Macromolecules **2005,** *38,* 4124−4132

Synthesis of Arborescent Isoprene Homopolymers

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Received October 4, 2004; Revised Manuscript Received March 4, 2005

ABSTRACT: A method was developed for the preparation of isoprene homopolymers with a dendritic architecture using an anionic “grafting onto” methodology. A linear polyisoprene substrate with a high (95%) 1,4-content was first epoxidized to introduce grafting sites randomly along the chain. Coupling of the epoxidized polyisoprene with polyisoprenyllithium yielded a comb-branched or generation G0 arborescent polyisoprene. *N,N,N′,N′*-Tetramethylethylenediamine, BF_3, Me_3Al, LiCl, and LiBr were investigated as promoters for the coupling reaction. Lithium salts were most effective, increasing the grafting yield from 78% to 92% for a linear substrate. Further epoxidation and grafting of the G0 polyisoprene led to arborescent isoprene homopolymers of generations G1 and G2. The attempted synthesis of a G3 arborescent polyisoprene was unsuccessful. The graft polymers were purified by precipitation fractionation and characterized by size exclusion chromatography (SEC), light scattering, and NMR spectroscopy. The products have narrow molecular weight distributions ($M_w/M_n \leq 1.05$) consistent with a uniform molecular size and display geometric increases in molecular weight and branching functionality for successive generations. The absolute weight-average molecular weight values determined from light scattering measurement are much higher than the apparent SEC values because of the highly branched structure of the molecules.

Introduction

Dendrimers, hyperbranched, and arborescent polymers are characterized by a treelike or dendritic architecture incorporating multiple branching levels. These materials have unique properties making them potentially useful in a wide range of applications including controlled drug delivery vehicles, rheology modifiers for polymer processing, and catalyst carriers.[1−4]

Arborescent polymers are typically synthesized using cycles of substrate functionalization and anionic grafting reactions.[5] Coupling sites are first introduced randomly on a linear substrate and reacted with a “living” polymer to yield a comb-branched or generation zero (G0) arborescent polymer. Repetition of the functionalization and grafting cycles leads to upper generation (G1, G2, ...) arborescent polymers, with a molecular weight and branching functionality increasing geometrically for successive generations. Both chloromethyl[6] and acetyl[7] functionalities have been used as coupling sites for the preparation of arborescent styrene homopolymers. Copolymers were also obtained by grafting other macroanions onto arborescent polystyrene substrates.[8,9] Anionic grafting was likewise used by Hempenius et al.[10] for the synthesis of arborescent butadiene homopolymers. Coupling sites were introduced by exhaustive hydrosilylation with dimethylchlorosilane of the pendent vinyl group of 1,2-units on a polybutadiene substrate and reacted with polybutadienyllithium. Unfortunately, the chlorosilane intermediate obtained was hydrolytically unstable, which precluded its storage prior to the reaction. Another problem encountered in this approach is that it would be difficult to vary the branching density of the graft polymers, since the 1,2-butadiene units content of the substrate is determined by the polymerization conditions used.

A technique was proposed by Ruckenstein and Zhang[11] for the synthesis of comb copolymers by reacting “living” macroanions with random copolymers of alkyl methacrylates and glycidyl methacrylate. The reaction of the pendent (terminal) epoxide functionalities of glycidyl methacrylate units proceeded quantitatively with polystyryllithium and polyisoprenyllithium. The comb polymers obtained had narrow molecular weight distributions, since anionic polymerization served to generate the backbone copolymer as well as the macroanions used as side chains in the reaction. Unfortunately, this synthetic strategy could not lend itself to the generation of dendritic architectures.

We now report on the synthesis of arborescent (dendrigraft) diene homopolymers based on epoxide coupling sites. While grafting onto terminal (unhindered) epoxide functionalities has been achieved with success,[11] this is not the case for intrachain (hindered) epoxide species. Correspondingly, much effort was devoted to optimizing the reaction conditions in order to maximize the grafting yield attained. Controlled epoxidation of the polyisoprene substrates provides a flexible method to vary the branching density of the molecules. The epoxidized substrates are stable and may be stored before the subsequent coupling step. The grafting reaction proceeds in up to 92% yield in the presence of lithium salts. The success of the synthetic methods used is demonstrated with light scattering, size exclusion chromatography, and NMR spectroscopy analyses for arborescent isoprene homopolymers of generations up to G2.

Experimental Section

Solvent and Reagent Purification. Hexane (BDH, mixture of isomers, HPLC Grade) was purified by refluxing with *n*-butyllithium in the presence of 2,2′-bipyridyl (30 mg/L) under nitrogen[12] and introduced directly from the still into the polymerization reactor through poly(tetrafluoroethylene) (PTFE) tubing. Tetrahydrofuran (THF, Caledon, reagent grade) was refluxed and distilled from sodium−benzophenone ketyl under nitrogen. Isoprene (Aldrich, 99%) was first distilled from CaH_2

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10.1021/ma0479565 CCC: $30.25

and further purified immediately before polymerization by addition of *n*-BuLi (2.5 M solution in hexane, 1 mL solution per 20 mL isoprene) and degassing with three freezing–evacuation–thawing cycles, before recondensation into an ampule with a PTFE stopcock.[8,9] The monomer ampules were stored at −78 °C before use. Boron trifluoride diethyl etherate (Aldrich, redistilled) was distilled twice before use. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA, Aldrich, 99%) was first distilled from CaH_2 and then from *n*-butyllithium. The initiator *tert*-butyllithium (*t*-BuLi, Aldrich, 1.7 M solution in pentane) was used as received; its exact concentration was determined to be 1.90 M by the method of Lipton et al.[13] 2,2′-Bipyridyl (Aldrich, 99+%) was dissolved in dry hexane to give a 0.10 M solution. LiCl (Aldrich, 99.9%), LiBr (Aldrich, 99+%), Me_3Al (Aldrich, 2.0 M in toluene), toluene (BDH, HPLC grade), hydrogen peroxide (BDH, 29–32% w/w), and formic acid (BDH, 96%) were used as received from the suppliers.

Isoprene Polymerization. An isoprene monomer ampule (30.0 g, 0.441 mol), the hexane line from the purification still, and a rubber septum were mounted on a four-neck 500 mL round-bottomed flask with a magnetic stirring bar. The flask was flamed under high vacuum and filled with purified nitrogen. Hexane (100 mL) was added to the flask, followed by 0.5 mL of 0.10 M 2,2′-bipyridyl solution in hexane, and the solvent was titrated with *t*-BuLi to give a persistent light orange color.[12] The initiator (3.2 mL, 6.0 mmol *t*-BuLi, for a calculated $M_n = 5000$) was injected in the reactor, and the isoprene was added dropwise from the ampule. The flask was maintained in a water bath at room temperature (25 °C) for 5 h, and the reaction was terminated with nitrogen-purged 2-propanol. The crude product (29.5 g) was recovered by precipitation in methanol and drying under vacuum for 24 h. The polymer had an absolute $M_w = 5400$ ($M_w/M_n = 1.06$) as determined by SEC analysis with a multiangle laser light scattering (MALLS) detector and a microstructure with 75% *cis*-1,4-, 20% *trans*-1,4-, and 5% 3,4-units as determined by ^{13}C NMR spectroscopy analysis from the integrated methyl carbon resonances for *cis*-1,4- (23.5 ppm), *trans*-1,4- (16.0 ppm), and 3,4-microstructures (18.7 ppm).[14]

Epoxidation of Polyisoprene. The reaction conditions used for all polyisoprene substrates were derived from the methods reported by Gnecco et al.[15] and Wang et al.[16] The epoxidation of a linear polymer is provided as an example. Toluene (200 mL), polyisoprene (10.0 g, 0.147 equiv isoprene units, absolute $M_w = 5400$, $M_w/M_n = 1.10$), and 7.50 g of formic acid (0.156 mol) were combined in a 500 mL jacketed round-bottomed flask with a magnetic stirring bar. The flask was heated to 40 °C with a circulating water bath, and 17.7 g of H_2O_2 solution (about 0.16 mol) was added dropwise with stirring over 20 min. The reaction was continued at 40 °C for 50 min. The organic phase was washed with water until the aqueous layer reached pH 7. The polymer solution was filtered, precipitated in methanol, and dried under vacuum for 24 h (yield 10.3 g, apparent $M_w = 6800$, $M_w/M_n = 1.10$). The epoxidation level of the sample, determined by ^1H NMR analysis from the relative intensities of the C=C−*H* resonance in 1,4-units (5.10 ppm) and the corresponding proton resonance in epoxidized 1,4-units (2.70 ppm), and assuming that 3,4-isoprene units were unreacted, was 23 mol %.

Grafting Reaction. The preparation of a G0 (comb-branched) polyisoprene sample using the optimized reaction conditions is provided as an example of a graft polymer synthesis. The linear epoxidized polyisoprene substrate (1.9 g, 23% epoxidation, 6.2 mmol equiv epoxide units) was purified in an ampule with three azeotropic drying cycles using THF[6] before redissolution in 100 mL of dry THF. A four-neck 500 mL round-bottomed flask with a magnetic stirring bar was set up with an isoprene ampule (28.3 g, 0.416 mol), the epoxidized substrate ampule, the dry hexane inlet, and a septum. Solid LiBr (3.0 g, 34.5 mmol) was loaded in the polymerization reactor before the flask was evacuated, flamed, and then purged with nitrogen. Isoprene was polymerized with 3.0 mL of *t*-BuLi solution (5.6 mmol, for a target $M_n = 5000$) in 50 mL of hexane under the conditions described above. After 5 h a sample was removed and terminated with degassed 2-propanol to determine the side chain molecular weight. The epoxidized substrate solution was added to the flask, and the grafting reaction was allowed to proceed for 60 h at room temperature. Sample aliquots were removed by syringe every 6 h and terminated with degassed water to monitor the progress of the reaction. Residual macroanions were terminated with degassed water, and the crude product (28.7 g) was recovered by precipitation in methanol and dried under vacuum. The crude graft polymer was purified by precipitation fractionation from hexane/2-propanol mixtures to remove the linear polyisoprene contaminant. The fractionated G0 polymer (absolute $M_w = 87\,000$, $M_w/M_n = 1.10$) was further epoxidized and grafted with polyisoprene side chains according to the procedures described above to yield upper generation polymers.

Polymer Characterization. Size exclusion chromatography (SEC) served to determine the grafting yield as well as apparent and absolute molecular weight and polydispersity index (M_w/M_n) values for the side chain and graft polymer samples. Routine analysis, used to determine the grafting yield and apparent molecular weight, was done at 25 °C on an instrument consisting of a Waters 510 HPLC pump, a 500 mm × 10 mm Jordi DVB mixed-bed linear column (molecular weight range 10^2–10^7), and a Waters 410 differential refractometer (DRI) detector. Tetrahydrofuran at a flow rate of 1 mL/min served as eluent, and linear polystyrene standards were used to calibrate the instrument. The absolute weight-average molecular weight (M_w) and polydispersity index of selected samples were determined from SEC-MALLS (multi-angle laser light scattering) measurements using a Wyatt Dawn DSP-F instrument operating at 632.8 nm. The effect of the second virial coefficient was not considered in the molecular weight calculations, which may result in slightly (<5%) underestimated molecular weight values.[6] The SEC-MALLS system used consists of a Waters 590 programmable HPLC pump coupled with Waters Ultrastyragel columns (10^4, 10^5, and 10^6 Å pore sizes) using THF at a flow rate of 1 mL/min. Polymer concentration measurements in the eluent were accomplished with a Waters 2410 DRI detector operating at 660 nm. The refractive index increment of the samples was measured at 25 °C on a Brice-Phoenix differential refractometer equipped with a 632 nm band-pass interference filter.

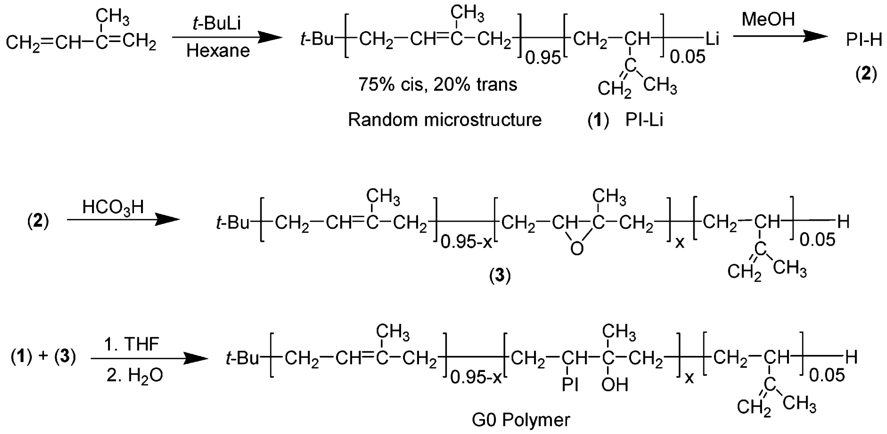
Dynamic light scattering measurements were performed on a Brookhaven BI-200SM instrument equipped with a BI-2030AT 201-channel correlator at a temperature of 25 °C and a scattering angle of 90°, using a Lexel 2 W argon ion laser operating at 514.5 nm. The polymer samples were dissolved in THF at concentrations of 0.01–0.1% w/v and filtered with 0.2–0.5 μm PTFE filters, depending on the generation number. The correlator was operated in the exponential sampling mode, the last four data acquisition channels being used for baseline measurements. The translational diffusion coefficients used in the hydrodynamic diameter calculations were determined from second-order analysis of the normalized electric field correlation function $|g^1(\tau)|$.

^1H NMR spectra were acquired for the polyisoprene, epoxidized polyisoprene, and graft polyisoprene samples on a Bruker-300 (300 MHz) instrument in $CDCl_3$ at a concentration of 5%. ^{13}C NMR inverse gated spectra for quantitative microstructure analysis of polyisoprene samples were acquired at 75.5 MHz (25 °C) on the same instrument in $CDCl_3$ at a concentration of 40%. The ^{13}C acquisition parameters used were pulse width 3.27 μs (flip angle of 30°), acquisition time 0.92 s (sweep width of 17 730 Hz), and pulse spacing 3 s (6 × relaxation time for sp^3-hybridized carbon in polyisoprene as determined by Schaefer[17]).

Results and Discussion

The reaction sequence serving in the preparation of arborescent polyisoprenes is depicted in Scheme 1. Linear polyisoprene (**2**) was first functionalized by partial epoxidation to introduce grafting sites randomly along the polymer chain. The epoxidized substrate (**3**), upon reaction with polyisoprenyllithium (**1**), yielded a

Scheme 1. Grafting Reaction



comb-branched (G0) isoprene homopolymer. The G0 polymer was subjected to additional cycles of epoxidation and grafting to obtain upper generation arborescent polymers under similar conditions. Different promoters were investigated to increase the rate and yield of the coupling reaction. Scheme 1 is somewhat oversimplified since possible residual epoxide functionalities, likely present in the grafting product, have been omitted for the sake of clarity.

Polymerization of Isoprene. The microstructure of polyisoprene chains obtained is strongly dependent on the polarity[18] of the solvent used and, to a lesser extent, on the initiator and monomer concentration in the reaction.[19] In nonpolar (hydrocarbon) solvents a predominantly *cis*-1,4-microstructure resembling natural rubber is obtained, while the polymerization in THF (a more polar solvent) leads to a mixed microstructure with 1,4-, 1,2-, and 3,4-isoprene units. In hydrocarbon solvents, the *cis*-1,4-content increases when the initiator concentration is decreased or the monomer concentration is increased. Because of the good elastomeric properties of *cis*-1,4-polyisoprene and its high reactivity in the epoxidation reaction, hexane was preferred as a polymerization solvent in the present study. The ^{1}H NMR spectrum shown in Figure 1a is for a linear polyisoprene sample obtained under the conditions described. By comparing the NMR peak areas at 5.10 ppm (olefinic protons of the *cis*- and *trans*-1,4-microstructures) and the doublet at 4.73 and 4.66 ppm (two vinylic protons of the 3,4-microstructure), the content of 1,4-units (*cis*- and *trans*-isomers combined) and 3,4-units was estimated to be 95% and 5%, respectively.[20] The microstructure of the polyisoprene chains was also analyzed by ^{13}C NMR spectroscopy according to the procedure of Morèse-Séguéla et al.[14] The analysis using methyl substituent resonances yielded a microstructure consisting of 73 ± 2% *cis*-1,4-, 22 ± 2% *trans*-1,4-, and ~5% 3,4-isoprene units.

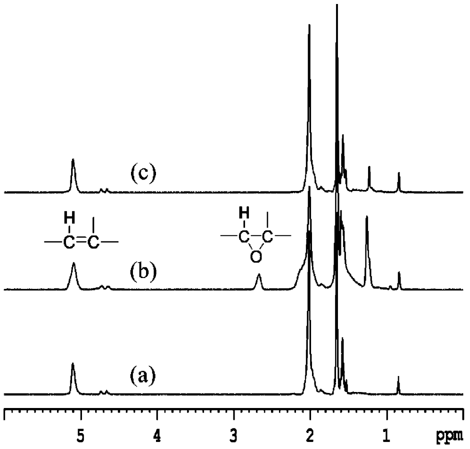


Figure 1. ^{1}H NMR spectra for the synthesis of G0 arborescent polyisoprene under optimized conditions: (a) linear polyisoprene (absolute $M_w = 5400$), (b) epoxidized linear polyisoprene (23 mol % substitution), and (c) fractionated G0 graft polymer (absolute $M_w = 87\,000$).

Epoxidation Reaction. The epoxidation of alkenes by organic peracids is an electrophilic reaction, so a higher electron density at the double bond favors epoxidation. Alkyl substitution increases the electron density at the double bond and hence its reactivity. The reaction is also relatively insensitive to steric effects.[21] Consequently, the reactivity order for substituted alkenes toward epoxidation decreases in the order tetra → tri → di → mono → unsubstituted.[21,22] The ^{1}H NMR spectrum for an epoxidized linear polyisoprene sample is provided in Figure 1b. The 3,4-isoprene units, less substituted than 1,4-units, appear to be essentially unreacted, although this is difficult to quantify reliably due to their low concentration in the polymer (5%). Upon epoxidation, the alkene proton on 1,4-units (5.10 ppm) is shifted upfield to 2.70 ppm.[15,23] The methylene protons at 2.00 ppm in 1,4-polyisoprene are shifted slightly downfield after epoxidation and visible as a shoulder on the peak at 2.00 ppm. Peaks also appear upon epoxidation at 1.26 and 0.96 ppm. These resonances are attributed to the methyl group of epoxidized 1,4-isoprene units and *tert*-butyl groups connected to terminal epoxidized 1,4-isoprene units, respectively. If the 3,4-units are assumed to be unreacted, the epoxidation level can be estimated by comparing the area of the peaks at 5.10 and 2.70 ppm (one proton on unreacted and epoxidized double bonds of 1,4-isoprene units, respectively).

Side reactions, and in particular ring opening of the epoxide, take place at high acid concentrations and reaction temperatures.[24] The alcohol functionality resulting from ring opening would interfere with the grafting reaction by terminating the living chains. Ring opening was avoided under the conditions used (no resonance at 3.3 ppm).[15] Because epoxidation is a heterogeneous reaction, variations in the stirring efficiency can cause fluctuations in the epoxidation level attained. Nevertheless, by controlling the stirring rate, substrates with 23−28 mol % epoxidation levels were consistently obtained for grafting substrates of all generations (Table 1). Performic acid, generated in situ

Table 1. Results of Epoxidation Reactions for Linear-G2 Polyisoprene Substrates with Performic Acid in Toluene at 40 °C

polyisoprene substrate			product	
generation	M_w [a]/10^3	M_w/M_n [b]	E[c]/mol %	M_w/M_n [b]
linear	5.4	1.10	23	1.10
G0	87	1.10	26	1.10
G1	1100	1.09	24	1.09
G2	10000	1.08	28	1.09

[a] Absolute M_w measured by MALLS. [b] Apparent M_w/M_n measured by SEC analysis with linear polystyrene calibration curve. [c] Epoxidation level determined by ^{1}H NMR analysis.

from formic acid and hydrogen peroxide, is an excellent epoxidation reagent due to its low cost and the relatively good reproducibility of the substitution level achieved in the reactions. The apparent molecular weight and molecular weight distribution of the polymers display little variation upon epoxidation, with only a slight increase in apparent molecular weight and without broadening of the molecular weight distribution due to chain scission observed for long reaction times and high temperatures.[25]

Optimization of Grafting Reaction. A series of reactions were carried out to maximize the grafting yield, defined as the fraction of polyisoprenyllithium chains generated in the reaction that becomes attached to the substrate. Optimization of the reaction conditions is a critical aspect of arborescent polymer synthesis because of the multiple functionalization and grafting cycles used to obtain polymers of successive generations. Increasing the yield of the grafting reaction not only improves the overall product yield but also simplifies purification of the crude product by minimizing the amount of linear contaminant present.

The grafting yield can be approximated in SEC analysis of the crude product by dividing the peak area (from the DRI detector) of the graft polymer by the total peak areas for the graft polymer and the residual linear chains. While the molecular weights of the linear epoxidized substrate and the side chains are similar, the hydrodynamic volume of the graft polymer is significantly larger, and two well-resolved peaks are observed in the SEC trace for the graft polymer and for residual side chain material (see, for example, Figures 2a and 3c). This approach is sufficient for the purpose of optimizing the reaction conditions but slightly overestimates the grafting yield. This is because part of the response for the graft polymer peak is due to the grafting substrate. A more accurate calculation method, requiring knowledge of either the absolute molecular weight of the substrate and the graft polymer or the reaction stoichiometry used, will be described subsequently. Polyisoprenyllithium and linear epoxidized polyisoprene substrates with $M_w \approx 5000$ and $M_w/M_n \leq 1.10$ were used for all test reactions. Either hexane or hexane−THF mixtures, alone or in combination with various promoters, served as solvent for the grafting reactions.

Grafting without Promoters. The grafting yields obtained without promoters under different solvency conditions are summarized in Table 2. Polyisoprenyllithium was synthesized from 5.6 mmol of *t*-BuLi and 28 g of isoprene in 50 mL of hexane prior to grafting in all cases; THF, when present, was added as a solvent in the epoxidized substrate ampule. A mole ratio of living chains to epoxide functionalities of 0.8 (corresponding to 25% excess epoxide) was used initially in the optimization procedures.

Table 2. Influence of Solvent Composition and Temperature on Grafting Yield Attained for Linear Epoxidized Polyisoprene and Polyisoprenyllithium in the Absence of Promoters[a]

hexane:THF/mL:mL	temp/°C	time[b]/h	grafting yield/%
150:0	25	24	31
		48	68
100: 50	25	24	61
		36−48[c]	69
75:75	25	12	73
		24−44[c]	76
50:100	25	6	74
		12−18	78
50:150	25	9−12	75
50:100	0	12	55
		24	67
50:100	40	6−9[c]	72

[a] All reactions with 26% epoxidized linear polyisoprene substrate (apparent $M_w = 6100$, $M_w/M_n = 1.10$), with a living end-to-epoxide ratio of 0.8 (25% excess epoxide); 5.6 mmol initiator used to generate side chains. [b] A time range indicates that the grafting yield did not change significantly (±1%) over that interval. [c] Reaction stopped after living ends coloration disappeared.

It is quite clear, on the basis of the results reported in Table 2, that the coupling reaction is very slow under all conditions investigated. For comparison, Ruckenstein et al.[11] reported quantitative coupling of polyisoprenyl and polystyryl anions with linear glycidyl methacrylate copolymers after 30 min at −30 °C, using THF−benzene or THF−cyclohexane mixtures with LiCl added. In this case, the polyisoprenyl anion:epoxide ratio was varied from 0.22 to 0.35, while the polystyryl anion:epoxide ratio ranged from 0.18 to 0.72. The quantitative grafting yields and faster reactions observed for polyisoprenyl anion grafting onto glycidyl moieties could be explained in part by the larger excess of epoxide functionalities used in the reactions. More importantly, the better accessibility and minimal steric crowding of pendent (terminal) epoxide sites in the glycidyl methacrylate copolymers likely explains the fast coupling rates observed. The intrachain epoxidized 1,4-units of the polyisoprene substrates are much more hindered.

The results of Table 2 clearly show that THF enhances the rate of the coupling reaction. While only 31% of the side chains were coupled with the substrate after 24 h in pure hexane at 25 °C, the yield increased to 74% after only 6 h in a 1:2 hexane/THF mixture. The maximum grafting yield attained without promoters is 78%, in the same solvent mixture after 12 h. Further increase in THF content to a 1:3 ratio led to an insignificant decrease in grafting yield to 75% after 12 h at 25 °C. It should be pointed out that, strictly speaking, THF does act as a promoter for the coupling reaction by increasing the ionic character (and reactivity) of the polyisoprenyl anions. In the current context, however, the definition of a promoter is restricted to an additive having a notable influence on the grafting reaction when used at low concentration (up to a 10:1 ratio relative to the living ends).

The coupling reaction proceeds more rapidly under ambient conditions than at low temperature: A grafting yield of only 67% was obtained after 24 h at 0 °C in 1:2 hexane/THF. While further increasing the temperature to 40 °C might be expected to enhance the rate of the coupling reaction, no significant change in yield was observed relative to 25 °C after 6 h. The susceptibility of THF to proton abstraction by organolithium com-

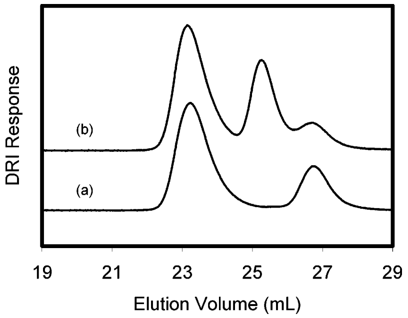


Figure 2. SEC elution curves for test reaction of linear epoxidized polyisoprene and polyisoprenyllithium (a) after 24 h reaction, limiting yield of 79% reached; (b) after addition a new monomer aliquot, chain extension is observed for the portion of polyisoprenyllithium side chains still active.

Table 3. Grafting Yield Attained for Linear Epoxidized Polyisoprene and Polyisoprenyllithium Using *N,N,N′,N′*-Tetramethylethyklenediamine (TMEDA) as Promoter at 25 °C[a]

hexane:THF/mL:mL	TMEDA:LE[b]	time[c]/h	grafting yield/%
150:0	1.5:1	12	28
		24	41
150:0	4:1	6	70
		12	73
150:0	10:1	12	70
50:100	4:1	3−12	80
50:100	10:1	3−6	80

[a] Living end (LE) to epoxide ratio of 0.8 (25% excess epoxide functionalities) used for all reactions; PDI ≤ 1.10 for side chains, substrate and graft polymers. [b] TMEDA:living end ratio, TMEDA added by syringe after backbone. [c] A time range indicates that the grafting yield did not change significantly (±1%) over that interval.

pounds is well-documented,[26] and polyisoprenyllithium likewise decays slowly at temperatures above 0 °C.[27] Other possible deactivation reactions are proton abstraction from the epoxide ring[28] and its methyl substituent[29] by the polyisoprenyl anions, although these side reactions are less likely for delocalized organolithium compounds such as polyisoprenyllithium. The rate of these side reactions is clearly temperature-dependent as expected: In a 1:2 hexane/THF mixture, the yellow coloration of polyisoprenyl anions faded after only 9 h at 40 °C. In comparison, the color was still very noticeable at 25 °C after 18 h but faded after 40 h. Under the conditions used the grafting yield attained presumably results from competition between the coupling reaction and chain termination by THF and possibly proton abstraction from the coupling substrate. Chain termination should be minimized at low temperature; unfortunately, the coupling reaction is slow under these conditions.

One rather puzzling aspect of the grafting reaction is that the grafting yield attained seems to reach a limiting value after a certain time, despite the presence of a 25% excess of epoxide functionalities in the reaction and the persistent color of the living polyisoprene throughout the reaction. It can be seen in Table 2 that the grafting yield remained constant (±1%) over periods extending up to 20 h. It could be tempting to attribute this effect to steric crowding of the coupling substrate, but this explanation cannot suffice since over 90% grafting yield was achieved under optimal conditions. The presence of an equilibrium in the grafting reaction is highly unlikely: While the polymerization of alkyl-substituted epoxides is subject to equilibration, these compounds are still able to react with delocalized organolithium compounds in high yield.[28] The cis−trans isomerization of chain termini of polyisoprenyllithium[30] in THF is also unlikely to suffice to explain incomplete grafting because the isomerization occurs on a much faster time scale than the grafting reaction.

The presence of “living” polyisoprenyllithium after reaching the limiting conversion was confirmed with a chain extension experiment. The initial conditions used were identical with entry 4 of Table 2, and the SEC elution curve for the crude product after 24 h is provided in Figure 2a. Peak area analysis for Figure 2a reveals the presence of 21% linear side chains in the crude product after the maximum grafting yield (79%) was reached. In this case, the grafting yield remained constant from 15 to 24 h after the beginning of the reaction. The elution curve for the product obtained upon addition of a second portion (6.3 g) of isoprene monomer after 24 h is provided in Figure 2b. A new peak appeared in the chromatogram due to chain extension for the fraction of polyisoprene side chains still active. Deconvolution of the peaks in Figure 2b and mass balance considerations show that around 13% of the chains were deactivated at the time when the second monomer aliquot was added. Therefore, at least 8% of the polyisoprenyllithium chains were still active after the second monomer addition.

On the basis of the above considerations, an explanation is suggested for the limiting grafting yield observed in the absence of promoters. The polymerization of isoprene in nonpolar solvents is rather slow[18] and by no means complete after 5 h. The small amount of residual monomer may react with the chain ends in the presence of THF to produce 1,2- and 3,4-isoprene units, thereby modifying the reactivity of the macroanions. The nucleophilic ring-opening reaction of epoxides should be sensitive not only to chain end structure but also to solvent composition via changes in ionic character or aggregation level. To a first approximation, however, 1,2-units are expected to be less reactive than either 3,4- or 1,4-units because they are more sterically hindered. Chain end reactivity modification may thus be responsible for the limiting grafting yields observed in the absence of promoters.

Grafting Reactions with Promoters. Three distinct strategies can be identified to increase the rate and yield of the grafting reaction: A Lewis base such as *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) may be added to complex the lithium counterion and increase the nucleophilicity of the polyisoprenyl anions; Lewis acids can serve to increase the reactivity of the epoxide ring via coordination; finally, lithium salts can decrease the reactivity of polyisoprenyl anions by a common ion effect but also increase the reactivity of the epoxide ring via coordination because they are weak Lewis acids. With the exception of lithium salts (as described above), all promoters were added to the reactor by syringe after addition of the epoxidized substrate.

***N,N,N′,N′*-Tetramethylethylenediamine as Promoter.** TMEDA may sometimes increase the reactivity of organolithium compounds via complexation with the lithium counterion.[31] The usefulness of TMEDA to improve the coupling reaction was investigated both in pure hexane and in hexane−THF mixtures. Comparison of the grafting yields attained after 24 h at 25 °C in pure hexane (Table 2) and in the presence of 1.5 equiv of TMEDA with respect to the living ends (Table 3) shows that this additive increased the grafting yield significantly from 31% to 41% under otherwise identical

Table 4. Grafting Yield Attained for Linear Epoxidized Polyisoprene and Polyisoprenyllithium with Lewis Acid Promoters under Different Reaction Conditions[a]

hexane:THF/mL:mL	additive	Add:LE[b]	temp/°C	time[c]/h	grafting yield/%
150:0	BF_3	0.5	−15	1	61
				2	63
				12	65
150:0	BF_3	1	−15	1	76
				2	78
				12	78
150:0	BF_3	1.5	−15	1	77
				2	78
50:100	BF_3	1	−15	2	36
				12	55
50:100	$AlMe_3$	0.05	25	12	83
50:100	$AlMe_3$	0.1	25	12	84
50:100	$AlMe_3$	0.2	25	12	79

[a] All reactions at room temperature with a living end-to-epoxide ratio of 0.8 (25% excess epoxide functionalities); PDI ≤ 1.10 for side chains, substrate and graft polymers. [b] Additive (Add):living end (LE) ratio, promoter added by syringe after backbone.

Table 5. Grafting Yield Attained for Linear Epoxidized Polyisoprene and Polyisoprenyllithium with Lithium Salts as Promoters[a]

LE:Epx[b]	additive	add:LE[c]	temp/°C	time[f]/h	grafting yield/%
0.8	LiCl	1	25	12	81
				24	86
0.8	LiCl	3	25	24−30	91
0.8	LiCl	6	25	18−24	92
0.8	LiCl	6	0	18	88
				24	86
0.9	LiCl	6	25	24	89
				48	90
0.8	LiBr	6	25	12	91
				15	92
0.9	LiBr	6	25	18	83
				24−60	92
1.0	LiBr	6	25	24	67
				48−60	83
0.9[d]	LiBr	6	25	36	86
				48−60	91
0.9[e]	LiBr	6	25	36	81
				48	83

[a] Mixed solvent system (50 mL hexane + 100 mL THF) used; $M_w/M_n \leq 1.10$ for side chains and graft polymers. [b] Living end (LE):epoxide (Epx) ratio (substrate with 26% epoxidation unless otherwise noted). [c] Additive (Add):living end (LE) ratio. [d] 12% substrate epoxidation. [e] 35% substrate epoxidation. [f] A time range indicates that the grafting yield did not change significantly (<1%) over that interval.

reaction conditions. A TMEDA:living end ratio of 4 increased the yield to 70% in only 6 h. For a TMEDA:living end ratio of 10 the solution was turbid, due to the low solubility of TMEDA in hexane, and no further improvement in grafting yield was observed. Even in the hexane−THF mixed solvent system the addition of TMEDA increased the rate of the grafting reaction to reach 80% over 3−12 h.

Lewis Acid Promoters. Lewis acids such as BF_3[32] and $AlMe_3$[33] can be used as modifiers for reactions of organolithium compounds or Grignard reagents with epoxides and ketones by coordination with the oxygen atom of the substrate. The results obtained for a series of grafting reactions in either pure hexane or hexane−THF mixtures using BF_3 or $AlMe_3$ as promoters are summarized in Table 4. Even in a nonpolar solvent (hexane), the grafting yield reached 78% in 2 h with BF_3 for a promoter:living end ratio of 1. It did not increase further for a ratio of 1.5. No activity was observed for BF_3 in the presence of THF, presumably because of competitive coordination by the solvent acting as a Lewis base and the reaction of living chain ends with BF_3.[34] The data of Table 4 also show that $AlMe_3$, a weaker Lewis acid than BF_3, is active in hexane−THF mixtures and increases the grafting yield to 84% when added in a 0.1 ratio relative to the living ends. Further increases in the promoter/living end ratio did not improve the grafting yield. The role of BF_3[32] and $AlMe_3$[33] in promoting ring opening of small molecule epoxides has been discussed in the literature. Because B and Al are strongly oxophilic atoms, Lewis acids containing them can coordinate efficiently with the oxygen atom in the epoxide ring. Complexation leads to a decreased electron density on the epoxide ring, facilitating the nucleophilic attack. While Me_3Al does work better as a promoter than BF_3 it may not be ideal because Me_3Al can also attack the epoxide ring.[35,36] This could explain why the grafting yield decreased slightly when the $AlMe_3$:living end ratio was increased from 0.1 to 0.2.

Lithium Salt Promoters. Considering possible side reactions as well as the potential for the formation of poorly soluble byproducts upon hydrolysis of BF_3 and $AlMe_3$, the use of lithium salts, known to have weak Lewis acid character,[37] was also investigated to modify the grafting reaction. In a 1:2 hexane/THF mixture, the grafting yield greatly increased from 78% without promoter (Table 2) to 91−92% in the presence of 6 equiv of LiCl in the reaction (Table 5). Since it takes a long time for LiCl to dissolve in the mixed solvent system used, LiBr was also investigated because of its higher solubility. The results obtained with LiBr are very similar (Table 5, entry 6). Since the lithium ion is a weak Lewis acid and an oxophile, it can coordinate with the epoxide ring to increase its reactivity in analogy to BF_3 and $AlMe_3$. At the same time, however, the lithium ions suppress the ionization of living polymer chains through a common ion effect, thus necessitating longer reaction times. The suppression of chain end ionization has a further advantage in that it also improves the stability or living characteristics of the macroanions.

All the reactions discussed so far were based on an epoxide:living end ratio of 0.8, corresponding to a 25% excess of epoxide in the reaction. While relatively unreactive, intrachain residual epoxide functionalities could potentially participate in cross-linking reactions under certain conditions. For that reason, grafting was also attempted under optimized conditions with living end:epoxide ratios closer to the exact 1:1 stoichiometry. For a living end:epoxide ratio of 0.9 a high grafting yield of 90−92% can still be achieved using LiBr, although the reaction time must be increased to 24 h (Table 5,

Table 6. Synthesis of Higher Generation Graft Polymers[a]

								$M_w/10^3$				
gen	hexane:THF/ mL:mL	M_w^{br} [b]/10^3	time[c]/h	M_w/M_n	yield[d]/%	G_y[e]/%	d*n*/d*c*[f]/ mL g^{-1}	DRI[g]	MALLS[h]	R_g/R_h	f_w[i]	C_e[j]/%
G0	50:100	5.3	24–60	1.04	91	90	0.130	46	87	1.00	15	84
G1	50:150	5.4	32–72	1.04	83	82	0.129	300	1100	0.94	180	54
G2	50:200	5.5	36–75	1.05	76	74	0.130	880	10000	0.73	1630	44
G3[k]	50:200	4.70[f]	120	1.08[f]	10	3		900				

[a] Characteristics of substrates used in the reactions provided in Table 1; $M_w = 5400$ and $M_w/M_n = 1.05$ for linear polymer; target $M_n = 5000$, M_w/M_n 1.05 for side chains; all reactions using a living end:epoxide ratio = 0.9, LiBr:living end ratio = 6, at 25 °C. [b] Absolute molecular weight of side chains. [c] Grafting yield constant (±1%) over specified time interval. [d] Approximate grafting yield based on relative peak areas. [e] Grafting yield corrected for substrate contribution to graft polymer peak. [f] Measured at 633 nm; d*n*/d*c* = 0.131 mL/g for linear polyisoprene. [g] Apparent value from SEC analysis using a differential refractometer detector and a linear polystyrene standards calibration curve. [h] Absolute molecular weight from multiangle laser light scattering. [i] Number of side chains added in the last grafting reaction. [j] Coupling efficiency. [k] Reaction mixture turbid, products not characterized by light scattering due to low yield.

entry 7). For stoichiometric amounts of living ends and coupling sites, the grafting yield drops significantly to 83% under the same conditions (entry 8). Finally, the influence of branching density on the grafting yield was also explored. For a substrate with an epoxidation level of 26%, corresponding to ca. 1 coupling site for every 4 repeating units along the chain, a grafting yield of 92% was achieved after 48 h (entry 7). Decreasing the epoxidation level to 12% (ca. 1 coupling site for every 8 repeating units, entry 9) yields identical results (91%), while only 83% grafting is achieved after 48 h for an epoxidation level of 35% (ca. 1 coupling site for every 3 repeating units, entry 10), presumably as a result of increased steric crowding.

Synthesis of Arborescent Polyisoprenes of Successive Generations. The results obtained for the synthesis of G0–G2 arborescent polyisoprenes using the optimized reaction conditions are summarized in Table 6. A living chain end-to-epoxide ratio of 0.9 and 6 equiv of LiBr were used in all cases. For the synthesis of higher generations of arborescent polyisoprenes it was necessary to use more solvent to maintain a sufficiently low viscosity, leading to slightly increased reaction times.

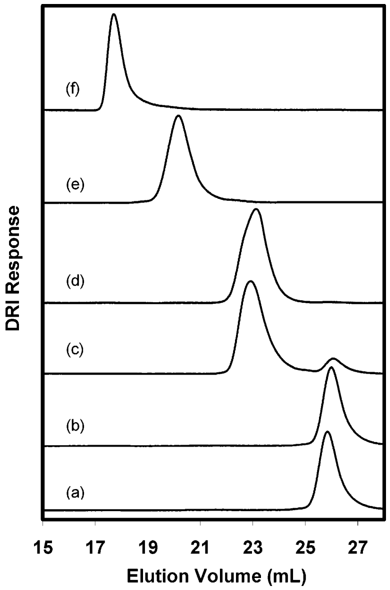


Figure 3. Synthesis of arborescent polyisoprenes of successive generations: SEC elution curves for (a) linear epoxidized polyisoprene substrate, (b) polyisoprene side chains used in the synthesis of the G0 polymer, (c) crude G0 grafting product, and (d–f) G0–G2 polymers after purification by precipitation fractionation.

A series of SEC elution curves are provided in Figure 3 to illustrate the synthesis of the G0 arborescent polyisoprene sample (curves a–d) and for the G1 and G2 purified graft polymers using the optimized conditions. Reaction of the linear epoxidized polyisoprene substrate (curve a) with the polyisoprenyl anions (curve b) yielded a crude sample (curve c) consisting of the coupling product (leftmost peak) and the linear polyisoprene contaminant (rightmost peak). As pointed out earlier, the grafting yield (fraction of polyisoprenyl anions coupled with the substrate) can be approximated from the SEC peak area determined using the differential refractometer (DRI) detector. If the concentration response of the detector is assumed to be identical for the graft polymer and the nongrafted side chains (identical refractive indices), the area of the graft polymer peak is defined as A_1, and the area for the nongrafted side chains is A_2, the grafting yield can be approximated as $A_1/(A_1 + A_2) \times 100\%$. This approach (method 1) slightly overestimates the grafting yield because part of the response for the graft polymer (A_1) is due to the substrate.

For a more accurate determination of the grafting yield, peak area A_1 can be corrected by subtracting the contribution from the substrate (method 2). The corrected peak area corresponds to $A_1' = A_1 \times$ weight fraction of the side chains in the sample, i.e., $A_1' = A_1[M_w(G) - M_w(G-1)]/M_w(G)$, where $M_w(G)$ and $M_w(G-1)$ represent the absolute molecular weight of the graft polymer of generation G and of the preceding generation, respectively. This approach requires knowledge of the molecular weight of the product, which could be determined reliably for all but the G3 sample. In this case, an alternate approach (method 3) was used to calculate the grafting yield (G_y) based on the stoichiometry of the reaction. Using the exact weight of grafting substrate (w_1) and monomer (w_2) employed and assuming complete monomer conversion, the peak areas A_1 and A_2 can be considered proportional to contributions from the substrate and the side chains, leading to the relation

$$\frac{A_1}{A_2} = \frac{w_1 + w_2 G_y}{w_2(1 - G_y)} \qquad (1)$$

The approximate grafting yields determined for polymers of successive generations according to method 1 are compared to the more accurate results based on peak area correction (method 2 for G0–G2, method 3 for G3) in Table 6. Discrepancies between the approximate and the more accurate methods are minor (±1–2%) for all samples except G3. Method 1 clearly overestimated the grafting yield attained for the G3 sample because most of the peak response for the graft polymer was due to the substrate. Grafting yield calculations are typically reproducible within ca. ±1–2% because they are based on relative (rather than absolute) peak areas for the graft polymer and the linear component. Since the two peaks are resolved to the baseline in all cases, the main contributions to errors in the calculations are slight variations in baseline selection and in setting the integration limits for the peaks.

For the reaction conditions selected, the grafting yield progressively decreased from 90% for the G0 polymer (grafting onto a linear substrate) to 74% for the G2 product (grafting onto a G1 substrate). Decreases in grafting yield have been reported on many occasions in the synthesis of arborescent polymers[5] due to steric congestion limiting the accessibility of coupling sites. Additionally to steric hindrance, chain end deactivation by hydroxyl functionalities present at branching points of the substrates may also have contributed to lowering the grafting yield for polymers of generations G1 and G2. Chain end deactivation by hydroxyl groups on G0 and G1 substrates, while not insignificant, is rather small. Taking the specific example of the G0 substrate in Table 1 (used to synthesize the G1 polymer) with $M_w = 87\,000$ and 26% epoxidation, each of the 15 side chains ($f_w = 15$ in Table 5) has one $-$OH group at the branch junction. Since the structural unit molecular weight $M_0 = 68.1$ for isoprene, the degree of polymerization of the G0 substrate is $87000/68.1 = 1280$. The number of coupling sites on the G0 substrate is therefore $1280 \times 0.26 = 332$. The fraction of living chains that could be deactivated due to the presence of the 15 $-$OH groups on the substrate is $15/332 = 0.0452$ or ca. 4.5% at most. The true fraction of living chains deactivated by this mechanism is likely lower in practice, however, since some of the $-$OH groups located near the center of the molecules are presumably inaccessible to the living anions. The attempted synthesis of a G3 arborescent polymer clearly failed, the corrected grafting yield being limited to 3%. The reason for this disappointingly low yield is not completely clear, although it seems that poor solubility of the epoxidized substrate in the reaction medium may have been a factor.

The linear contaminant was easily removed from the G0 crude product by precipitation fractionation (Figure 3, curve d) as well as from the G1 and G2 arborescent polymers (curves e and f). The apparent (polystyrene equivalent) M_w of the graft polymers, determined by SEC analysis using a differential refractometer (DRI) detector, ranges from 4.6×10^4 (G0) to 8.8×10^5 (G2), as indicated in Table 6. The absolute M_w of the same polymers, determined using the MALLS detector, ranges from 8.7×10^4 (G0) to 1.0×10^7 (G2). The large underestimation of M_w by SEC analysis with a DRI detector, reaching over 10-fold for the G2 sample, is clearly the result of the very compact structure of the arborescent isoprene homopolymers, in analogy to former observations in different arborescent systems.[5]

The branching functionality of the graft polymers, also reported in Table 6, was calculated from the equation

$$f_w = \frac{M_w(G) - M_w(G-1)}{M_w^{br}} \tag{2}$$

where M_w^{br} is the absolute molecular weight of the side chains. It corresponds to the number of side chains added in the last grafting reaction. From Table 6, it can be seen that both the absolute molecular weight and the branching functionality increase in an approximately geometric fashion for successive generations, as expected when the side chain molecular weight and branching density remain constant.[5] There is nonetheless a noticeable decrease in the growth *rate* of the molecules from generations G0 to G2.

The coupling efficiency (C_e), defined as the fraction (percentage) of epoxide coupling sites consumed in the reaction, can be calculated as the ratio of f_w to the number of coupling sites on the substrate or alternately from the equivalent equation

$$C_e = \frac{f_w M_0}{M_w(G-1)E} \times 100\% \tag{3}$$

where M_0 is the molecular weight of the isoprene unit (68.1) and E is the epoxidation level of the substrate polymer (Table 1). The coupling efficiencies calculated on the basis of the MALLS results are provided in Table 6. The decrease in coupling efficiency observed from G0–G2 reflects the decreasing growth rates observed for higher molecular weight polymers. Even with a living end:epoxide ratio of 0.9 (corresponding to an 11% excess of living ends), the coupling efficiency reaches at most 84% (sample G0, Table 6) as a result of either side reactions or inaccessibility of the coupling sites. Unfortunately, the concentration of coupling sites in the final product is too low to allow an in-depth analysis of factors limiting the coupling efficiency.

The grafting reaction was intentionally optimized in terms of grafting yield rather than coupling efficiency, mainly for practical reasons: The grafting yield determines the amount of linear contaminant which must be removed in purifying the crude product. A higher grafting yield greatly simplifies sample purification by precipitation fractionation, requiring dilute (ca. 1%) solution conditions and therefore large amounts of solvents. Furthermore, because the coupling sites are randomly distributed on the substrates, incomplete coupling has no significant consequences on the structure and the molecular weight distribution of the graft polymers: Structural defects should be likewise randomly distributed. While forcing the reaction by increasing the excess of living ends used may potentially increase the coupling efficiency and the branching functionality attained (if no side reactions of coupling sites are involved), sample purification would certainly be more difficult.

The radius of gyration (R_g) measured by SEC-MALLS and the hydrodynamic radius (R_h) measured by dynamic light scattering were combined to calculate the R_g/R_h ratio also reported in Table 6. This ratio is expected to decrease and reach a limiting value of $(3/5)^{1/2}$ or 0.775 for rigid spheres of uniform density. The arborescent polyisoprenes have R_g/R_h ratios decreasing from 1 (G0) to 0.73 (G2). This result shows that the density of arborescent polymers in solution increases over successive generations. The 0.73 value determined for the G2 polymer is actually below the 0.775 limit for rigid spheres. This discrepancy could be due either to the uncertainties on R_g measurements by SEC-MALLS or to a nonuniform distribution of the chain segments in arborescent polymer molecules. More accurate R_g measurements for arborescent polystyrenes of generations G0–G3 using small-angle neutron scattering (SANS) have indeed indicated that the radial segment density of polystyrenes follows a power law model with maximum density in the center of the molecules and a more diffuse layer on the outside.[38]

A ^{1}H NMR spectrum obtained for the purified G0 graft polymer is compared in Figure 1c with spectra for linear polyisoprene (curve a) and linear epoxidized polyisoprene (curve b). The peak assignments have been provided above. The G0, G1, and G2 arborescent polyisoprenes have NMR spectra very similar to linear polyisoprene, since the chains grafted in the last reaction account for 89−94% of the total mass of the molecules.

Conclusions

A new method, based on coupling of polyisoprenyllithium with epoxidized polyisoprene substrates, was presented for the synthesis of arborescent isoprene homopolymers. The additives TMEDA, BF$_3$, AlMe$_3$, and lithium salts were shown to influence the reaction rate and grafting yield. Most useful were LiCl and LiBr by minimizing the termination of polyisoprenyllithium as well as promoting the reaction with epoxide functionalities. The graft polymers of generations G0−G2 obtained all had narrow molecular weight distributions ($M_w/M_n \leq 1.05$). The higher absolute molecular weights observed by MALLS analysis relative to the apparent molecular weights obtained from the DRI detector, reaching over 10 times for the G2 polymer, is evidence for the highly compact structure of arborescent molecules. The molecular weight and branching functionality of the graft polymers increased in an approximately geometric fashion for successive generations, while the growth rate of the molecules decreased noticeably.

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support and Dr. Neil McManus, Chemical Engineering Department, University of Waterloo, for providing access to the SEC-MALLS equipment.

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MA0479565