Synthesis and Characterization of Polybutadiene and Poly(ethylene−1-butene) Combs

C. M. Fernyhough* and R. N. Young

Department of Chemistry, University of Sheffield, Brookhill, Sheffield, U.K. S3 7HF

D. Poche

The Dow Chemical Company, Plaquemine, Louisiana 70765-0400

A. W. Degroot

The Dow Chemical Company, 2301 North Brazosport Boulevard, Freeport, Texas 77541-3257

F. Bosscher

The Dow Chemical Company, 4530 AA Terneuzen, The Netherlands

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ABSTRACT: A series of polybutadiene "combs" with polydispersities less than 1.2 have been synthesized using anionic polymerization techniques. Control was exerted over the average number and length of branches but not on their placement along the polybutadiene backbone. Hydrogenation of the materials resulted in the formation of the corresponding poly(ethylene-*co*-butene) combs. The effects of branching on the solution properties of the polybutadiene combs have been examined. As predicted using the Berry−Orofino model, the "shrinking factor" g' decreases with increasing branch length. The effect of branching on the Zimm−Stockmayer parameter, g, has also been investigated.

Introduction

The rheology of H-polymers,[1] super-H polymers,[2] and star-shaped polymers[3−12] has been examined in detail in the past few years and modeled theoretically. Solution properties of stars[13−16] and highly branched combs[17] have also been determined. It is immediately clear that the physical properties of polymers having branched architectures are significantly different than those of linear polymers and that, by synthesizing "model" polymers, the influence of variables such as the number and the length of the branches can be systematically examined.

Anionic polymerization provides a useful route for the preparation of model polymer architectures having narrow molecular weight distributions and controllable molecular mass. The utilization of chlorosilanes as linking agents has allowed well-defined nonlinear architectures such as stars and H-polymers to be produced.[18−23] Other complex architectures have been created via the functionalization of polymer chains by means of the hydrosilylation reaction whereby a silicon−hydrogen moiety can add across a carbon−carbon double bond in the presence of a platinum catalyst. For example, reaction of chlorodimethylsilane with polybutadiene results in the attachment of chlorodimethylsilyl groups. The reaction takes place, under mild conditions, exclusively at pendant vinyl groups, i.e., the double bonds resulting from 1,2-addition of butadiene during polymerization. By incorporating a block of 1,2-enchained polybutadiene at the end of a polystyrene chain, hydrosilylating with dichloromethylsilane, and subsequently adding polybutadienyllithium, Wang et al.[24] were able to produce "umbrella"-shaped polymers. Multiarm starlike polybutadienes have been produced by hydrosilylating low molecular weight 1,2-polybutadiene and then introducing living anionic polymer chains.[25] Aborescent graft copolymers were produced by Hempenius et al.[26] by hydrosilylating polybutadiene having approximately 7% 1,2-content, introducing polybutadienyllithium, and then repeating the cycle. Similarly, comb copolymers have been synthesized[27,28] by grafting polystyrene branches onto a functionalized polybutadiene backbone using similar methodology, and recently, polybutadiene combs have been synthesized via a hydrosilylation route.[29] *tert*-Butyl methacrylate has also been grafted onto polybutadiene to yield a precursor for a liquid-crystalline comb.[30] Presently, direct "living" anionic synthesis of polyolefins is not possible. However, certain polyolefins are accessible indirectly through hydrogenation of polybutadienes. For example, ethylene-*co*-1-butene polymers with controlled weight and narrow molecular weight distribution have been produced by hydrogenating anionically produced polybutadiene,[31−33] and their rheology[34] and melt dimensions[35] were then determined.

The present work is part of a larger and ongoing program to investigate the role of long-chain branching on the processing characteristics of polyethylene. To that end, the synthesis of "comb" polymers has been undertaken. The availability of polybutadiene combs having irregularly spaced branching, but where the average number and the length of the branches have been well-characterized, is the prerequisite for the examination of the solution and melt properties of the parent polybutadienes and, subsequently, their hydrogenated counterparts. Examination of the solution and melt properties of these parent polybutadienes has much novelty in its own right as the literature does not appear to contain any previous systematic studies on polybutadiene combs. Furthermore, comparison of the properties with those of the corresponding polyolefins formed on hydrogenation was anticipated to be revealing.

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Experimental Section

Hydrosilylation of a Polybutadiene Backbone: Method "a". The solvents, initiator, and butadiene were purified using standard techniques for anionic polymerization.[36] Chlorodimethylsilane (Aldrich) and chlorotrimethylsilane (Aldrich) were distilled under reduced pressure and the middle fractions collected.

Butadiene was polymerized in *n*-hexane using *sec*-BuLi as the initiator in an all-glass apparatus which had been flamed under vacuum before use. Reagents were added from ampules by the rupturing of glass break-seals. Reactions were carried out under high vacuum at 30 °C for a minimum of 48 h to ensure completion. Once the polymerization was complete and the polymer had been dried thoroughly, the polybutadiene (no more than 10 g) was dissolved in dry THF. Chlorotrimethylsilane (2 cm^3, 0.016 mol) and platinum−divinyltetramethyldisiloxane (80 μL) were added to the reactor prior to the introduction of chlorodimethylsilane (5 cm^3, 0.045 mol). The hydrosilylation reaction[29,26] was performed under vacuum, a little oxygen being allowed to enter to vessel prior to the commencement of the reaction. A sample was taken from the reactor after 18 h reaction time at 70 °C, the chlorosilyl moieties were deactivated using *n*-BuLi, and the polymer was recovered and analyzed by ^{1}H NMR and size exclusion chromatography (SEC). THF and unreacted chlorodimethylsilane were removed from the remaining contents of the reactor under reduced pressure for several days; the polymer was dissolved in dry benzene, and the process was repeated to ensure complete removal of the silane. The hydrosilylated polymer was finally dissolved in benzene and isolated in a glass ampule.

Hydrosilylation of a Polybutadiene Backbone: Method "b". Method "b" is similar to method "a", but after completion of the *sec*-BuLi initiated polymerization on a 20 g scale, the polybutadienyllithium was terminated using chlorotrimethylsilane from an ampule. A small sample of the backbone was taken for SEC and ^{1}H NMR analysis. The hydrosilylation was then performed, the platinum catalyst and chlorodimethylsilane were added directly to the reaction vessel, and the excess silane was removed in a manner similar to method "a".

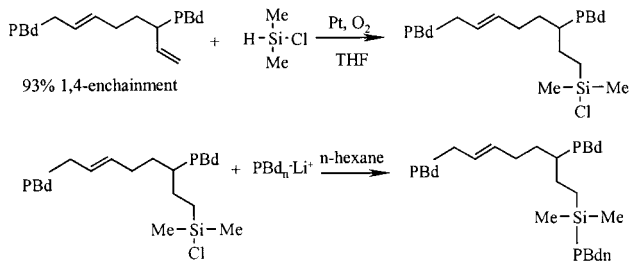
Synthesis of Combs. Polybutadienyllithium "branches" were prepared in a manner similar to the backbone as detailed above. A sample was taken for SEC analysis prior to the addition of the hydrosilylated polybutadiene backbone. *n*-BuLi was added to the reaction mixture after 24 h in order to destroy unreacted chlorosilane functionalities which had not been utilized. The excess *n*-BuLi was destroyed after 6 h using degassed methanol, and the polymer precipitated in bulk methanol and 2,6-di-*tert*-butyl 4-methylphenol were added as antioxidant.

Hydrogenation of Combs. Diimine hydrogenation was carried out in a method similar to that of Hahn[37] with polybutadiene, toluenesulfonylhydrazide, and tri-*n*-propylamine being refluxed together in *o*-xylene for 4−5 h. The resulting poly(ethylene-*co*-1-butene) was precipitated in methanol, filtered, and washed with dilute hydrochloric acid and then hot water.[38] The polymer was dissolved in hot toluene and precipitated in methanol, and the purification process was repeated.

Characterization. The products of the hydrosilylation reaction were analyzed by ^{1}H NMR spectroscopy in $CDCl_3$ at 30 °C using a Bruker AC250 MHz spectrometer. Poly(ethylene-*co*-butene) samples were analyzed by ^{1}H NMR in d_8-toluene using a Bruker 400 MHz spectrometer at 80 °C.

The molecular mass and chain dimensions of the polybutadiene combs were determined by SEC/triple detector consisting of a Waters 150-C pump equilibrated at 35 °C with 2 Polymer Laboratories gel mixed-C columns, a differential refractive index (DRI) detector fitted with a 12 V light source and externally powered at 11 V, a Viscotek model 150R viscometer, and a Chromatix KMX-6 LALLS (low-angle laser light scattering) detector (633 nm). The DRI and viscometer were calibrated with a 68K narrow polystyrene standard and Dow 1683 broad polystyrene. The mobile phase was THF with a flow rate of 0.929 mL/min. The sample concentration ranged from 0.1 to 3.5 mg/mL depending on the sample. Concentrations for viscosity data were 0.45−0.65 mg/mL, except for side chains (branch material) which were 2.5−3.5 mg/mL. The instrument constant for the LALLS unit was derived through measurement of the attenuator constants. The specific refractive index (d*n*/d*c*) was calculated from the calibrated DRI detector and determined to be in the range 0.122−0.127 mL/g. The values are similar to those reported by Hempenius,[26] who found linear polybutadienes to have d*n*/d*c* values of 0.13 mL/g and aborescent grafts to exhibit values in the region of 0.121−0.122 mL/g in THF at 633 nm.

Scheme 1. Reaction Scheme for the Synthesis of Polybutadiene Combs



The molecular mass and branching distributions of the hydrogenated polybutadienes were measured at 140 °C using high-temperature SEC with a Waters Alliance GPCV 2000 and a Wyatt multiangle laser light scattering (MALLS). The MALLS was equipped with an ultrahigh-temperature cell and an argon ion laser (488 nm). The specific refractive index (d*n*/d*c*) of polyethylene was determined to be 0.106 mL/g, calculated from the calibrated DRI detector. The mobile phase was trichlorobenzene, stabilized with 200 ppm of bis(hydroxytoluene) at a flow rate of 1.12 mL/min. The sample concentration ranged from 1 to 4 mg/mL depending on the sample. Three Polymer Laboratories 10 μm mixed B columns were used for the separation and the injection volume was 200 μL. Astra software (Wyatt) was used to calculate the absolute molecular weights at each retention time and the molecular weight moments M_n, M_w, and M_z. Fourier transform infrared (FTIR) measurements were performed using a Mattson 2020 Galaxy series FTIR spectrophotometer and WinFirst software. Spectra of thin (0.03 mm) hydrogenated polybutadiene films were collected plus Nujol mulls of toluenesulfonylhydrazide, toluenesulfinic acid, and toluenesulfonic acid. The background spectrum of Nujol was taken as a reference.

Results and Discussion

Method a. The reaction scheme employed to produce polybutadiene combs is shown in Scheme 1. The backbones of the combs were made in 50 g batches, one of approximately 60 000 g/mol and the other of 120 000 g/mol molecular mass. By using a few grams of these polymers in each of several hydrosilylation reactions, it was possible to prepare two sets of comb samples where the backbone molecular weight was a common factor.

Method b. For these reactions, a large amount of polybutadiene backbone (up to 30 g) was subjected to hydrosilylation, and therefore it was decided that residual impurities of water/methanol would, in all likelihood, be difficult and time-consuming to remove from such an amount of a highly viscous polymer. A quicker, easier route was therefore devised, the polybutadienyllithium being terminated with excess chlorotrimethylsilane which acted also to dry the hydrosilylation catalyst before commencing the next stage of the reaction. The *n*-hexane in which the butadiene had been polymerized was removed under vacuum prior to termination of the polybutadienyllithium and replaced

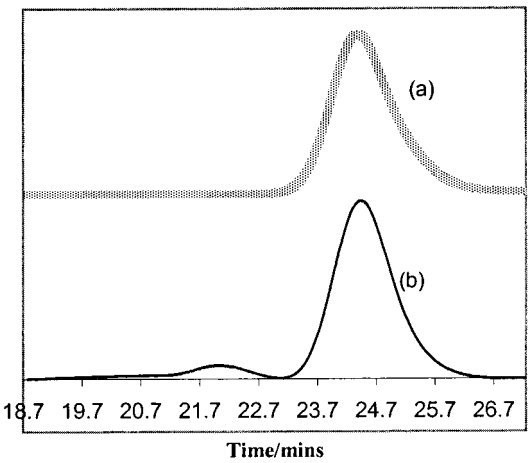


Figure 1. SEC trace of 120 000 g/mol polybutadiene backbone before and after hydrosilylation: (a) backbone before hydrosilylation; (b) backbone after hydrosilylation.

with dry THF. At this point, the solution became bright yellow in color. The capping reaction was fast, the solution rapidly becoming colorless after the introduction of the chlorotrimethylsilane.

Hydrosilylation. Oxygen has been reported to be a key element in the hydrosilylation reaction,[39] and although the reaction itself is carried out under vacuum, it is possible, by using a series of greaseless stopcocks, to add a cocatalytic amount of oxygen to a THF solution of the catalyst prior to admitting it into the main reactor vessel. A yellow color appeared after a few minutes—this is a characteristic of the hydrosilylation reaction.[40] ^{1}H NMR was used to monitor the reaction. Hydrosilylation takes place exclusively at the 1,2-enchained polybutadiene units (pendant vinyl groups) under mild conditions.[41] SEC was used to check the sample once the hydrosilylation was complete. Figure 1 shows the trace for 120 000 g/mol polybutadiene before and after hydrosilylation. The peak at 22 min corresponds to coupled material; it is exactly twice the molecular weight of the original backbone. It is apparent that coupling, typically around 5%, occurs during the course of the reaction and is most likely due to Si−O−Si linking caused by the presence of residual moisture despite the careful procedures employed. Linking of this type becomes more apparent when the backbone is extensively functionalized, an analogous observation having been made during the synthesis of multiarmed star polymers using chlorosilane linking agents of varying functionalities.[23] The removal of volatiles from the polymer was performed with the vessel undergoing evacuation for several days before redissolving the polybutadiene and again removing the solvent and silanes. Although chlorodimethylsilane is highly volatile, the polybutadiene in which it is dissolved is of a sufficiently high molecular weight to make its removal quite problematic—the viscosity being very high and stirring not being possible. Once purification of the functionalized backbone was complete, a benzene solution of the polymer was isolated under vacuum in an ampule. Polybutadienyllithium was added under vacuum (typically a 10:1 molar ratio of branch:backbone) in order to obtain polybutadiene combs with around 8−9 branches; a small amount of the polybutadienyllithium was terminated by residual chlorodimethylsilane present in the backbone solution. Typically, 10−20% of unreacted branch material was present in the final comb

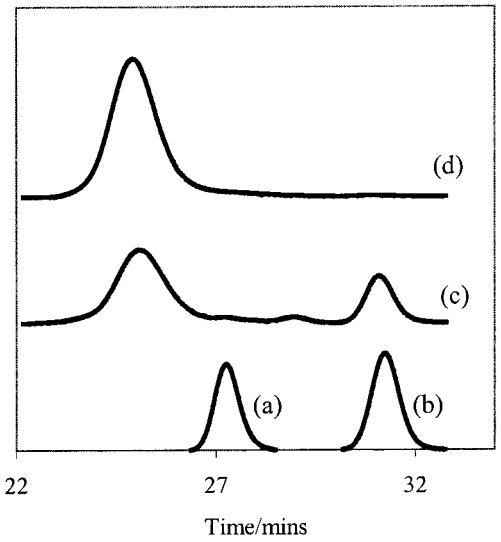


Figure 2. SEC traces for the synthesis of comb b54-15 (a) shows the backbone trace, (b) the branches, (c) the unfractionated comb, and (d) the fractionated polymer.

product. The minimization of excess branch material is a distinct advantage over the alternative method recently reported by Hadjichristidis[29] whereby very large excesses of polybutadienyllithium are added to backbone material of limited functionality in order to produce comb material. The other advantage is the increased control exerted over the number of branches present on the final comb polymer. Addition of very low silane concentrations inhibits the catalytic cycle with platinum, and the hydrosilylation reaction fails.[27] It is accordingly difficult to control the extent of the hydrosilylation reaction and thereby the extent of branching of the final comb product. Instead, approximately 20 sites were hydrosilyated per polymer chain in a typical reaction, but the results varied significantly between experiments. Limiting the quantity of polybutadienyllithium introduced afforded flexible control over the number of branches. Once the subsequent reaction with polybutadienyllithium branches was complete (24 h), the remaining reactive sites were deactivated using *n*-BuLi, thus avoiding any possibility of combs subsequently coupling via hydrolysis of residual chlorosilane bonds by atmospheric water. The *n*-BuLi addition led to the comb polybutadiene product having several randomly placed $C_2H_4-Si(Me)_2-C_4H_{10}$ short chain branches in addition to pendant vinyl groups. Figure 2 shows the progress of comb formation for sample b54-15. The backbone peak was eluted at 27.5 min. The unfractionated polymer comb was contaminated by unreacted (prematurely terminated) branch material eluted at around 31.5 min. The comb was fractionated from a 1% solution in toluene using propan-2-ol as the nonsolvent. Initially, the branch material was removed then the remainder of the polymer was fractionated so that high molecular weight material present due to the coupling of polymer chains during the hydrosilylation reaction could also be removed. LALLS analysis proved the removal of high molecular weight material to be successful. It was found that method b for hydrosilylation gave superior results compared to method a with regard to the molecular weight distribution and the amount of material obtained. Method b employed cleaner conditions, thus minimizing the formation of high molecular weight species, and an increased number of fractionation steps

Table 1. Molecular Mass Data for Polybutadiene Combs[a]

	side-chains/"branches"			backbone			comb			
polymer[b]	M_n (g/mol)	M_w (g/mol)	PD	M_n (g/mol)	M_w (g/mol)	PD	M_n (g/mol)	M_w (g/mol)	PD	no. of branches
a60-12	11 500	11 900	1.04	60 600	63 900	1.06	142 300	166 800	1.17	8.6
a60-22	21 300	22 700	1.07	59 700	61 400	1.03	228 800	252 200	1.10	8.4
a60-28	28 000	28 800	1.03	59 000	60 500	1.03	281 600	320 100	1.14	9.0
a120-10	10 100	10 300	1.02	121 400	123 200	1.02	411 100	449 200	1.09	31.6
a120-17	17 300	17 700	1.02	117 700	124 600	1.06	185 300	210 800	1.14	4.9
b60-6	5 570	5 750	1.03	61 100	62 700	1.03	105 100	110 000	1.05	8.2
b54-15	14 800	14 900	1.00	53 800	53 800	1.00	168 500	172 400	1.02	8.0
b80-20	20 100	20 100	1.00	81 700	81 800	1.00	231 700	237 300	1.02	7.7
b105-6	6 070	6 090	1.00	104 900	105 100	1.00	153 600	156 100	1.02	8.4
b120-23	22 700	22 700	1.00	116 300	118 500	1.02	182 000	194 700	1.07	3.4

[a] Samples were characterized using a GPC/triple detector. M_n is the number-average molecular weight; M_w is the weight-average molecular weight, PD is polydispersity = M_w/M_n. [b] Prefixes a and b indicate whether hydrosilyation procedure a or b was employed.

Table 2. Intrinsic Viscosity and Shrinking Factors of Polybutadiene Combs

sample	$[\eta]_{linear}$ (g/mL)	$[\eta]_{comb}$ (g/mL)	g'	g_{pred}	λ	ϵ
a60-12	1.613	0.893	0.554	0.483	0.383	0.81
a60-22	2.179	1.090	0.500	0.414	0.243	0.78
a60-28	2.591	1.196	0.461	0.378	0.189	0.79
a120-10	3.314	1.451	0.438	0.317	0.274	0.72
a120-17	1.910	1.142	0.597	0.644	0.591	1.17
b60-6	1.192	0.836	0.701	0.607	0.570	0.71
b54-15	1.652	0.990	0.599	0.454	0.312	0.65
b80-20	2.084	1.207	0.579	0.474	0.345	0.73
b105-6	1.537	1.147	0.746	0.686	0.673	0.78
b120-23	1.804	1.371	0.760	0.674	0.609	0.70

were possible, when necessary, due to the larger scale of these reactions.

Table 1 gives the absolute weight-average molecular mass determination of backbone and side-chain (branches) samples. The combs with backbone of approximately 60 000 g/mol can be seen to have similar numbers of branches. From the weight-average molecular mass of the comb and its components, the average number of branches present per comb can be calculated.

$$p = \frac{M_{w,comb} - M_{w,backbone}}{M_{w,branch}} \quad (1)$$

where p is the number of branches/arms, $M_{w,comb}$ is the molar mass of the comb, $M_{w,backbone}$ is that of the backbone, and $M_{w,branch}$ is the mass of the branch.

Solution Properties. The Mark−Houwink relationship (eq 2)

$$[\eta] = KM^a \quad (2)$$

was used to calculate the constants a and K from the backbone and branch linear polybutadiene samples, and they were determined to be 0.727 and 2.58×10^{-4}, respectively. The intrinsic viscosity values $[\eta]_{lin}$ for linear samples having the same molar mass as the corresponding comb polybutadienes could then be calculated.

Table 2 lists the intrinsic viscosities of the combs together with the values calculated for linear samples of the same molecular mass. A plot of log $[\eta]$ against log molecular mass (M_w) is shown in Figure 3 for comb samples a60-12, a60-22, a60-28, b60-6, and b54-15, which have a similar backbone molecular mass and number of branches and are therefore most useful for the examination of structure−property relationships. These samples exhibit a steady, near linear, increase in comb viscosity with increasing molecular

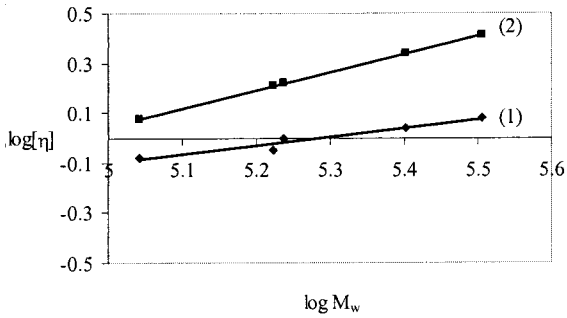


Figure 3. Graph showing the rise in intrinsic viscosity with increasing molecular weight for the comb series with backbone mass of around 60 000 g/mol. Series (1) shows the measured intrinsic viscosities of the comb series, and (2) shows the corresponding (calculated) intrinsic viscosities for linear polybutadienes having equivalent molecular mass.

mass. A linear graph of log $[\eta]$ against log M_w can be generated from the intrinsic viscosities of the linear polybutadienes. However, the extrapolated viscosities of the corresponding linear polybutadienes are always greater and rise much faster with increasing molecular mass compared to the actual results for the comb series.

The ratio of the intrinsic viscosities of linear and branched samples of identical molar masses provides a quantitative measure of how the dimensions of a polymer are altered by branching. This ratio, commonly known as the g' factor, is given by eq 3.

$$g' = \frac{[\eta]_{comb}}{[\eta]_{lin}} \quad (3)$$

It is found that for comb samples a60-12, a60-22, a60-28, b60-6, and b54-15, as the arm length approaches the backbone length, g' steadily decreases as illustrated in Figure 4; the x-abscissa is a measure of the ratio of arm length to backbone. The results are consistent with the prediction made by Berry and Orofino[42] and similar to results found by Roovers[17] for polystyrene combs. The number of branches on the comb also exerts a profound effect on the shrinking factor. The lowest value for g' in this study is that of comb a120-10, which has an average of 31 branches and is thus very compact. Figure 5 shows the effect exerted by both the length of the branches and the number of branches; the greater the fraction of the molecule which is branch material, the lower the g' value.

Another measure of the relative compactness of branched polymers is known as the g factor[43] (Zimm−Stockmayer), which is the ratio of the radius of gyration

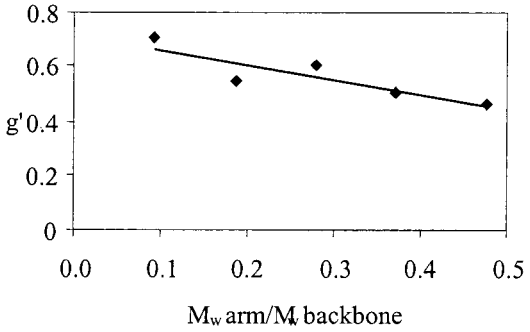


Figure 4. Variation of the shrinking factor g' with increasing comb branch length.

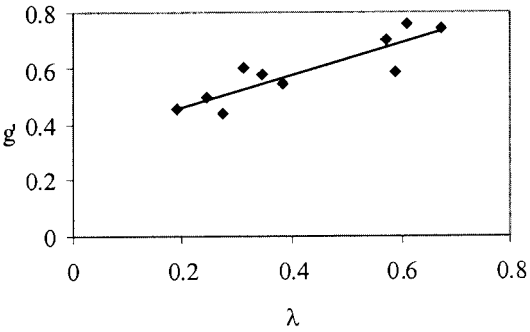


Figure 5. Plot of λ vs g' where λ is the fraction of backbone material present in the comb.

squared, $\langle R_g^2 \rangle$, between a branched polymer molecule and a linear polymer of the same molecular weight.

$$g = \frac{\langle R_g^2 \rangle_{br}}{\langle R_g^2 \rangle_{lin}} \quad (4)$$

Although it is possible to measure the radius of gyration of the comb polymers, it would be laborious to obtain a set of linear polymers with exactly the same molecular weights. The typical way around this is to produce a series of linear polymers in the molecular weight range needed and use the measured R_g vs molecular weight relationship to obtain the linear R_g value.

Using random-flight statistics, Berry, Casassa, and Orofino[42,44,45] derived a relationship for computing g from the molar mass properties of regular comb shaped chains. This is shown in eq 5:

$$g_{pred} = \lambda^3 + \frac{2p+1}{p+1}\lambda^2(1-\lambda) + \frac{p+2}{p}\lambda(1-\lambda)^2 + \frac{3p-2}{p^2}(1-\lambda)^3 \quad (5)$$

where g_{pred} is the predicted value of g (to differentiate it from experimentally determined g), p is the number of branches per backbone chain (eq 1), and λ is the backbone fraction of the comb molecule.

$$\lambda = \frac{M_{w,backbone}}{M_{w,comb}} \quad (6)$$

Again, using the series of combs having a backbone of around 60 000 g/mol, a trend can be seen between g_{pred} and branch length, g_{pred} leveling out as the branch molecular mass tends toward the backbone molecular mass as shown in Figure 6.

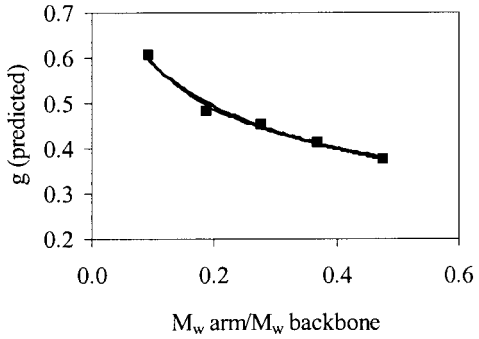
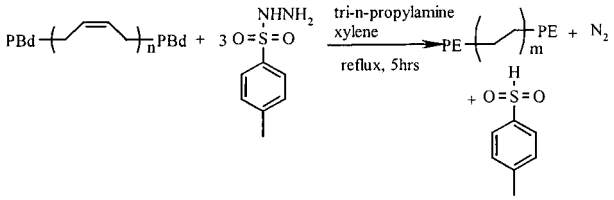


Figure 6. Plot of the variation of the shrinking factor g_{pred} with increasing comb branch length.

Scheme 2. Polymer Hydrogenation



The parameters g' and g are related by the exponent ϵ as shown in eq 7:

$$g' = g^{\epsilon} \quad (7)$$

Zimm and Kilb[46] suggested that $\epsilon = 1/2$ is a reasonable approximation for all types of branching. However, subsequent studies by Berry[47] indicate that values of ϵ are sensitive to structure and chain configuration, and although $\epsilon = 1/2$ may hold for star branch polymers, ϵ tends to a theoretical limit of 1.5 for combs having long backbones and short branches. From the present study of polybutadiene combs, it can be seen (Table 2) that ϵ, calculated from eq 7 using g_{pred}, varies little with structure have a value of 0.73 ± 0.08 apart from an anomalous value of 1.17 for a120-17. However, the theoretical models are based on perfectly monodisperse combs under θ conditions, and eq 5 was derived for regular combs, i.e., where the branches are regularly spaced which may account for deviations between our results and theory. The results agree well with other studies performed on combs. Hadjichristidis et al.[29] determined g and g' empirically for comb-shaped polyethylenes and subsequently calculated ϵ values around 1.05. When they predicted g using eq 5, their calculated ϵ values fell in the 0.7−0.8 range. Roovers[48] also found that $\epsilon = 0.75$ for comb polystyrenes in a good solvent when g was predicted. For polystyrene comb samples where both $[\eta]$ and R_g values were measured, Roovers found ϵ in the range 0.90−1.20 in good solvents and 0.83−1.20 in Θ conditions.

Hydrogenation of Linear Polybutadiene and Comb Samples. Scheme 2 shows the reaction used to hydrogenate the polybutadiene combs. Because of the wish to use the samples synthesized in this study for rheological evaluation, it was imperative that[37] side reactions previously identified to occur with the use of toluenesulfonyl hydrazide were prevented. Toluenesulfinic acid formed as a byproduct of the reaction is believed to protonate polybutadiene, leading to a subsequent tosylation reaction. To avoid tosylation, tri-*n*-propylamine was added in a 1:1 stoichiometric ratio to the hydrazide. After the reaction was completed, thor-

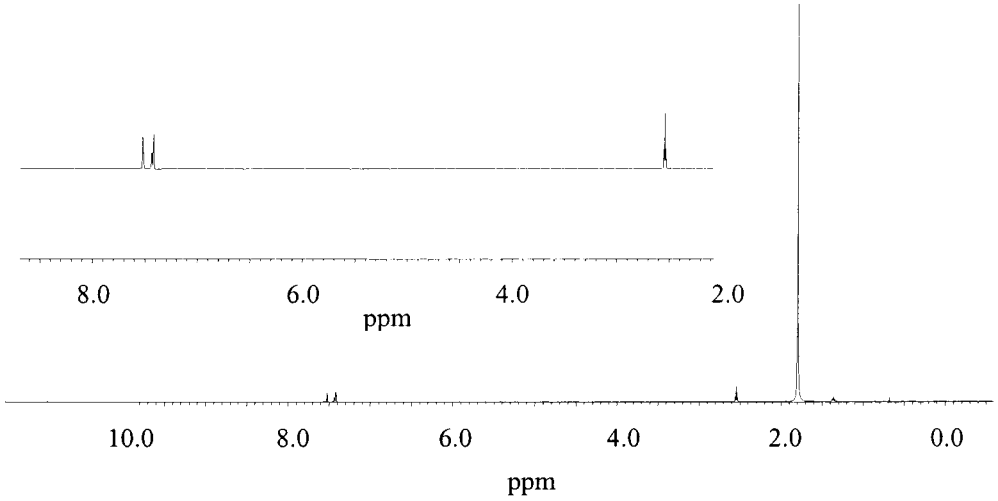


Figure 7. High-temperature ^{1}H NMR of 60-28 comb polybutadiene after hydrogenation with tosyl hydrazide.

Table 3. Results of Hydrogenation

name[a]	M_n[b] (g/mol)	M_w[b] (g/mol)	PD[b]	no. of branches[c] (p)	$\langle Rg\rangle_z$[b] (nm)	R_g(lin)[d] (nm)	g_{exp}[e]	g_{pred}[f]
lin50	52 800	53 000	1.00		11.6			
lin100	110 300	114 300	1.02		18.8			
lin250	225 700	240 400	1.07		30.6			
lin500	429 800	472 500	1.10		51.8			
a60-28 comb	265 600	317 200	1.19	8.5	22.2	38.3	0.34	0.39
b120-23 comb	143 600	157 700	1.09	1.5	21.4	23.8	0.81	0.79
b80-20 comb	166 800	190 800	1.14	5.1	19.8	27.1	0.53	0.57

[a]lin denotes linear material, and the number indicates the approximate molecular mass in g/mol. [b] From SEC/MALLS. [c] Calculated using eq 1. [d] Calculated from data in ref 29. [e] Calculated using eq 4 and MALLS data. [f] Calculated from eq 5.

ough washing with dilute (0.1 M) HCl and hot water was employed to remove toluenesulfinic acid/amine impurities.[38] ^{1}H NMR results shown in Figure 7 indicate that this procedure was successful in that very little (i.e., less than 0.5%) residual unsaturation was present in any of the samples tested, and no signals were present which would indicate the presence of tosyl derivatives, the signals at δ 2.1 and around δ 7.0 being due to a little hydrogenous toluene. FTIR was performed on polybutadiene films, and no signals were present in the 1100−1200 cm^{-1} region of the spectrum, indicating the sample to be free of SO_2-containing species such as toluenesulfinic acid. Elemental microanalysis was unable to detect the presence of sulfur in the hydrogenated polybutadiene samples. Table 3 displays the results collected from GPC/MALLS for selected hydrogenated polybutadiene fractions. M_n and M_w results differ slightly from those listed in Table 1 for polybutadiene due to the different polymer fractions which were used for hydrogenation. The SEC-LALLS trace of a polybutadiene comb a60-28 is shown in Figure 8, and the same comb hydrogenated is shown in Figure 9. The branching distribution of a hydrogenated comb b80-20 is shown in Figure 10. Figure 10 indicates that a little branch or backbone material may be present with 2% of the material having between no branches and small amounts of comb having 1, 2, and 3 branches per backbone molecule. Around 60% of the material consists of comb with 4 or 5 branches, perhaps somewhat surprising as the functionalization of the backbone and the addition of the branches are both random processes, although fractionation will help to narrow the molecular weight distribution of the sample. Both Figures 10 and 11 show the presence of high molecular weight material, illustrating that even after careful fractionation, some high molecular weight species are still detectable by MALLS.

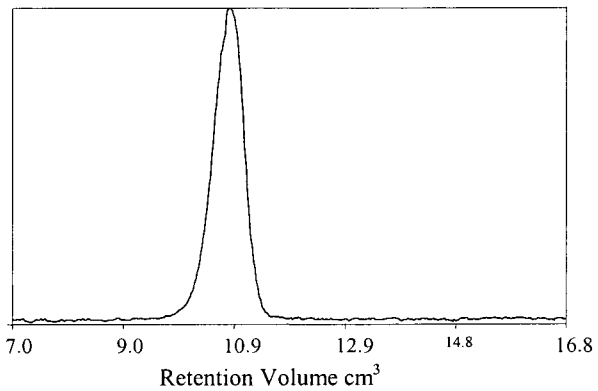


Figure 8. LALLS response vs elution volume for a60-28 comb polybutadiene prior hydrogenation with tosyl hydrazide.

The linear hydrogenated polybutadiene samples were used to determine a relationship between the weight-average molecular mass and radius of gyration (z-average) as measured using MALLS as shown in Figure 11. The resulting relationship was calculated to be $R_g = 0.00695M_w^{0.68}$. The experimental g factors (eq 4) can be compared to those calculated by Berry[42] using eq 5, which assumes random-flight statistics, branching to be regular, and the polymer chain to be in a Θ solvent. Figure 11 indicates that hydrogenated polybutadiene in trichlorobenzene acts as an expanded coil (the slope of the graph is 0.68, the theoretical slope for an expanded coil being 0.67) but is not a Θ solvent for hydrogenated polybutadiene. Despite expected discrepancies between theoretical and experimental values of g, the maximum difference is 15%, which is for sample a60-28 which has

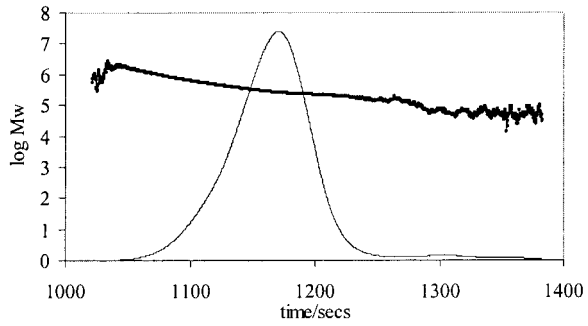


Figure 9. Plot of log M vs retention time for a60-28 comb polybutadiene after hydrogenation with tosyl hydrazide.

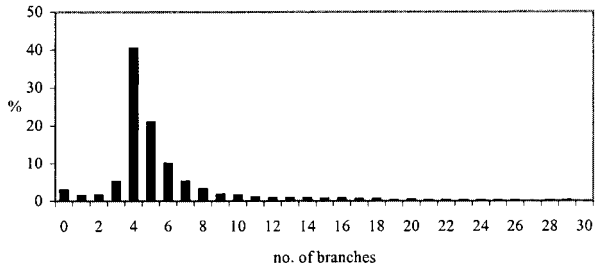


Figure 10. Branching distribution for comb b80-20 after hydrogenation with tosyl hydrazide.

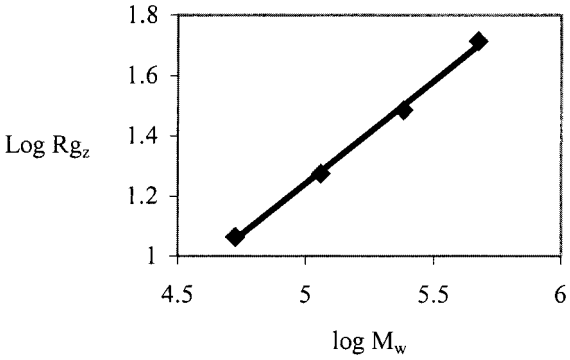


Figure 11. Graph showing the relationship between R_g and M_w for linear hydrogenated polybutadiene samples.

most branches; as the number of branches decreases, the percentage disparity between g_{theor} and g_{exp} also decreases.

Conclusions

A series of polybutadiene combs have been synthesized successfully; the number of branches per molecule has been shown to be controlable by functionalizing the comb's backbone by hydrosilylation in modest excess over requirement and then coupling with a limited number of "living" branches. This protocol was found to be superior to using limited hydrosilylation to control branch number. The hydrogenation of the polybutadiene combs has been performed successfully by using the homogeneous, relatively mild, diimine technique. Both the number and the length of the branches are seen to affect the intrinsic viscosity of the comb polybutadienes, and further research is now being conducted into the linear (melt) and extensional rheology of the materials.

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