^{-1})	DP[a]
GSI 25-35	72	71	0.168	13
GSI 60-25	48	46	0.155	10
GSI 70-15	27	25	0.145	11
GSI 90-7	13	11.5	0.141	9

[a] Degree of polycondensation reaction. DP= (M_w (graft) − M_n(PI))/(2M_n(PS) + M_n(PI)).

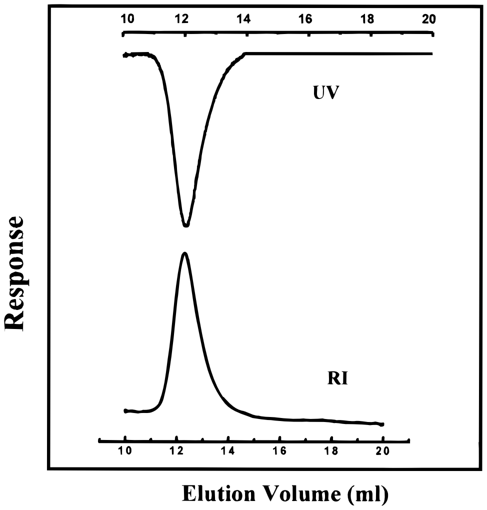


Figure 6. SEC chromatograms of fractionated GSI 60−25 (RI and UV detectors).

Here M_{wgraft}, M_{ncon}, and M_{narm} are the molecular weights of graft, connector, and arm, respectively.

The degree of polymerization calculated from the experimental results was higher than expected (Table 3). This is due, at least in part, to the fractionation of the raw products, from which only the higher molecular weight fractions were obtained. The molecular characteristics of the fractionated graft copolymers are given in Tables 3 and 4.

The synthesis reported herein relies on the inability of the sterically hindered PS anions to undergo complete reaction with silicon tetrachloride. On the other hand the less hindered PI anions are able to react with the last two chlorine atoms to form the graft copolymer. SEC chromatograms obtained by both RI and UV detectors for fractionated copolymers reveal that they exhibit high degrees of compositional homogeneity (Figure 6). This is also supported by (a) the agreement between the composition of the grafts found by ^{1}H NMR and the one calculated from the M_n of the arms and (b) the agreement between the overall d*n*/d*c* value found experimentally and the one calculated by using the equation $dn/dc(\text{graft}) = x(dn/dc)(PS) + (1 - x)(dn/dc)(PI)$ where x is the amount of PS indicated by NMR spectroscopy.

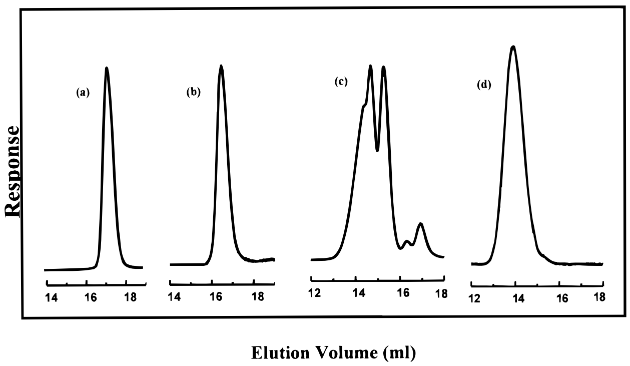


Figure 7. SEC chromatograms of PS arms (a), PS connector (b), and unfractionated (c) and fractionated (d) comb homopolymer (GS 15-35).

Table 5. Molecular Characteristics of the PS Graft Homopolymers

sample	M_n(PS arm)[a] $\times 10^{-4}$	M_n(PS con)[a] $\times 10^{-4}$	$I^b(M_w/M_n)$	$M_w \times 10^{-5\,c}$	DP[e]
GS 15-35	3.44	1.57[d]	1.19	4.28	5
GS 40-25	2.88	4.12	1.20	4.53	4
GS 60-15	1.35[d]	5.70	1.19	3.29	3

[a] Membrane osmometry in toluene at 37 °C. [b] Polydispersity index obtained by SEC in THF at 25 °C. [c] LALLS in THF at 25 °C. [d] Obtained by MALDI/TOF/MS measurements. [e] Degree of polymerization. DP= (M_w(graft) − M_n(con))/(2M_n(arm) + M_n (con)).

PS-*g*-PS2 Comb Homopolymers (Homocentipedes). In this case, where there is no concern about control of microstructure, a small amount of THF was added prior the addition of the initiator. THF is a strong base, which disrupts the aggregates and promotes the initiation of styrene with DLI. To accelerate the addition of the PS connector to the difunctional macromolecular linking agent $(PS)_2SiCl_2$, three to four units of butadiene (Bd) were added to each anion. Figure 7 shows a typical chromatogram of the raw product which is a mixture of polycondensation products with different DP. In the same figure the chromatogram of the fractionated product is given. A significant amount of connector did not react with the difunctional macromolecular linking agent, and the extent of the polymerization was much lower than in the case of the copolymers (Table 5). No comparison with the theoretical values of DP_N can be made, because the extent of polymerization p of the raw product cannot be evaluated. The presence of THF in the polymerization system results in a PBd with high vinyl content during end capping. The steric hindrance of 1,2-PBd is higher than the steric hindrance of the 1,4 moiety, and as a consequence, the linking reaction with the last two Si−Cl groups was not complete. Due to the large amounts of $(PS)_2SiCl_2$ and LiPSLi that were left unreacted the polydispersity indices were 2.5−3.0. The molecular characteristics of these polymers along with the DP_N values are given in Table 5.

Conclusions

In this paper, the synthesis of regularly spaced PI-*g*-PS_2 graft copolymers (cocentipede) and PS-*g*-PS_2 homopolymers (homocentipede) with two PS branches at each linking point is described. The step polymerization of $(PS)_2SiCl_2$ with a difunctional PI or PS resulted in a raw product with polydispersity of 2.0−3.0. After fractionation, the polydispersity of the graft copolymers was reduced to 1.2−1.3. More careful fractionation could be employed to obtain fractions of even lower heterogeneity.

The PEB-based DLI proved to be a highly difunctional initiator with high stability at room temperature. The effect of *s*-BuOLi as a polar additive in the polymerization of isoprene was investigated. It was found that when the [*s*-BuOLi]/[C−Li] ratio was as high as 14, a difunctional polymer with very low polydispersity was obtained. In the case of styrene where no microstructure requirements are imposed, the presence of THF enhanced the initiation rate of the polymerization and a low polydispersity difunctional polymer was obtained.

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