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Articles

Synthesis of Combs, Centipedes, and Barbwires: Poly(isoprene-*graft*-styrene) Regular Multigraft Copolymers with Trifunctional, Tetrafunctional, and Hexafunctional Branch Points

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ABSTRACT: The synthesis of poly(isoprene-*graft*-styrene) copolymers with multiple, regularly spaced branch points is reported. The synthetic strategy employs classical anionic polymerization techniques and utilizes a modular approach in which polystyryllithium and α,*ω*-poly(1,4-)isoprenyldilithium are sequentially incorporated into chlorosilane linking centers. Previous syntheses employing this basic strategy have yielded graft copolymers with trifunctional ("combs") and tetrafunctional ("centipedes") branch points. Here we further develop and extend this methodology to include a novel regular multigraft material with hexafunctional branch points ("barbwires"); these materials possess polystyrene side chains of uniform length attached in clusters of four at regularly spaced points along a narrow molecular weight distribution polyisoprene main chain. In the synthesis of barbwires, PSLi is added first to 1,6-bis(trichlorosilyl)hexane, in an incremental fashion, until 4 equiv has been incorporated into the linking silane; LiPILi is next added in a slight stoichiometric excess, resulting in a condensation between macromolecular dinucleophiles and dielectrophiles. Homogeneous multigraft samples of all three architectures were synthesized, with a polydispersity index of about 1.2, through fractionation of the raw condensation products.

Introduction

There have been great advances in the synthesis of well-defined graft copolymers over the past decade.[1,2] A tightly controlled polymerization mechanism, coupled with judicious choice of synthetic strategy and careful characterization methods, can yield complex macromolecules with a high level of homogeneity, with respect to not only molecular weight characteristics but also architectural structure. One strategy that can lead to a moderately well-defined graft copolymer is the "grafting from" approach;[3] the expedience of this strategy holds obvious appeal. Alternatively, "grafting onto" is attractive from the standpoint of allowing one to sample both the main and side chains for characterization.[4] Unfortunately, the previous strategies become less satisfactory in exercising control over branch point placement. A sequential "macromonomer" synthetic scheme does offer a solution to this.[5,6] However, the need for repeated efficient initiations and no termination poses a challenge. Another method that allows control over branch point placement is based on a "modular" synthetic approach.[7,8] In this strategy, the main chain is polymerized in discrete segments (or "modules"), which are subsequently linked together, along with the side chains, using suitable linking chemistry. Under the tight control that may be gained through a combination of anionic polymerization and chlorosilane linking strategies, the potential of this modular strategy toward macromolecules with a single branch point has been quite thoroughly explored.[7−12]

Extension of the controllable chlorosilane-based linking strategies employed in the synthesis of simple grafts and miktoarm stars may lead to materials of more complex architectures. To facilitate synthesis of such materials, the use of well-defined difunctional macromolecular precursors is essential. Earlier work has explored the potential of this method for synthesis of well-defined double grafts such as pi and H.[13,14] More recently, the strategy has been exploited for synthesis of regularly spaced multiple grafts (multigrafts) with trifunctional ("combs") and tetrafunctional ("centipedes") branch points.[15,16]

The work described herein extends this earlier work and targets the production of multigraft copolymers with systematic variation of branching functionality, number of branch points per molecule, and composition with respect to relative mass of the main and side chains. Figure 1 illustrates the multigraft architectures targeted in this work. A new graft copolymer architecture has been afforded through the use of a hexafunctional chlorosilane linking agent, 1,6-bis(trichlorosilyl)hexane ("hexachlorosilane" subsequently in this paper). This chlorosilane leads to a material with regularly

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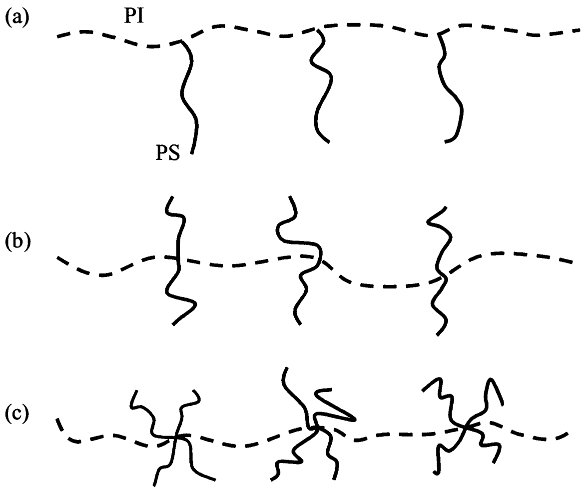


Figure 1. Regular multigraft poly(isoprene-*graft*-styrene) architectures: (a) $A(BA)_N$ "comb", (b) $A(B_2A)_N$ "centipede", (c) $A(B_4A)_N$ "barbwire".

spaced hexafunctional branch points (i.e., polystyrene grafts in clusters of four attached to each branch point). We refer to this new architecture as "barbwire".

Experimental Description

Reagents. The purification of isoprene (Aldrich), styrene (Aldrich), hexanes, and benzene to the standards required for anionic polymerization was done using established procedures.[17] Tetrahydrofuran (Fisher) was dried over CaH_2, refluxed over Na, and finally distilled under vacuum into a reservoir containing liquid K/Na (3:1 by weight); a rich teal blue color developed, indicating a high level of purity.

Trichloromethylsilane (United Chemical Technologies) and tetrachlorosilane (UCT) were dried and neutralized over CaH_2, degassed, and distilled under vacuum; a middle fraction was collected. 1,6-Bis(trichlorosilyl)hexane ("hexachlorosilane") was purified by distillation using a specially prepared all-glass short-path apparatus, allowing collection of the purified chlorosilane at 75 °C under a dynamic vacuum. Tetrachlorosilane and hexachlorosilane were diluted using purified hexanes.

sec-Butyllithium (*sec*-BuLi) was prepared in vacuo through the reduction of *sec*-BuCl with Li metal.[18] (1,3-Phenylene)bis(3-methyl-1-phenylpentylidene)dilithium initiator (DLI) was prepared from the 2-fold adduction of *sec*-BuLi to 1,3-bis(1-phenylethenyl)benzene.[18,19] *sec*-BuOLi was prepared in vacuo from the alcohol, using Li metal.

Manipulative Technique. The synthetic manipulations were conducted using classical high-vacuum techniques, using all-glass BuLi-washed and benzene-rinsed reactors, equipped with break-seals for the addition of reagents and constrictions for the removal of intermediate products.[17,18]

Detailed Synthetic Account. *Comb Synthesis.* An all-glass linking reactor was charged with ~2 mL of $MeSiCl_3$ in a small quantity of benzene. A ~5% w/v solution of PSLi, in benzene at 20 °C, was added in one continuous increment to the silane ([silane]/[CLi] = 100), with the reactor contents briskly stirring in a 0 °C bath. The solution was then allowed to warm to 20 °C.

The contents of the reactor were out-distilled until the solution was too viscous to stir, fresh benzene was in-distilled to make a ~10% w/v solution, and the contents were well mixed; this sequence was repeated until a total of three out-distillations had been accomplished. The reactor was left open to a high vacuum at 20 °C and pumped for 1 week. Benzene was in-distilled to make a ~3% w/v solution.

LiPILi was prepared as a ~3% w/v solution in benzene, initiated from DLI in the presence of *sec*-BuOLi ([COLi]/[CLi] = 7). The LiPILi solution and the $(PS)MeSiCl_2$ from the linking reactor were adjusted to a stoichiometric ratio of [CLi]/[SiCl] = 1.2, and the solutions were mixed. After 1 day, several milliliters of THF was added (~0.5% v/v of the finally resulting solution; THF/Li = 100).

Centipede Synthesis. An all-glass linking reactor was charged with 0.200 mmol of $SiCl_4$ in a small quantity of hexane and benzene. A ~3% w/v solution of PSLi was incrementally added to the silane. The first addition was made such that ~0.27 mmol of PSLi was added quickly to the chilled reactor (0 °C bath; colder than the flask of PSLi at 20 °C) with brisk stirring. After the first addition was made, the reactor was allowed to warm slowly to 20 °C (isothermic with the flask of PSLi), and further dropwise additions of PSLi were made. The progress of the linking reaction was monitored by removing small aliquots from the reactor and analyzing them with SEC. After ~2 equiv of PSLi (~0.40 mmol) had been added to the reactor, and more importantly the end point was judged by SEC, the titration was stopped.

A ~3% w/v solution of LiPILi in benzene and the $(PS)_2SiCl_2$ in the linking reactor were mixed in a stoichiometric ratio of [CLi]/[SiCl] = 1.2. After 1 day THF was added (~0.5% v/v of the finally resulting solution; THF/Li = 100).

Barbwire Synthesis. An all-glass linking reactor was charged with 0.200 mmol of hexachlorosilane in a small quantity of hexane and benzene. A ~3% w/v solution of PSLi was incrementally added to the silane. The first addition was made such that ~2 equiv (~0.40 mmol) was added to the reactor. After the first addition ~0.5 mL of THF was slowly distilled into the reactor (less than 0.5% v/v of the resultant linking solution; THF/Li = 30). Further additions were made slowly to a calculated (stoichiometry of reagents and concentration of PSLi) stopping point of ~4.3 equiv of PSLi (~0.87 mmol). The progress of the linking reaction was monitored by removing small aliquots from the reactor and analyzing them with SEC. It was noticed that, after addition of beyond ~3.7 equiv of PSLi, the color in the linking reactor steadily grew more intensely golden.

A ~3% w/v solution of LiPILi in benzene and the contents of the linking reactor were mixed in a stoichiometric ratio of [CLi]/[SiCl] = 1.2. After 1 day THF was added (~0.5% v/v of the finally resulting solution; THF/Li = 100).

Workup and Fractionation. The linking solutions were permitted to react for 3 weeks before quenching. The raw final polymers were stabilized with butylated hydroxytoluene (BHT) and precipitated into a large excess of methanol. Fractionation was performed using toluene/methanol as the solvent/nonsolvent pair.

Three cycles of fractionation were found to give optimal results. The first cycle was conducted at a polymer concentration of ~1.3% w/v, and two large down-fractions were taken. In the second fractionation cycle, the first two down-fractions were consolidated and refractionated at a concentration of ~1.0% w/v, and three down-fractions were taken. During the final fractionation cycle, the previous down-fractions were *not* consolidated; rather, a staggered sequence was used: the first (highest MW) intermediate down-fraction was refractionated, alone, into the first final down-fraction and a remaining up-fraction; to this up-fraction the second (middle MW) intermediate down-fraction was added, and these were refractionated into the second final down-fraction and another remaining up-fraction; to this up-fraction the third (lower MW) intermediate down-fraction was added, and these were refractionated in order to obtain the third final down-fraction. By following this iteration, more dilute concentrations were able to be used during the final fractionation round (~0.4−0.7% w/v).

Molecular Characterization Methods. Size exclusion chromatography with refractive index detection (SEC-RI) was performed using a Waters model 510 pump, Waters Ultrastyragel columns (with a continuous porosity range from 10^6 to 10^3 Å), and a Waters model 410 differential refractometer. SEC-RI was used routinely to monitor synthetic products and fractionation workups.

Multiple detection SEC methods, combining refractive index (SEC-RI), ultraviolet (SEC-UV), and multiangle laser light scattering (SEC-MALLS), were also used in this work. UV detection is primarily useful for distinguishing between species of differing absorbance profiles; since PI is transparent at 260 nm, the PS content of analyte is easily established through calibration of the detector response at this wavelength to the mass of injected PS. Since molecular weights established using SEC-MALLS are not retention dependent, these values are more accurate, especially for analytes that are compositionally and architecturally complex.

Multidetector SEC analyses (SEC-UV and SEC-MALLS) were performed using a Waters Alliance separations module 2690, Waters Ultrastyragel columns (HR-4, HR-5E, HT-3, HT-6E with a continuous porosity range from 10^6 to 10^3 Å), a Waters refractive index detector 2410, a Waters photodiode array detector 996, and a Wyatt Technology Dawn DSP laser photometer. THF solutions were chromatographed at 30 °C and detected at 25 °C. SEC-MALLS and SEC-UV were accomplished using dried and distilled THF.

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) measurements were taken using a Bruker 300 MHz instrument. Samples were prepared in $CDCl_3$. To obtain quantitative spectra, 5 s relaxation times were used.

Results and Discussion

Each of the regular multigrafts was derived from the same two active macromolecular precursors. Styrene was polymerized using *sec*-BuLi, while isoprene was polymerized using the difunctional initiator, DLI.

$$\textit{sec}\text{-BuLi} + \text{S} \rightarrow \text{PSLi}$$

$$\text{DLI} + \text{I} \rightarrow \text{LiPILi}$$

The result of these two polymerizations is that polystyryllithium (PSLi) is nucleophilic at one end, while α,ω-polyisoprenyldilithium (LiPILi) is nucleophilic at both ends.

The architecture of the multigraft is controlled through the choice of a chlorosilane of the appropriate functionality. In the preparation of combs, trichloromethylsilane was used:

$$\text{PSLi} + \text{excess MeSiCl}_3 \rightarrow (\text{PS})(\text{Me})\text{SiCl}_2 + \text{LiCl} + \text{MeSiCl}_3\uparrow$$

$$\text{LiPILi} + (\text{PS})(\text{Me})\text{SiCl}_2 \rightarrow \text{PI}[(\text{PS})(\text{Me})\text{SiPI}]_N + \text{LiCl}$$

This approach leads to trifunctional branch points, thus these materials are subsequently referred to as “trifunctional multigrafts”. A large excess of $MeSiCl_3$ was used in order to prevent dimerization of PSLi. After successful end-capping of the PSLi, the remaining $MeSiCl_3$ was removed on the vacuum line. The second reaction is simply a condensation of macromolecular reagents, dinucleophiles and dielectrophiles. In other words, the regular multigraft is created through a step-growth polymerization using two macromolecular reactants. The statistical nature of the final linking is such that N is not strictly controlled, but its average value can be targeted through the ratio of C−Li to Si−Cl used. C−Li is used in excess so that a polyisoprenyl unit is tethered at each end of the multigraft.

Centipedes (“tetrafunctional multigrafts”) were synthesized using tetrachlorosilane:

$$2\text{PSLi} + \text{SiCl}_4 \rightarrow (\text{PS})_2\text{SiCl}_2 + 2\text{LiCl}$$

$$\text{LiPILi} + (\text{PS})_2\text{SiCl}_2 \rightarrow \text{PI}[(\text{PS})_2\text{SiPI}]_N + \text{LiCl}$$

Although it is possible to add 1 equiv of PSLi to excess $SiCl_4$ and titrate the second equivalent after removing the leftover silane, in this work the strategy was to use a stoichiometric quantity of silane and titrate both arms at once.

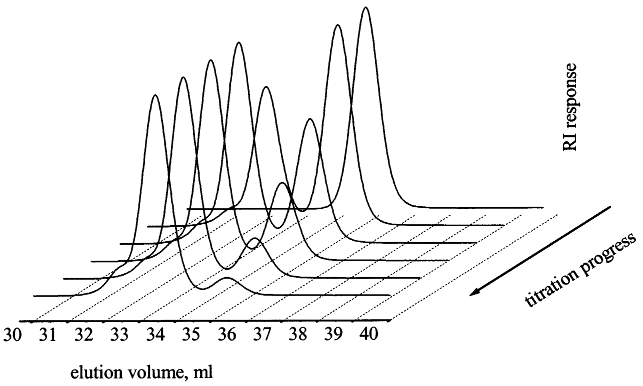


Figure 2. SEC traces following the titration of tetrafunctional multigraft 3.

Barbwire molecules (“hexafunctional multigrafts”) were synthesized using a hexachlorosilane according to the following reactions:

$$4\text{PSLi} + \text{Cl}_3\text{Si}(\text{CH}_2)_6\text{SiCl}_3 \rightarrow \text{Cl}(\text{PS})_2\text{Si}(\text{CH}_2)_6\text{Si}(\text{PS})_2\text{Cl} + 4\text{LiCl}$$

$$\text{LiPILi} + \text{Cl}(\text{PS})_2\text{Si}(\text{CH}_2)_6\text{Si}(\text{PS})_2\text{Cl} \rightarrow \text{PI}[(\text{PS})_2\text{Si}(\text{CH}_2)_6\text{Si}(\text{PS})_2\text{PI}]_N + \text{LiCl}$$

This synthesis also makes use of titration techniques. The prerequisite for success is that PSLi must be able to substitute for chloride anions cleanly 4-fold (i.e., twice upon each Si atom).

In this report, a sample identification format “MG*X Y*” has been adopted in which *X* indicates the grafting architecture (i.e., the branch point functionality) of the multigraft product and *Y* denotes the synthetic experiment. For example, using this nomenclature, the product of the second trifunctional multigraft (comb) synthesis is tagged MG3 2.

To monitor the progress of the synthesis, SEC-RI was employed throughout the experimental protocol. Aliquots of PSLi and LiPILi were quenched with methanol and analyzed in order to verify MW and concentration of CLi chain ends before linking reactions were conducted.

The end-capping of PSLi with $MeSiCl_3$, in the synthesis of the combs, does not intrinsically forbid the dimerization of PS anions. Comparison of the PS solution before and after end-capping with the silane by using SEC indicates that a successful result was achieved: the SEC traces are indistinguishable. The end-capping was resultant in 99+% $(PS)(Me)SiCl_2$ unimer for each of the five comb syntheses.

In the synthesis of the centipedes, PSLi was titrated into $SiCl_4$, as followed in Figure 2. In this figure a series of SEC eluograms taken throughout the titration procedure are “stacked” toward the viewer in a sequential manner. All of the traces have been normalized with respect to maximum peak height for visual comparison. The SEC eluogram of the precursor PSLi is shown in the trace furthest away from the viewer. The eluogram of the first aliquot, the trace immediately nearer the viewer from the back, indicates that the composition in the reactor was approximately 40% $(PS)_2SiCl_2$ and 60% $PSSiCl_3$ by mass. At the point of the second aliquot, the

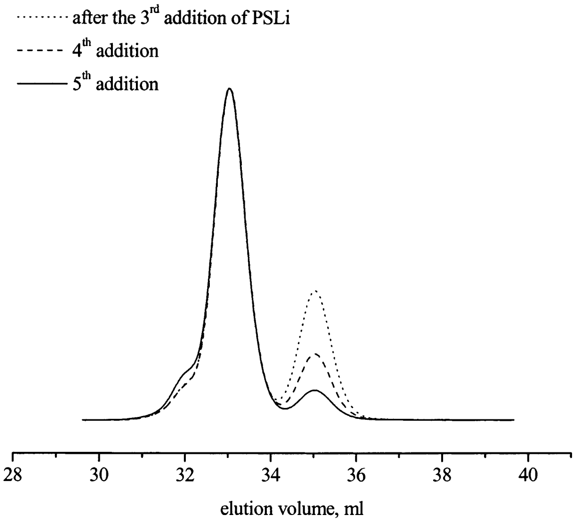


Figure 3. SEC overlays monitoring the titration of tetrafunctional multigraft 3.

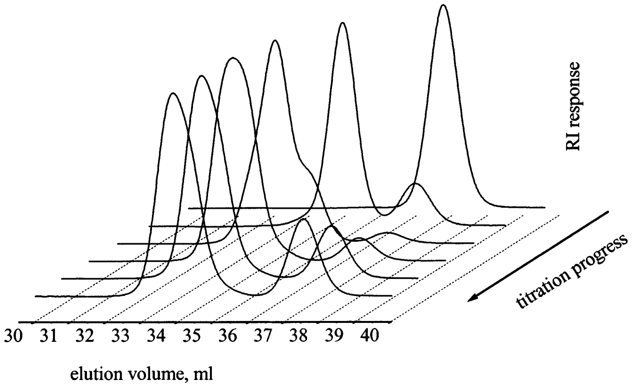


Figure 4. SEC traces following the titration of hexafunctional multigraft 2.

amount of dimer had increased to approximately 60%. Small additions of PSLi resulted in a continuing decrease of unimer content. Equally important to notice is that toward the end of the procedure a small shoulder of higher molecular weight $(PS)_3SiCl$ trimer becomes apparent. This may be seen more clearly in Figure 3, which is a direct overlay of the last three traces in Figure 2. Because of the formation of a small quantity of trimer, the titration was stopped at the point of the last aliquot shown. The titration resulted in 90−95% $(PS)_2SiCl_2$ dimer for each of the three centipede syntheses. Formation of a small quantity of trimer and residual unimer was consistently observed.

In the synthesis of the barbwires, PSLi was titrated into the hexachlorosilane linking agent. Figure 4 shows a series of six eluograms that follow this procedure. The back-most trace corresponds to the PSLi titrant. The next five traces correspond to five aliquots taken throughout the course of the procedure, stoichiometrically calculated as follows: first aliquot, ∼2.0 equiv of PSLi added to the silane; second aliquot, ∼3.0 equiv; third aliquot, ∼3.7 equiv; fourth aliquot, ∼4.0 equiv; fifth aliquot, ∼4.3 equiv. The progress of linking at the end point is more clearly seen in Figure 5, which is a direct overlay of the eluograms corresponding to the aliquots taken at ∼3.0, ∼3.7, and ∼4.3 equiv of added PSLi. It appears that as the $(PS)_4Si_2C_6H_{12}Cl_2$ tetramer is finally formed, further adduction of PSLi becomes sterically prohibited, and excess active unimer begins to accumulate in the reactor. The titration progressed in this manner for both of the barbwire syntheses.

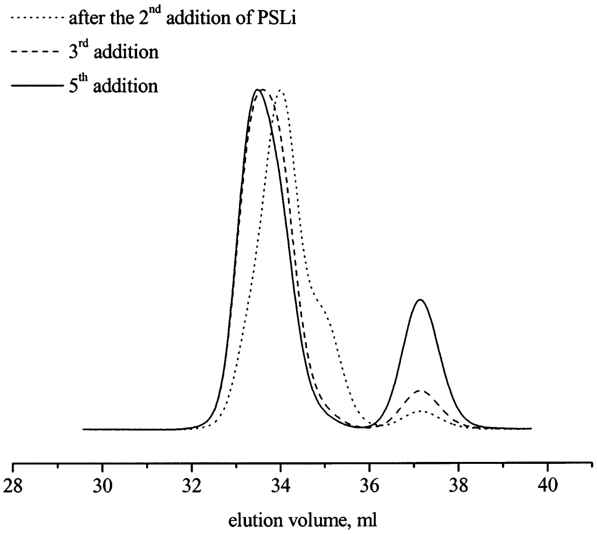


Figure 5. SEC overlays following the titration of hexafunctional multigraft 2.

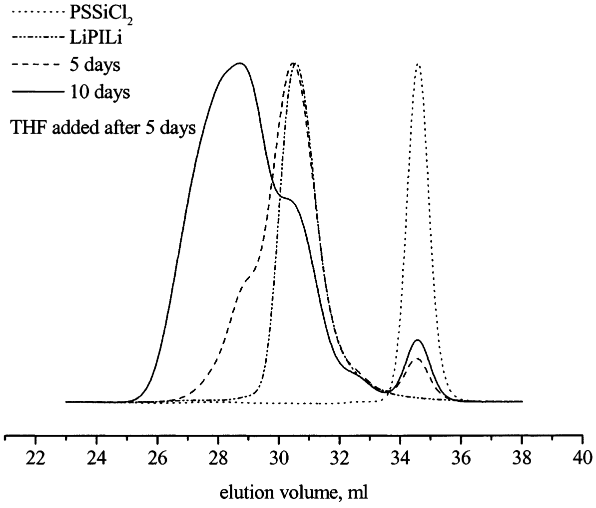


Figure 6. SEC overlays following the linking progress of trifunctional multigraft 2.

Final linking progress was also monitored using SEC. Figure 6 is an SEC overlay composition illustrating the linking progress in the synthesis of one of the combs. The traces have been normalized with respect to maximum peak height. It is apparent that, even though there is alkoxide present in the system, the initial linking progress was extremely retarded. However, with the addition of THF the final product was formed within 1 week. Figures 7 and 8 illustrate the linking of a centipede and a barbwire with respect to their precursors. Several of the multigrafts were also monitored for much longer periods of linking time (up to 1 month). Surprisingly, in no case was it observed that any further shift toward higher MW material had taken place beyond that which had already occurred within the first week in the presence of THF.

All syntheses were conducted on a ∼20 g scale. Afterward, a "staggered" refractionation strategy (as detailed in the Experimental Section) was chosen; the desire was both to obtain a good separation of the product into *different* (MW) narrow fractional cuts and also to distribute the final polymer more *equally* (yield)

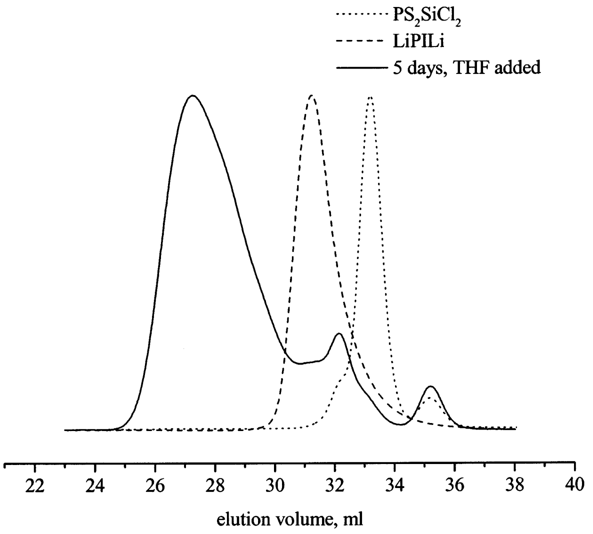


Figure 7. SEC overlays following the linking progress of tetrafunctional multigraft 3.

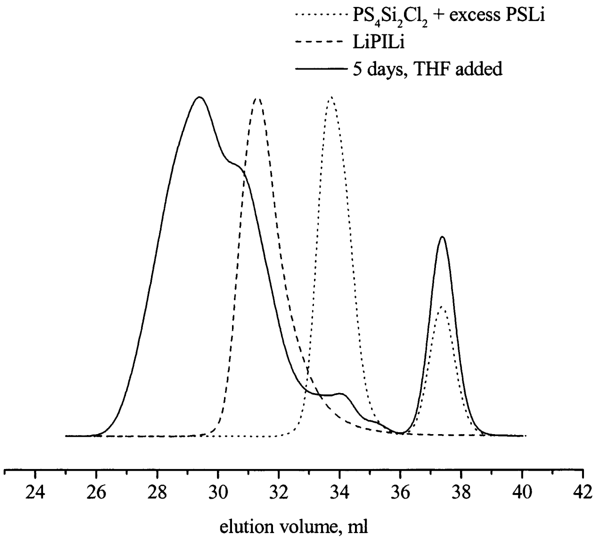


Figure 8. SEC overlays following the linking progress of hexafunctional multigraft 2.

into the three final fractions taken of each raw polymer sample.

SEC-RI was employed to monitor the products of the fractionation procedure. Figure 9 illustrates the final fractionation result for one of the combs in an overlay. The traces have been normalized with respect to maximum peak height. Table 2 displays a summary of the fractionation results of the complete multigraft series along with the fractionated yields obtained. The synthetic experiments have been arranged primarily with respect to architecture and secondarily in order of increasing PS content of the target material.

Reflection upon these data reveals several similarities and one interesting dissimilarity. Polydispersity indices of the unfractionated multigraft materials were consistently ~1.5. In the case of the MG4 and MG6 syntheses it must be pointed out that this value reflects an integration of the main peak (the linked product) while neglecting unlinked material (which was well resolved from the main peak); an integration of *all* material (i.e., including excess unincorporated PSLi titrant) results in a PDI of ~2.5 for the MG4s and a PDI of 4+ for the MG6s. Polydispersities of the finally fractionated materials were in all cases ≤1.25 and in most cases <1.2.

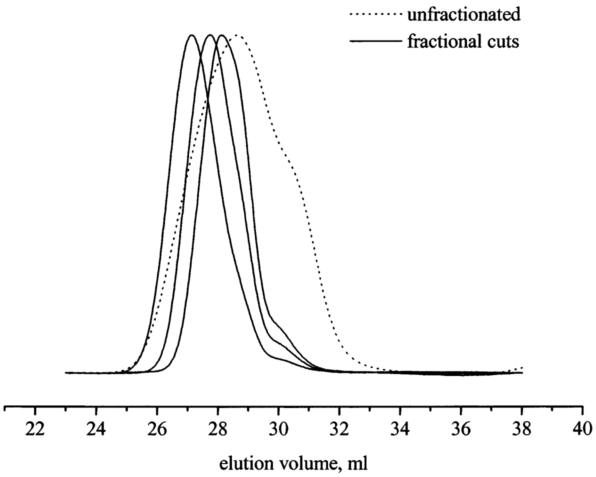


Figure 9. SEC chromatograms showing raw trifunctional multigraft 1 and fractions.

Table 1. Trifunctional Multigraft Series, LiPILi Spacer Characteristics

sample	LiPILi spacer, characteristics	
	M_w, kg/mol[a]	I, M_w/M_n[b]
MG3 1	105.0	1.07
MG3 2	86.0	1.09
MG3 3	48.0	1.15
MG3 4	34.2	1.29
MG3 5	23.6	1.42

[a] SEC-MALLS. [b] SEC-RI.

The yields were, however, noticeably different even though each of the syntheses was conducted on the same scale. In six of the syntheses, MG3 1, MG3 2, the three MG4 syntheses, and MG6 1, the cumulative fractionated yields were >50%. In the cases of MG3 3, MG3 4, and MG6 2 the yields were ~30%. MG3 5 led to a fractionated recovery of only ~15%.

Molecular weight distributions of all PSLi precursors were very narrow (PDI ≤ 1.04). In contrast, the LiPILi precursors exhibit broader, although still narrow, polydispersities. MWD data for the five LiPILi used in the synthesis of the MG3 series are collected in Table 1.

All of the multigraft samples and their precursors were rigorously characterized with regard to molecular weights using SEC experiments with on-line light-scattering detection. The multigraft samples were characterized for composition using ^{1}H NMR and SEC with ultraviolet detection.

Detailed molecular characteristics are tabulated specifically for one comb, one centipede, and one barbwire in Tables 3, 4, and 5, respectively. Since the MW of the repeating graft unit, or "constituting block copolymer" following the terminology of Lee and Gido,[20] of a multigraft cannot be actually measured, this is calculated from the measured values of the PS and PI precursors. The constituting block copolymer of a comb is an A_2B miktoarm star; the constituting block copolymer of a centipede, A_2B_2; and the constituting block copolymer of a barbwire, A_2B_4. It should be understood that the "cutting" of the graft copolymer into its repeating unit is a mental dissection, and as such, it is more logical to cut the PI main chain at the *midpoint* between the grafts in order to arrive at a repeating symmetric simple graft structure. Thus, in the MW calculation of the repeat unit, each PI arm of the miktoarm star is *one-half* of the LiPILi spacer. With this value, the

Table 2. Multigraft Complete Series, Fractionation Summary

	unfractionated		fractionated multigraft		
sample[a]	V_e, mL	I, M_w/M_n[b]	V_e	I	yield, g
MG3 1	28.60	1.51	27.10	1.18	6.46
			27.70	1.17	4.63
			28.08	1.15	2.46
MG3 2	28.82	1.86	27.46	1.25	5.27
			28.09	1.24	4.06
			28.24	1.21	1.93
MG3 3	28.93	1.77	27.83	1.22	2.93
			28.20	1.23	2.05
			28.50	1.23	1.25
MG3 4	29.30	1.54	28.29	1.16	2.03
			28.65	1.13	1.72
			29.14	1.13	2.07
MG3 5	<29.8	1.40	28.67	1.12	2.81
			29.13	1.08	0.31
MG4 1	27.78	1.5	26.97	1.15	4.88
			27.57	1.15	4.60
			28.02	1.15	2.81
MG4 2	27.15	1.5	26.62	1.17	6.14
			27.14	1.19	6.16
			27.61	1.19	2.53
MG4 3	27.24	1.5	26.82	1.18	4.13
			27.26	1.17	4.17
			27.62	1.17	2.49
MG6 1	27.73	1.5	26.99	1.15	3.84
			27.51	1.16	4.55
			27.98	1.17	2.80
MG6 2	29.34	1.5	28.29	1.19	1.44
			28.72	1.22	2.27
			29.07	1.22	1.76

[a] Each synthesis represents a material that was ultimately fractionated into three multigraft products. MG3 denotes a trifunctional multigraft; MG4, tetrafunctional; and MG6, hexafunctional. [b] I values were determined for the MG3 unfractionated samples by integrating all peaks. For MG4 and MG6 only the main peak was integrated, without considering residual excess PS titrant.

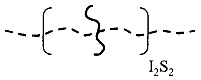
Table 3. Trifunctional Multigraft 1, Molecular Characteristics

PS Graft	SEC-MALLS	M_w, kg/mol	9.5		
	SEC-RI	I, M_w/M_n	1.03		
PI Spacer	SEC-MALLS	M_w	105.0		
	SEC-RI	I	1.07		
Repeat Unit	 I_2S		[a]Calculated M_w 115 kg/mol		
Multigraft Product		fractional cut	1	2	3
	^{1}H NMR	mass% PS	6.1	6.1	5.9
	SEC-UV	mass% PS	7.4	7.2	7.1
	SEC-MALLS	M_w	601	406	316
	SEC-RI	I	1.18	1.17	1.15
	[b]Calculated Number of Branch Points		4.3	2.6	1.8

[a] M_w\|miktoarm star\| = M_w\|PS graft\| + M_w\|PI spacer\|. [b] # = (M_w\|multigraft\| − M_w\|PI spacer\|)/M_w\|repeating miktoarm star\|.

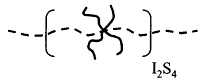
number of branch points per molecule is then calculated. Since excess LiPILi spacer was used in all syntheses, the MW of one PI spacer is first subtracted from the MW of graft before the quantity is divided by the MW of the repeat unit.

Table 4. Tetrafunctional Multigraft 1, Molecular Characteristics

PS Graft	SEC-MALLS	M_w, kg/mol	11.1		
	SEC-RI	I, M_w/M_n	1.02		
PI Spacer	SEC-MALLS	M_w	97.2		
	SEC-RI	I	1.09		
Repeat Unit	 I_2S_2		[a]Calculated M_w 119 kg/mol		
Multigraft Product		fractional cut	1	2	3
	^{1}H NMR	mass% PS	15.2	15.1	15.1
	SEC-UV	mass% PS	16.5	16.6	16.1
	SEC-MALLS	M_w	691	475	372
	SEC-RI	I	1.15	1.15	1.15
	[b]Calculated Number of Branch Points		5.5	3.5	2.5

[a] M_w\|miktoarm star\| = M_w\|PS graft\| + M_w\|PI spacer\|. [b] # = (M_w\|multigraft\| − M_w\|PI spacer\|)/M_w\|repeating miktoarm star\|.

Table 5. Hexafunctional Multigraft 1, Molecular Characteristics

PS Graft	SEC-MALLS	M_w, kg/mol	8.2		
	SEC-RI	I, M_w/M_n	1.04		
PI Spacer	SEC-MALLS	M_w	86.8		
	SEC-RI	I	1.13		
Repeat Unit	 I_2S_4		[a]Calculated M_w 120 kg/mol		
Multigraft Product		fractional cut	1	2	3
	^{1}H NMR	mass% PS	23.5	23.2	23.1
	SEC-UV	mass% PS	24.7	24.5	24.3
	SEC-MALLS	M_w	705	515	411
	SEC-RI	I	1.15	1.16	1.17
	[b]Calculated Number of Branch Points		5.2	3.6	2.7

[a] M_w\|miktoarm star\| = M_w\|PS graft\| + M_w\|PI spacer\|. [b] # = (M_w\|multigraft\| − M_w\|PI spacer\|)/M_w\|repeating miktoarm star\|.

Table 6 displays a summary of molecular weight characteristics for the entire multigraft series. Inspection of the molecular characteristics in this table reveals several interesting trends. Within the MG3 series, the number of branch points is quite similar. However, there is a subtle steady decrease in molecular weight of products from MG3 1 through MG3 5. Data obtained for the two MG6s reveal a more stark contrast: compared to MG6 1, the MG6 2 products are markedly lower both in molecular weight and in number of branch points. The MG4s are higher in molecular weight and number of branch points than either the MG3s or the MG6s. Additionally, the variance of molecular weight and number of branch points within the MG4 series is opposite that found within the MG3 series and the MG6 pair.

To obtain polyisoprene with the desired 1,4 microstructure through anionic polymerization, it is necessary to employ a lithium counterion in hydrocarbon media.[21] This limits the selection of difunctional initiators, and DLI remains one of the best choices available. It should be recalled that the polydispersities of LiPILi were

Table 6. Multigraft Complete Series, Molecular Weight Characteristics Summary

sample[a]	PS graft M_w[c]	PI spacer M_w[c]	unit[b] M_w[e]	multigraft M_w[c]	multigraft % PS[d]	multigraft #[f]
MG3 1	9.5	105.0	115	601	6.1	4.3
				406	6.1	2.6
				316	5.9	1.8
MG3 2	31.6	86.0	118	515	18.4	3.7
				391	19.0	2.6
				315	19.0	2.0
MG3 3	60.3	48.0	108	464	44.6	3.8
				400	47.5	3.3
				360	48.5	2.9
MG3 4	77.3	34.2	112	421	65.4	3.5
				338	67.2	2.7
				268	67.8	2.1
MG3 5	79.5	23.6	103	382	82.2	3.5
				291	82.4	2.6
MG4 1	11.1	97.2	119	691	15.2	5.5
				475	15.1	3.5
				372	15.1	2.5
MG4 2	16.8	87.6	121	891	24.9	6.6
				624	24.7	4.4
				472	24.5	3.2
MG4 3	26.6	63.6	117	930	43.5	7.4
				681	43.7	5.3
				572	43.9	4.4
MG6 1	8.2	86.8	120	705	23.5	5.2
				515	23.2	3.6
				411	23.1	2.7
MG6 2	13.0	63.3	115	409	38.3	3.0
				328	37.9	2.3
				287	38.2	1.9

[a] Each sample represents a material that was ultimately fractionated into three multigraft products. MG3 denotes a trifunctional multigraft; MG4, tetrafunctional; and MG6, hexafunctional. [b] The constituting block copolymer (repeat unit) of a MG3 is an I_2S miktoarm star; MG4, I_2S_2; and MG6, I_2S_4. [c] SEC-MALLS. [d] ^{1}H NMR. [e] Calculated from graft and spacer M_w values. [f] Number of branch points calculated from multigraft, unit, and spacer M_w values.

larger than those of PSLi. With *sec*-BuLi the initiation step is much faster than the subsequent propagation reaction. Thus, all of the molecules thus grow to nearly the same size. Unfortunately, in the case of DLI, the initiation event is presented with a higher energetic barrier than the following propagation since the carbanionic sites of DLI are themselves more stabilized than ensuing PILi chain ends.

A further difficulty with DLI is that the resultant anion remaining at the initiator, after the first of two initiations has taken place, is even more stable than it was before the primary initiation reaction, since the mesomeric resources of the center phenyl ring of DLI are no longer shared by two anions. That is, in kinetic terms, *the two initiation rate constants of DLI toward a dienic monomer are irreconcilably chemically inequivalent*.

Additives, such as the *sec*-BuOLi employed in this work, do have a great effect upon aggregation equilibria and rates of both propagation and initiation and thus the polydispersity of the LiPILi product.[16] Yet at low molecular weight it becomes increasingly difficult to mask the chemical disparities. The data in Table 1 show the effect of the targeted MW upon polydispersity of the LiPILi product, showing that polydispersities become smaller as MW increases. Thus, the DLI initiator is not *ideal* with respect to synthesis of model multigraft materials but nevertheless has been employed for lack of a better difunctional initiator.

What is already somewhat clear from the characterization data alone becomes visually obvious in Figure 10. This figure presents SEC eluograms for unfractionated and fractionated products of the MG3 syntheses. The MG3 samples are arranged in order, from left to right, of increasing mass percent PS content of the multigraft material. The bold traces represent the unfractionated multigraft samples; these are normalized to each other with respect to total area. The fine traces represent the final fractional cuts taken of each synthesis. These are overlaid, each upon its parent unfractionated multigraft, and are normalized with respect to height of the parent trace. In the MG3s which are rich in PI, the linking proceeded much more completely toward high molecular weight multigraft material. In the MG3s which are rich in PS, there remained a great amount of unlinked and slightly linked material.

In the earlier work of Iatrou et al.,[16] two types of centipedes (MG4s) were synthesized. One type of centipede was composed of a PI main chain with PS side chains, such as the ones synthesized in this report. The other type was homopolymers composed entirely of PS (with a few units of butadiene added to the LiPSLi before the final condensation reaction). The PI-*graft*-PS copolymers were characterized by a high degree of condensation, yielding high MW product, as was found here. The homopolymers, despite the butadiene end-capping, did not undergo efficient linking, exhibiting behavior such as was found here in the synthesis of MG3 4 and MG3 5 (the combs rich in PS content).

Steric barriers will have a great effect on these linking reactions. An active PILi chain end-tethered at the opposite end by PS grafts could be greatly encumbered by both the mass of those grafts and especially their proximity to the PILi chain end. In the scenario of long PS branches and short PI spacers, the bulkiness of the grafts tends to hinder reactivity. Thus, PILi chain ends can remain chemically active but be physically hindered from reacting.

Table 7 shows the results on compositional characterization of the multigraft products. There is agreement between experimental ^{1}H NMR values and SEC-UV values within 1.5 mass % PS. The calculated value is obtained through use of the previously calculated number of branch points and the MWs of the PS and PI precursors. In the calculation of the number of branch points, two assumptions were made: (1) the condensation of the macromolecular precursors proceeds in a statistical manner that does not discriminate among LiPILi anions with respect to molecular size; (2) only linearly assembled final grafted architectures result. Thus, comparison of the calculated and measured compositional values can offer insight as to whether the assumptions made in the earlier calculations are valid. In the cases of MG3 4 and MG3 5, the experimental values are significantly higher ($>$5 mass% PS) than the calculated values. This may be explained by intramolecular cyclization. If cyclization occurs after several initial intermolecular condensations, then the expected mass % PS would be greater (since there would be N, instead of $N + 1$, spacers per molecule) (see Figure 11a).

Interestingly, persistence of low MW shoulders in the eluograms depicting final linking progress (Figures 6−8) suggests the formation of PI loops (perhaps "Q" architectures). These low MW shoulders were removed through fractionation. Likely, cyclic products must be present at some level in all the raw products.

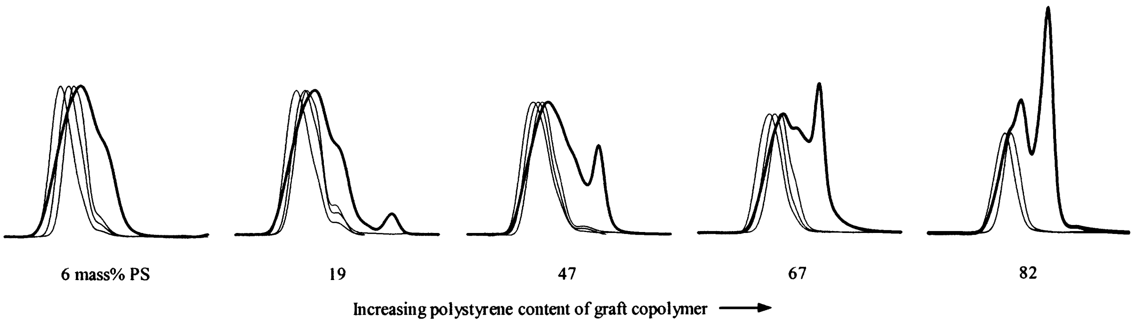


Figure 10. SEC template composition: trifunctional multigraft series, final product of synthesis before and after fractionation. The bold traces represent the finally linked unfractionated product of each of the MG3 syntheses. The fine traces represent the fractional cuts taken of each raw polymer product.

Table 7. Multigraft Complete Series, Compositional Characterization

multigraft sample[a]		measured, mass % PS		
		^{1}H NMR	SEC-UV	calculated[b]
MG3 1	f 1	6.1	7.4	6.8
	f 2	6.1	7.2	6.2
	f 3	5.9	7.1	5.5
MG3 2	f 1	18.4	19.8	22.4
	f 2	19.0	19.9	21.0
	f 3	19.0	20.2	19.5
MG3 3	f 1	44.6	45.0	49.9
	f 2	47.5	47.9	49.0
	f 3	48.5	49.8	48.3
MG3 4	f 1	65.4	65.0	63.7
	f 2	67.2	66.9	62.3
	f 3	67.8	67.1	60.5
MG3 5	f 1	82.2	81.5	72.4
	f 2	82.4	81.7	70.9
	f 3			
MG4 1	f 1	15.2	16.5	17.6
	f 2	15.1	16.6	16.3
	f 3	15.1	16.1	15.1
MG4 2	f 1	24.9	26.6	25.0
	f 2	24.7	25.7	23.8
	f 3	24.5	25.6	22.6
MG4 3	f 1	43.5	44.5	42.4
	f 2	43.7	44.7	41.3
	f 3	43.9	44.5	40.5
MG6 1	f 1	23.5	24.7	24.0
	f 2	23.2	24.5	22.8
	f 3	23.1	24.3	21.6
MG6 2	f 1	38.3	39.0	38.1
	f 2	37.9	38.9	36.4
	f 3	38.2	39.1	35.2

[a] Specific multigraft samples are here identified by both synthesis and fractionation. [b] Calculated compositional values are obtained through the use of both measured M_w values of PS graft and PI connector and earlier calculated number of branch points per molecule (see text for full explanation).

During the synthesis of the MG4s, the impurities observed at the conclusion of the titration procedure were indicative of small amounts of both $(PS)_3SiCl$ and $PSSiCl_3$. These species would lead to branching irregularities such as those depicted in Figure 11b. It is likely that the MG4 products are contaminated with some quantity of species containing one or both of the possible defects. Moreover, the type (c) defect would go quite a way toward explaining why the MWs of the MG4s are consistently higher than both the MG3s and the MG6s.

Conclusions

A systematic investigation into the synthesis of poly(isoprene-*graft*-styrene)s having multiple regularly spaced branch points was conducted. The strategy involved the synthesis of polystyrene and polyisoprene segments having reactive anions at one or both chain ends, respectively. The segments were then controllably linked at their reactive sites using chlorosilane chemistry. Materials having trifunctional, tetrafunctional, and hexafunctional branch points were synthesized by varying the choice of chlorosilane. The linking reaction is a step-growth polymerization employing two macromonomers; thus, polydisperse products were obtained. Well-defined multigrafts having well-defined complex architectures were obtained by fractionation. These products were rigorously characterized in terms of composition, molecular weight, and extent of branching. The effects of functionality, molecular weight, and composition on the linking reaction were investigated, and potential side reactions and byproducts of the syntheses were identified.

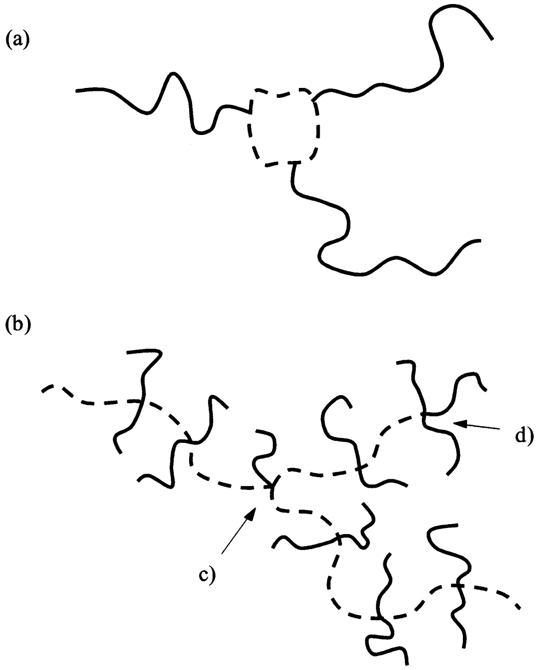


Figure 11. Irregular multigraft architectures: (a) cyclic comb structure; (b) centipede with branching defects, for example (c) I_3S branch point and (d) IS_3 branch point.

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References and Notes

(1) Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Adv. Polym. Sci.* **1998**, *135*, 1.
(2) Mays, J. W. Recent Developments in Anionic Synthesis of Model Graft Copolymers. In *Ionic Polymerization and Related Processes*; Puskas, J. E., Ed.; Kluwer: Dordrecht, The Netherlands, 1999; pp 268−81.
(3) Edgecombe, B. D.; Stein, J. A.; Frechet, J. M. J.; Xu, Z.; Kramer, E. J. *Macromolecules* **1998**, *31*, 1292.
(4) Xenidou, M.; Hadjichristidis, N. *Macromolecules* **1998**, *31*, 5690.
(5) Fujimoto, T.; Zhang, H.; Kazama, T.; Isono, Y.; Hasegawa, H.; Hashimoto, T. *Polymer* **1992**, *33*, 2208.
(6) Reutenauer, S.; Hurtrez, G.; Dumas, P. *Macromolecules* **2001**, *34*, 755.
(7) Mays, J. W. *Polym. Bull. (Berlin)* **1990**, *23*, 247.
(8) Lee, C.; Gido, S. P.; Pitsikalis, M.; Mays, J. W.; Beck Tan, N.; Trevino, S.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 3732.
(9) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 4649.
(10) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 2479.
(11) Allgaier, J.; Young, R. N.; Efstratiadis, V.; Hadjichristidis, N. *Macromolecules* **1996**, *29*, 1794.
(12) Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857.
(13) Pochan, D.; Gido, S. P.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1996**, *29*, 7022.
(14) Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N. *Macromolecules* **1994**, *27*, 6232.
(15) Hong, K.; Uhrig, D.; Iatrou, H.; Poulos, Y.; Hadjichristidis, N.; Mays, J. W. *Polym. Prepr.* **1999**, *40* (2), 104.
(16) Iatrou, H.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1998**, *31*, 6697.
(17) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.
(18) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211.
(19) Ignatz-Hoover, F. Ph.D. Thesis, University of Akron, 1989.
(20) Lee, C.; Gido, S. P.; Poulos, Y.; Hadjichristidis, N.; Beck Tan, N.; Trevino, S. F.; Mays, J. W. *J. Chem. Phys.* **1997**, *107*, 6460.
(21) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996.

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