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Synthesis of 4-, 8-, 12-arm star-branched polybutadienes with three different chain-end functionalities using a functionalized initiator

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Abstract

An array of well-defined 4-, 8-, and 12-arm, chain-end functionalized, star polymers and their deuterated analogs has been synthesized using a *t*-butyldimethylsiloxy-functionalized alkyllithium initiator and anionic polymerization. The design of the synthesis provides for unusually well-defined comparisons of the behavior of the polymers with different chain-end functionality. For each star architecture three polybutadiene polymers were synthesized with the same labeling, the same well-defined degree of branching and molecular weight, but different chain end functionality. Deprotection of the *t*-butyldimethylsiloxypropyl chain ends of the stars as first synthesized provided stars with hydroxypropyl chain ends. The hydroxypropyl chain ends were further converted to trifluoroethanesulfonyloxypropyl chain ends by tresylation with 2,2,2-trifluoroethanesulfonyl chloride. Measurements of intrinsic viscosities for the hydrogenous and deuterated linear PBs made in the course of characterizing the star functionalities confirm that the dimensions of the linear chains are not affected by isotopic substitution.
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1. Introduction

In order to perform the most incisive studies of the effect of polymer chain molecular characteristics on polymer properties, targeted synthesis of well-defined molecules and analogs is essential [1–5]. The molecular characteristics that can be controlled by synthesis include molecular weight and its distribution, microstructure and tacticity, degree of branching and architecture, and chain end functionality. One family of synthetic methods that has been particularly useful for creating polymers of various well-defined architectures with narrow molecular weight distributions relies on living anionic polymerization, which is characterized by no chain termination and no chain-transfer reactions [6].

One research area opened by the development of controlled anionic polymerization is the study of the bulk thermodynamics of binary blends of homopolymers containing components of very similar chemical composition, but different architecture or topology [7–10] for which

experimental results have recently appeared [11–15]. Such blends are of practical importance because the addition of a long-branched component to a melt of linear chains can substantially alter the flow characteristics [16,17], aiding processing [18].

There is also interest in how long-chain branching of a blend component might be tailored to impact the surface composition of polymer blends. Theories [19,20] have predicted that the long-chain branched component in a blend of star and linear chains will be preferentially segregated to the blend surface, all other factors being equal. Preferential segregation of stars has been seen in blends of star and linear isotopic pairs [12,21]. However, understanding the degree to which this phenomenon is dictated by architectural effects is complicated by the fact that the chemical structure of the chain ends is inevitably distinct from the chemical structure of the repeat units [22]. Explicit study of the effect of chain end functionalization is of interest not only to address this question of the driving forces for surface segregation, but also to address the possibility of tailoring blend properties by varying the functionality of the chain ends.

The creation of star-branched polymers with controlled

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functionalization of the arm ends poses significant synthetic challenges [23–25]. Quirk and coworkers [26] have proposed a route to the synthesis of uniformly functionalized star-branched polymers using a functionalized initiator. Their approach produces a star-branched polymer with uniform arms and with a functional group at every branch chain end. In the present study this method has been applied to create an unprecedented array of 4-, 8-, and 12-arm star polymers and perdeuterated analogs with variously functionalized chain ends. In each series of a particular labeling and architecture, arm molecular weight, molecular weight dispersity, and average number of arms are all identical because all members of the series are derived from the same star polymer precursor. Only the chemistry at the star arm ends differs. Such an array of polymers allows for the most discriminating study of the effect of chain end functionalization. Furthermore, the synthesis of perdeuterated analogs allows for studies of a number of effects in blends using various techniques, particularly neutron scattering, that are sensitive to deuterium labeling.

2. Experimental

2.1. Synthesis

Cyclohexane (Fisher, 99%), hydrogenous 1,3-butadiene (Matheson, 99%), and deuterated 1,3-butadiene (Cambridge Isotope Laboratories, 98%) were purified as described elsewhere [27]; methanol (Fisher, 99%), toluene (Aldrich, 99.5%), tetrahydrofuran (THF) (Fisher, 99.5%), HCl (Fisher, 37%), and 2,2,2-trifluoroethanesulfonyl chloride (tresyl chloride, TrCl) (Aldrich, 99%) were used as received. The solution of 3-(t-butyldimethylsiloxy)-1-propyllithium (FMC, Lithium Division, 15.4% in cyclohexane) was used as initiator after double-titration analysis [28]. Tetrachlorosilane (Aldrich, 99%) was purified by stirring over CaH_2 and diluted with cyclohexane. Octa- and dodecachlorosilane were synthesized as described elsewhere [29] and diluted with cyclohexane. Less than 0.5 wt% of 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) (Aldrich, 99%) was added to each polymer to prevent oxidation. Triethylamine (TEA) (Aldrich, 99.5%) and dichloromethane (Fisher, 99.6%) were purified with CaH_2 and stored over molecular sieves. The molecular sieves (Union Carbide, 4 Å) were dried at 150 °C for at least 24 h and cooled in a vacuum oven under a dry N_2 atmosphere before using.

Polymerizations were carried out using all-glass reactors and standard high-vacuum techniques [27]. The target overall molecular weight of the 4-, 8-, and 12-arm star polymers was constant at 100,000 g/mol. So the target molecular weights for the base polymers to serve as arms were 25,000, 12,500, and 8300 g/mol, respectively. For the synthesis of the 4-arm star polymer, 1,3-butadiene (29.8 g, 0.55 mol) was polymerized in cyclohexane (350 ml) using

3-(t-butyldimethylsiloxy)-1-propyllithium (1.33 mmol, 0.74 M in 1.8 ml of cyclohexane). After 24 h at 40 °C, about 65 ml of living poly(butadienyl)lithium solution was transferred from the reactor into an ampoule and this solution was terminated with degassed methanol to obtain a sample of the base polymer that could be characterized. This ampoule was opened after another 24 h and less than 0.5 wt% of BHT was dissolved in the solution before precipitating the base polymer slowly into 650 ml of methanol. The polymer was collected and dried in the vacuum oven at 30 °C.

Addition of the linking agent to form the 4-arm stars was done in two steps. An amount of linking agent, corresponding to 0.4 molar equiv. with respect to the living poly-(butadienyl)lithium remaining in the reactor, was added into the reaction solution 48 h after removing the base polymer aliquot. A small amount of reaction solution was then taken and terminated after 24 h to check the linking reaction using size exclusion chromatography (SEC). After this check, another aliquot of linking agent corresponding to 0.4 molar equiv. with respect to the remaining living poly(butadienyl)lithium was added, and this step of the reaction was completed after 48 h. The reaction was terminated by adding degassed methanol and the rest of the procedure was the same as for the base polymer, except for the addition of a fractionation step. The product of the linking reaction was a mixture of linked star-branched polymer and unlinked excess base polymer from which the star-branched polymer had to be isolated by fractionation. Fractionation was done using toluene as a good solvent and methanol as a nonsolvent. Usually 2500 ml of toluene were used to fractionate 3–5 g of the linked polymer mixture and 4–5 fractionation steps were sufficient to complete a fractionation.

The deprotection was performed in the following manner. A t-butyldimethylsiloxypropyl-functionalized, star-branched polybutadiene (1 g) was dissolved in 10 ml of THF with 0.1 ml of concentrated HCl and 1 mg of BHT. Under nitrogen this solution was heated under reflux for 1 h and cooled before precipitation into 100 ml of methanol. The polymer was separated and dried in a vacuum oven at 30 °C.

The procedure of Sofia et al. [30] was followed in performing the tresylation. The deprotected star-branched polybutadiene with hydroxypropyl chain ends (1 g) was dissolved in 20 ml of dichloromethane and 5 ml of molecular sieves was added. This solution was stored in the refrigerator for 24 h and then moved into a drybox with other chemicals and glassware that had been dried at 150 °C for more than 24 h. The solution was transferred into a 50 ml, round-bottomed flask with a stir bar. Then TEA was added dropwise into the reactor, followed by TrCl. The amounts of TEA and TrCl added corresponded to 1.5 times the calculated number of moles of hydroxypropyl chain ends. After 90 min at room temperature, the light brown colored reaction solution was taken out of the drybox and

connected to a vacuum line to remove the solvent and excess reagents. The vacuum dried reaction product was redissolved in 20 ml of cyclohexane with BHT, washed three times with water to remove triethylamine hydrochloride (TEA·HCl) salt formed as a result of the tresylation reaction, and precipitated into methanol. Unremoved salt remaining in the sample forms thin, rod-shaped crystals that make the vacuum-dried polymer cloudy and that can be observed with an optical microscope.

2.2. Characterization

The molecular weight was determined for all polymers using multiangle laser light scattering (LS) at a wavelength of 690 nm (DAWN-EOS, Wyatt Technology) coupled to SEC (TriSEC, Viscotek) with THF as eluent at 35 °C. ^{1}H and ^{13}C NMR spectra were measured in deuterated chloroform using a Varian Gemini-300 spectrometer. Viscosities were measured in toluene at 30 °C using an Ubbelohde capillary viscometer. Flow times were measured for 4 concentrations and an average of 5 trials recorded for each concentration. The intrinsic viscosity was determined by extrapolation to zero concentration using both the Huggins [31] and Kraemer [32] equations and averaging the results. The reported uncertainties in the intrinsic viscosities reflect the error in the viscosity measured at a particular concentration as well as the uncertainty of the extrapolation to zero concentration.

3. Results and discussion

3.1. Polymerization

Scheme 1 shows schematically the synthetic route to matching stars with three different chain-ends. Star-branched functionalized polybutadienes with 4, 8, and 12 arms were synthesized anionically using 3-(*tert*-butyldimethylsiloxy)-1-propyllithium as initiator. Some of these chains were then used to obtain a second series of polymers that were deprotected to obtain hydroxypropyl chain ends. Reaction of the polymers with hydroxypropyl chain ends with 2,2,2-trifluoroethanesulfonyl chloride gave a third type of star with 2,2,2-trifluoroethanesulfonyloxypropyl chain ends. In this way we obtained well-controlled polymer samples of the same architecture and molecular weight, but having different chain-ends.

Fig. 1 shows the SEC chromatograms of the base polybutadiene (a), the corresponding the mixture of base polybutadiene and 4-arm star polymer before fractionation (b), and the fractionated 4-arm star polymer (c). Since the star has four arms, the peaks corresponding to the base polymer and star polymer overlap slightly in the case of the chromatogram for the mixture. This overlap is not observed in the cases of the 8- and 12-arm polymer. The peak retention volume of the fractionated 4-arm star is slightly
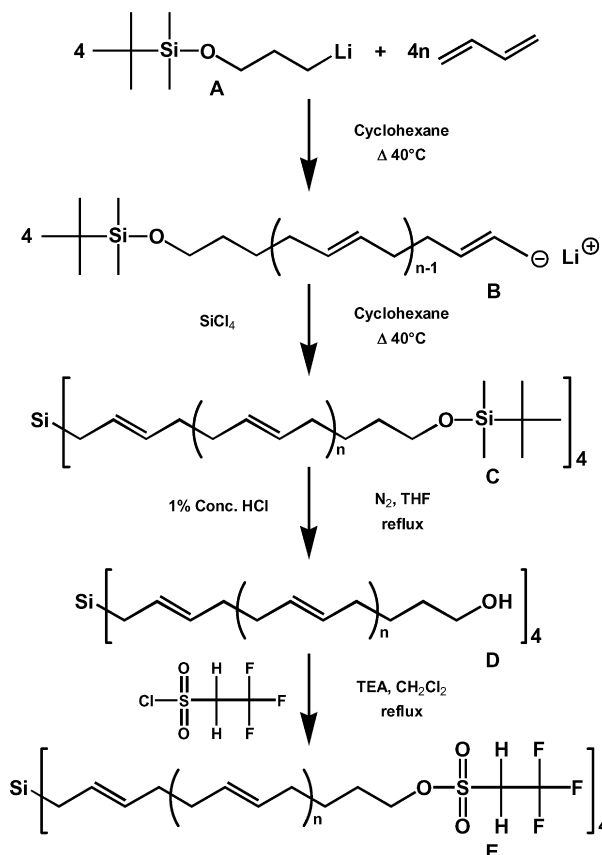
Scheme 1.

smaller than that of the 4-arm star in the mixture since fractionation collects preferentially the higher molecular weight polymer. Molecular weights of the base and star-branched polymers were determined by light scattering and are summarized in Table 1. The degree of branching (*f*) was calculated as $f = M_{w,star}/M_{w,arm}$ using weight averaged molecular weights since light scattering provides an absolute measurement of M_w. The molecular weight used for the star was that determined after fractionation, while the molecular weight of the arm refers to that determined from the unfractionated reaction mixture. Since the fractionation preferentially collects the higher molecular weight stars, the degree of branching calculated in this way is slightly higher
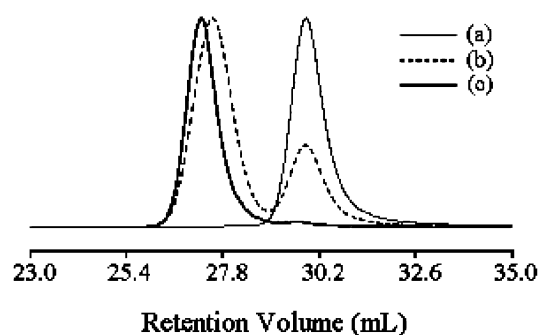
Fig. 1. SEC chromatograms of (a) base polybutadiene, (b) crude mixture of base and 4-arm star-branched polybutadiene, and (c) fractionated 4-arm star-branched polybutadiene.

Table 1
Molecular weights and microstructures of base polybutadienes and star-branched polybutadienes

Sample	Target f	Base polymer			Star polymer			f^a	1,4-Addition[b] (%)
		M_w^c (g/mol)	M_n^c (g/mol)	M_w/M_n^c	M_w^c (g/mol)	M_n^c (g/mol)	M_w/M_n^c		
h-PB	4	22,000	21,000	1.05	85,000	83,000	1.03	3.8	92 ± 0.5
	8	16,000	15,000	1.06	91,000	89,000	1.03	5.8	92 ± 0.5
	12	9400	9000	1.04	104,000	102,000	1.02	11.1	92 ± 0.5
d-PB	4	26,000	25,000	1.04	98,000	95,000	1.03	3.7	91 ± 1
	8	15,000	14,000	1.06	94,000	91,000	1.03	6.5	91 ± 1
	12	9400	8900	1.05	94,000	93,000	1.02	10.0	90 ± 1

[a] The degree of branching; $f = M_{w,star}/M_{w,base}$.
[b] Determined by ^{1}H NMR for hydrogenous samples and ^{13}C NMR for deuterated samples.
[c] Obtained from light scattering coupled to SEC.

than the true value characteristic of the reaction mixture. However, the difference between the mean molecular weights of the star polymers before and after fractionation was less than 5%, which is less than the uncertainty in f arising from other sources. The degree of branching was more than 80% of the target value except for the hydrogenous 8-arm star-branched polybutadiene, for which the actual degree of branching was 73% of the target value. This lower value for the linking efficiency might have been caused by unknown impurities in the linking agent solution or lower functionality of the linking agent.

The degrees of branching were also checked by comparing experimentally measured branching factors (g^l) of the star-branched polymers with reference values [33]. The branching factor is the ratio of the intrinsic viscosities ($[\eta]$) of the branched and linear polymers of the same molecular weight. The intrinsic viscosities of the star-branched polymers were measured in toluene at 30 °C, while the intrinsic viscosities of the corresponding linear polybutadienes were calculated using the Mark–Houwink equation. The values of the parameters K and a for linear polybutadiene were obtained by regression of the results of our measurements of the intrinsic viscosities of 3 hydrogenous and 6 deuterated linear polybutadienes in the range of M_w from 10,000 to 110,000 g/mol in toluene at 30 °C as shown in Fig. 2. The slopes, corresponding to the exponent a, of the two lines are both 0.708, in good agreement with literature value of 0.713 [34]. The intercepts, the logarithms of the coefficients K, for the two isotopic analogs are different. The value of K for the deuterated polybutadiene, 0.000309 dl/g, is 18% lower than that for the hydrogenous PB, 0.000377 dl/g, which also agrees well with literature value of 0.00039 dl/g [34].

It is of interest to consider if, in fact, the dimensions of the hydrogenous and deuterated chains are perceptibly different. There have been a few studies of the influence of isotopic labeling on chain dimensions in polymer solutions. Schäfer [35] has shown that deuterated polystyrene (d-PS) and hydrogenous polystyrene (h-PS) have similar conformations in cyclohexane at the θ-temperature, while Wang et al. [36] reported that d-PS

has a smaller conformation than h-PS under the same conditions. Strazielle and Benoit [37] reported viscosity measurements with d-PS and h-PS in benzene and suggested that those data indicated a larger dimension for d-PS. When viscosity vs. chain length data for the isotopic analogs were plotted on a log–log plot in a manner that accounted for the differences in repeat unit molecular weight, different exponents were observed.

We consider our viscosity data in the same way as did Strazielle and Benoit. Substituting the degree of polymerization for M_w on the ordinate normalizes for the different repeat molecular weights in the description of chain length. Secondly, since the intrinsic viscosity is based on measurements using concentrations expressed in weight per volume, the value for the d-PS must be normalized to account once again for the difference in repeat unit molecular weight. When the data are plotted in this fashion the two lines for the deuterated and hydrogenous PBs nearly coincide, with the values of the corresponding prefactors (call them K^l) varying by only 2%, which is within our experimental uncertainty. Thus the unperturbed dimensions of the deuterated and hydrogenous PBs are found to be the
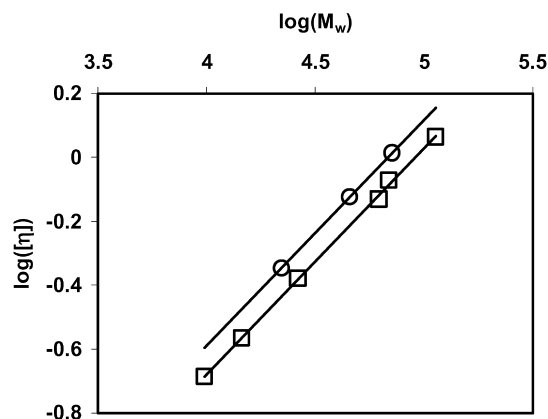

Fig. 2. Plot of the intrinsic viscosity vs. the weight averaged molecular weight for linear hydrogenous (circles) and deuterated (squares) polybutadienes in toluene at 30 °C. The lines are linear regressions which give $K = 0.000377$ dl/g for hydrogenous polybutadiene and $K = 0.000309$ dl/g for deuterated polybutadiene. The slope, a, is 0.708 for both.

same and one is justified in estimating the Mark–Houwink coefficient for the deuterated species simply by proper consideration of the effect of repeat unit molecular weight.

The linear polybutadienes were made using the same reaction conditions as used in the synthesis of the star-branched polybutadienes so that the microstructures of the star and linear analogs were the same. Table 2 summarizes the intrinsic viscosities of star-branched and linear polybutadiene, and their branching factors. The observed variation of the branching factor (g') with degree of branching (f), plotted in Fig. 3, agrees well with that expected from reports for other star-branched polymers in the literature [33], as indicated in the figure.

Although it had been anticipated that the linking reactions should go essentially to completion, 100% linking was not accomplished. Hadjichristidis et al. [29] reported complete linking reactions in the syntheses of 8- and 12-arm star-branched polyisoprenes. To aid completion of the linking, they added about five repeat units of butadiene onto the living ends of the arms before linking because polybutadiene links more readily than does polyisoprene [38]. However, in their work the degree of branching was calculated differently, using the equation $f = M_{w,star}/M_{n,arm}$. This leads to somewhat higher apparent degrees of branching, which are misleading. Table 3 summarizes from their report some selected results on degrees of branching and molecular weights of the arm and star-branched polyisoprenes together with degrees of branching calculated in other ways. When f is recalculated in a manner that reflects a better estimate of the actual degree of branching one finds that they achieved about 90% of their target value as well. We also note that in the present authors' laboratories, linking smaller polybutadiene arms ($M_{w,arm} = 2000$ g/mol) with the same linking agents showed more nearly complete linking than seen when linking larger arms [39]. The degrees of branching for 4-, 8-, and 12-arm linking agents in the case of short arms, determined also by light scattering, were 3.9, 7.7, and 11.1, respectively. This suggests that the incomplete linking of both the polyisoprene star polymers and our larger polymers is due to some steric hindrance or mobility effect in the linking process rather than impurities.

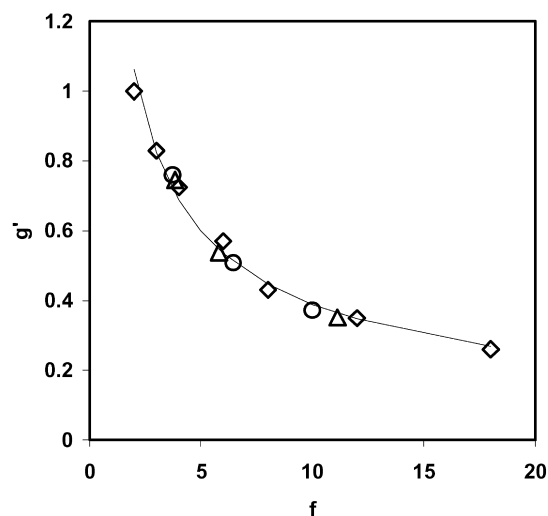The microstructures of the stars were determined using

Fig. 3. Branching factor (g') determined by viscosity measurements vs. degree of branching (f) determined by light scattering. Values from the literature [30] are shown with diamonds, values for the hydrogenous star-branched polybutadienes with triangles, and values for the deuterated star-branched polybutadienes with circles. The thin solid curve is intended as a guide for the eye.

^{1}H NMR for the hydrogenous polybutadienes [40] and ^{13}C NMR for the deuterated polybutadienes [41]. With the reaction conditions used in our study, more than 90% 1,4-addition microstructure was expected [6] and this is also what was found (Table 1). The lower resolution of ^{13}C NMR results in larger uncertainties for the values for the deuterated polybutadienes, but the microstructures of all the samples were the same within the experimental uncertainties.

3.2. Deprotection

The deprotection reaction to remove the *t*-butyldimethyl-silyl group followed a procedure developed by Jang [42] for analogously protected linear polybutadiene using hydrochloric acid in THF. The progress of the reaction was checked by observing the characteristic ^{1}H NMR peaks corresponding to the dimethylsilyl (δ 0.05 ppm, s) and *t*-butyl silyl (δ 0.9 ppm, s) groups at the chain-ends. As the reaction proceeded, these two peaks from the protected

Table 2
Intrinsic viscosities and branching factors for star-branched polybutadienes

Hydrogenous polybutadiene				Deuterated polybutadiene			
f	$[\eta]_{branched}$[a] (dl/g)	$[\eta]_{linear}$[b] (dl/g)	g'[c]	f	$[\eta]_{branched}$[a] (dl/g)	$[\eta]_{linear}$[d] (dl/g)	g'[c]
3.8	0.87 ± 0.008	1.16	0.75	3.7	0.81 ± 0.006	1.06	0.76
5.8	0.66 ± 0.004	1.23	0.54	6.5	0.52 ± 0.003	1.02	0.51
11.1	0.47 ± 0.002	1.35	0.35	10.0	0.38 ± 0.001	1.03	0.37

[a] Measured intrinsic viscosity of star-branched polybutadiene in toluene at 30 °C.
[b] Calculated intrinsic viscosity of hydrogenous linear polybutadiene in toluene at 30 °C using $K = 0.000377$ dl/g and $a = 0.708$.
[c] Branching factor; $g' = [\eta]_{branched}/[\eta]_{linear}$.
[d] Calculated intrinsic viscosity of deuterated linear polybutadiene in toluene at 30 °C using $K = 0.000309$ dl/g and $a = 0.708$.

Table 3
Molecular weights of star-branched polyisoprenes from reference [29] and recalculated degree of branching

Sample	f^a	Arm		Star		f'^b	f''^c
		M_n ($\times 10^{-4}$, g/mol)^d	M_w ($\times 10^{-4}$, g/mol)^e	M_n ($\times 10^{-5}$, g/mol)^d	M_w ($\times 10^{-5}$, g/mol)^f		
8-IAA	7.4	3.74	3.90	2.70	2.76	7.2	7.1
8-IIAAA	6.9^g	8.80	9.20	5.90	6.04	6.7	6.6
12-1A	11.7	3.56	3.70	4.10	4.15	11.5	11.2

[a] The degree of branching; $f = M_{w,star}/M_{n,arm}$.
[b] Recalculation of the degree of branching; $f' = M_{n,star}/M_{n,arm}$.
[c] Recalculation of the degree of branching; $f'' = M_{w,star}/M_{w,arm}$.
[d] Membrane osmometry.
[e] Gel permeation chromatography.
[f] Light scattering in cyclohexane.
[g] This sample was not capped with butadiene prior to linking.

chain end became smaller and finally disappeared after complete deprotection of the chain ends.

For the linear polybutadiene Jang heated a 10 w/v% polymer solution in THF under reflux for 1 h with 1 v/v% concentrated HCl with no problems. However, for the protected star-branched polybutadienes containing the silicon linking agent, this procedure produced some cleaved arm polymer and a trace amount of higher molecular weight polymer in some cases. This side reaction increased with increasing reaction time and concentration of HCl in the reaction solution. Fig. 4 shows SEC chromatograms of deprotected 8-arm star after various reaction times. As reaction time passed 1 h, the cleaved base polymer concentration reached 2.1 wt%. With a further increase in the reaction time to 24 h the base polymer concentration reached 4.5 wt% and a higher molecular weight peak appears as a shoulder of the star polymer peak.

The effect of both reducing the reaction time and reducing the concentration of HCl were tested separately to solve this problem. However, complete deprotection was promoted by longer reaction times and higher concentrations of HCl. Fig. 5 shows how the NMR spectra of the 12-arm star-branched polybutadiene varied as reaction time

increased with 0.3 v/v% (5 equiv. relative to the calculated chain end) of concentrated HCl. With an HCl concentration of 0.3 v/v% the reaction progressed with time, but was not completed within 1 h and required overnight to complete.

One possible explanation for the arm cleavage is oxidation of the star-branched polymer, but neither running the reaction under N_2, nor adding additional antioxidant to the reaction solution provided substantial alleviation of the problem. After considering the two competing issues of arm cleavage and reaction yield, a reaction time of 1 h and HCl concentration of 1 v/v% were chosen to produce 100% deprotection, with the unwanted side products being removed by fractionation if needed.

3.3. Tresylation

In contrast to the deprotection reaction, with the tresylation reaction it was essential to control moisture content to obtain a high yield for the chain-end transformation. So special care was needed in preparing all materials to minimize moisture content. All glassware was dried more than 24 h at 150 °C and TEA and CH_2Cl_2 were dried with CaH_2 and stored over molecular sieves. The polymer reactant with hydroxypropyl chain-ends was also dried by
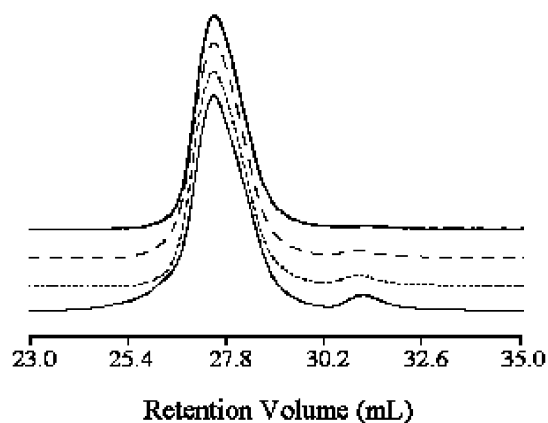

Fig. 4. SEC chromatograms of products of the deprotection reaction of 8-arm star-branched polybutadiene after different reaction times: thick solid line, 0 h; broken line, 1 h; dotted line, 5 h; thin solid line, 24 h.
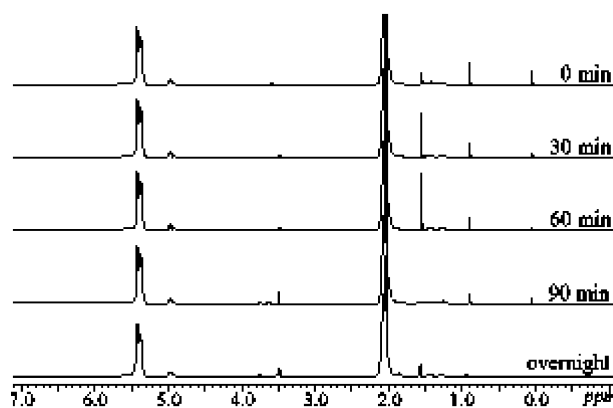

Fig. 5. ^{1}H NMR spectra of the 12-arm star-branched polybutadiene after different reaction times for deprotection with 0.3 v/v% HCl.

adding molecular sieves into a CH_2Cl_2 solution of the reactant and leaving this solution in a refrigerator overnight.

The amounts of TEA and TrCl added to the reaction and the reaction time should not be much in excess of that required, otherwise side reactions become a problem. Fig. 6 shows the SEC chromatogram of 4-arm star-branched polybutadiene before and after the tresylation reaction when using reaction times greater than 12 h and amounts of TEA and TrCl corresponding to more than 10 times the calculated number of moles of hydroxypropyl chain ends. These reaction conditions resulted in cleavage of the star to form arm polymer and higher molecular weight polymer in a manner similar to that seen for the deprotection reaction.

The yield of trifluoroethanesulfonyl-substituted, star-branched polymers could have been checked using elemental analysis if the polymer were pure, but since it is essential to keep BHT in the polymer to avoid oxidation, this method was not used. Instead, ^{1}H NMR was used to estimate the yield of functionalization. Fig. 7 shows the changes in the ^{1}H NMR spectra of the 12-arm, star-branched polybutadiene as the chain end changes from $-C_3H_6OH$ to $-C_3H_6OSO_2CH_2CF_3$ as the reaction time increases. The characteristic ^{1}H NMR peaks from the protons at the double bonds of either the 1,4- or 1,2-addition (δ 5.7–5.2 ppm, m and δ 5.1–4.8 ppm, m) were first used to calculate the microstructure. Then the peak from protons of 1,2-addition (δ 5.1–4.8 ppm, m) was compared to the characteristic ^{1}H NMR peak from the protons of the 2,2,2-trifluoroethane-sulfonyl group (δ 3.88 ppm, q) with the estimated number of repeating units from the molecular weight results. The yields for different reaction times calculated using this method are summarized in Fig. 8. The reaction yield increased with reaction time for times up to about 40 min and then leveled off at 100% yield.

By way of comparison we note that the yield of a tresylation reaction of linear poly(ethylene oxide) (PEO) by Sofia et al. [30] was 75–80% by elemental analysis. They used the same procedure to tresylate $-OH$ chain ends of PEO of molecular weights ranging from 3400 to 20,000 g/mol; this range is very similar to that for the molecular weights of our polybutadienes (9000–25,000 g/mol). Their system may have had lower yield than ours because it is
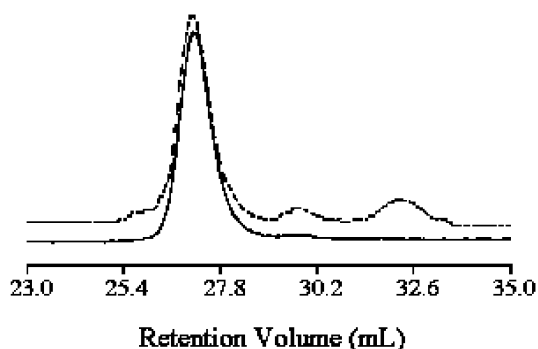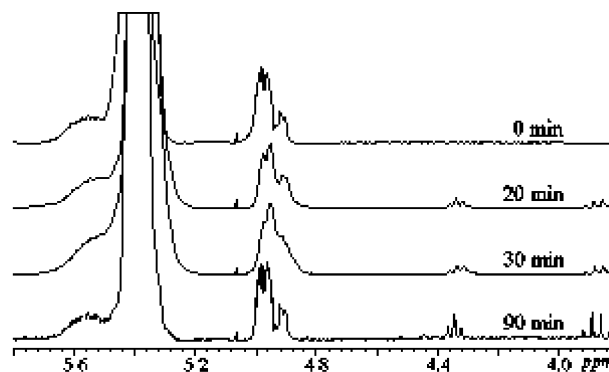

Fig. 7. ^{1}H NMR spectra of the 12-arm star-branched polybutadiene after being subjected to the tresylation reaction for reaction times of 0, 20, 30, and 90 min. The growth of the peaks at δ 3.88 ppm indicates the progression of the reaction.

difficult to remove the moisture completely from hydrophilic poly(ethylene oxide). These polymers are currently under investigation for the effect of chain-end functionalization on bulk thermodynamics of blends of linear and star-branched polybutadienes and these results will be reported shortly.

4. Conclusions

Star-branched polybutadienes with 4, 8, and 12 arms and with $-C_3H_6OSi(CH_3)_2C(CH_3)_3$, $-C_3H_6OH$, and $-C_3H_6OSO_2CH_2CF_3$ chain ends were synthesized. Anionic polymerization of butadiene initiated with 3-(*tert*-butyldimethylsiloxy)-1-propyllithium and then linking with silicon chloride linking agents produced star-branched polymers with *t*-butyldimethylsiloxypropyl chain end functional groups. The degree of branching was generally greater than 80% of the target value. Deprotection of the *t*-butyldimethylsiloxypropyl chain ends was effected using HCl and produced hydroxypropyl chain ends; it was observed that the reaction conditions should be optimized to increase yields and to reduce side reactions which lead to formation of cleaved arm polymer and higher molecular weight polymer. The reaction of the hydroxypropyl-functionalized star-branched polybutadienes with TrCl

Fig. 6. SEC chromatograms of 4-arm star-branched polybutadiene before (solid line) and after (dotted line) tresylation.
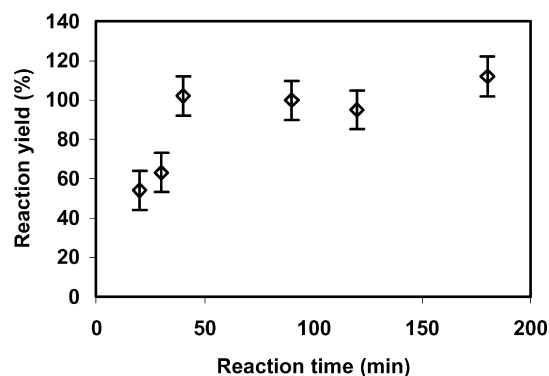

Fig. 8. Variation of reaction yield of the tresylation reaction of 12-arm star-branched polybutadiene with reaction time.

produced star-branched polymers with trifluoroethanesulfo-nyloxypropyl chain ends. In this way, we obtained three series of well-controlled polymer samples having the same architecture and molecular weight, but different chain-ends.

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