Synthesis of Arborescent Polystyrene-*graft*-polyisoprene Copolymers Using Acetylated Substrates

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Received July 29, 2003; Revised Manuscript Received November 12, 2003

ABSTRACT: A new method is presented for the preparation of arborescent copolymers containing polyisoprene (PIP) segments. The technique uses acetyl coupling sites randomly distributed on polystyrene substrates. Isoprene was polymerized with *sec*-butyllithium in tetrahydrofuran to yield polyisoprenyllithium, and the living polymer was titrated with an acetylated substrate to generate a copolymer. The grafting yield was maximized at 25 °C using 5 equiv of LiCl to attenuate the reactivity of polyisoprenyllithium. Arborescent copolymers were synthesized by grafting PIP side chains with a weight-average molecular weight M_w of either 5000 (PIP5) or 30 000 (PIP30) onto linear, comb-branched (G0), G1, and G2 acetylated polystyrenes. The copolymers with short (PIP5) side chains contain 84−91% w/w polyisoprene. For long (PIP30) side chains, the polyisoprene content varies from 92 to over 97% w/w. The graft copolymers exhibit a geometric increase in branching functionality and molecular weight for successive generations ($f_w = 11-4000$, $M_w = 6.5 \times 10^4-2.5 \times 10^7$ for the PIP5 series, and $f_w = 11-1530$, $M_w = 3.2 \times 10^5-4.9 \times 10^7$ for the PIP30 series). A narrow molecular weight distribution ($M_w/M_n = 1.06-1.09$) was maintained after grafting. Film formation by the arborescent copolymers was investigated using tapping mode atomic force microscopy after spin-casting from different solvents. When heptane, a solvent selective for the polyisoprene segments, was used, phase separation between the polystyrene core and the polyisoprene shell was clearly visible in phase contrast imaging, even for copolymers with longer PIP side chains. In nonselective solvents (toluene and chloroform) phase contrast was reduced, presumably due to enhanced mixing of the polystyrene and polyisoprene phases.

Introduction

The synthesis of arborescent polymers typically relies on a "graft-upon-graft" strategy,[1] whereby grafting sites are randomly introduced along a linear polymer chain and coupled with a "living" polymer to generate a comb-branched (G0) structure. Repeated functionalization and grafting reaction cycles lead to higher generation arborescent polymers G1, G2, etc. An important feature of the "graft-upon-graft" method is that the branching density and branch molecular weight can be varied independently for each generation, allowing the synthesis of tailor-designed polymers. It was shown recently that acetyl functionalities are efficient coupling sites for the preparation of arborescent styrene homopolymers[2] and arborescent polystyrene-*graft*-poly(2-vinylpyridine) copolymers.[3]

Arborescent polystyrenes provide an excellent opportunity for the investigation of structure−property relations in dendritic graft polymers. The influence of structural variations, in terms of branching functionality and side chain molecular weight, on the physical properties of arborescent polymers was clearly demonstrated in a series of investigations on arborescent polystyrenes.[4−9] The compact structure of arborescent polymers leads to hard-sphere-like behavior in solution, characterized by features such as insensitivity of the intrinsic viscosity to molecular weight.[5] An increase in branching functionality (generation) or a decrease in side chain molecular weight leads to increasingly hard-sphere-like behavior.[4] Fluorescence quenching measurements have shown that the segmental density in arborescent polystyrenes is significantly higher than for linear polystyrenes.[6] Small-angle neutron scattering experiments further indicated that the segmental density increases for higher generation polymers.[8,9] Atomic force microscopy visualization of monolayer films confirmed the compact structure and uniform size of arborescent polystyrenes:[7] The most regular packing was achieved for the more rigid (higher generation, short side chain) polymers.

The examples cited above illustrate many of the distinctive properties of arborescent polystyrenes. From a practical viewpoint, however, it is desirable to extend the arborescent polymer synthesis to the preparation of copolymers, to provide materials with a wider range of physical and chemical properties for different applications. These copolymers could be synthesized by grafting macroanions with a different composition onto polystyrene substrates containing randomly distributed acetyl coupling sites. Variations in structural parameters for the side chains or the substrates may lead to copolymers with different morphologies. For example, by grafting side chains with a low molecular weight, the structure expected is best described as a branched block copolymer with spherical symmetry (Figure 1a). For large side chains, the structure should be closer to a highly branched starlike molecule, since the dimensions of the core are small relative to the outer branches (Figure 1b).

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10.1021/ma035099j CCC: $27.50
Published on Web 01/08/2004

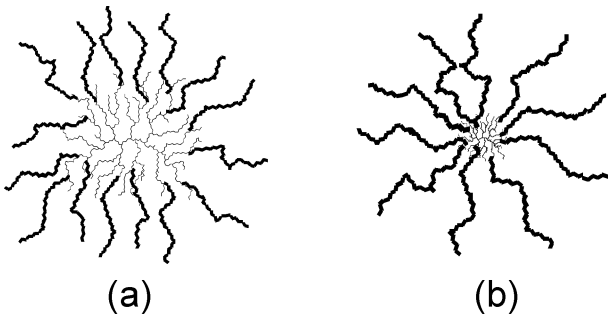


Figure 1. Comparison of structures obtained when a G1 acetylated polystyrene substrate is grafted with (a) short and (b) long polyisoprene side chains.

The successful synthesis of arborescent polystyrenes by coupling isoprene-capped polystyryl anions with acetylated polystyrene substrates[2] provides a basis for the synthesis of arborescent polystyrene-*graft*-polyisoprene copolymers. In this paper, the synthesis of arborescent isoprene copolymers by a "grafting onto" scheme is demonstrated by grafting polyisoprene segments of different molecular weights onto linear, comb-branched (G0), G1, and G2 acetylated polystyrene substrates. Atomic force microscopy measurements on monomolecular films of these materials clearly show phase separation between the core and shell portions of the molecules. The combination of a narrow molecular weight distribution, highly branched structure, and heterogeneous morphology characterizing the arborescent polystyrene-*graft*-polyisoprene copolymers should lead to interesting properties and applications for these materials.

Experimental Section

Solvent and Reagent Purification. Tetrahydrofuran (THF; Caledon, reagent grade) was purified by refluxing and distillation from sodium benzophenone ketyl under dry nitrogen. The dry solvent was introduced directly from the still into the polymerization reactor or ampule preparation manifolds through poly(tetrafluoroethylene) (PTFE) tubing. Styrene (Aldrich, 99%), 2-vinylpyridine (2VP, Aldrich, 99%), and *N*,*N*,*N*′*N*′-tetramethylethylenediamine (TMEDA; Aldrich, 99%) were purified by distillation at reduced pressure after stirring over CaH_2 overnight. Isoprene (Aldrich, 99%) was first purified by stirring with CaH_2 and distillation under nitrogen. A second purification step before polymerization, using *sec*-butyllithium, is described subsequently. The purified reagents were stored under nitrogen at −20 °C until needed. *sec*-Butyllithium (Aldrich, 1.3 M in cyclohexane) was used as received. The exact concentration of the solution was determined using the procedure of Lipton et al.[10] Lithium chloride (99.99+%, Aldrich) was first oven-dried at 110 °C, further dried by azeotropic distillation, and dissolved in THF. Acetyl chloride (Aldrich, 99%) and nitrobenzene (Aldrich, 99%) were purified by distillation. All other reagents were used as received. The reagent ampules used in the polymerization and grafting procedures were prepared with the help of high-vacuum techniques and then filled with nitrogen.[11] The ampules were equipped with Young high-vacuum PTFE stopcocks and ground glass joints, so they could be mounted directly on the polymerization reactor.

Preparation of Acetylated Polystyrene Substrates. The linear, comb-branched (G0), G1, and G2 partially acetylated polystyrenes serving as substrates were synthesized in a previous study using cycles of acetylation, grafting, and fractionation.[3] The substrates were synthesized from $M_w \approx 5000$ polystyrene core and side chains.

Synthesis of Polystyrene-*graft*-polyisoprene Copolymers. Isoprene was further purified on a high-vacuum manifold by three successive freezing−evacuation−thawing cycles in the presence of *sec*-butyllithium solution (0.5 mL for 20 mL monomer) and slow distillation to a glass ampule. The ampule was filled with nitrogen and stored at −5 °C until needed.

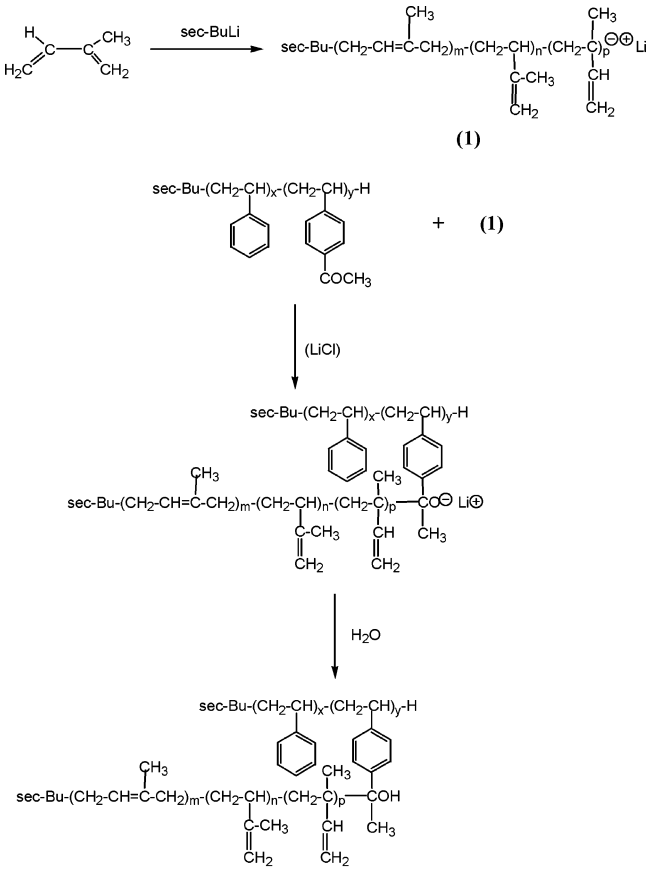
The first step in the preparation of the copolymers was the polymerization of isoprene (15 g) with *sec*-butyllithium at 0 °C in THF either with or without additive (LiCl or TMEDA). After complete conversion of the monomer, a sample was removed with a syringe and terminated with degassed methanol for characterization of the side chains. The remaining polymer solution was then maintained at a desired temperature and titrated with a solution of the acetylated polystyrene substrate over ca. 30 min to a pale yellow color, taking care not to overtitrate the living chains. Further fading of the coloration was observed after stirring was continued for 30 min. Residual anions were terminated with degassed methanol. The graft copolymer was separated from nongrafted polyisoprene linear chains by precipitation fractionation in a hexane−2-propanol mixture. Successful fractionation was confirmed by comparison of size exclusion chromatography (SEC) traces for the fractionated and nonfractionated samples. Copolymers with different polyisoprene (PIP) contents and branching functionalities were prepared by grafting PIP side chains with a weight-average molecular weight $M_w \approx 5000$ or 30 000 onto linear, comb-branched (G0), G1, and G2 acetylated polystyrenes.

Sample Characterization. Routine SEC analysis was performed for the polystyrene substrates, the polyisoprene side chains, the raw grafting products, and the fractionated graft copolymers using a Waters 510 HPLC pump equipped with a Jordi 500 mm × 10 mm DVB linear mixed-bed column (molecular weight range 10^2−10^7) and a Waters 410 differential refractomer (DRI) detector. The polymers were analyzed in THF at 25 °C and a flow rate of 1 mL/min. Apparent molecular weights were determined for the graft copolymers and for the side chain samples using a linear polystyrene standards calibration curve.

The absolute weight-average molecular weight (M_w) and molecular weight distribution of the polystyrene grafting substrates and most arborescent graft copolymers and side chain samples were determined by SEC-MALLS (multiangle laser light scattering) analysis, using a Wyatt Dawn DSP-F detector at a flow rate of 1 mL/min in THF. The system consisted of a Waters 590 HPLC pump coupled with Waters Ultrastyragel columns (10^4, 10^5, and 10^6 Å pore sizes). The polymer concentration in the eluent was measured with a Waters 2410 DRI detector. The absolute M_w of samples G2PS−PIP5 and G2PS−PIP30, which were not eluted from the SEC column, was determined using batch static light scattering measurements in THF. The refractive index increment (dn/dc) for the graft copolymers was calculated as a composition-weighed average of the values determined for the core polymers and for linear polyisoprene samples with the same microstructure and molecular weight as the side chains.[12] The dn/dc values for the homopolymers were measured at 25 °C using a Brice-Phoenix differential refractometer equipped with 510 and 632 nm band-pass interference filters. A Brookhaven BI-200 SM light scattering goniometer with a Lexel 2 W argon ion laser operating at 514.5 nm was used for the static and dynamic light scattering measurements.[11] The absolute M_w was determined by Zimm extrapolation to zero angle and concentration for a series of measurements for 6−8 solutions at angles ranging from 30° to 150°. Hydrodynamic radii in THF were determined from the normalized electric field correlation function $|g^1(\tau)|$ using second-order analysis to better account for polydispersity effects.

Composition analysis of the arborescent copolymers was performed using ^{1}H NMR spectra obtained on a Bruker AM-250 nuclear magnetic resonance spectrometer in $CDCl_3$. The PIP contents are reported as a weight percentage of PIP in the graft copolymers. Copolymer compositions were also determined by UV absorption measurements on a Hewlett-Packard HP8452 spectrophotometer. A linear polystyrene standard ($M_n = 50\,000$) dissolved in THF was used to generate an absorbance vs concentration calibration curve using the characteristic polystyrene absorbance maximum at $\lambda = 262$

Scheme 1. Preparation of Polystyrene-*graft*-polyisoprene Copolymer by Grafting onto a Linear Acetylated Polystyrene Substrate



nm. The PIP contents reported were calculated from the polystyrene content in the graft copolymers determined in THF by comparing the absorbance at $\lambda = 262$ nm to the calibration curve.

Atomic force microscopy (AFM) characterization of the samples was carried out using a Multimode Nanoscope IIIa instrument, Veeco Inc., Santa Babara, CA. The copolymers were dissolved in heptane, toluene, or chloroform at a concentration of about 0.5−1 mg/mL. Monomolecular films were obtained by spin-casting of the solutions onto mica (spinning rate 2500 rpm). The AFM measurements were done at room temperature (25 °C) and relative humidity of 30−40%, in the tapping mode using a silicon cantilever with a spring constant of ∼50 N/m and resonance frequency of ∼160 kHz.

Results and Discussion

A "grafting onto" scheme was selected for the preparation of arborescent isoprene copolymers, based on the technique developed for the preparation of arborescent polystyrenes previously described.[2] This approach provides extensive control over the total molecular weight, branching functionality, and composition of the graft copolymers by varying the acetylation level of the substrate and the size of the polyisoprene side chains or by using arborescent polystyrene substrates of different structures (generation and/or side chain molecular weight). Isoprene was first polymerized using *sec*-butyllithium to generate a macroanion solution with a bright greenish-yellow color. The living polymer solution was then titrated with a solution of acetylated polystyrene substrate to consume nearly all anions and yield the corresponding arborescent graft copolymer. Scheme 1 describes the grafting procedure by coupling polyisoprenyl anions with an acetylated linear polystyrene substrate, involving nucleophilic addition of the macroanion on the carbonyl group. Each reaction step will be discussed in more details below.

Polystyrene Substrates. The characteristics of the linear and G0−G2 polystyrene substrates used in the preparation of the graft copolymers are summarized in Table 1. All substrates were synthesized using $M_w \approx 5000$ polystyrene side chains with a narrow molecular weight distribution (MWD), $M_w/M_n = 1.07-1.09$, as determined by the SEC-MALLS analysis. The polystyrene substrates exhibit an absolute molecular weight increasing geometrically for successive generations, while a narrow MWD is maintained ($M_w/M_n = 1.07-1.09$). The branching functionality of the graft homo- and copolymers, defined as the number of chains added in the last reaction, is calculated from the equation

$$f_w = \frac{M_w(G) - M_w(G-1)}{M_w^{br}} \qquad (1)$$

where $M_w(G)$, $M_w(G-1)$, and M_w^{br} are the absolute weight-average molecular weights (determined from SEC-MALLS or batch static light scattering measurements) of graft polymers of generation G, of the preceding generation, and of the side chains, respectively. The acetylation level of the substrates was maintained in the range of 20−30 mol %, corresponding to 10−15 grafting sites per $M_w \approx 5000$ side chain. The number of potential grafting sites introduced on the substrates, reported in Table 1, is calculated from the molecular weight and the acetylation level.

Isoprene Polymerization and Optimization of Grafting Conditions. Isoprene polymerization was carried out in THF at 0 °C to yield living polymers with a controlled molecular weight and a narrow molecular weight distribution.[13] Side chains with a "mixed" microstructure, containing roughly equal proportions of 1,4-, 1,2-, and 3,4-units, are obtained under these conditions.[14] Characterization data for side chains removed before the grafting reaction (e.g., Table 2) demonstrate that good control over molecular weight and a narrow molecular weight distribution are maintained under the conditions used.

The influence of the reaction temperature and additives (LiCl and TMEDA) on the *grafting yield*, defined as the fraction of living chains generated that is grafted on the substrate, as determined by SEC analysis (vide infra), was investigated in a series of reactions using a linear acetylated polystyrene substrate. For the grafting reaction to proceed in high yield, the macroanions must remain active ("living") during the time required to complete the reaction, and coupling must be favored over side reactions leading to premature termination of the chain ends. This requires the macroanions to be stable but still sufficiently nucleophilic. The reactivity of polyisoprenyllithium toward the acetyl functionality should be similar to that of isoprene-capped polystyryllithium already investigated.[2] The stability and reactivity of the macroanions can be controlled to some extent by varying the temperature at which the grafting reaction is carried out or using additives as reactivity modifiers. These parameters were systematically investigated to maximize the grafting yield. For each test reaction, short ($M_w \approx 5000$) PIP side chains were grafted onto a partially acetylated $M_w = 5100$ linear polystyrene

Table 1. Characteristics of Polystyrene Substrates[a]

	branches [b]		substrates				
polymer	M_w[c]	M_w/M_n[c]	M_w[c]	M_w/M_n[c]	f_w[d]	CH_3CO-,[e] mol %	grafting sites
PS (linear)			5.1×10^3	1.07		25	12
G0PS	4400	1.09	5.3×10^4	1.08	11	22	100
G1PS	4500	1.07	4.3×10^5	1.08	84	27	980
G2PS	5000	1.08	3.9×10^6	1.09	690	20	6600

[a] Substrates obtained by cycles of acetylation−grafting−fractionation using $M_w \approx 5000$ polystyrene core and side chains. The acetylated polystyrene substrates used in the reactions are the same as in ref 3. [b] Polystyrene branches end-capped with 3 equiv of 2-vinylpyridine. [c] Absolute values determined by SEC-MALLS measurements before acetylation. [d] Number of branches added in the last grafting reaction. [e] Acetylation level determined by ^{1}H NMR spectroscopy.

Table 2. Effect of Reaction Temperature and Additives on Grafting Yield[a]

temp,		PIP side chains		grafting	graft copolymer	
°C	additive[b]	M_w[c]	M_w/M_n[c]	yield,[d] %	M_w[c]	M_w/M_n[c]
−78	none	5300	1.08	75	38 900	1.08
−30	none	5000	1.07	69	35 600	1.08
0	none	5200	1.08	66	35 100	1.09
25	none	5400	1.07	61	34 500	1.09
−78	LiCl	5100	1.09	87	42 300	1.08
−30	LiCl	5500	1.07	90	47 500	1.07
0	LiCl	5300	1.06	91	45 900	1.08
25	LiCl	5400	1.08	94	47 200	1.07
0	TMEDA	5200	1.07	42	22 300	1.10

[a] All reactions in THF with linear polystyrene substrate (M_w = 5100, M_w/M_n = 1.07, acetylation level = 25 mol %). [b] 5 equiv of additive (LiCl or TMEDA) added relative to the number of macroanions in the reaction. [c] Apparent values determined by SEC analysis based on a linear polystyrene standards calibration curve. [d] Fraction of side chains generated attached to the substrate.

substrate with an acetylation level of 25 mol %. The results obtained for the test reactions are summarized in Table 2.

The influence of reaction temperature on the grafting yield was examined at −78, −30, 0, and 25 °C after polymerization of isoprene at 0 °C in THF either with or without a coordinating additive (LiCl or TMEDA). In the absence of additive, the grafting yield increases from 61 to 75% as the reaction temperature is decreased from 25 to −78 °C. The increased grafting yield at lower temperatures could be explained by reduced susceptibility of the macroanions toward side reactions, while maintaining a high reactivity in the coupling reaction. As discussed for the synthesis of arborescent polystyrenes,[2] the abstraction of a proton from the acetyl functionality of the substrate by the macroanion likely constitutes the main side reaction. The increased grafting yield thus reflects either a decreased frequency of proton abstraction at lower temperatures or alternately increased living character and stability of the macroanions.

Additives can either increase or decrease the stability (and reactivity) of PIP anions, depending on their nature. The influence of additives on the grafting yield was investigated using either LiCl or TMEDA for comparison with reactions in the absence of additives. It is known that the addition of a common ion salt to an anionic polymerization reaction shifts the ion pair vs free anion equilibrium in favor of ion pairs.[15] These ion pairs are characterized by a decreased nucleophilicity (reactivity) and a higher stability relative to the free ions. The addition of LiCl to the anionic polymerization of acrylates and methacrylates in polar solvents has been shown to increase the initiation efficiency and decrease the breadth of the MWD.[16] The reactivity of the chain ends is expected to decrease in the presence of excess lithium ions, thereby minimizing detrimental side reactions. Experimentally, the grafting yield is found to increase substantially in the presence of a 5-fold excess of lithium ions at all reaction temperatures investigated to reach a maximum of 94% at 25 °C. This increase is attributed to a larger reduction in the rate of chain-terminating side reactions than in the rate of the coupling reaction.

To confirm that the increased grafting yield with LiCl results from the decreased concentration of free ions or solvent-separated ion pairs in the reaction, the dissociation equilibrium was also perturbed with TMEDA, which can act as a ligand for lithium ions.[17] This may increase the concentration of both solvent-separated ion pairs and free ions in the reaction at the expense of tight ion pairs, thus enhancing the average reactivity of the PIP macroanions. It was reported that the addition of TMEDA prior to grafting polyisoprenyllithium onto partially chloromethylated polystyrenes increased the grafting yield by suppressing side reactions such as metal−halogen exchange and cross-linking reactions.[18] The situation is very different in the coupling reaction with acetyl functionalities since the addition of TMEDA decreases the grafting yield from 66% to 42% at 0 °C, presumably due to enhanced chain termination.

On the basis of the results obtained, grafting of LiCl-modified polyisoprenyl anions onto acetylated polystyrene substrates in THF at 25 °C was selected as a standard procedure for the preparation of arborescent polystyrene-*graft*-polyisoprene copolymers.

Arborescent Polystyrene-*graft*-polyisoprene Copolymers. Using the conditions optimized for the synthesis of comb-branched isoprene copolymers, two series of arborescent copolymers with either short ($M_w \approx 5000$, PIP5) or long ($M_w \approx 30\,000$, PIP30) PIP side chains grafted onto acetylated polystyrene substrates of different generations were prepared. Characterization data for the copolymers are provided in Table 3. In keeping with previous nomenclature,[19] graft copolymer sample identification specifies the composition and structure of the molecules. For example, G1PS−PIP5 refers to a graft copolymer with $M_w \approx 5000$ PIP side chains grafted onto a G1 (twice-grafted) arborescent polystyrene substrate.

The results listed in Table 3 clearly demonstrate that the grafting yield decreases as the generation (or branching functionality) of the substrate increases. This is true for both the PIP5 and PIP30 series. An important factor contributing to deactivation of the living PIP anions under the grafting conditions used may be their reaction with residual protic impurities introduced with the substrate polymer solution during the grafting process. Higher generation substrates are more difficult to purify after the acetylation reaction and are thus susceptible to contain more protic impurities. Moreover,

Table 3. Characteristics of Arborescent Isoprene Copolymers of Successive Generations[a]

sample	PIP side chains		grafting yield,[c] %	graft polymer					coupling efficiency,[f] %	% w/w PIP	
	M_w[b]	M_w/M_n[b]		M_w[b]	M_w/M_n[b]	M_w[d]	f_w[e]	R_h, nm		NMR[g]	UV[h]
PS−PIP5	5300	1.08	94	6.5×10^4	1.07	4.7×10^4	11	6	92	91	85
G0PS−PIP5	4900	1.07	91	4.9×10^5	1.06	1.3×10^5	89	11	89	88	84
G1PS−PIP5	5000	1.08	85	3.7×10^6	1.08	6.5×10^5	650	22	66	85	82
G2PS−PIP5	5200	1.09	75	2.5×10^7			4000	46	60	84	80
PS−PIP30	29800	1.09	90	3.2×10^5	1.08	2.0×10^5	11	10	92	>97	95
G0PS−PIP30	29200	1.08	82	2.1×10^6	1.08	4.6×10^5	70	23	70	97	93
G1PS−PIP30	29900	1.07	38	1.1×10^7	1.09	6.9×10^5	350	40	36	94	91
G2PS−PIP30	29400	1.08	23	4.9×10^7			1530	54	23	92	89

[a] All reactions in THF at 25 °C with 5 equiv of LiCl added. [b] Absolute values determined by SEC-MALLS or laser light scattering measurements. [c] Fraction of side chains generated attached to the substrate. [d] Apparent values determined by SEC analysis based on a linear polystyrene standards calibration curve; G2PS−PIP5 and G2PS−PIP30 not eluted from the column in SEC analysis. [e] Number of branches added in the last grafting reaction. [f] Fraction of available coupling sites on the substrate consumed. [g] PIP content determined by ^{1}H NMR spectroscopy. [h] PIP content determined by UV absorption analysis.

for nearly complete discoloration of the PIP macroanions, a larger than stoichiometric amount of substrate is consumed in the titration for higher generation substrates, leading to the introduction of additional protic impurities. The acetylation level of the arborescent polystyrene substrates, determined by ^{1}H NMR analysis, was also confirmed by FT-IR spectroscopy. Consequently, the larger amounts of higher generation substrates required for discoloration of the living macroanion solution can be clearly attributed to reactive site inaccessibility rather than inaccurate acetylation level determinations. The dependence of the grafting yield upon the length of the PIP grafts is also observed: Comparison of the grafting yields obtained for substrates of the same generation shows that it is always lower for PIP30 than PIP5 side chains. This effect is most noticeable for the G2 substrates, with a decrease from 75% for G2PS−PIP5 to 23% for G2PS−PIP30. The effect of adventitious impurities is always more significant for higher molecular weight side chains because the concentration of living ends is lower.

The *coupling efficiency*, defined as the fraction of coupling sites on the substrate consumed in the reaction, is calculated as the ratio of the branching functionality of the copolymer (Table 3, column 8) to the number of grafting sites on the acetylated polystyrene precursor (Table 1, column 8). The variations in coupling efficiency follow trends similar to the grafting yield, as indicated in Table 3. The acetyl sites are presumably randomly distributed within the core polymer, and thus all sites should react independently from each other. However, as the substrate polymer becomes more highly branched, it also becomes increasingly congested. A fraction of the acetyl sites should become less accessible to the polyisoprenyl anions, resulting in decreased coupling efficiency. Two distinct "phases" were identified within arborescent polystyrenes in a fluorescence quenching investigation of the molecules.[6] The more rigid inner portion of the molecule was found to be less accessible to quencher species than the more flexible outer portion. The fraction of less accessible material was also found to increase for higher generation polymers. This differential accessibility effect explains the decreased coupling efficiency for higher generations in the polyisoprenyllithium grafting reaction. In addition to the steric crowding effects mentioned, incompatibility between the polystyrene and polyisoprene components, as well as excluded-volume effects minimizing the tendency for the living polymer coils and the acetylated polystyrene substrates to overlap, may also have contributed to lowering the coupling efficiency.

There are indications that the grafting reaction onto acetylated substrates becomes diffusion-limited in the synthesis of higher generation copolymers. The amount of acetylated substrate required in the titration of the living polymers based on linear and G1 substrates is approximately as expected from the stoichiometry of the reaction. For samples based on G1 and G2 substrates, however, 50−100% excess of acetylated substrate is required to deactivate all the living ends. This, again, suggests that surface overcrowding effects may be hindering the diffusion of the living chain ends to the acetyl sites. Surface overcrowding was also reported as a limiting factor in the preparation of dendrimers.[20]

A grafting reaction was designed to attempt to maximize the coupling efficiency by using a 30 mol % excess of side chains and allowing it to proceed for 4 h (instead of the usual 1 h). The coupling reaction of G1PS with $M_w \approx 30\,000$ PIP side chains was used for this purpose. The green-yellow coloration of the solution persisted over the course of the reaction, and residual anions were terminated with degassed methanol. As expected, the fraction of side chains grafted (grafting yield, as determined by SEC analysis) decreased from 38% to 28% due to the excess of living ends present. However, the total apparent molecular weight of the product was identical for both reactions, indicating that the coupling efficiency is limited by the extent of steric congestion within the molecules.

It should be noted that both the grafting yield and the coupling efficiency are useful parameters characterizing the extent of reaction. The coupling efficiency is of fundamental importance, as it describes the yield of the reaction based on the fraction of coupling sites reacted. This parameter should reflect the accessibility of coupling sites on the substrate to the living chain ends, irrespective of specific factors (steric hindrance, incompatibility, and/or excluded-volume effects) affecting their accessibility. The grafting yield, on the other hand, should depend mainly on the concentration of impurities in the reaction but is also important from a practical viewpoint: It determines how difficult is the removal of linear chain contaminant from the crude product in sample purification.

Polymer Characterization. SEC analysis was routinely used to characterize the acetylated polystyrene cores, the polyisoprene side chains, the raw grafting products, and the fractionated copolymers. Figure 2 illustrates the synthesis of a copolymer with a series of SEC traces for sample G0PS−PIP5. Generally two peaks, corresponding to the graft copolymer and nongrafted side chains, can be observed in the SEC trace

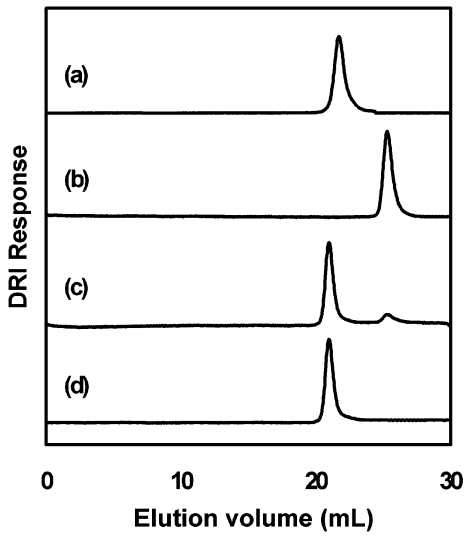


Figure 2. Preparation of sample G0PS−PIP5: SEC traces for (a) G0PS acetylated substrate, (b) PIP5 side chains, (c) crude product from the grafting reaction, and (d) fractionated copolymer.

for the raw product (curve c). The leftmost (high molecular weight) peak corresponds to the graft copolymer. The rightmost peak has the same molecular weight as the side chain sample removed from the reactor before the grafting reaction (curve b). It corresponds to polymer chains deactivated by side reactions or by residual protic impurities present in the acetylated polymer solution.

The grafting yield (fraction of living polymer chains grafted) can be quantified from the SEC trace for the raw product if the DRI response due to the copolymer and the grafted side chains is assumed to be identical. This is done by comparing the peak area for the graft copolymer to the total area for all peaks. Using sample G0PS−PIP5 (Figure 2c) as an example, the peak area obtained (in arbitrary units) for the side chain (rightmost) peak was 2348 units. The area of the leftmost (graft copolymer) peak was 26 682 units. This amounts to a grafting yield 26 682/(26 682 + 2348) = 91%. The grafting yields reported in Tables 2 and 3 were obtained by the SEC analysis method described (method I), except for samples derived from the G2PS substrate. Samples G2PS−PIP5 and G2PS−PIP30 were retained on the SEC column by an unknown mechanism, and only the nongrafted side chains were eluted. The grafting yield could still be determined by SEC analysis in this case, using the following modified analysis procedure (method II). Solutions of equal concentrations were prepared from the crude grafting product and the linear PIP side chains. For SEC traces obtained from these two polymer solutions, the peak areas for the linear PIP component were compared. Taking sample G2PS−PIP5 as an example, the peak area obtained for the linear polyisoprene sample was 82 400 units. The peak area for the side chains in the crude product was 20 500 units. The ratio of areas is 20 500/82 400 = 0.25, corresponding to 25% of nongrafted side chains or 75% graft polymer. The grafting yield was also confirmed gravimetrically by weighing the purified graft polymer recovered after fractionation. The grafting yields obtained gravimetrically for samples G2PS−PIP5 and G2PS−PIP30 are 73% and 31%, respectively, in good agreement with the SEC values in Table 3. The validity of SEC analysis method II was further confirmed by comparing the results obtained by methods I and II for a sample completely eluted from the SEC column. The grafting yield determined for G1PS−PIP5 by method II was 86% as compared to the 85% value reported in Table 3 for method I.

It should be noted that both methods I and II slightly overestimate the grafting yields obtained because they do not take into consideration the contribution of the polystyrene substrate to the total mass of the copolymer molecules. The grafting yield is defined as the fraction of living chains coupled with the substrate. For example, grafting yield calculations by method I, based on the relative peak areas for the graft copolymer and the side chains, implicitly assume a negligible polystyrene content in the copolymer, so that the response for the copolymer peak is due only to the polyisoprene component. While this assumption should be valid for high polyisoprene contents, it can lead to more significantly overestimated grafting yields for copolymers with a higher polystyrene weight fraction (e.g., error estimated at ca. 3% for sample G1PS−PIP5). Similar problems are encountered in applying method II to grafting yield determinations: In this case, since identical concentrations are used for the raw product and the linear polyisoprene sample injections on the SEC column, the overall concentration of the polyisoprene component is lower in the raw product because of the presence of the polystyrene substrate.

The *absolute* weight-average molecular weight (M_w) and polydispersity (M_w/M_n) of the polyisoprene side chains and the graft copolymers (determined by either SEC analysis using a MALLS detector or batch light scattering measurements) are presented in Table 3. The results demonstrate that a narrow molecular weight distribution was achieved for both the polyisoprene side chains and the graft copolymers. Also reported in Table 3 (column 7) are the *apparent* (or polystyrene-equivalent) M_w values determined by SEC analysis using only the DRI detector in combination with a linear polystyrene standards calibration curve. Comparison of the absolute and apparent M_w values shows that the apparent molecular weights are strongly underestimated, especially for the higher generation copolymers. This result, expected for branched polymers, is a consequence of the very compact structure of the molecules. The hydrodynamic radii (R_h) of the copolymers, determined from dynamic light scattering measurements in THF, are provided in Table 3. The size of the molecules progressively increases for successive generations at a rate comparable to that previously reported for arborescent styrene homopolymers.[5]

The branching functionality (f_w) of the copolymers, calculated according to eq 1 using absolute M_w values, ranges from 11 to 4000 for the PIP5 series and 11 to 1530 for the PIP30 series. The f_w values determined for the copolymers are lower than the number of grafting sites (Table 1) on the acetylated polystyrene substrates in all cases. The branching functionality is always lower for polymers with longer PIP side chains than for short side chain materials, in particular for higher generation substrates. This unfortunately leads to difficulties in accurately controlling the branching functionality within a series of copolymers based on the same polystyrene grafting substrate. To establish structure−property relations in these materials, it would clearly be preferable to generate series of samples for which the branch-

ing functionality remains constant and only the side chain molecular weight varies.

The crude grafting products were purified to remove linear polyisoprene contaminant by precipitation fractionation from a hexane−2-propanol mixture (e.g., Figure 2, curve d), and the composition of the purified copolymers was determined by ^{1}H NMR spectroscopy. The results obtained, summarized in Table 3, indicate that the composition of the graft copolymers is dominated by the PIP component, ranging from 84 to 91% and 92 to 97%+ by weight for the PIP5 and PIP30 series, respectively. The polyisoprene contents determined by UV analysis are also provided in Table 3. The results from UV analysis are consistent, although systematically slightly lower (3−6% w/w) than the values obtained by NMR spectroscopy. While the differences in polyisoprene contents obtained by NMR and UV analysis are relatively small, they are more significant in terms of the uncertainty on the polystyrene content of the copolymers. The arborescent copolymers with short PIP side chains contain a significant weight fraction of polystyrene. When longer polyisoprene side chains are grafted on the substrate, the polystyrene content becomes negligible. It is thus possible to control the composition of the copolymers by varying parameters such as the length and number of the PIP segments and the size (generation) of the polystyrene substrate.

AFM Measurements. The arborescent polymers form uniform monolayers on mica, and each molecule can be clearly resolved by atomic force microscopy in the tapping mode (Figure 3). The dimensions of the molecules, determined by analysis of the height images, are summarized in Table 4. The uncertainties reported correspond to the standard deviations obtained by statistical analysis of the whole images. The molecules are flattened on the mica surface due to strong adhesion, as noticed from the larger lateral size of the molecules relative to their thickness. The particles clearly increase in size for copolymers based on generations G0−G2 polystyrene substrates at constant PIP chain length. Molecular volumes V were calculated (Table 4) for dense hexagonal packing of spherical particles on the basis of measured film thickness and intermolecular distance. A volume polydispersity of about 15%, determined from the AFM images, is in agreement with the low polydispersity indices (below 1.10) determined by SEC-LALLS analysis. The fact the size polydispersity does not rise for higher generations is a particularly important indication that the synthetic strategy developed is useful to synthesize nanoscopic spherical molecules of uniform size. Also included in Table 4 is the molecular volume V_m calculated from the independently measured molecular weight. For the majority of the copolymers investigated, V_m was larger than the molecular volume determined from the AFM images. Although the disagreement was usually within experimental errors, lower AFM values were expected due to additional flattening of the molecules induced by the AFM tip.

Phase separation between the polystyrene core and the polyisoprene side chains is clearly visible for films obtained by spin-casting from heptane, a solvent selective for polyisoprene, when the images are examined in the phase mode (Figure 3). The images depict lighter particles of the harder polystyrene-rich core embedded in the gray matrix of the softer polyisoprene corona chains. For the G1 and G2 substrates grafted with PIP30, one can even observe peculiar star-shape structures in the polystyrene core, providing direct evidence for a core−shell morphology. Films were also prepared for samples G0PS−PIP30 and G1PS−PIP30 using two nonselective solvents, toluene and chloroform (Figure 4). In this case the contrast achieved between the polystyrene cores and the polyisoprene shell is strongly decreased, as evidenced by comparison to parts B and

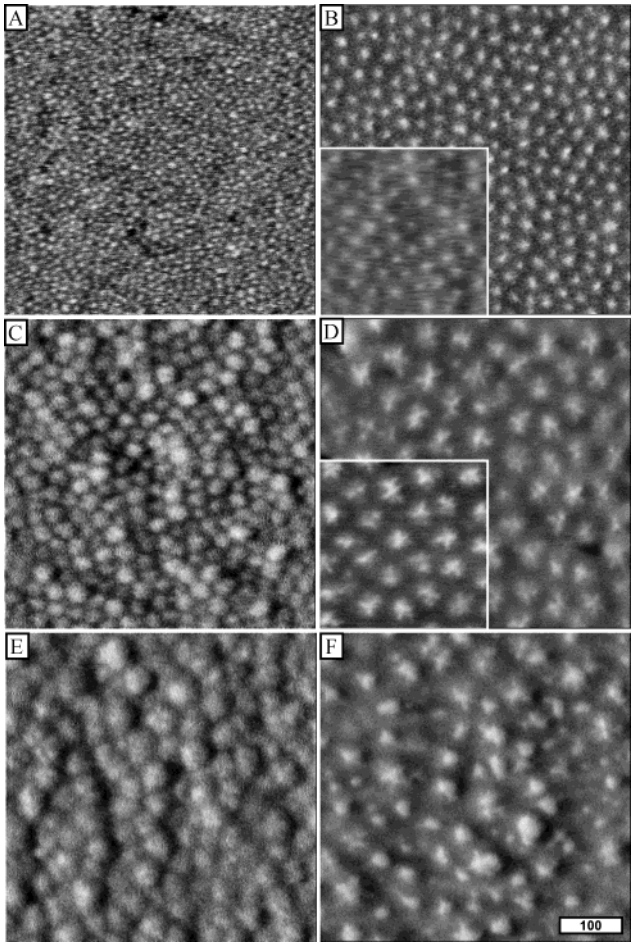


Figure 3. AFM images of samples prepared by spin-casting from heptane solutions (concentration ~1 mg/mL): (A) G0PS−PIP5, (B) G0PS−PIP30, (C) G1PS−PIP5, (D) G1PS−PIP30, (E) G2PS−PIP5, (F) G2PS−PIP30. All images are shown in the phase mode to allow visualization of the molecular morphology due to differences in viscoelastic behaviors of polystyrene and polyisoprene chains. The insets of (B) and (D) are the height images, showing the topology of the monolayers. The 100 nm scale bar shown in (F) is identical for all images.

Table 4. Thickness and Interparticle Distance in Monomolecular Films of Arborescent Polystyrene-*graft*-polyisoprene Copolymers on Mica

sample	thickness, nm	distance, nm	V,[a] nm^3	V_m,[b] nm^3	V/V_m
G0PS−PIP5	3.8 ± 0.1	13 ± 1	556	904	0.61 ± 0.07
G0PS−PIP30	3.4 ± 0.1	33 ± 2	3200	3880	0.8 ± 0.1
G1PS−PIP5	7.4 ± 0.2	35 ± 3	7840	6830	1.1 ± 0.2
G1PS−PIP30	6.6 ± 0.2	51 ± 2	14800	20300	0.7 ± 0.1
G2PS−PIP5	17 ± 1	50 ± 3	36800	46100	0.8 ± 0.2
G2PS−PIP30	16 ± 3	56 ± 14	43400	90400	0.5 ± 0.3

[a] Molecular volume $V = (\sqrt{3}/2)hd^2$ calculated for a dense hexagonal packing of spherical particles, based on the film thickness h and interparticle distance d determined from AFM measurements. [b] Molecular volume $V_m = M_w/\rho N_A$ calculated from the absolute molecular weights M_w reported in Table 3 (column 5) and a bulk density $\rho = 800$ kg/m^3 for polyisoprene.

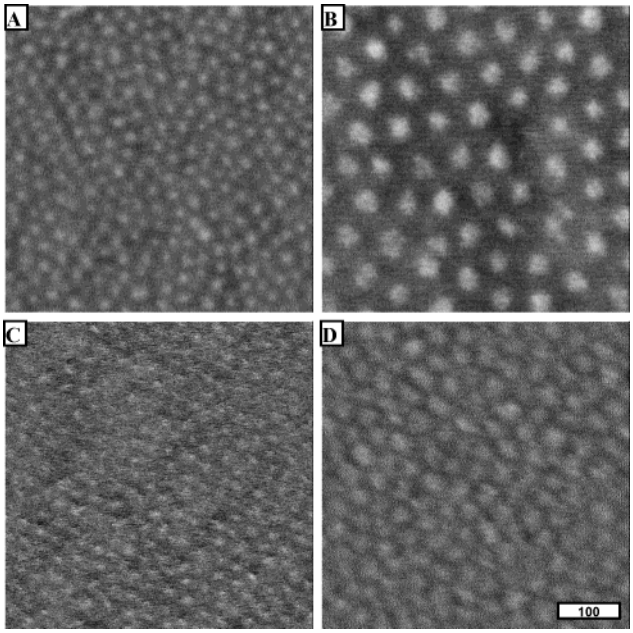


Figure 4. AFM phase image of films obtained by spin-casting (concentration ~1 mg/mL): G0PS−PIP30 in toluene (A) and chloroform (C); G1PS−PIP30 in toluene (B) and chloroform (D). The 100 nm scale bar shown in (D) is the same for all images.

D of Figure 3 for samples G0PS−PIP30 and G1PS−PIP30, respectively, obtained from heptane solutions. The starlike shape of the polystyrene-rich core is not clear or barely visible in the films prepared from the nonselective solvents, probably due to better mixing between the two polymer phases. The films obtained from the chloroform solutions display the least phase contrast (Figure 4C,D), suggesting that chloroform promotes mixing between the polystyrene and polyisoprene phases more strongly than toluene.

Conclusions

The results obtained demonstrate that acetyl coupling sites are useful to synthesize arborescent isoprene copolymers. The grafting yield varies with the reaction temperature and is maximized in the presence of LiCl. A narrow molecular weight distribution ($M_w/M_n = 1.06-1.09$) is maintained for the graft copolymers. The method was demonstrated for the special case of a dense polystyrene substrate with a large number of grafting sites. Different materials with a wider range of properties could presumably be obtained if the structure of the polystyrene substrate was varied. Likewise, the efficiency of the coupling reaction may be increased if substrates with a lower acetylation level are used, to decrease the influence of steric exclusion effects. The arborescent copolymers prepared provide an excellent opportunity to investigate the physical properties of these unique materials. The characterization results obtained clearly confirm the occurrence of phase separation between the polystyrene core and the polyisoprene shell of the molecules on a nanometric scale. The extent of phase separation achieved strongly depends on the selectivity of the solvent used in the spin-casting process.

Acknowledgment. This work was supported by the Natural Science and Engineering Research Council of Canada (NSERC), the 3M Canada Co., and the National Science Foundation (DMR-0306787). The authors also thank Dr. Neil McManus, Department of Chemical Engineering, University of Waterloo, for his help with the SEC-MALLS measurements.

References and Notes

(1) For an overview of the synthesis of arborescent and other dendritic graft polymers, see: Kee, R. A.; Gauthier, M.; Tomalia, D. A. In *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds.; Wiley: Chichester, 2001; Chapter 9.
(2) Li, J.; Gauthier, M. *Macromolecules* **2001**, *34*, 8918.
(3) Gauthier, M.; Li, J.; Dockendorff, J. *Macromolecules* **2003**, *36*, 2642.
(4) Gauthier, M.; Möller, M.; Burchard, W. *Macromol. Symp.* **1994**, *77*, 43.
(5) Gauthier, M.; Li, W.; Tichagwa, L. *Polymer* **1997**, *38*, 6363.
(6) Frank, R. S.; Merkle, G.; Gauthier, M. *Macromolecules* **1997**, *30*, 5397.
(7) Sheiko, S. S.; Gauthier, M.; Möller, M. *Macromolecules* **1997**, *30*, 2343.
(8) Choi, S.; Briber, R. M.; Bauer, B. J.; Topp, A.; Gauthier, M.; Tichagwa, L. *Macromolecules* **1999**, *32*, 7879.
(9) Choi, S.; Briber, R. M.; Bauer, B. J.; Topp, A.; Gauthier, M.; Tichagwa, L. *Macromolecules* **2000**, *33*, 6495.
(10) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155.
(11) Gauthier, M.; Tichagwa, L.; Downey, J. S.; Gao, S. *Macromolecules* **1996**, *29*, 519.
(12) Kratochvíl, P. *Classical Light Scattering from Polymer Solutions*; Elsevier: Amsterdam, 1987; Chapter 5.
(13) (a) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1. (b) Bywater, S. *Prog. Polym. Sci.* **1994**, *19*, 287.
(14) Bywater, S.; Worsfold, D. J. *Can. J. Chem.* **1967**, *45*, 1821.
(15) Szwarc, M.; Van Beylen, M. *Ionic Polymerization and Living Polymers*; Chapman & Hall: New York, 1993; Chapter 2.
(16) Varshney, S. K.; Hauteker, J. P.; Fayt, R.; Jérôme, R.; Teyssié, P. *Macromolecules* **1990**, *23*, 2618.
(17) Collum, D. B. *Acc. Chem. Res.* **1992**, *25*, 448.
(18) Price, C.; Woods, D. *Polymer* **1973**, *14*, 82.
(19) Kee, R. A.; Gauthier, M. *Macromolecules* **1999**, *32*, 6478.
(20) (a) Tomalia, D. A.; Baker, H.; Dewald, J. R.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J. (Tokyo)* **1985**, *17*, 117. (b) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466. (c) Tomalia, D. A.; Hall, M.; Hedstrand, D M. *J. Am. Chem. Soc.* **1987**, *109*, 1601.

MA035099J