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Synthesis of Dendrigraft Star−Comb Polybutadienes by Anionic Polymerization and Grafting-onto Methodology

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ABSTRACT: A series of dendrigraft star−comb polybutadienes (PBs), from generation zero to four (G0−G4), were synthesized by anionic polymerization and grafting-onto methodology. The 4-arm star PB (G0 PB) with high 1,4-content and narrow molecular weight distribution (MWD) was selectively epoxidized at the 1,4-PB sites to introduce grafting sites randomly along the polymer arms. The G1 PB was prepared by grafting of the epoxidized G0 PB with polybutadienyllithium (PBLi) anions. The dendrigraft star−comb PBs of higher generations (G2, G3, and G4) were synthesized by repeating the epoxidation and grafting reaction cycles. The dendrigraft star−comb PBs had high molecular weights ($M_w = 8.3 \times 10^3 - 1.4 \times 10^7$) and narrow MWDs ($M_w/M_n = 1.01 - 1.20$). Moreover, the molecular weight and branching functionality increased geometrically for the successive generations. The solution properties and the characteristic parameters ($[\eta]$, R_g, R_h, and g') of the dendrigraft star−comb PBs were determined and compared with those of the corresponding linear PBs. All results pointed to a much higher compactness of the dendrigraft star−comb macromolecular structure.

Introduction

Dendritic polymers, characterized by a cascade-branched structure, represent the fourth major class of macromolecules that can be further subdivided into four categories of hyperbranched polymers, dendrons, dendrimers, and dendrigraft polymers.[1] Of the four categories, dendrigraft polymers combine features of dendrimers and those of hyperbranched polymers, owing to generation-based growth of dendrimers and the randomly distributed grafting sites of hyperbranched polymers, respectively. In general, dendrigraft polymers are achieved mainly by three synthetic methods: grafting-onto, grating-from, and grafting-through.[2] The dendrigraft polymers obtained by the grafting-from technique are difficult to characterize and usually have relatively broad MWDs.[3] The grafting-through method (macromonomer method) is a convergent approach more closely resembling the hyperbranched polymer synthesis. When the grafting-through method is used, the one-pot reaction leads to a poorly defined architecture and MWD of 2 or greater.[4] And the grafting-onto has been by far the most widely applied technique for the preparation of dendrigraft polymers, due to the advantage of easy characterization on each of the successive generation.[5]

In recent years, great efforts have been made to synthesize well-defined long chain dendritically branched polymers by mean of the methodology based on the iterative divergent approach, especially dendrimer-like star-branched polymers;[6] the grafting sites of almost all these polymers are limited at the polymer chain ends. Hempenius and Möller[7] have reported the synthesis of arborescent PBs with the grafting sites located randomly on the main chain. However, the instability of the chlorosilane intermediate and the difficulty of varying the branching density of the graft polymers are two drawbacks encountered in this approach. On recognizing the relatively high stability of the epoxidized polyisoprene, Yuan and Gauthier[5f] have reported the synthesis of arborescent polyisoprenes from linear core with epoxy groups as grafting sites. Bender and Knauss[8] have reported the synthesis of the dendritic polystyrenes (PS) with hydroxyl-functionalized branch points, also utilizing epoxy groups as grafting sites. Schappacher and co-worker[9] have synthesized highly branched starlike comb polystyrenes having new polymer chain architecture. The developed strategy is based on the highly selective coupling reaction of living polystyryllithium onto starlike poly(chloroethyl vinyl ether) chains. Koutalas and co-workers[10] have reported the synthesis of well-defined star−comb PB by virtue of the macromonomer technique coupled with the high-vacuum technique. Nevertheless, this synthetic strategy seems difficult to achieve the dendritic architectures of high generation.

In this study, the dendrigraft star−comb PB with 4-arm star PB was first prepared by anionic polymerization and grafting-onto techniques. The 4-arm star PB chains with high 1,4-content were epoxidized to generate randomly distributed epoxide functionality along the PB arms, and these epoxide functional groups were used as grafting sites. The grafting of the living PBLi anions onto a 4-arm star PB led to a G1 dendrigraft star−comb PB; the dendrigraft star−comb PBs of higher generation were synthesized by the iterative reactions of epoxidation and grafting (Scheme 1). The structural characterizations of dendrigraft star−comb PBs of generations G = 0, 1, 2, 3, and 4 with ^{1}H and ^{13}C NMR spectroscopy, differential scanning calorimetry (DSC), size exclusion chromatography (SEC), and SEC coupled with two-angle laser light scattering detector (SEC-TALLS) techniques are presented.

Experimental Section

Materials. Butadiene (Yanshan Petrochem. Co., China, polymerization grade) was treated with a small amount of *n*-butyllithium (*n*-BuLi) to remove the moisture and inhibitor

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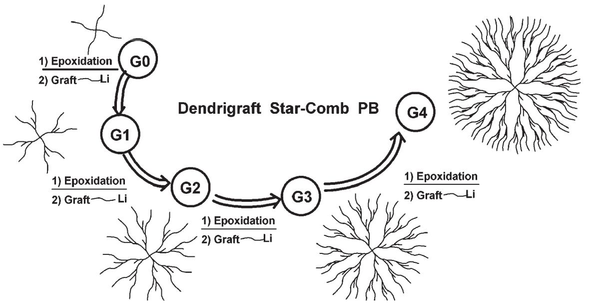
Scheme 1. Synthetic Scheme of Dendrigraft Star−Comb PBs by the Iterative Approach



and was condensed in a flame-dried flask prior to use. The exact concentration of the initiator, *n*-BuLi (JK Chemical, 2.5 M solution in *n*-hexane), was determined by Gilman−Haubein double titration prior to use.[11] Cyclohexane (Jinxi Chemical Plant, China, polymerization grade) was dried and stored over activated 5 Å molecular sieve and deoxygenated. Tetrachlorosilane ($SiCl_4$, JK Chemical, 98 wt %), dried over CaH_2 and distilled, was diluted with the dry cyclohexane prior to use. Tetrahydrofuran (THF, Fuchen Chemical Regent Factory, China, analytical reagent) was dried over sodium benzophenone ketyl under nitrogen and freshly distilled prior to use. The terminating agent 2-propanol (Tianjin Bodi Chemical Co., Ltd., China, analytical reagent) was degassed via three freezing−evacuation−thawing cycles prior to use. Formic acid (HCOOH, 88 wt %, Tianjin Hengxingong Chemical Manufacturing Co., Ltd., China), hydrogen peroxide (H_2O_2, 30 wt %, Shenyang Lianbang Chemical Regent Factory, China), and all other reagents were used as received. The 5 Å molecular sieve was activated at 400 °C for at least 4 h and then cooled to ambient temperature under a dry nitrogen atmosphere before use.

Synthesis of Dendrigraft Star−Comb PBs. All syntheses were carried out under an inert atmosphere via standard Schlenk techniques and cannula transfer. A typical anionic polymerization reaction was performed in a round-bottomed flask connected to the Schlenk line and equipped with an inert gas (N_2) inlet and a rubber septum. The glass assembly was dried with three cycles of a flaming/N_2-purging/evacuating, before introducing all the reagents, and the anionic polymerization reaction initiated.

Synthesis of 4-Arm Star PB. The living PBLi was synthesized by the anionic polymerization of butadiene (35.0 g, 648 mmol) with *n*-BuLi (18 mmol) and THF (1.8 mmol) in 359 mL of cyclohexane in a flask at 50 °C for 3 h. An aliquot of the living PBLi was withdrawn and quenched with degassed 2-propanol to determine the molecular weight. The coupling agent $SiCl_4$ was added to the flask via a syringe. After 3 h, the reaction mixture was quenched by adding degassed 2-propanol. The crude polymer was collected by removal of volatiles using a rotary evaporator and dried in a vacuum oven at 40 °C to constant weight. THF/ethanol was used as the solvent/nonsolvent pair in the present study to separate the star polymer and the deactivated linear PB. Then 5.0 g of crude G0 PB was dissolved in 200 mL of THF to make an ≈2.5% w/v solution at 20 °C. Ethanol was added dropwise to the solution until the solution turned slightly turbid. Finally, 3−5 mL of ethanol was then added to the solution, and the turbid solution was sufficiently warmed until it became clear. After slowly cooling the solution to 4 °C, a concentrated layer containing the high molecular weight component was separated from the solution. The fractionation step was repeated once or twice to obtain the pure polymer.[12] Successful fractionation was confirmed by the comparison of SEC curves of the fractionated and crude polymers.

Epoxidation of PB. The epoxidation reaction of PB was carried out under the conditions described in the method reported by Zuchowska.[13a] The epoxidation of fractionated G0 PB was provided as a representative example. Toluene (300 mL), fractionated G0 PB (30.1 g), and formic acid (11.2 g) were mixed in a 500 mL round-bottomed flask with a magnetic stirring bar. The reaction mixture was heated to 45 °C, and 31.6 g of H_2O_2 solution in water (30 wt %) was added dropwise to the mixture with stirring within 15 min. The reaction was continued for 2 h at 45 °C. The organic phase was washed with distilled water until the aqueous layer reached pH 7. The polymer solution was concentrated using a rotary evaporator and further dried under vacuum at 40 °C to constant weight. The epoxidized polybutadiene was purified by azeotropic drying[5b] and was diluted with dry cyclohexane (Figure S1). The epoxidation degree of the sample, determined by the ^{1}H NMR,[14] was 25 mol %.

Grafting Reaction. The dendrigraft star−comb PB was prepared by reaction of the epoxidized PB substrate with the linear living PBLi with a target $M_n = 3000$. The synthesis of a G1 dendrigraft star−comb PB was provided as a representative example.

The living PBLi was prepared by anionic polymerization of butadiene with *n*-BuLi at 50 °C. After anionic polymerization for 3 h, an aliquot was withdrawn and quenched with degassed 2-propanol to determine the PBLi molecular weight. The epoxidized G0 substrate solution ([epoxy group]/[*n*-BuLi] = 1.0) was added to the living PBLi solution via a syringe, and then the grafting reaction was allowed to proceed for 3 h at 50 °C. The reaction mixture was quenched with degassed 2-propanol. The crude product was collected by evaporation of all volatiles and purified by precipitation fractionation. The fractionated G1 polymer (66% yield) was further epoxidized and grafted with PBLi anions with a target $M_n = 3000$ to yield the G2 polymer. By iterative cycles of epoxidation and grafting, G3 and G4 PBs were prepared. The grafting reaction times for G2, G3, and G4 PBs were about 4, 5, and 6 h, respectively.

Molecular Characterization. *SEC and SEC-TALLS.* Two size exclusion chromatography instruments were used: the first one (SEC-TALLS) was used to precisely characterize the intermediate and final fractionated polymers, and the second one (SEC) was used only to determine the final fractionated polymers. The first instrument is a Viscotek TDA-302 size exclusion chromatograph (Viscotek Corp., Houston, TX) equipped with tetra detectors [refractive index (RI), UV, viscosity (VISC), and two-angle laser light scattering (7° and 90°, laser wavelength, $\lambda = 670$ nm)]. PS sample (Viscotek Corp.) with a stated peak molecular weight of 99 500 g/mol and a MWD of 1.03 was used to calibrate the instrument. The d*n*/d*c* value and intrinsic viscosity of this standard are 0.185 mL/g and 0.477 dL/g, respectively. Two Viscogel mixed bed columns (GMMXL, GMLXL, with a linear range of molecular weights from 10^3 to 10^7 g/mol) were employed; THF was used as the mobile phase at a flow rate of 1.0 mL/min and the column temperature of 30 °C. The samples were dissolved in THF with the sample concentrations of 2.0−5.0 mg/mL, depending on molecular weight of graft polymers, and 100 μL of such solution was injected to start data collection. The data obtained were analyzed using OmniSEC software version 4.5 (Viscotek Corp.). Weight-average molecular weights [M_w(LS)] were calculated based on absolute measurements with a light scattering detector relative to narrow PS standards.

The second instrument was a SEC PL-220 (Polymer Laboratories Ltd., England) equipped with a Waters 410 differential refractometer and was calibrated using the universal calibration method, which was created from a series of narrow PS standards with molecular weights from 0.58×10^3 to 7.5×10^6 g/mol. THF was used as the mobile phase at a rate of 1 mL/min and the column temperature of 30 °C.

NMR Analysis. The samples were analyzed by ^{1}H NMR and ^{13}C NMR spectroscopy on a Varian Inova (USA) or Bruker Avance (Switzerland) 400 MHz NMR spectrometer in $CDCl_3$

at 25−30 °C at a concentration of 4% w/v (for ^{1}H NMR) and 15% w/v (for ^{13}C NMR), respectively. The chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane in $CDCl_3$. Data were processed using MestReC software version 4.7.0.0. (Mestrelab Research, Spain).

Intrinsic Viscosity. The intrinsic viscosities ($[\eta]_{br}$) of dendrigraft star−comb PBs were determined in toluene with a Schott Ubbelohde viscometer. The temperature was regulated at 35.0 ± 0.1 °C. Flow time of the solvent and that of each of polymer solutions with four different concentrations below the overlap concentration c^* were measured to determine $[\eta]_{br}$ as described elsewhere.[15]

Differential Scanning Calorimetry (DSC). The glass transition temperatures (T_g) of the dendrigraft star−comb PBs were measured on differential scanning calorimeter with a NETZSCH DSC 204 instrument (Netzsch, Selb, Germany). The samples were dried under vacuum for 2 days, and each sample of 7 ± 2 mg was sealed in an aluminum pan. Each sample was scanned in the range of −150 to 0 °C at a heating rate of 10 °C/min, and sample cooling was achieved with a stream of N_2 gas flowing from liquid nitrogen. Data were processed using NETZSCH Proteus software version 4.3 (Netzsch, Germany). The T_g values reported corresponded to the midpoint change in heat capacity in the transition region.

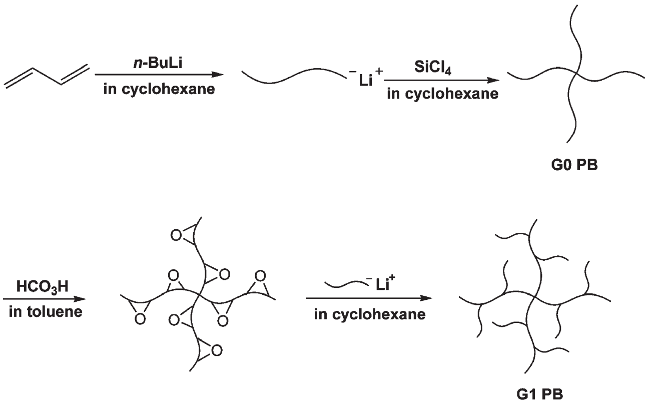
Results and Discussion

The synthesis of the dendrigraft star−comb PB is depicted in Scheme 2. The 4-arm star PB was first functionalized by partial epoxidation to introduce grafting sites randomly along each PB arm. The reaction of the epoxidized polybutadiene substrate with living PBLi yielded G1 dendrigraft star−comb PB. The G1 polymer was subjected to additional cycles of epoxidation and grafting to obtain dendrigraft star−comb PBs of the higher generations under similar conditions with increased reaction time for each successive generation.

Butadiene Polymerization. The polymerization of butadiene in cyclohexane yielded a polymer with high 1,4-content, while a high 1,2-content polymer was obtained in THF. The association phenomena of alkyllithium initiators (*n*-BuLi) in nonpolar solvents resulted in very low polymerization rates.[16] Owing to high reactivity of the 1,4-PB in the epoxidation reaction,[13] cyclohexane was preferred as a polymerization solvent with a small amount of THF as a modifier in this study. The ^{1}H NMR spectrum of a 4-arm star PB obtained under the conditions described is shown in Figure 1a. By comparing areas of the ^{1}H NMR peaks at 5.4 ppm (olefinic protons of the *cis*- and *trans*-1,4-units) and 4.9 ppm (two terminal protons of the 1,2-units), the contents of 1,4-units (*cis*- and *trans*-isomers combined) and 1, 2-units were 89% and 11%, respectively.[17]

The microstructures of the dendrigraft star−comb PBs were also examined via ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of the 4-arm star PB is shown in Figure 2a. By comparing areas of the ^{13}C NMR peaks at approximately 114 and 143 ppm assigned to the two different carbons in 1,2-units and complex resonance peaks between 127 and 133 ppm assigned to the *cis*-1,4 and *trans*-1,4 olefinic carbons, the 1,2-unit content can be calculated.[18a] Calculation based on the relative peak areas of the methylene carbon atoms located at 27.4 ppm (*cis*-1,4) and 32.7 ppm (*trans*-1,4) provided a polybutadiene composition of 38 ± 2% *cis*-1,4, 50 ± 2% *trans*-1,4, and 12 ± 2% 1,2-units.[18b]

Scheme 2. Synthetic Route of Dendrigraft Star−Comb PBs



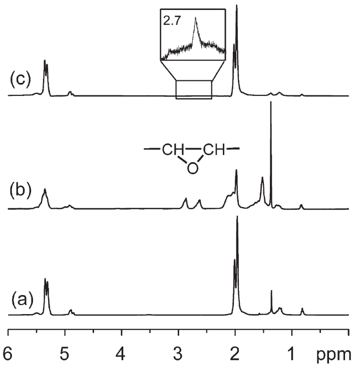


Figure 1. ^{1}H NMR spectra of G1 dendrigraft star−comb PB: (a) fractionated G0 PB (M_w = 8300), (b) epoxidized G0 PB (25 mol % substitution), and (c) fractionated G1 graft polymer (M_w = 72 000).

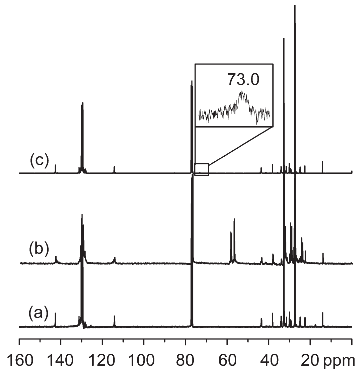


Figure 2. ^{13}C NMR spectra of G1 dendrigraft star−comb PB: (a) fractionated G0 PB (M_w = 8300), (b) epoxidized G0 PB, and (c) fractionated G1 graft polymer (M_w = 72 000).

Figure 3 illustrates the SEC curves of the PB arm (a) and the corresponding mixture of the arm PB and 4-arm star PB (b). The peaks corresponding to the arm PB and 4-arm star PB overlap slightly in the chromatogram of the mixture. The ratio of the 4-arm star PB to unlinked arm PB prior to fractionation was approximately 4:1 based on SEC RI peak areas (Figure 3b). Subsequent purification via precipitation fractionation from its THF solution by ethanol improved this peak ratio to more than 100:1 (Figure 5 G0 curve). The molecular weights of both the polymers were determined by SEC-TALLS (Table 2). The degree of branching (f) was 3.6, which can be calculated from the following equation:[19]

$$f = \frac{M_{w,star}}{M_{w,arm}} \qquad (1)$$

where $M_{w,star}$ and $M_{w,arm}$ are the M_w(LS)s of the 4-arm star PB and linear arm PB determined by SEC-TALLS, respectively.

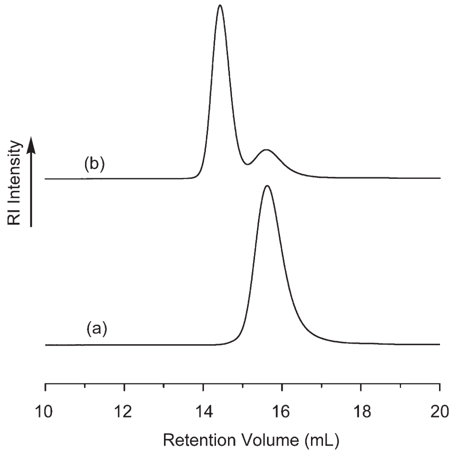


Figure 3. SEC curves of (a) the arm PB and (b) crude mixture of the arm PB and 4-arm star PB before fractionation.

Epoxidation of PB. The epoxidation of olefins by peroxyformic acid is an electrophilic reaction, so a higher electron density at the double bond favors the epoxidation, which is relatively insensitive to steric effect.[20] The reactivity of PB in the epoxidation reaction depends on the microstructures and decreases in the following order: *cis*-1,4 > *trans*-1,4 > 1, 2-units.[13,21] The ^{1}H NMR spectrum of an epoxidized G0 PB is shown in Figure 1b. The increase in epoxidation degree is confirmed by the decrease area of the olefinic peak at 5.4 ppm (*cis*- and *trans*-1,4 units) and the increase areas of epoxy peaks at 2.9 and 2.7 ppm, assigned to *cis*- and *trans*-1,4 epoxy protons, respectively.[22] The ^{13}C NMR spectrum of the epoxidized G0 PB is shown in Figure 2b. The two new peaks at 58.5 and 56.8 ppm indicative of the presence of *trans*- and *cis*-1,4 epoxy carbons, respectively, are observed.[21] In the case of 1,2-units of PB, no peak at 48.0 ppm in the ^{13}C NMR spectrum was detected (Figure 2b), which confirms that the reaction of epoxidation did not occur.[23]

Side reactions, particularly the ring-opening of the epoxide, could happen at high acid concentrations and elevated reaction temperatures.[14] No significant side reactions, such as ring-opening, occurred in this epoxidation system because of no characteristic absorption peaks of any byproduct at 3.0−4.5 ppm in ^{1}H NMR or 50−75 ppm in ^{13}C NMR (Figures 1b and 2b).[22] These results indicate that the successful epoxidation of polybutadiene proceeded smoothly under such conditions and selectively only at the 1,4-PB sites.

Since epoxidation is a heterogeneous reaction, the stirring efficiency affects the epoxidation degree.[5f] Nevertheless, substrates with 22−28 mol % epoxidation degrees were successfully obtained by controlling the amount of H_2O_2 added and the stirring rate. The slight increase of M_w(LS)s and the constant MWDs of the dendrigraft star−comb polymers after epoxidation (Table 1) strongly suggest the absence of chain scission and cross-linking reactions during the epoxidation.[24]

Grafting Reaction. The SEC curves of G1 dendrigraft star−comb PB are depicted in Figure 4. The reaction of the epoxidized G0 PB with living PBLi (Figure 4a) yielded a crude product (Figure 4b) consisting of the grafting product (left peak) and the linear PB residue (right peak). The grafting yield (fraction of living PBLi anions grafted with the substrate) can be approximately estimated from the SEC peak area using a RI detector. If the concentration response of the detector is assumed to be identical with those of the graft polymer and the linear polymer (identical refractive indices), the area of the graft polymer peak is defined as A_1 and the area of the nongrafted side chains as A_2; hence, the grafting yield (G_y) can be approximately calculated by virtue of the following equation:[5f]

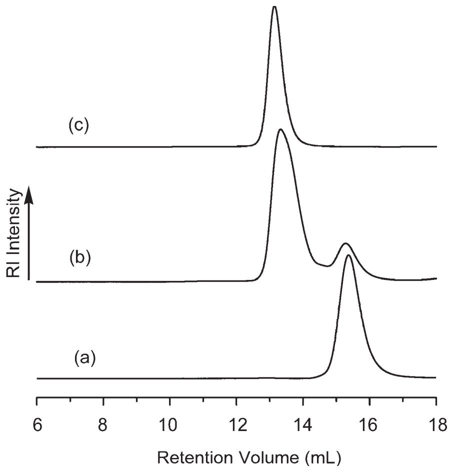


Figure 4. SEC curves of (a) PB side chains used in the synthesis of the G1 graft polymer, (b) crude G1 graft product, and (c) fractionated G1 graft polymer.

$$G_y = \frac{A_1}{A_1 + A_2} \times 100\% \qquad (2)$$

The grafting yield of the G1 polymer was 72%. Thus, some linear PB chains were remained in the G1 crude product and easily removed by precipitation fractionation (Figure 4c). A living PB chain to epoxide ratio of 1.0 was used for the grafting reaction in the present study. The excess linear PB chains remained in the crude product indicate that certain amount of epoxy groups still remained in the G1 polymer. In addition, the epoxy groups remained in the graft polymer can be confirmed by the appearance of a very weak peak at 2.7 ppm (Figure 1c and inset). However, the concentration of epoxy groups in dendrigraft star−comb polymer is too low to allow an in-depth analysis.

The grafting yield progressively decreased as generation number increased. Decrease in grafting yield has been reported in the synthesis of dendrigraft polymers[2a] due mainly to the excluded volume effect. The relatively poor solubility of epoxidized higher generation substrates in this study also contributed to the lower grafting yield. Furthermore, partial PBLi anions deactivation by the hydroxyl groups at branching points of the dendrigraft star−comb polymers may also be an obviously intractable factor for the lower grafting yield of G2−G4 polymers. NMR spectra were measured, confirming that the hydroxyl groups were attached to the dendrigraft star−comb polymers. Peaks in the region 3.6−4.0 ppm corresponding to the methine protons and at 73.0 ppm corresponding to the methine carbons could not be unambiguously identified due to the high amount of butadiene units (Figures 1c and 2c). The PBLi anions deactivation by the hydroxyl groups on G1−G3 dendrigraft star−comb polymer substrates is, however, substantially small. For example, the G1 substrate in Table 1 (used to synthesize the G2 polymer) had a M_w(LS)=73 000, an epoxidation degree of 22 mol %, and 19 hydroxyl groups (Table 2), because of each side chain having one hydroxyl group at the junction point. Since the molecular weight per butadiene unit is 54.09, the polymerization degree and the number of grafting sites of the G1 substrate are 73 000/54.09 = 1350 and 1350 × 0.22 = 297, respectively. The fraction of living chains that may be deactivated due to the presence of the hydroxyl groups on the G1 substrate is 19/297 = 0.064. The true fraction of living chains deactivated by the hydroxyl groups is most likely low in practice which may be due to the excluded volume effect.[5f]

Characterization of Dendrigraft Star−Comb PBs of Successive Generations. The absolute M_w(LS)s of the dendrigraft star−comb PBs, determined by SEC-TALLS, are reported in Table 2 along with the apparent M_w(RI)s determined by SEC with a RI detector. A living chain end-to-epoxide ratio of 1.0 and side chain target $M_n = 3000$ were used for the G1−G4 dendrigraft star−comb PBs, while the side chain target $M_n = 2500$ was used for the G4′ dendrigraft star−comb PB. All the side chains had narrow MWDs (M_w/M_n = 1.01−1.04). To synthesize dendrigraft star−comb PBs of higher generation, it is necessary to use low concentration of reactant to keep the sufficiently low viscosity and increase the grafting reaction time in the grafting reaction (Table 2).

Table 2 shows the dn/dc values of G0−G4 dendrigraft star−comb PBs ranged from 0.116 to 0.108, which agree very well with the literature values.[25] Moreover, the downward trend was similar to that of the results obtained by Hempenius et al.[7] Large discrepancies between the apparent M_w(RI)s and absolute M_w(LS)s determined for the dendrigraft star−comb PBs were observed. For example, the absolute molecular weight of the G4 polymer is more than an order higher [$M_w(\mathrm{LS}) = 1.4 \times 10^7$] than that of the apparent [$M_w(\mathrm{RI}) = 1.1 \times 10^6$]. This phenomenon is obviously due to highly compact structure of the dendrigraft star−comb polymers. The M_w(LS)s of the graft polymers were in a range from 8.3×10^3 (G0) to 1.4×10^7 (G4). The molecular weight of the dendrigraft star−comb PBs increased significantly after each iterative cycle, since polybutadiene chains are used as grafting-onto building blocks. The MWDs of the dendrigraft star−comb PBs of successive generations remained relatively narrow (M_w/M_n=1.01−1.20).

The branching functionality of the graft polymers (Table 2) can be calculated from the following equation:[26]

$$f_w = \frac{M_w(G) - M_w(G-1)}{M_{w,br}} \tag{3}$$

where $M_w(G)$, $M_w(G-1)$, and $M_{w,br}$ represent the M_w(LS)s of the graft polymers of generation G, of the previous generation, and of the side chains, respectively. The branching functionality corresponds to the number of side chains grafted in the last grafting reaction. The results indicate that both the molecular weight and the branching functionality increased geometrically with increasing generation number.

The SEC curves of fractionated G0−G4 dendrigraft star−comb PBs are shown in Figure 5. All the resulting polymers exhibit sharp monomodal distributions, and the peak moves to a higher molecular weight side with the increase of generation number.

Figure 6 shows SEC curves (results of three detectors responses) for the fractionated G4 dendrigraft star−comb PB. These curves overlap and show symmetrical monomodal distributions. The low angle lighting scattering detector (LALS) signal slightly moves to lower retention volume than the concentration (RI) signal and because the LALS signal response more depends on sample molecular weight than sample concentration.

The ratio of the radius of gyration in solution (R_g from light scattering detector) to the hydrodynamic radius in solution (R_h from viscosity detector) was calculated (Table 2). The R_g/R_h values of the G4 and G4′ dendrigraft star−comb PBs are 0.65 and 0.77, respectively, suggesting that both polymers have a highly compact structure. In particular, the G4′ dendrigraft star−comb PB has a value of R_g/R_h 0.77, which is close to the value of 0.775 expected for rigid spheres of uniform density.[7]

Table 3 shows the intrinsic viscosity values ($[\eta]_{br}$) of the dendrigraft star−comb PBs were determined by a Schott Ubbelohde viscometer in toluene at 35.0 ± 0.1 °C, and the intrinsic viscosity ($[\eta]_{lin}$) values of linear polymers of molecular weights [M_w(LS)] were identical to the corresponding

Table 1. Results of Epoxidation Reactions of G0−G3 Dendrigraft Star−Comb PB Substrates with Performic Acid in Toluene at 45 °C

	polybutadiene substrates		epoxidized polymers		
gen	$M_w \times 10^{-3}$[a]	M_w/M_n[a]	$M_w \times 10^{-3}$[a]	M_w/M_n[a]	E[b]/mol %
G0	8.3	1.01	8.6	1.02	25
G1	72	1.07	73	1.08	22
G2	230	1.12	240	1.11	28
G3	1300	1.19	1400	1.18	27

[a] Measured by SEC-TALLS. [b] Epoxidation degree determined by ^{1}H NMR analysis.

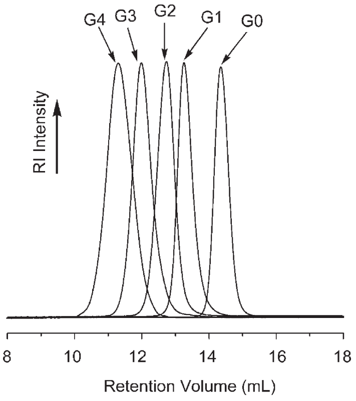


Figure 5. SEC curves of G0−G4 dendrigraft star−comb PBs after fractionation.

Table 2. Characterization Results of Dendrigraft Star−Comb PBs[a]

	side chains			graft polymers						
gen	$M_{w,br} \times 10^{-3}$[b]	M_w/M_n[b]	time/h	dn/dc /mL g^{-1}	$M_w(\mathrm{RI}) \times 10^{-3}$[c]	$M_w(\mathrm{LS}) \times 10^{-3}$[d]	M_w/M_n[d]	f_w[e]	R_g[f]/nm	R_g/R_h
G0	2.4	1.01	3−4	0.116	9.8	8.3	1.01	4		
G1	3.3	1.01	3−4	0.113	52	72	1.07	19		
G2	3.4	1.03	4−5	0.112	110	230	1.12	48		
G3	3.1	1.02	4−5	0.110	290	1300	1.19	420		
G4	3.7	1.02	6−7	0.108	1100	14000	1.17	3700	22.9	0.65
G4′	2.4	1.04	6−7	0.109		46000	1.19	5880	18.6	0.77

[a] Side chains for G1−G4 polymers: target $M_n = 3000$, $M_w/M_n = 1.05$; side chains for G4′ polymer: the target $M_n = 2500$, $M_w/M_n = 1.05$; for all graft polymer (G1−G4 and G4′): [epoxide]/[living end] = 1.0 (molar ratio), grafting temperature at 50 °C. [b] Determined by SEC-TALLS, dn/dc = 0.129 mL/g for linear PB. [c] Determined by SEC with a RI detector (PS as standard). [d] Determined by SEC-TALLS, dn/dc = 0.116−0.108 mL/g for the dendrigraft star−comb PBs. [e] Number of side chains grafted in the last grafting reaction. [f] Determined by SEC-TALLS.

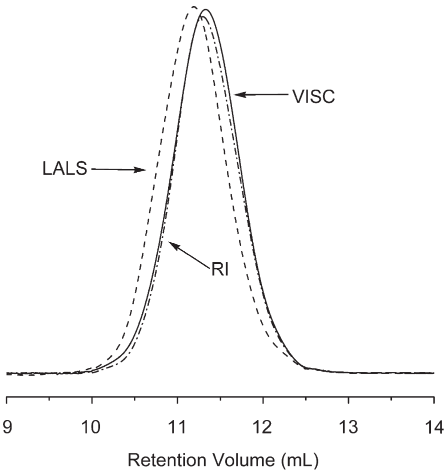


Figure 6. RI, VISC, and LALS curves of fractionated G4 dendrigraft star–comb PB determined by SEC-TALLS. Note: RI = refractive index detector; VISC = viscosity detector; LALS = low angle light scattering detector.

Table 3. Intrinsic Viscosities and Branching Factors of G0–G4 Dendrigraft Star–Comb PBs

gen	$[\eta]_{br}{}^{a}$/mL g^{-1}	$[\eta]_{lin}{}^{b}$/mL g^{-1}	g'^{c}
G0	13	17	0.75
G1	19	86	0.22
G2	25	208	0.12
G3	24	800	0.030
G4	20	5000	0.0040

[a] In toluene at 35.0 ± 0.1 °C. [b] Calculated using $[\eta]_{lin} = KM_w{}^a$. [c] $g' = [\eta]_{br}/[\eta]_{lin}$.

ones of the dendrigraft star–comb PBs calculated using the Mark–Houwink equation with values of $a = 0.765$ and $K = 0.0169$ mL/g.[27] The $[\eta]_{br}$ values of dendrigraft star–comb PBs almost remained constant from G2 to G4 dendrigraft star–comb polymers that were almost independent of the molecular weight of the whole molecule, which shows the intrinsic viscosity of dendrigraft star–comb polymer was determined by the molecular weight of the side chain rather than the generation number (branching functionality) of the molecule. Similar results have been reported for dendrigraft polystyrenes.[28]

To further investigate the branched nature of the molecular architecture, the branching factor (g'), which was defined as the ratio of the intrinsic viscosity of the dendrigraft polymer to that of a linear polymer of the molecular weight identical to that of the corresponding dendrigraft polymer, was calculated. The g' value of a branched polymer could be less than 1.0 because branched polymers have relatively lower intrinsic viscosities. The g' values of the dendrigraft star–comb polymers fell in a range from 0.75 (G0) to 0.004 (G4), indicating that the dendrigraft star–comb polymers have the increasingly compact structure. Furthermore, these data are consistent with those reported by Yuan et al.[15] whose values of the G0 and G1 series dendrigraft polystyrenes are between 0.69 ± 0.09 and 0.15 ± 0.01, respectively. Moreover, the g' values of G3 and G4 dendrigraft star–comb PBs were as low as 0.03 and 0.004, respectively, which confirms that the dendrigraft star–comb PBs have high branch density and very compact structure.[6a]

The hydrodynamic radius of the graft polymer in THF ($R_{h,THF}$) can be determined by SEC-TALLS, while $R_{h,TOL}$ can be calculated from eq 4, where N_A, $[\eta]$ and M are Avogadro's number, the intrinsic viscosity in toluene, and the mass of the spheres, respectively.

$$R_{h,TOL} = \left(\frac{3[\eta]M}{10\pi N_A}\right)^{1/3} \tag{4}$$

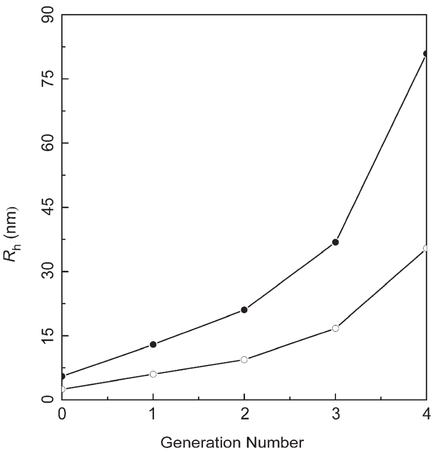


Figure 7. Hydrodynamic radius from viscometry as a function of the dendrigraft star–comb PBs' generation number: (●) PB in toluene at 35 °C; (○) PB in THF at 30 °C.

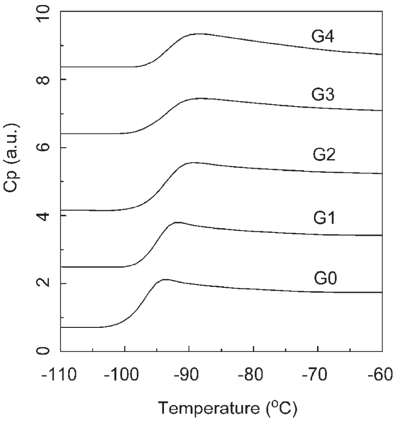


Figure 8. DSC thermograms of G0–G4 dendrigraft star–comb PBs.

As seen from Figure 7, the hydrodynamic radius (R_h) increases quickly in toluene with increasing generation number, while R_h of the dendrigraft star–comb PB increases to a much less extent in a relatively poor solvent (THF), which again strongly suggests that the dendrigraft star–comb PBs have a highly branched and relatively rigid structure.

The glass transition temperatures of the dendrigraft star–comb PBs were determined by DSC. The T_g values of the dendritic polymers can be affected by the molecular weight, composition, and number of chain ends.[29] The dendrigraft star–comb PBs synthesized in this study had similar microstructures, M_w(LS)s of the side chains, and ratio of chain ends to molecular weight. The only substantial difference was the total molecular weights of the different generation number polymers. The T_g value was found to increase slightly with increasing generation number and became almost constant from G2 to G4 dendrigraft star–comb PBs (Figure 8). Furthermore, these data are consistent with the data reported by Gauthier et al.[28a]

Conclusions

A new method, based on anionic polymerization, region selective and random epoxidation, and grafting-onto method, was developed for the synthesis of dendrigraft star−comb PBs from 4-arm star PB. All the dendrigraft star−comb PBs of generations G0−G4 prepared had relatively narrow MWDs (M_w/M_n = 1.01−1.20). The molecular weight of G4 dendrigraft star−comb polymer determined by SEC-TALLS was higher than that obtained from SEC with RI detector, which clearly illustrates the highly branched compact structure. Moreover, the g' value of the G4 dendrigraft star−comb PB was as low as 0.004, indicating that the dendrigraft star−comb PB had high branch density and very compact macromolecular structure. The molecular weight and branching functionality of the dendrigraft star−comb PBs increased geometrically with the increasing generation number.

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, and FT-IR spectra of the intermediate epoxides and final products from G0 to G4 and the purification of epoxidized polybutadiene substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

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