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Synthesis and Dilute Solution Properties of Well-Defined H-Shaped Polybutadienes

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ABSTRACT: A novel and advantageous approach to synthesis of H-shaped polybutadienes (H-PBd) is reported. The synthetic strategy employs classical anionic polymerization using high-vacuum techniques and utilizes a difunctional linking agent 4-(dichloromethylsilyl)diphenylethylene (DCMSDPE). The synthesis involves (a) growing a living PBd chain using *s*-BuLi as initiator in benzene at room temperature, (b) titration of DCMSDPE with living PBdLi, (c) addition of *s*-BuLi to activate the double bond of DPE, (d) subsequent addition of butadiene to generate a living "$^1/_2$ H", which has two arms and half of the final cross-bar, and (e) finally coupling the two "$^1/_2$ H" molecules with dichlorodimethylsilane to produce an H-PBd, which has two arms attached to each end of the cross-bar. The weight-average molecular weight, number-average molecular weight, molecular weight distribution, intrinsic viscosity, and radius of gyration were characterized by multidetector size exclusion chromatography (SEC) coupled with a refractive index detector, a two-angle (15° and 90°) light scattering detector, and a Viscotek differential viscometer in tetrahydrofuran at 40 °C. The H-PBds showed narrow and symmetrical molecular weight distributions (polydispersity indices, PDI = 1.03−1.06). Furthermore, the use of light scattering detectors showed that there were no detectable high molecular weight, more highly branched components present in these materials. This is an important advantage of this novel approach over previous synthetic routes to H-polymers. The values of the branching parameters g (0.58−0.77) and g' (0.60−0.75) in the thermodynamically good solvent, tetrahydrofuran, are consistent with values reported previously by Roovers and Toporowski for H polystyrenes in the good solvent toluene. Effects of architecture on the branching parameters are elucidated.

Introduction

The importance of branched polymers is rapidly growing due to their interesting solution, rheological, and mechanical properties.[1] The effects of long chain branching on the properties of polymers and their industrial applications make these materials highly fascinating.[2] However, branched polymers as produced commercially are generally extremely complex mixtures exhibiting polydispersity in molecular weight, extent of branching, and branching architectures. Thus, macromolecules of precisely controlled architectures and narrow molecular weight distributions (MWD) are necessary to understand the effects of branching on polymer properties. Much attention has thus been given to the synthesis of regular star, comb, graft, and dendritic polymers[3−8] in the past, but relatively few studies have focused on H-shaped polymers due to their difficult synthesis.

H-shaped polymers have been synthesized by anionic polymerization using a chlorosilane coupling agent and following a three-step strategy: (a) the difunctional cross-bar was synthesized by anionic polymerization, (b) the cross-bars were end-functionalized by reaction with methyltrichlorosilane, and (c) the monofunctional arms were produced and then coupled with the reactive cross-bars.[7−10] However, this procedure can result in a significant amount of high molecular weight side products with two cross-bars and up to five arms due to the rapid coupling reaction of difunctional cross-bars with trichloromethylsilane.[10] The molecular weights of these byproducts are not too different from that of the H polymer, and therefore it is difficult to separate them by fractionation and difficult to detect them by conventional concentration sensitive size exclusion chromatography (SEC) detectors. Furthermore, the use of difunctional initiators, especially in nonpolar solvents, generates broader MWDs for the connectors as compared to chains produced using monofunctional initiators such as *s*-BuLi.[7] As a result, the disparities between the MWDs of the arms and cross-bars cannot be avoided.

Coupling of two side arms first prior to reaction with the cross-bars appears to offer a superior approach to the more common strategy described above. Roovers et al. reported the first H-shaped polystyrene, where the two living arms (prepared by *s*-BuLi in benzene) were coupled with trichloromethylsilane and then added to the difunctional living cross-bars (prepared by using a difunctional initiator in THF/benzene 50/50 v/v).[11] This procedure can significantly reduce the amount of high molecular weight undesirable products. However, the use of a difunctional initiator and mixed solvent system limits the application of this strategy to the synthesis of polybutadienes with high 1,4-microstructure as well as structural homogeneity of the side arms and cross-bars.

The use of a monofunctional initiator and a special linking agent 4-(chlorodimethylsilane) (CDMSS) or 4-chloromethylsilane provides another alternative approach for the synthesis of H-shaped polymers. A key aspect of this synthesis is the faster coupling of living anions with the Si−Cl bonds of CDMSS to produce a macromonomer with two side arms as opposed to a mixture of macromonomer and initiated living polymers.[12] In the next step, addition of living polymers to the CDMSS results in an off-center living polymer, which then can be coupled with a dichloromethylsilane to obtain the desired H-shaped polymers. However, during the coupling reaction the styrenic double bond also reacts to some degree, which results in a small percentage of graft or comb-shaped polymers with nearly the same or higher molecular weight than the H-shaped polymers, and they are difficult to eliminate by fractionation.

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The Hirao group and the Hadjicristidis group recently reported the synthesis of a number of star and heteroarm star, comb, and dendritic polymers using a 1,1-diphenylethylene (DPE) derivative.[13] The end-capping or coupling of living polymers with these DPE derivatives is more selective than that obtained when using CDMSS. The steric hindrance and inductively electron-donating character of the two phenyl groups of DPE greatly enhance the reactivity of living polymers to the chlorosilyl groups versus reacting with the double bond of DPE. In a later stage the activation of the double bond of DPE and subsequent addition of monomer lead to well-defined branched polymers.

Herein, we report a controlled synthesis of H-shaped high 1,4-polybutadienes by anionic polymerization using high-vacuum techniques with the use of a difunctional DPE-based linking agent 4-(dichloromethylsilyl)diphenylethylene (DCMSDPE). We also report the characterization and dilute solution properties of these materials using SEC coupled with two-angle laser light scattering (TALLS).

Experimental Section

Materials. The monomer butadiene (Bd) (Aldrich, 99%) was distilled twice on the vacuum line over *n*-BuLi before final distillation into calibrated ampules and dilution with a 2.5-fold excess of benzene. The solvents (benzene and hexane, treated with concentrated sulfuric acid to remove olefinic impurities) and coupling agent dichlorodimethylsilane (Aldrich, 99%) were dried over CaH_2 and vacuum-distilled. The initiator *sec*-butyllithium (*s*-BuLi) was prepared[14] from the reaction of distilled *sec*-butyl chloride (Aldrich, 99%) with excess of Li (Aldrich, 99%).

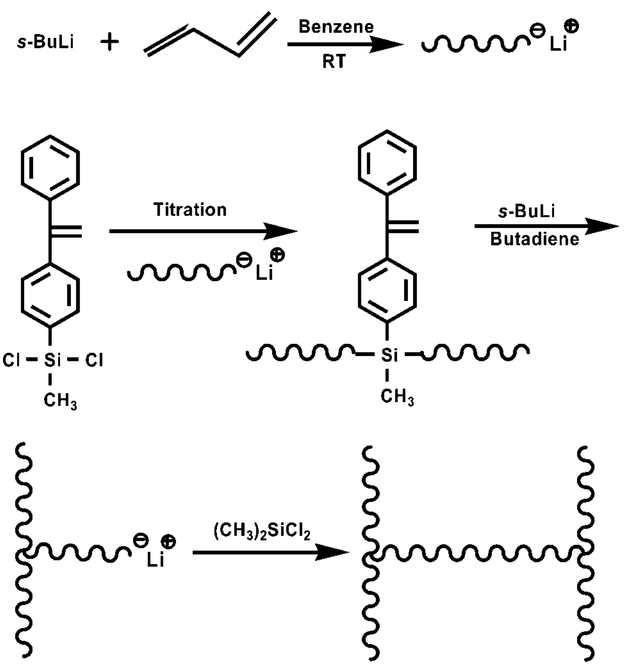
4-(Dichloromethylsilyl)diphenylethylene. The linking agent DCMSDPE was prepared using high-vacuum techniques as reported previously.[15] Briefly, the starting material 4-bromobenzophenylehylene was prepared by the Wittig reaction of 4-bromobenzophenone and methyltriphenylphosphonium iodide in the presence of *n*-BuLi. In a second step the Grignard coupling reaction of 4-bromobenzophenylehylene with trichloromethylsilane produced the linking agent DCMSDPE. It was vacuum-distilled and sealed in glass ampules with break-seals. An adequate concentration of DCMSDPE was diluted prior to use.

Manipulative Techniques. The synthetic manipulations were conducted using classical high-vacuum techniques, using all-glass *n*-BuLi-washed and benzene-rinsed reactors, equipped with break-seals for the addition of reagents and constrictions for the removal of intermediate products.[16]

Synthesis of H-Shaped Polybutadienes (H-PBd). The synthesis involves growing a living linear PBd and then slowly adding the living chain to DCMSDPE, followed by an addition of *s*-BuLi to activate the double bond of DCMSDPE, polymerization of Bd from newly generated anionic site to produce the third living arm, and finally coupling with dichlorodimethylsilane to produce H-shaped PBd (Scheme 1).

The living PBdLi arm was synthesized by the polymerization of butadiene (6 g, 111 mmol) with *s*-BuLi (0.55 mmol, titrated twice with 1,2-dibromobutane to determine the exact concentration of the initiator) in benzene (100 mL) at room temperature for 24 h. The small amount of PBdLi was separated by heat-sealing the constriction for characterization. The rest of the living PBdLi was then collected in a precalibrated ampule with break-seals and used for the coupling of DCMDPE. The PBdLi ($M_n = 10.6$ kg/mol, 0.55 mmol) was added dropwise to the DCMDPE (0.05 g, 0.17 mmol) in benzene (100 mL) under vigorous stirring. The slow addition was carried out over a period of 36 h, and the progress of the coupling reaction was monitored by taking several aliquots out and characterizing them using SEC. After the addition of ~2 equiv of PBdLi relative to DCMSDPE, the end point was observed from SEC and the titration was stopped. The excess PBdLi was then removed from the apparatus by heat-sealing the constriction.

Scheme 1. Synthetic Scheme of H-Shaped Polybutadienes



The desired amount of initiator *s*-BuLi (0.17 mmol) was then added to the flask. The solution color immediately turned to deep red, indicating the opening of the double bond of the DPE. The solution was stirred over 48 h to ensure all the DPE group reacted with *s*-BuLi. A fresh portion of the butadiene monomer (3.33 g, 61.66 mmol) was added to produce half-cross-bars of H-shaped PBd. The linking agent dichlorodimethylsilane (0.01 g, 0.08 mmol) was then added to connect two “$^{1}/_{2}$ Hs” to produce H-shaped PBd. The reaction was monitored by taking a small amount out via constrictions for SEC analysis. The linking solutions were permitted to react for 3 weeks before quenching. The raw final polymers were stabilized with butylated hydroxytoluene (BHT) and precipitated into a large excess of methanol. Fractionation was performed using toluene/methanol as the solvent/nonsolvent pair. Fractionation was repeated to obtain optimal results. The fractionated polymer was precipitated in an excess of methanol and vacuum-dried prior to characterization.

Molecular Characterization Methods. Size exclusion chromatography/two-angle laser light scattering (SEC-TALLS) connected with a refractive index (RI) detector and Viscotek differential viscometer was used to characterize precursors and final H polymers. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1.0 mL/min at 40 °C. This system features a Waters 1525 high-pressure pump, Waters Ultrastyragel columns (HR-2, HR-4, HR-5E, HR-5E, and HR-6E with pore sizes 10^3, 10^4, and 10^5 Å), a Waters 2410 differential refractometer detector (at 680 nm), a Precision Detectors PD-2040 two-angle (15°, 90°) light scattering detector, and a Viscotek differential viscometer. The Precision Detectors software “Discovery 32” was used to calculate the M_w values from SEC-TALLS data. The refractive index increment (d*n*/d*c*) value was measured on a Wyatt Optilab DSP detector at a wavelength of 690 nm and temperature of 40 °C in THF. After d*n*/d*c* was measured for five different concentrations of each sample, the average value 0.130 mL g^{-1} was used. The same instrument was used to study the solution properties (intrinsic viscosity and radius of gyration) of H-shaped PBd. We have previously demonstrated that SEC-TALLS provides reliable (±5%) molecular weights and radii of gyration for linear and branched polymers up to sizes between 13 and 42 nm based on experiment. However, theoretically it was shown that values of R_g measured for Gaussian coils by TALLS should only be at most 2% less than the true values up to $R_g < 72$ nm.[17]

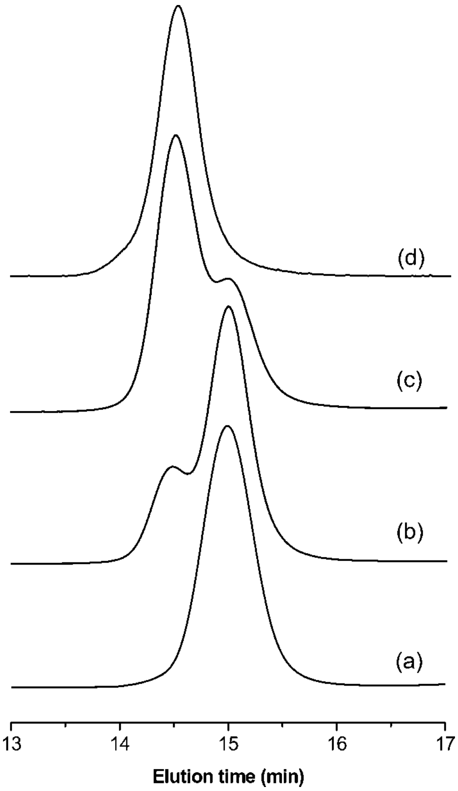


Figure 1. Size-exclusion chromatography (SEC) profiles during the coupling reaction of living PBd with DCMSDPE: (a) PBd-DPE-SiCl, (b) and (c) mixture of PBd-DPE-PBd and PBd-DPE-SiCl, (d) PBd-DPE-PBd (99%). The samples were analyzed in THF at 40 °C.

Results and Discussion

Synthesis of H-Shaped PBd. The general synthetic route used for the synthesis of H-shaped polybutadienes is given in Scheme 1.

The titration of DCMSDPE by slow addition of living PBdLi yields what is in effect a coupled PBd with the double bond of DPE in the center of the chain. The key factor for this synthesis is the selective substitution reaction of the two chlorines of DCMSDPE with two polyanions. The reaction of polyanions is much more selective with the DPE derivative relative to the styrene derivative, and this is a key advantage of this approach. The titration was monitored by taking aliquots by the heat-sealing sample tubes with constrictions to obtain samples that were then analyzed using SEC. Figure 1 shows the typical chromatograms obtained at various times during the coupling reaction. Initially, the SEC profile was monomodal (Figure 1a), which indicates the selective reaction of one chlorine of DCMSDPE with the PBd. As the titration continues, the SEC profile becomes bimodal, and finally the SEC peak corresponding to the reaction product of the reaction of DCMSDPE with one PBd disappears (Figure 1d). At this point the sharp change of the colorless reaction solution to pale yellow also indicates the end point of the titration. By careful and very slow addition of living PBdLi to DCMSDPE, ~99% coupling can be achieved. However, balancing the stoichiometry is always vital to get pure in-chain DPE, and thus great caution and patience should be exercised when performing the titration. If the titration is incomplete and SiCl remains in the system, it will react with the *s*-BuLi added in the next step, while the addition of excess living PBdLi will initiate polymerization of the butadiene monomer added in the next step. Both cases will lead to undesirable products.

Table 1. Molecular Characteristics of the Precursors, Intermediates, and Fractionated H-Shaped Polybutadienes

sample	M_n (arm),[a] kg/mol	M_n ($^1/_2$ H),[a] kg/mol	M_n (cross-bars),[b] kg/mol	M_n (H),[a] kg/mol	M_w/M_n (H)[a]
1	10.6	41.0	39.9	82.3	1.03
2	11.3	49.5	53.3	98.5	1.03
3	15.3	82.4	97.0	158	1.04
4	29.6	80.2	42.6	161	1.06
5	41.6	105	45.6	212	1.05

[a] Molecular weight (M_n) and polydispersity indices (M_w/M_n) were measured by size-exclusion chromatography—two angle laser light scattering (SEC-TALLS) in THF at 40 °C. [b] M_n is calculated using the relation M_n(cross-bar) = {M_n(H) − M_n(arm) × 4}.

The addition of *s*-BuLi initiator activates the double bond of the in-chain DPE derivative. The immediate color change from pale yellow to deep red indicates that the in-chain double bond of DPE was initiated. Subsequent addition of butadiene monomer leads to growth of the half-cross-bar of the H-shaped PBd with two arms attached. The target molecular weight of the cross-bar was estimated from the moles of DPELi and Bd added. A small aliquot was taken for characterization by SEC-TALLS. The observed M_n was in good agreement with the calculated M_n of the off-center living $^1/_2$ H (Table 1). However, the polydispersity of the $^1/_2$ H (PDI = 1.09) (Figure 2c) was broader than that of the precursor arms (PDI = 1.01−1.03). Their broader PDI likely reflects a small amount of a low molecular weight component (Figure 2c) that is attributable to addition of a slight excess of *sec*-BuLi when activating the in-chain DPE.

Dichlorodimethylsilane was added to the reactor to connect two $^1/_2$ Hs and produce the desired H-shaped PBd. The stoichiometry of this coupling reaction was also balanced carefully to obtain the maximum yield of final H polymer. In general, an excess of living polymer is usually added to chlorosilane coupling/linking agents, which leads to about 70−80% of the desired product. Earlier work suggested that the addition of equimolar living polymer to the coupling agent (living anion:coupling agent 2:1) or even 5−10% excess of coupling agent compared to living polymers resulted in nearly ~95% yield of polymer.[18] In the present case, we have used equimolar concentrations of living polymers to the coupling agent (2:1). The resulting H polymer was isolated with ~90% yield. Each step of the synthesis to produce H-shaped PBd was monitored by SEC. Figure 2 shows the SEC-TALLS (15° angle) profiles of arm, coupled arm, $^1/_2$ H, unfractionated H, and pure H polymers after fractionation. The SEC of pure H polymers shows no visible shoulder or tailing, suggesting that the H-shaped PBd was formed successfully. It is particularly significant for these materials, which are to be used in rheology studies, that there are no shoulders detected at the high molecular weight end of the MWD, which would indicate the presence of higher molecular weight, more highly branched polymer species which could dominate the rheology even at very low levels. In our experience, H samples produced by the conventional routes described above usually contain readily detectable levels of such contaminants when characterized by SEC with low-angle light scattering detection.[19] This has also been confirmed by temperature gradient interaction chromatography.[10]

The molecular characteristics of a series of H-shaped PBds with different arm lengths and different cross-bars are given in Table 1. The polymers exhibit narrow MWDs as well as controlled molecular weights of the H polymer, which also indicate that the symmetric H-shaped polymer has been achieved as desired.

Dilute Solution Properties of H-PBd. The dilute solution properties of H-shaped polybutadiene samples were characterized using a multidetector SEC, which characterizes the polymer in each elution volume as it emerges from the column to produce plots of radius of gyration and intrinsic viscosity as a function of the molecular weight of each fractionated polymer. For each sample the values of molecular weight (Table 1), radius of gyration (R_g),

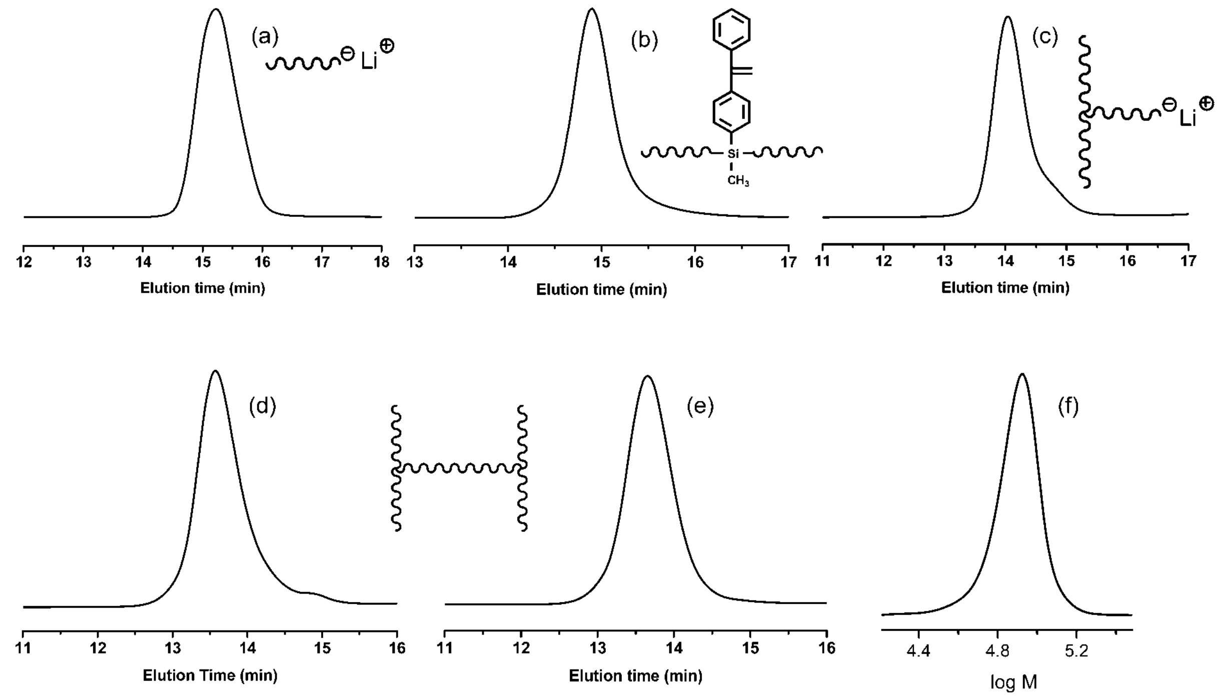


Figure 2. Size-exclusion chromatography/two-angle laser light scattering (SEC-TALLS) elution profiles of precursors and H-shaped PBd (entry 1, Table 1) (for the LS response at 15°): (a) living PBd arm, (b) coupled PBd arm, (c) off center living PBd ($^1/_2$ H), (d) H-PBd before fractionation, (e) pure H-PBd after fractionation, and (f) log *M* profile of a pure H-PBd.

and intrinsic viscosity ([η]) (Table 2) at the maximum of concentration detector chromatogram peak were used, rather than any average values, in order to minimize errors due to differences in PDI between the samples.[20] The typical error bars associated with SEC-TALLS have been shown experimentally to be ±5%.[17] The R_g values in Table 2 are relatively small and may therefore be susceptible to errors as large as ±10%. However, it should be noted that SEC columns are generally very effective filters for removal of extraneous matter from the sample, thus aiding in the determination of R_g from scattering data obtained at angles ≤90° for samples with small R_g.

It can be seen from the Table 2 that even though there is not much difference in the molecular weights of samples 1 and 2, the intrinsic viscosities differ quite appreciably. Sample 3 exhibits a higher value of [η] than sample 4, although the latter has a slightly higher M_w. The higher [η] value for sample 4 can be attributed to the increase in backbone length. The R_g values show a similar trend as well. However, the R_g values are less affected by the change in backbone length than are the [η] values for the corresponding samples, although the R_g of sample 3 is nevertheless higher than that of sample 4.

Table 3 presents the calculated values of branching contraction parameters *g* and *g*′ where

$$g = \langle R_g^{\ 2}\rangle_b / \langle R_g^{\ 2}\rangle_l \tag{1}$$

and

$$g' = [\eta]_b/[\eta]_l \tag{2}$$

Table 2. Dilute Solution Properties of H-Shaped Polybutadienes in THF at 40 °C Using Multidetector SEC

sample	R_g (nm)	[η] (dL/g)
1	10.7	0.678
2	12.9	0.812
3	18.3	1.39
4	16.5	1.22
5	21.1	1.52

Table 3. Branching Parameters of H-Shaped Polybutadienes in THF

sample	g	g_{th}	λ	g'	ε	R_v/R_g
1	0.58	0.85	0.48	0.60	0.94	0.91
2	0.68	0.87	0.54	0.70	0.92	0.85
3	0.77	0.90	0.61	0.75	1.10	0.84
4	0.60	0.74	0.26	0.64	0.87	0.90
5	0.72	0.72	0.22	0.74	0.92	0.83

The subscripts “b” and “l” stand for branched and linear polymers, respectively, of the same molecular weight and the same composition. The measurements of *g* and *g*′ were carried out for polybutadienes in the thermodynamically good solvent THF via multidetector SEC at 40 °C. To obtain [η] and R_g for the linear 1,4-polybutadiene corresponding to the same molecular weight as a given H polymer, we utilized data on linear high 1,4-polybutadienes in THF published by Jackson et al.[20] which are

$$R_g = 1.6 \times 10^{-2} M^{0.597} \text{ (nm)} \tag{3}$$

$$[\eta] = 2.52 \times 10^{-4} M^{0.73} \text{ (dL/g)} \tag{4}$$

The values of *g* and *g*′ are always <1, indicating the expected smaller dimensions of branched species relative to linear ones of the same molecular weight. The observed values of *g* and *g*′ for H-shaped polybutadienes are in the range of 0.58−0.77 and 0.60−0.75, respectively, indicating that the systems are lightly branched—not surprising since they have only four arms of equal length separated by a linear cross-bar. λ in Table 3 is the weight fraction of polymer in the backbone (taken as the cross-bar). It is generally expected that as λ increases, which imparts more linear-like behavior to these molecules, there will be an increase in *g* and *g*′. Polymers with very short cross-bars, on the other hand, approach the behavior of 4-arm stars.[21] The sample with the highest λ value, sample 3, exhibits the highest values of *g* and *g*′, but the experimental data do not consistently follow the expected trend. To further illustrate this point, a comparison of theoretical branching parameter (g_{th}) with the experimentally observed g values is provided in Table 3. The theoretical g_{th} values were calculated using eq 5, which was proposed by Pearson et al.[22] for H-shaped molecule having four arms of equal length connected via a backbone of variable length:

$$g_{th} = \lambda^3 + 3\lambda^2(1 - \lambda) + (9/4)\lambda(1 - \lambda)^2 + (5/8)(1 - \lambda)^3 \quad (5)$$

It should be noted this expression is for H polymers in the melt or under theta conditions, but we nevertheless compare our results obtained in thermodynamically good solvents with this theory because theory has shown there to be little difference between g values for H polymers measured in good vs theta solvents.[23] The g_{th} value of sample 5 with equal four arms and backbone is 0.72, which is identical to our experimental g value of 0.72. The other samples 1−4 show significant differences between the experimental and theoretical g values. For samples 1 and 2 this may reflect experimental errors in the determination of R_g, since these polymers are approaching the lower size limit for measuring R_g by light scattering. However, the trends reflected by the g' values follow those of the g values, since the intrinsic viscosity is accurately measured even at low molecular weights and the combined data appear to suggest that the variations cannot be accounted for by experimental errors only.

Although experimental results on dilute solution properties of well-defined combs and "centipede" molecules are plentiful, there are not many results available on well-defined H-shaped polymers.[21] The most detailed study of dilute solution properties on H-shaped polymers (polystyrenes) in a good solvent (toluene) was reported by Roovers and Toporowski.[11] They reported good solvent values of g and g' to be 0.69 and 0.73, respectively, for H polymers with 20% of their mass in the cross-bar. Our values of g appear to be in very good to fair agreement with these reported values, with samples 2 and 5 yielding the closest values. Since sample 5 has around 20% of its mass in the cross-bar, the similarity in the values of g and g' for the Roovers and Toporowski polymers and our sample 5 is reassuring. In addition, the g value for sample 5 with $\lambda = 0.22$ can be directly compared with the renormalization group theory g value reported for an H polymer consisting of five segments of equivalent length in a thermodynamically good solvent.[23] The measured value for sample 5 (0.72) is in perfect agreement with this theoretical value.

The branching parameters g and g' are related by the empirical factor ε as follows:

$$g' = g^{\varepsilon} \quad (6)$$

where ε is the structure factor or branching exponent and is dependent on the type of branching (star, comb, centipedes).[24] The reported values of ε for regular comb and centipedes range from 0.7 to 1.0.[25] The values of ε for H polystyrenes in toluene have been reported to be 0.92.[11] Our ε values for samples 1, 2, 4, and 5 (0.94, 0.92, 0.87, and 0.92, respectively) are close to this reported value. The value of sample 3 shows a slightly higher value (1.1) and is in agreement with theory reported by Berry, who suggested that as the fraction of monomer units increases in the backbone the ε value tends toward unity.[26]

We calculated the viscometric radius (R_v) using

$$R_v = \left(\frac{3[\eta]M}{10\pi N_A}\right)^{1/3} \quad (7)$$

where M is taken as the weight-average molecular weight and N_A is Avogadro's number. The ratios of the viscometric radii to the radii of gyration are presented in Table 3 and are essentially constant in the range of 0.87 ± 0.04. Corresponding good solvent values for R_v/R_g of linear polymers are in the range of approximately 0.63−0.71,[27] and thus this parameter for H polymers exhibits values intermediate to those of linear polymers and hard spheres, as expected for lightly branched polymers.[21]

Conclusions

H-shaped polybutadienes (H-PBd) with controlled architecture have been synthesized by using a novel dual functional linking agent. This method uses only monofunctional initiators (*s*-BuLi) in nonpolar solvents for the preparation of both side arms and cross-bars, which allows a high degree of control over the microstructure, molecular weight distribution, and structural homogeneity of both side arms and cross-bars. Several H-PBd's were synthesized, and the products were characterized by multidetector SEC. The H-PBds obtained by fractionation showed narrow molecular weight distributions, with M_w/M_n values of 1.03−1.06. The dilute solution properties of H-shaped polybutadienes with different backbone contents and different arm lengths have been studied. Results for H polymers having about 20% of their mass in the backbone are in good agreement with theoretical predictions and previously published experimental data on H polystyrenes. For H polymers having higher mass fractions in the backbone, discrepancies between theory and experiment are noted.

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