Arborescent Polystyrene-*graft*-polyisoprene Copolymers

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ABSTRACT: A synthetic technique is presented for the preparation of a novel type of arborescent copolymer containing polyisoprene (PIP) segments. Isoprene is polymerized with *sec*-butyllithium in cyclohexane or tetrahydrofuran, to yield a predominantly *cis*-1,4- or a mixed microstructure, respectively. The graft copolymers are obtained by capping the polyisoprenyl anions with 1,1-diphenylethylene and titration with a solution of a chloromethylated polystyrene substrate. Copolymers containing PIP side chains of different molecular weights are prepared by grafting onto linear, comb-branched (G0) and twice-grafted (G1) chloromethylated polystyrenes. The samples with short ($M_w \approx 5000$) PIP branches contain 77−83% w/w polyisoprene. For PIP side chains with $M_w \approx 30\,000$ and 90 000, the polystyrene content is negligible. A low apparent polydispersity ($M_w^{app}/M_n^{app} \leq 1.15$) is maintained after grafting. Characterization of these materials using size exclusion chromatography and light scattering indicates that they have a highly compact structure. Scanning force microscopy measurements in the phase contrast mode show that the copolymers display phase-separated morphologies (glassy core surrounded by a rubbery shell) to different extents, depending on their structure.

Introduction

Dendritic polymers encompass a broad range of compounds with a cascade-branched structure including dendrimers and hyperbranched and arborescent polymers.[1] Numerous synthetic methods have been suggested for the preparation of these materials. Dendrimers are typically obtained in a series of protection−condensation−deprotection cycles (generations) of AB$_n$ monomers. The rate of increase in molecular weight is relatively low in these systems, however, and many generations are required to reach a significant molecular weight. Hyperbranched polymers can be obtained with a high molecular weight in simple one-pot condensation procedures but suffer from a poorly defined branched structure and a broad molecular weight distribution. Alternately, arborescent polymers can be prepared from grafting reactions using polymeric building blocks, making it possible to attain high branching functionalities and molecular weights in a few reaction steps, while maintaining a narrow molecular weight distribution.[2−4]

The synthesis of arborescent polystyrenes[2] relies on the random introduction of grafting sites (chloromethyl groups) along a linear polystyrene chain, followed by coupling with polystyryl anions to give a comb-branched (generation 0 or G0) polymer. Further chloromethylation and grafting cycles lead to higher generation arborescent polymers (G1, G2, etc.), characterized by a compact, spherelike highly branched structure.[5] This strategy, described as a "graft-on-graft" technique, was also used for the synthesis of polyethylenimines[3] and polybutadienes[4] with an arborescent structure. The fact that the branching density *and* the size of the branches can be varied independently for each generation is an important feature of the graft-on-graft technique.

The synthesis of arborescent *copolymers* has also been described. Amphiphilic copolymers incorporating an arborescent polystyrene core and a poly(ethylene oxide) shell were obtained in a *grafting from* approach.[6] Arborescent polystyrene molecules carrying hydroxyl groups at the *chain ends* were first synthesized. Titration of the hydroxyl groups with a strong base and addition of ethylene oxide resulted in extension of the core chains, to give covalently bound poly(ethylene oxide) segments forming a "shell" around the polystyrene core.

A new approach for the preparation of arborescent copolymers, described in this report, is based on a *grafting onto* scheme similar to the arborescent polystyrene synthesis. In this case, macroanions with a different composition are grafted on a substrate containing *randomly* distributed coupling sites. This extension of the graft-on-graft technique was used to synthesize copolymers incorporating polyisoprene segments of different molecular weights grafted onto linear, comb-branched (G0), and G1 chloromethylated polystyrene cores. For 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). The combination of a narrow molecular weight distribution, a highly branched structure, and a heterogeneous morphology characterizing the polystyrene−polyisoprene arborescent graft copolymers, not attainable by other synthetic methods, should lead to interesting elastomeric properties. Characterization results for these copolymers using size exclusion chromatography, light scattering, UV spectrometry, and atomic force microscopy, aimed at demonstrating the success of the synthetic methods used and morphology control, are discussed in this study.

Synthetic Strategy

There are numerous examples of star-branched polyisoprenes prepared by coupling polyisoprenyllithium with chlorosilanes.[7] In all cases the coupling reaction

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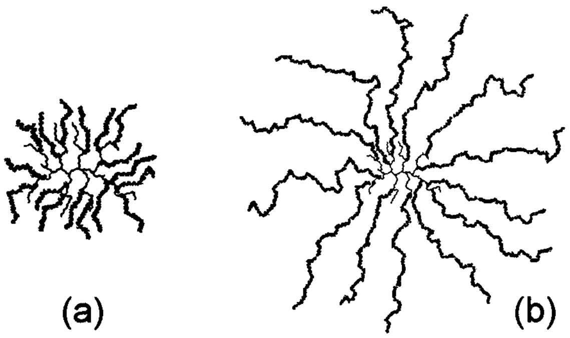


Figure 1. Comparison of structures obtained when a G0 (comb) chloromethylated polystyrene substrate is grafted with (a) short and (b) long polyisoprene side chains.

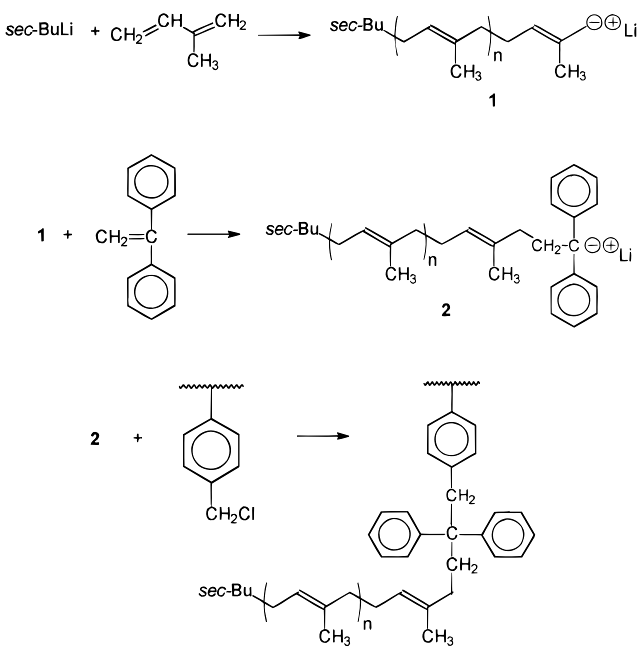
was efficient (often >90%) but required long reaction times. The coupling efficiency of polystyryl anions with chlorosilanes was also improved by adding a small amount of isoprene monomer to "cap" the polystyryllithium chains.[8]

Although the reaction of polyisoprenyllithium and chlorosilanes has been extensively studied, the coupling of polyisoprenyllithium with chloromethyl substituents has received little attention. In one report, the addition of linear chloromethylated polystyrene to a solution of polyisoprenyllithium in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was used to synthesize comb-branched polystyrene-*graft*-polyisoprene.[9] The amine was shown to suppress side reactions such as metal−halogen exchange and cross-linking and to improve the overall grafting efficiency. The analogous reaction of polystyryllithium with chloromethylated polystyrene is limited to ca. 50% grafting, also because of metal−halogen exchange. In this case, it was shown that the side reaction could be virtually eliminated, and the grafting yield increased to >95% by capping the macroanions with 1,1-diphenylethylene (DPE) prior to coupling with the substrate.[2] A similar coupling efficiency would, therefore, be expected in the reaction of DPE-capped polyisoprenyllithium with chloromethylated polystyrene.

The method selected for the preparation of arborescent PIP copolymers using a grafting onto scheme is based on the arborescent polystyrene synthesis. Isoprene is first polymerized using an organolithium initiator (Scheme 1), and the chains are capped with DPE. The resulting deep red solution is then titrated with a solution of chloromethylated polystyrene, to fully consume the anions. This approach provides extensive control over the total molecular weight, branching functionality, and composition of the graft copolymers, by varying the chloromethylation level of the substrate or the size of the polyisoprene side chains or by using arborescent polystyrene substrates of different structures (generation and/or side chain molecular weight).

The microstructure of the polyisoprene side chains can be varied by selection of appropriate polymerization conditions,[10] providing further control over the physical and chemical properties of the copolymers. A high proportion of *cis*-1,4-linkages is obtained using alkyllithium initiators in hydrocarbon solvents. In polar solvents such as THF, a microstructure high in 1,2- and 3,4-units is typically obtained, the balance being primarily *trans*-1,4-polyisoprene.[11,12] The flexibility of the graft-on-graft technique in the preparation of arborescent PIP graft copolymers will be demonstrated by using side chains with either a high *cis*-1,4-content or a mixed microstructure in the grafting reaction.

Scheme 1. Synthesis of Arborescent Isoprene Copolymers by Grafting onto a Chloromethylated Polystyrene Substrate



Experimental Procedures

Reagents. Styrene (Aldrich, 99%), 1,1-diphenylethylene (DPE; Aldrich, 97%), tetrahydrofuran (THF; Caledon, ACS Reagent), and CCl_4 (Caledon, ACS Reagent) were purified as previously described.[6] 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. Cyclohexane (BDH, ACS Reagent) was refluxed with oligostyryllithium under dry nitrogen atmosphere and distilled directly into the polymerization reactor. *sec*-Butyllithium (Aldrich, 1.3 M in cyclohexane) was used as received; the exact concentration of the solution was determined by the procedure of Lipton et al.[13] Purified chloromethyl methyl ether (CMME) was prepared as described earlier.[6] The procedures using CMME should be carried out in a well-ventilated fume hood with great care, since it is a known carcinogen.[14] All other reagents were used as obtained from the suppliers.

Linear Core Polymer. A polystyrene sample with a weight-average molecular weight $M_w \approx 5000$ and a low polydispersity index was synthesized as previously described.[6] Partial chloromethylation of the linear polystyrene was achieved by dissolving the vacuum-dried polymer (5 g) in dry CCl_4 (500 mL) and CMME (50 mL) and adding a solution of anhydrous $AlCl_3$ (3 g) in 1-nitropropane (100 mL). After 30 min stirring at room temperature the reaction was quenched with glacial acetic acid (10 mL), and the solvent was removed under vacuum. The polymer residue was dissolved in $CHCl_3$, extracted with three portions of 50% (v/v) glacial acetic acid, and precipitated into methanol.

Comb-Branched (G0) and G1 Core Polymers. A comb-branched polystyrene was obtained by reacting the chloromethylated linear polystyrene sample with DPE-capped polystyryl anions with $M_w \approx 5000$, as previously described.[2] After purification by precipitation fractionation to remove non-grafted side chains, the G0 polymer was further chloromethylated and reacted with $M_w \approx 5000$ polystyryl anions, to yield the G1 core. Samples of the linear, G0, and G1 polystyrenes were also chloromethylated according to the method described, to serve as grafting substrates for the polyisoprenyl anions.

Graft Copolymers. Isoprene was purified on a high-vacuum line by three successive freezing−evacuation−thawing cycles in the presence of *sec*-butyllithium solution (0.5 for 50 mL monomer) and slow distillation to a glass ampule with a poly(tetrafluoroethylene) (PTFE) stopcock. The ampule was filled with purified nitrogen and stored at −5 °C until needed.

The first step in the preparation of a graft copolymer was the polymerization of isoprene (50 g) with *sec*-butyllithium. To obtain a high proportion of *cis*-1,4-units, the polymerization was performed in cyclohexane at 25 °C. Alternately, polymerization was carried out at 0 °C in THF to yield a mixed microstructure. When the reaction was performed in cyclohexane, the reactor was cooled to 0 °C after complete conversion of the monomer, while slowly adding dry THF (for an overall THF content of ca. 30% v/v), before adding the DPE solution. If the polymerization was carried out in pure THF at 0 °C, the content of the DPE ampule was simply added to the reactor after complete conversion of the monomer. The DPE was left to react 30 min before removal of a sample of the side chains for characterization. The polymer solution was cooled to −30 °C and then titrated with a solution of the chloromethylated polystyrene, over 30 min, to a pale orange-red color. Further fading of the coloration was observed after stirring was continued for 30 min. Residual anions were terminated with degassed methanol. After workup, the graft copolymer was separated from nongrafted polyisoprene side chains by precipitation fractionation in a cyclohexane−2-propanol mixture. Successful fractionation was confirmed by comparison of size exclusion chromatography (SEC) diagrams for the fractionated and nonfractionated samples.

Four series of graft copolymers with different side chain molecular weights were prepared according to the same procedure. Three series used polyisoprene side chains with a predominantly *cis*-1,4-microstructure grafted onto linear, G0, and G1 chloromethylated polystyrenes. One series of copolymers with mixed microstructure polyisoprene side chains grafted onto G0 chloromethylated polystyrene was also prepared.

Characterization. Size exclusion chromatography was used to characterize the polystyrene and polyisoprene side chains, the raw grafting products, and the fractionated graft copolymers. The instrument used a Waters 510 HPLC pump, a Jordi 500 mm linear mixed bed column, and a Waters 410 differential refractometer (DRI) detector. Tetrahydrofuran served as the eluent, at a flow rate of 1 mL/min. Apparent molecular weights were determined for the graft copolymers and for the mixed microstructure side chain samples using a linear polystyrene standards calibration curve. Absolute molecular weights for the linear polyisoprene side chains with a high *cis*-1,4-content were determined using a calibration curve prepared from linear polyisoprene standards having the same microstructure.

The absolute M_w of the polystyrene grafting substrates and of the arborescent graft copolymers was determined using static light scattering measurements. Refractive index increments (dn/dc) for the graft copolymers were calculated as a composition-weighted average of the values determined for the core polymers and for linear polyisoprenes with the same microstructure as the side chains.[15] The dn/dc values of the homopolymers were measured at 25.0 ± 0.1 °C using a Brice-Phoenix differential refractometer equipped with a 510 nm band-pass interference filter. Measurements on the linear polyisoprene sample with a predominantly *cis*-1,4-microstructure were done in cyclohexane. The sample with a mixed microstructure was characterized in THF. A Brookhaven BI-200 SM light scattering goniometer equipped with a Lexel 2 W argon ion laser operating at 514.5 nm was used for the static light scattering measurements.[6] 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 40° to 140°.

Composition and microstructure analysis was performed using ^{1}H NMR spectra obtained on a Bruker AM-250 nuclear magnetic resonance spectrometer. The graft copolymers prepared in cyclohexane were dissolved in $CDCl_3$, and the samples prepared in THF were dissolved in benzene-d_6. Microstructure analysis of the predominantly *cis*-1,4-polyisoprene samples was carried out according to the method described by Chen.[16] The microstructure of the polyisoprene samples prepared in THF was determined by the method of Essel and Pham.[17] The composition of the copolymers was also analyzed by UV−vis spectroscopy on a Hewlett-Packard HP8452 spectrophotometer. The characteristic polystyrene absorbance maximum at $\lambda = 262$ nm was used to generate an absorbance vs concentration curve using linear polystyrene standards ($M_n = 50\,000$) dissolved in cyclohexane. The PIP contents reported are calculated from the polystyrene content in the graft copolymers determined in cyclohexane by comparing the absorbance at $\lambda = 262$ nm to the calibration curve.

Table 1. Characteristics of Arborescent Polystyrene Substrates

polymer	M_w^{br} (SEC)[a]/ g mol^{-1}	M_w^{br}/M_n^{br}	M_w (LS)[b]	f_w	CH_2Cl[c]/ mol %	grafting sites
PS (linear)			4 360		27	11
G0PS	4430	1.04	49 700	10	23	110
G1PS	5750	1.03	797 000	130	16	1220

[a] Absolute M_w of the side chains determined by SEC analysis. [b] Absolute M_w of the graft polymers determined by light scattering (linear sample analyzed by SEC). [c] Chloromethylation level determined by ^{1}H NMR spectroscopy analysis of substrate.

Scanning force microscopy measurements were done on a Digital Instruments Nanoscope IIIa operated in the tapping mode at a resonance frequency of ~360 kHz. The measurements were performed under ambient conditions using Si probes with a spring constant of ~50 N/m. The samples were prepared by spin-casting at 1000 rpm of a solution of the copolymer 0.05% w/w in chloroform on a freshly cleaved mica substrate.

Results and Discussion

The characteristics of the linear and branched polystyrene substrates used in the preparation of the copolymers are summarized in Table 1. The branching functionality of the polymers, defined as the number of chains added in the last grafting reaction, was calculated from the equation

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

where $M_w(G)$, $M_w(G-1)$, and M_w^{br} are the absolute weight-average molecular weight of graft polymers of generation G, of the preceding generation, and of the side chains, respectively. The number of grafting sites introduced on the substrates was calculated from their molecular weight and chloromethylation level. The nomenclature used for the polystyrene samples and the graft copolymers specifies the composition and the structure of the molecules. For example, G1PS−PIP30 refers to a copolymer with $M_w \approx 30\,000$ PIP side chains grafted onto a G1 arborescent polystyrene substrate. The suffix (THF), when used, indicates that the PIP side chains were synthesized in tetrahydrofuran.

The synthesis of an arborescent copolymer (G0PS−PIP5) is demonstrated in Figure 2 with a series of SEC traces for (a) the chloromethylated polystyrene core (G0PS), (b) the polyisoprene side chains with $M_w \approx 5000$, (c) the raw grafting product, and (d) the fractionated copolymer. Three peaks can be observed in the SEC trace for the raw product (curve c). The leftmost (highest molecular weight) peak corresponds to the graft copolymer. The intermediate peak, with a molecular weight twice as high as the rightmost peak, is attributed to the formation of linear “dimer”. This occurs following a

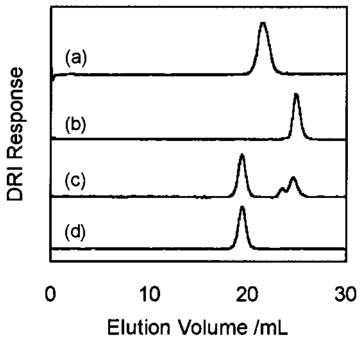


Figure 2. SEC chromatograms for the preparation of sample G0PS−PIP5: (a) chloromethylated G0 polystyrene, (b) polyisoprene side chains, (c) raw product from the grafting reaction, (d) fractionated graft copolymer.

metal−halogen exchange reaction with the chloromethylated polystyrene backbone,[2] to give a chlorine-terminated chain that couples with another polyisoprenyllithium molecule. The rightmost peak has the same molecular weight as the side chain sample removed from the reactor before the grafting reaction (curve b). It may correspond to either the nonreacted chlorine-terminated intermediate mentioned above or to polymer chains deactivated by residual protic impurities present in the chloromethylated polymer solution. Comparison of curves a and c demonstrates that no excess polystyrene substrate is present in the product, because the colorimetric titration procedure used allows exact monitoring of the reaction stoichiometry.

The grafting efficiency can be quantified from the size exclusion chromatography trace for the raw product, if the DRI detector response due to the polystyrene component of the copolymer is considered negligible. This is done by comparing the integrated peak area for the graft copolymer to the total area of all peaks. For sample G0PS−PIP5 (Figure 2c), the grafting efficiency amounts to 65%.

To demonstrate the necessity for DPE capping prior to grafting, the preparation of a comb-branched graft copolymer with short ($M_w \approx 5000$) side chains was attempted without capping agent, under conditions otherwise identical with those used to synthesize sample PS−PIP5. Virtually complete reaction of the linear polyisoprene side chains and backbone polymer was observed. However, linear dimer was formed as the main product, with only 44% graft copolymer yield. In contrast, the grafting yield for the reaction using DPE was 80%.

Anionic grafting processes are known to be sensitive to the polarity of the reaction medium. For example, reduced solvent polarity was reported to have a negative influence on the coupling yield of *uncapped* polystyryllithium with polychloromethylstyrene.[18] On the other hand, grafting efficiencies of up to 96% were observed with chloromethylated polystyrene in a benzene:THF 1:2 v/v mixture, when the polystyryllithium species were capped with DPE prior to grafting. The higher grafting efficiency is clearly linked to the suppresion of metal−halogen exchange reactions: In grafting DPE-capped polystyryl anions at −30 °C, dimer formation is almost nonexistent. In the present investigation, the grafting reaction was carried out with DPE-capped polyisoprenyl anions either in a cyclohexane:THF 7:3 v/v mixture or in pure THF. The results obtained for both reaction conditions are compared in Figure 3, when $M_w \approx 5000$ PIP side chains are grafted onto a G0 chloromethylated polystyrene sample. The graft polymer is not only obtained in lower yield in the less polar cyclohexane/THF mixture than in pure THF, but more dimer is also produced in the reaction. A series of copolymers were prepared by grafting different M_w PIP side chains onto a chloromethylated G0 polystyrene core in pure THF (Table 2). The grafting efficiencies achieved under these conditions are significantly higher than for the corresponding reactions in the cyclohexane−THF mixture, providing further evidence for the influence of solvent polarity on grafting efficiency.

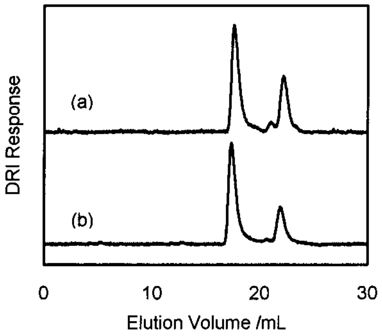


Figure 3. SEC chromatograms for raw grafting products: (a) G0PS−PIP5 and (b) G0PS−PIP5(THF).

An alternate explanation for the lower grafting yield in less polar environments could be a decreased efficiency of the capping reaction with DPE. Chains not capped with DPE are more susceptible to metal−halogen exchange, because of the higher reactivity of the anions. According to a related study on the synthesis of epoxide-terminated styrene−butadiene block copolymers using DPE capping, however, this seems unlikely to be the source of the problem: The reaction of polybutadienyl anions with DPE was shown to proceed rapidly and quantitatively, even at low THF concentrations in the reaction mixture.[19]

It is apparent from Table 2 that as the molecular weight of the polyisoprene side chains increases, the grafting efficiency tends to decrease for each core polymer. The effect is most pronounced for the G1PS substrate. Since the chloromethyl sites are, presumably, randomly distributed within the core polymer, all sites should react independently from each other. However, as the core polymer becomes more highly branched, it also becomes increasingly congested. A fraction of the chloromethyl sites should become less accessible to the polyisoprenyl anions, resulting in a decreased grafting efficiency. In a recent fluorescence quenching investigation of arborescent polystyrenes, two distinct “phases” could be identified within the molecules.[20] The inner, more rigid portion of the molecule was shown to be less accessible to quencher species than the outer, more flexible portion. The fraction of less accessible material was also shown to increase for higher generation polymers. This differential accessibility effect explains the decreases in grafting efficiency observed for higher generation chloromethylated polystyrene substrates.[2] An additional factor that may have contributed to a lower grafting efficiency is the inherent immiscibility of polystyrene and polyisoprene, making the grafting sites even less accessible to the macroanions.[21]

The molecular weights for the polyisoprene side chains and the fractionated graft copolymers, determined by either SEC analysis or light scattering, are summarized in Table 2. Some M_w(LS) values are miss-

Table 2. Characterization Data for the Arborescent Graft Copolymers Synthesized

	polyisoprene side chains			graft copolymers			
sample	M_w^{br} (SEC)[a]/ 10^3 g mol^{-1}	M_w^{br}/M_n^{br} (SEC)[a]	grafting efficiency	M_w^{app} (SEC)[b]/ 10^3 g mol^{-1}	M_w^{app}/M_n^{app} (SEC)[b]	M_w (LS)/ 10^3 g mol^{-1}	f_w
PS−PIP5	4.5	1.07	0.80	54	1.11	50.2	11
PS−PIP30	35	1.03	0.66	222	1.10	421	12
PS−PIP100	118	1.08	0.43	733	1.13		
G0PS−PIP5	4.7	1.06	0.65	169	1.07	575	112
G0PS−PIP30	32	1.06	0.63	461	1.13	2760	85
G0PS−PIP100	112	1.03	0.35	683	1.12	4010	35
G1PS−PIP5	5.1	1.09	0.71	393	1.11	5640	950
G1PS−PIP30	35	1.05	0.18	666	1.11	8180	225
G1PS−PIP100	118	1.07	0.06	901	1.07		
G0PS−PIP5(THF)	5.5[b]	1.06[b]	0.92	135	1.15	825	
G0PS−PIP30(THF)	30[b]	1.06[b]	0.69	168	1.07	3740	
G0PS−PIP100(THF)	99[b]	1.12[b]	0.60	540	1.13		

[a] SEC calibrated using linear standards with an average microstructure of 71% *cis*-1,4-, 22% *trans*-1,4-, and 7% 3,4-polyisoprene. [b] Apparent molecular weights determined using SEC calibrated with linear polystyrene standards.

Table 3. Microstructure and Polyisoprene Content Analysis

			polyisoprene microstructure/mol %			
sample	polyisoprene/ % w/w (UV)	polyisoprene/ % w/w (^{1}H NMR)	*cis*-1,4	*trans*-1,4	3,4	1,2
PS−PIP5	83	90	72	23	5	∼0
PS−PIP30	94	>98	72	22	6	∼0
PS−PIP100	>97	>98	63	28	8	∼0
G0PS−PIP5	87	84	67	27	6	∼0
G0PS−PIP30	88	94	71	24	5	∼0
G0PS−PIP100	>97	>98	79	17	4	∼0
G1PS−PIP5		80	63	29	8	∼0
G1PS−PIP30		94	70	24	6	∼0
G1PS−PIP100		>98	72	23	5	∼0
G0PS−PIP5(THF)	77	84	34		34	29
G0PS−PIP30(THF)	91	97	38		34	28
G0PS−PIP100(THF)	>97	>98	37		39	27

ing, due to the impossibility of purifying the copolymers in sufficiently large amounts for the light scattering measurements. The results from SEC analysis for the polyisoprene side chains demonstrate that a narrow molecular weight distribution was achieved. For the different graft copolymers prepared, the polydispersity index likewise remains relatively low ($M_w^{app}/M_n^{app} \approx$ 1.07−1.15). While the polydispersity indices obtained are only apparent values based on a polystyrene standards calibration curve, they still suggest that a narrow molecular weight distribution was maintained for the copolymers. It is evident from Table 2 that the M_w^{app} values determined by SEC analysis are strongly underestimated for the graft copolymers compared with the absolute M_w(LS) values obtained from light scattering, indicating a very compact structure.

The branching functionality (f_w) of the copolymers, calculated according to eq 1, ranges from 11 to 950. No branching functionality calculations were attempted for the copolymers prepared in THF, because only apparent characterization data were available for the side chains. The f_w values determined for the copolymers are either identical with (within error limits) or lower than the number of grafting sites calculated for the chloromethylated polystyrene substrates (Table 1). The trends observed among the different copolymer series are consistent with the variations in grafting efficiency discussed previously: f_w decreases relative to the theoretical (calculated) value for polymers with longer PIP side chains and for higher generation substrates. This unfortunately leads to variations in branching functionality within a series of copolymers based on the same polystyrene grafting substrate. It would obviously be preferable, in terms of establishing structure−property correlations, to generate a series of samples for which the branching functionality remains constant and only the side chain molecular weight varies. It was shown in a previous study that 128-arm star polybutadienes can be prepared by coupling with a dense carbosilane dendrimer substrate.[22] It was also pointed out that the use of a Θ-solvent is preferable to increase the coupling yield under these conditions. Unfortunately, it is not clear how this concept could be applied to the synthesis of arborescent graft copolymers, since both components are high molecular weight polymers, making it impossible to find a solvent for the grafting reaction that is simultaneously a Θ-solvent for both the polystyrene and polyisoprene components.

Composition analysis for the different graft copolymer samples (Table 3) indicates a polyisoprene content varying from 77% to over 98 wt %. This demonstrates that when short PIP side chains are grafted (or alternately if grafting substrates with a lower chloromethylation level were used), copolymers containing a significant polystyrene component are obtained. When longer polyisoprene side chains are grafted on the substrate, the polystyrene component becomes essentially undetectable. This is seen in comparing the ^{1}H NMR spectra in parts a and b of Figure 4 for graft copolymers with $M_w \approx$ 5000 and 30 000 polyisoprene side chains, respectively. The polyisoprene contents determined by UV−vis spectrophotometry are in good agreement with the values determined using ^{1}H NMR spectroscopy. The slightly higher (3−5 mol %) values found by UV−vis analysis could be due to differences in the relaxation characteristics of the polyisoprene and polystyrene components affecting the intensity of the peaks in the NMR spectra.

The microstructure of the polyisoprene side chains determined for the copolymers prepared (Table 3) using

^{1}H NMR spectroscopy consists of a high proportion of *cis*-1,4-polyisoprene units when cyclohexane is used as the polymerization solvent. The proportion of *cis*-1,4-polyisoprene varies from 63 to 79 mol %, while the *trans*-1,4-units content varies from 17 to 29 mol %, the balance of the monomer being incorporated as 3,4-units (4−8 mol %). The microstructure variations can be explained by the different initiator concentrations used in each experiment. Worsfold and Bywater[23] have shown that, for the anionic polymerization of isoprene, the proportion of 3,4-units remains constant (ca. 5−6%), while the *cis*-1,4-content decreases relative to the *trans*-1,4-content as either the initiator concentration is increased or the monomer concentration is decreased. At 20 °C and with an initiator concentration on the order of 10^{-3} M, the alkyllithium-initiated polymerization of isoprene is expected to yield a *cis:trans* ratio of approximately 70:30, with ca. 5−6% 3,4-polyisoprene units.[24] When short polyisoprene side chains were prepared, the initiator concentration was higher than for the longer side chains ($M_w \approx 30\,000$ and 90 000), and consequently, the *cis*-1,4-content is somewhat lower.

The polyisoprene side chains prepared in THF have a mixed microstructure, with roughly equal proportions of 1,4-, 3,4-, and 1,2-polyisoprene units (Table 3). No distinction can be made between *cis*-1,4- and *trans*-1,4-units in this case, because of peak overlap. The ^{1}H NMR spectrum for a graft copolymer with $M_w \approx 30\,000$ side chains prepared in THF is shown in Figure 4c. Individual peaks are not completely resolved in the spectrum, making it necessary to deconvolute the peaks of interest to calculate peak areas used in the microstructure analysis.[17] The calculated values are in agreement with those previously reported by Bywater and Worsfold[12] for the free-ion propagation of polyisoprenyllithium in THF.

Scanning force microscopy pictures were obtained for selected samples in the phase contrast mode. In this type of measurement, the phase lag between the stress applied on the sample by the scanning tip and the cantilever deflection is measured, in analogy to dynamic mechanical measurements. Phase contrast pictures obtained for samples G0PS−PIP5 and G1PS−PIP5 are compared in Figure 5. The copolymer based on a comb polystyrene substrate (G0PS−PIP5) displays little contrast, hinting at partial “mixing” or at least at a diffuse boundary between the polystyrene and polyisoprene components of the molecules. For the sample derived from a G1 core (G1PS−PIP5), however, more pronounced phase contrast (ca. 10°−12°) is observed between the two components. Isolated nodules with an average diameter of about 15 nm, corresponding to glassy polystyrene-rich cores, are clearly visible on the picture and surrounded by a darker polyisoprene-rich shell forming a nearly continuous rubbery matrix in the film. The average polystyrene core diameter of 15 nm is close to the diameter of 19 nm measured for monomolecular films of arborescent polystyrene molecules with a similar structure.[25] Phase contrast measurements were also attempted on sample G1PS−PIP30, but no significant contrast was obtained, indicating that the film surface probed was essentially homogeneous. This is presumably due to the very low polystyrene content in the copolymer (6% w/w) making the core undetectable, as would be expected for a star-branched structure of the type shown in Figure 1b. The microscopy characterization results show that arborescent copolymers with different morphologies can be obtained, depending on the synthetic conditions used. Well-defined core−shell morphologies are obtained for higher generation subtrates grafted with short side chains, but properties similar to branched homopolymers are observed for structures incorporating long side chains.

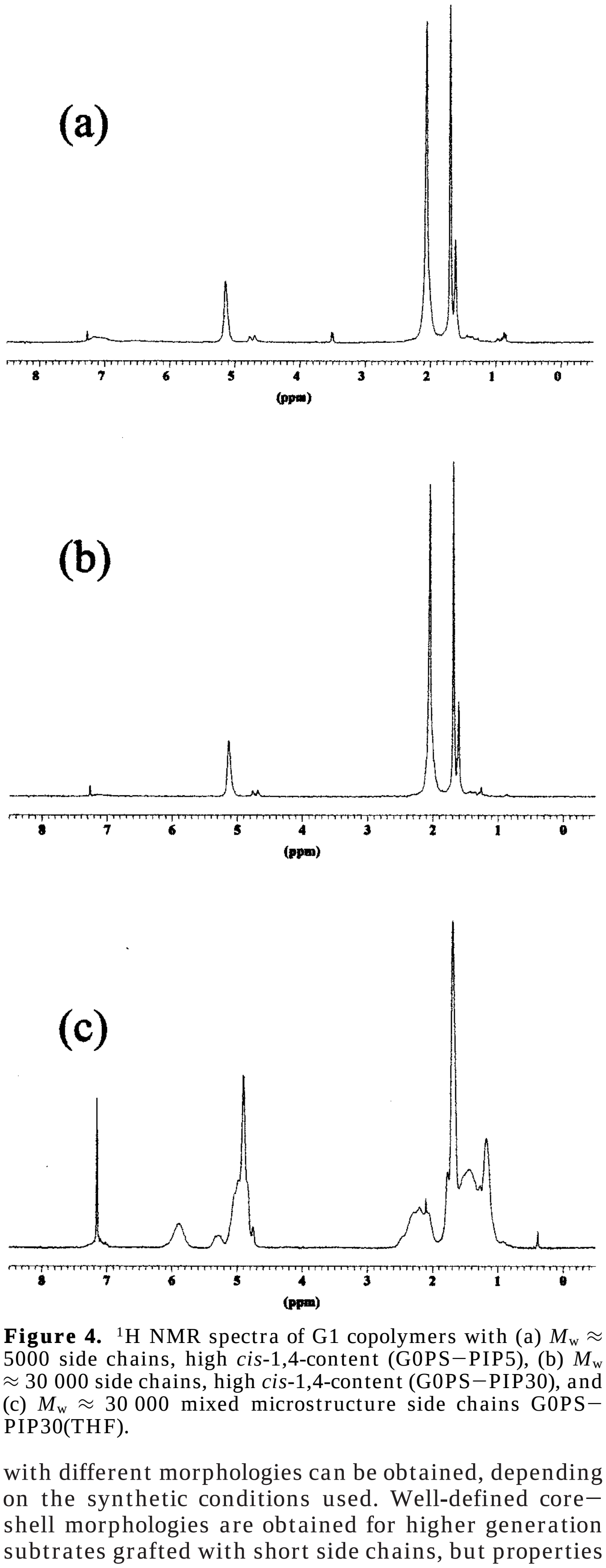


Figure 4. ^{1}H NMR spectra of G1 copolymers with (a) $M_w \approx$ 5000 side chains, high *cis*-1,4-content (G0PS−PIP5), (b) $M_w \approx 30\,000$ side chains, high *cis*-1,4-content (G0PS−PIP30), and (c) $M_w \approx 30\,000$ mixed microstructure side chains G0PS−PIP30(THF).

Conclusions

The results reported demonstrate that it is possible to extend the graft-on-graft technique to the preparation of highly branched graft copolymers containing side chains randomly grafted on a polystyrene substrate.

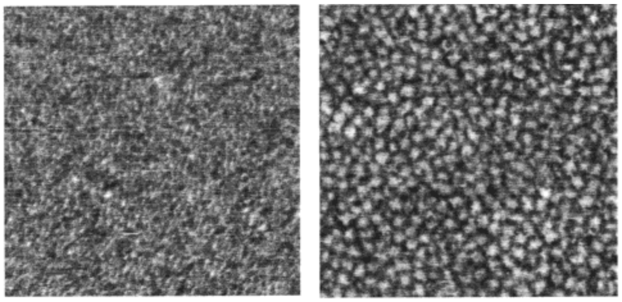


Figure 5. Phase contrast scanning force pictures for samples G0PS−PIP5 (left) and G1PS−PIP5 (right). The width of each picture is 500 nm.

Control over the polyisoprene side chain molecular weight and microstructure was achieved while maintaining a narrow apparent polydispersity for the graft copolymers ($M_w/M_n \approx 1.07-1.15$). The method was demonstrated for the special case of a dense polystyrene substrate with a high density of grafting sites. Different materials with a wider range of properties could presumably be obtained if the structure of the polystyrene substrate is varied. Likewise, the yield of the grafting reaction may be increased if grafting substrates with a lower chloromethylation level are used, to decrease the influence of steric exclusion effects. Scanning force microscopy measurements confirm the existence of microphase separation occurring to different extents for these molecules, depending on their structure. Detailed physical property investigations of these materials, in terms of dilute solution and rheological properties, will be the subject of future reports.

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References and Notes

(1) For an overview of the synthesis and properties of dendritic polymers, see for example: (a) *Advances in Dendritic Molecules*; Newkome, G. R., Ed.; JAI: Greenwich, CT, 1994−6; Vols. 1−3. (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules, Concepts, Syntheses, Perspectives*; VCH: New York, 1996.

(2) Gauthier, M.; Möller, M. *Macromolecules* **1991**, *24*, 4548.

(3) Tomalia, D. A.; Hedstrand, D. H.; Ferrito, M. S. *Macromolecules* **1991**, *24*, 1435.

(4) Hempenius, M. A.; Michelberger, W.; Möller, M. *Macromolecules* **1997**, *30*, 5602.

(5) Gauthier, M.; Möller, M.; Burchard, W. *Macromol. Symp.* **1994**, *77*, 43.

(6) Gauthier, M.; Tichagwa, L.; Downey, J. S.; Gao, S. *Macromolecules* **1996**, *29*, 519.

(7) (a) Fetters, L. J.; Morton, M. *Macromolecules* **1974**, *7*, 552. (b) Hadjichristidis, N.; Roovers, J. E. L. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2521. (c) Hadjichristidis, N.; Guyot, A.; Fetters, L. J. *Macromolecules* **1978**, *11*, 668. (d) Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1980**, *13*, 191.

(8) (a) Roovers, J. E. L.; Bywater, S. *Macromolecules* **1972**, *5*, 384. (b) Roovers, J. E. L.; Bywater, S. *Macromolecules* **1974**, *7*, 443.

(9) Price, C.; Woods, D. *Polymer* **1973**, *14*, 82.

(10) (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.

(11) Worsfold, D. J.; Bywater, S. *Can. J. Chem.* **1964**, *42*, 2884.

(12) Bywater, S.; Worsfold, D. J. *Can. J. Chem.* **1967**, *45*, 1821.

(13) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155.

(14) Weiss, W. *J. Occup. Med.* **1976**, *18*, 194.

(15) Kratochvíl, P. *Classical Light Scattering from Polymer Solutions*; Elsevier: Amsterdam, 1987; Chapter 5.

(16) Chen, H. Y. *Anal. Chem.* **1962**, *34*, 1134.

(17) Essel, A.; Pham, Q.-T. *J. Polym. Sci., Part B* **1970**, *8*, 723.

(18) (a) Takaki, M.; Asami, R.; Ichikawa, M. *Macromolecules* **1977**, *10*, 850. (b) Takaki, M.; Asami, R.; Kuwata, Y. *Polym. J.* **1979**, *11*, 425.

(19) Quirk, R. P.; Zhuo, Q. *Macromolecules* **1997**, *30*, 1531.

(20) Frank, R. S.; Merkle, G.; Gauthier, M. *Macromolecules* **1997**, *30*, 5397.

(21) Quirk, R. P. Personal communication.

(22) Roovers, J.; Zhou, L.-L.; Toporowski, P. M.; van der Zwan, M.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 4324.

(23) Worsfold, D. J.; Bywater, S. *Macromolecules* **1978**, *11*, 582.

(24) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1.

(25) Sheiko, S. S.; Gauthier, M.; Möller, M. *Macromolecules* **1997**, *30*, 2343.

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