Macromolecules

Synthesis and Structure–Property Relationships of Polypropylene-g-poly(ethylene-co-1-butene) Graft Copolymers with Well-Defined Long Chain Branched Molecular Structures

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ABSTRACT: A series of polypropylene-*g*-poly(ethylene-*co*-1-butene) (PP-*g*-EBR) graft copolymers with well-defined long chain branched (LCB) molecular structures were synthesized via the combination of coordination polymerization and anionic polymerization. The structure—property relationships of PP*g*-EBR were systematically investigated. The structural information was clarified by characterization of ¹H NMR and SEC equipped with triple detectors. The DMA measurements demonstrated that the amorphous EBR branches were miscible with the PP backbones. The melt behavior of the PP-*g*-EBRs



was studied with small-amplitude dynamic rheological measurements. Increasing branch length and branch density both led to increased zero-shear viscosity, more pronounced shear-thinning behavior, elevated value of storage modulus at low shear frequencies, more significant upshift deviation from linear behavior in the Han plot, and reduced loss angle. Comparatively, branch length contributed more to the improvement of rheological properties than branch density did. Interestingly, DSC results showed that the crystallization temperature of PP-g-EBR increased with the enhancement of branch length and branch density; however, when the LCB level exceeded a certain degree, further increasing the LCB level would reduce the crystallization temperature.

1. INTRODUCTION

Isotactic polypropylene (iPP) is one of the leading and fast growing thermoplastic polymers in the world due to its outstanding physical and chemical properties such as high melting point, low density, high tensile modulus, excellent chemical resistance, and low cost. However, commercial iPP, produced with Ziegler-Natta or metallocene catalysts, exhibits relatively low melt strength and no strain hardening behavior in the melt state because it consists of highly linear chains and has a relatively narrow molecular weight distribution, which limits its applications in blow molding, thermoforming, extrusion coating, and foaming. The melt strength of PP can be improved by many methods such as increasing the molecular weight, broadening the molecular weight distribution, or introducing long chain branches (LCBs), among which the most efficient way is to introduce LCBs onto PP's backbone. Apart from mediating rheological property, the presence of LCBs with different chemical structures from PP backbone may provide an opportunity to modify other properties of PP such as mechanical properties.

Since the presence of LCBs is generally known to enhance melt strength of a polymer,¹⁻³ several approaches have been developed to synthesize long chain branched polypropylene (LCBPP). Some of them are based on chemical modification of PP such as reactive extrusion⁴⁻⁹ and electron beam irradiation.¹⁰⁻¹² The branched structures in the irradiated or reactive extruded PP are usually generated via radical induced random chain scission followed by recombination. Thus, these techniques create branched PP with broadened molecular weight distributions and very complex topological structures, both of which lead to the difficulty in the structure characterization of the products.

¹ There are also some reports on the direct synthesis of LCBPP, such as the copolymerization of in situ generated PP macromonomer with propylene by using a single metallocene catalyst dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride¹³ or a binary single-site catalyst system.¹⁴ The addition of previously prepared macromonomers such as atactic PP,¹⁵ iPP and polyethylene (PE),¹⁶ poly(ethylene-*co*-propylene),¹⁷ or allyl-terminated syndiotactic PP¹⁸ to the propylene polymerization system catalyzed by a metallocene catalyst is another general strategy to synthesize LCBPP. This method can be used to synthesize LCBPP with relatively well-defined branches. However, the incorporation of macromonomers is difficult due to their less mobility to diffuse toward the active centers of catalyst, especially when the molecular weight for entanglements. As a

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consequence, the branch density of the resultant LCBPP is limited. It is also difficult to separate the unreacted macromonomer from the resulting LCBPP. On the other hand, as we know, the incorporation of comonomer will reduce molecular weight of PP backbone. Therefore, it is difficult to obtain LCBPP samples possessing a similar PP backbone but differing in branch densities for the macromonomer copolymerization method. Another important in situ in-reactor method for preparing LCBPP is the copolymerization of propylene with a nonconjugated diene comonomer.^{19–23} The branch density of thus obtained LCBPP could be calculated by the ¹³C NMR spectrum. Nevertheless, the branch length could not be determined, and a high concentration of diene copolymerized with propylene would yield polymer gels. Lu and Chung prepared LCBPP with a well-defined comblike structure through a graft-onto reaction between a maleic anhydride-grafted PP (PP-g-MA) and several amine-terminated PP (PP-t-NH₂).²⁴ Recently, Langston et al. reported a new method to synthesize LCBPP via the metallocenemediated polymerization of propylene with T-reagent p-(3butenyl)styrene.25

Although extensive studies have been reported in the literature about the synthesis and rheological characterization of LCBPP, the systematic study of the relationships between molecular structure and the rheological behavior of LCBPP has been seriously limited in the past compared to LCBPE. This is ascribed to the difficulty of preparing LCBPP samples with well-defined long chain branched molecular structures. Chung and co-workers reported a novel chemical route for preparing PP graft copolymers with a controlled molecular structure.²⁶ The poly(propylene-cop-methylstyrene) backbone was synthesized using heterogeneous Ziegler-Natta catalysts and subsequently lithiated in the *p*-methyl groups of *p*-methylstyrene (*p*-MS) units with sec-BuLi in order to form anionic active sites for initiating anionic polymerization of several monomers. However, the multisite heterogeneous Ziegler-Natta catalysts produce copolymers with wide molecular weight distribution and poor control of the copolymer composition. Chung and co-workers also succeeded in preparing poly(propylene-co-p-methylstyrene) copolymer with metallocene catalysts,²⁷ but they found that catalyst activity decreased sharply with increasing the content of *p*-MS in the feed and the molecular weight of the resultant copolymer was not high. The decrease of catalyst activity was speculated to result from a steric jamming during the consecutive insertion of 2, 1-inserted p-MS and 1,2-inserted propylene.^{27,28} The copolymerization of propylene with p-MS catalyzed by rac-SiMe₂ (2-Me-4-Ph-Ind)₂ZrCl₂/MAO predominantly gave *p*-MS-terminated PP (PP-t-p-MS).28

In order to prepare PP copolymer with high catalyst activity, high molecular weight, and narrow molecular weight distribution, we designed a new comonomer, p-(3-butenyl)toluene (p-BT), to be copolymerized with propylene using a metallocene catalyst. Compared to p-MS, a longer distance between the double bond and the bulky phenyl group in p-BT reduces the steric hindrance and consequently facilitates the incorporation of p-BT during copolymerization with propylene. In this work, we describe a new method that can be used to prepare LCBPP with well-defined molecular structure, i.e., known backbone molecular weight, branch length, branch density, and narrow molecular weight distribution of the LCBs. The poly(propylene-co-p-BT) (PP–BT) backbone was first synthesized using the catalyst system of rac-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂ (MBI)/MAO. Then the methyl groups in the p-BT units were lithiated by *sec*-BuLi. The

formed benzylic anion effectively initiated anionic polymerization of 1,3-butadiene at room temperature. At last, the polybutadiene (PB) side chains were subjected to a noncatalytic hydrogenation reaction, yielding comblike LCBPP samples containing iPP backbone and poly(ethylene-*co*-1-butene) (EBR) LCBs. A series of PP-*g*-EBR graft copolymers with controlled branch density and branch length were synthesized. Structure – property relationships of PP-*g*-EBRs were systematically investigated. One of the most important aims in this work is to give an insight into the influences of branch length and branch density of long chain branched polymers on their rheological properties.

2. EXPERIMENTAL SECTION

2.1. Materials. Toluene (AR grade, from Beijing Chemical Works) was refluxed over metallic sodium with benzophenone and distilled under argon atmosphere prior to use. Cyclohexane and hexane were refluxed over metallic sodium/potassium alloy with benzophenone and distilled under argon atmosphere before use. p-Toluenesulfohydrazide (TSH, from Aldrich) was recrystallized from methanol. 4-Methylbenzyl chloride (from Alfa Aesar), tripropylamine (TPA, from Sinopharm Chemical Reagent Co., Ltd.), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA, from J&K Chemical Ltd.) were vacuum-distilled over calcium hydride prior to use. Polymerization grade propylene (from YanShan Petrochemical Corp.) was used as received. Polymerization grade 1, 3-butadiene was purchased from Jinzhou Petrochemical Corp., purified by passing through four columns packed with 4 Å molecular sieves and solid KOH before use. Allylmagnesium chloride (2.0 mol/L solution in THF from Aldrich), diethyl ether (anhydrous, from Beijing Chemical Works), methylaluminoxane (MAO: 10 wt % in toluene, Ethyl Corp.), and rac-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂ (MBI) (from Mitsubishi Chemical Co.) were used as received. sec-Butyllithium (sec-BuLi: 1.3 mol/L solution in cyclohexane/hexane (92/8)) was purchased from Acros and used as received. All oxygen- and moisture-sensitive manipulations were carried out under dry and oxygen-free argon atmosphere using standard Schlenk techniques.

2.2. Synthesis of p-(3-Butenyl)toluene (p-BT). To a dry 500 mL three-necked round-bottom flask equipped with an isobaric dropping funnel, a condenser pipe, and a magnetic stir bar was transferred 100 mL (0.2 mol) of allylmagnesium chloride solution. Then, 20 mL (0.15 mol) of 4-methylbenzyl chloride diluted with 50 mL of diethyl ether was added dropwise to the flask through isobaric dropping funnel at ice bath temperature. After complete addition of 4-methylbenzyl chloride, the mixture was warmed to room temperature and stirred for 20 h. Then, 200 mL of distilled water was introduced to the mixture slowly. The aqueous layer was separated through a separatory funnel and extracted three times with diethyl ether. The solvent was removed under reduced pressure. The obtained crude product was dried with calcium hydride for 24 h and then distilled under vacuum to yield the comonomer (p-BT) as a colorless liquid (20.9 g, yield: 95%). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.11 (m, 4H, φ -H), δ 5.87 (m, 1H, C-CH=C), δ 5.04 (m, 2H, C-C=CH₂), δ 2.70 (t, 2H, φ -CH₂), δ 2.39 (m, 2H, CH₂-C=C), δ 2.34 (s, 3H, φ -CH₃).

2.3. Copolymerization of Propylene with *p***-BT.** All the polymerization runs were carried out in a 1 L stainless steel autoclave equipped with a mechanical stirrer. The autoclave was dried *in vacuo* at 100 °C for 2 h and then cooled to 40 °C. The autoclave was then charged with toluene, *p*-BT, MAO, and MBI catalyst solution. The total volume of the feeding liquid was 300 mL. The polymerization was initiated by introducing propylene gas. The autoclave was charged with propylene to a total pressure of 0.65 MPa. The reaction vessel was stirred and

Table 1	. Comp	parison o	f the l	Experin	nental I	Results	in the	rac-Me	₂ Si(2-	MeBenz	elInd	$_2$ ZrCl ₂	(MBI)	/MAO
Catalyz	ed Cop	olymeriza	ation	of Prop	ylene v	vith <i>p-</i> (3-But	enyl)tol	uene ^a					

sample	$[p-BT]^b \pmod{L}$	catalyst in feed (µmol)	activity (10 ⁶ g(mol Zr) ⁻¹ h ⁻¹)	<i>p</i> -BT in copolymer ^{<i>c</i>} (mol %)	$T_{\rm m}^{\ \ d} (^{\circ}{\rm C})$	$\Delta H_{\rm m}{}^d$ (J/g)	$M_{\rm w}^{\ e}$ (kg/mol)	$\mathrm{PDI}^{e}\left(M_{\mathrm{w}}/M_{\mathrm{n}} ight)$
РР	0	0.75	89.1	0	147.2	86.5	194	2.40
PP-BT1	0.023	1.80	35.3	0.20	143.2	82.6	196	2.32
PP-BT2	0.046	1.80	21.8	0.39	142.2	72.2	208	1.84
PP-BT3	0.092	1.80	7.1	0.73	140.5	65.5	221	1.83
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^{*a*} Experimental conditions: solvent, toluene; total volume, 300 mL; propylene pressure, 0.65 MPa; polymerization temperature, 40 °C; Al/Zr (mol/mol) = 10 000; polymerization time, 90 min. ^{*b*} *p*-BT denotes *p*-(3-butenyl)toluene. ^{*c*} Calculated by ¹H NMR spectra. ^{*d*} Determined by DSC measurements. ^{*e*} Measured by SEC with light scattering detector.

maintained at 40 °C and 0.65 MPa for 90 min. The polymerization was terminated by venting propylene gas and adding acidified ethanol solution. The product was filtered, washed with a large amount of ethanol, and then dried under vacuum at 60 °C for 24 h. The conditions and results of the copolymerization of propylene with *p*-BT are summarized in Table 1.

2.4. Synthesis of PP-*g*-PB Graft Copolymers. The graft-from polymerization was carried out according to the published literature.²⁶ In a typical experiment (sample 6 in Table 3), under an argon atmosphere, 2.0 g of PP–BT2 containing 0.39 mol % of *p*-BT was suspended in 60 mL of anhydrous cyclohexane in a dried Schlenk-type filtration reactor with a magnetic stir bar. 2.9 mL of 1.3 mol/L *sec*-BuLi solution and 1.2 mL of TMEDA were added to the reactor and then heated to 70 °C. After 4 h, the reaction was cooled to room temperature, and the resultant polymer was isolated by filtration and washed repeatedly with hexane under an argon atmosphere until complete decoloration of the filtrate.

A prescribed amount of 1,3-butadiene was dissolved in 90 mL of anhydrous cyclohexane and then transferred to the Schlenk-type filtration reactor containing lithiated PP-BT2 copolymer under an argon atmosphere. The lithiated copolymer initiated the anionic polymerization of 1,3-butadiene at 30 °C for a specific time (10–120 min). The graft-from reaction was terminated by adding ethanol. The precipitated polymers were filtered and then subjected to THF extraction to remove soluble PB homopolymer. Then the product was dried *in vacuo* at 40 °C. All the graft-from polymerizations were based on the same PP–BT2 backbone. The molar ratio of TMEDA and *sec*-BuLi used in all the lithiation reactions of PP-BT2 copolymer was 2/1.

2.5. Synthesis of PP-g-EBR Graft Copolymers. The PP-g-EBR graft copolymers were prepared by hydrogenation of the obtained PP-g-PB copolymers. In a typical reaction, to a 250 mL round-bottom flask equipped with a magnetic stir bar was added 1.5 g of PP-g-PB copolymer (sample 6 in Table 3 containing 20.1 mol % of 1, 3-butadiene), 3.62 g of p-toluenesulfohydrazide, 3.7 mL (2.78 g) of tripropylamine, and 100 mL of toluene under an argon atmosphere. The mixture was heated to reflux and stirred for 6 h. The mixture was then cooled and poured into a large amount of ethanol. The precipitated polymer was stirred in ethanol overnight, then filtered, washed with ethanol for several times, and dried at 60 °C for 24 h under vacuum.

2.6. Characterization. All high-temperature ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV400 spectrometer at 125 °C using *o*-dichlorobenzene- d_4 (*o*-C₆D₄Cl₂) as solvent. The measurements on the linear dynamic mechanical properties were conducted on a dynamic mechanical analyzer (DMA/SDTA861°). The test samples were first treated with 0.2 wt % Irganox B215 antioxidant and were formed into rectangular bars with a length of 9 mm, a width of 4 mm, and a thickness of 1 mm by compression-molding at 180 °C and 10 MPa. DMA was carried out between -100 and 130 °C at a constant frequency of 10 Hz and a heating rate of 2 °C/min. Melting temperatures (T_m) and

crystallization temperatures (T_c) of polymers were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 instrument operating at a heating rate of 10 °C/min from 30 to 200 °C under a nitrogen atmosphere. Absolute molecular weight, molecular weight distribution, and intrinsic viscosity were obtained by size exclusion chromatography (SEC) with triple detectors. The chromatographic system consisted of a Polymer Laboratories PL 220 high-temperature chromatograph equipped with a two-angle laser light scattering detector (TALLS), a viscosity detector, and a differential refractive index detector. Polymer solutions were prepared with amounts of about 20 mg of polymer in 10 mL of 1,2,4-trichlorobenzene containing a small amount of antioxidant 2,6-di-tert-butyl-4-methylphenol (BHT), and were eluted at 150 °C with a flow rate of 1 mL/min. Rheological measurements were preformed on a rotation rheometer (Physica MCR-300) at 180 °C. The parallel plate with a diameter of 25 mm and a gap height of 0.8 mm was used. The test samples were first treated with 0.2 wt %Irganox B215 antioxidant and formed into disks with a diameter of 25 mm and a thickness of 1 mm by compression-molding at 180 °C and 10 MPa. Then, the samples were quenched at room temperature. The range of the frequency sweeps was from 0.01 to 100 Hz (0.0628 to 628 rad/s), and a strain of 1% was used, which was in the linear viscoelastic regime for all samples. The rheometer oven was purged with dry nitrogen to avoid degradation of samples during measurements.

3. RESULTS AND DISCUSSION

3.1. Copolymerization of Propylene with p-BT. The copolymerization reaction is described in Scheme 1, and the experimental results are summarized in Table 1. A series of copolymerizations have been performed under variable p-BT comonomer feed ratios, in the presence of metallocene catalyst MBI activated by MAO, to prepare the copolymers with variable compositions. With the increase of the comonomer feed, the incorporation of p-BT in the copolymer increased while the catalyst activity decreased. The reduction of catalyst activity should result from the steric hindrance due to the large size of the pendant group of *p*-BT linked to the central metal of the catalyst, which is similar to the case of the copolymerization of propylene with α -olefins.²² Comparing with the experimental results for the copolymerization of propylene with p-MS using a similar catalyst (rac-SiMe₂(2-Me-4-Ph-Ind)₂ZrCl₂/MAO) in the literature (when 0.11 mol/L p-MS was added at 30 °C and under 0.51 MPa, the catalyst activity was less than 1/10000 of that in propylene homopolymerization),²⁷ one can observe that the negative influence of *p*-BT on the catalyst activity is much less than that of *p*-MS (for example, the catalyst activity of copolymerization of propylene with 0.092 mol/L p-BT was about 1/13 of that in propylene homopolymerization). The distance between the



double bond and the bulky phenyl group in p-BT is longer than that in p-MS, which reduces the steric hindrance, facilitates the incorporation of p-BT during copolymerization, and consequently favors the catalyst activity. The incorporation of p-BT comonomer almost did not affect molecular weights, but it decreased melting temperatures and melting enthalpies (see Table 1).

A typical ¹H NMR spectrum of PP–BT copolymer (sample PP–BT2 in Table 1) is shown in Figure 1a. In addition to the three major peaks centered at 0.99, 1.39, and 1.72 ppm, which correspond to the CH₃, CH₂, and CH protons of the PP backbone, respectively, two minor peaks at 2.28 and 2.67 ppm, corresponding to φ -CH₃ and φ -CH₂ of the *p*-BT units, respectively, can also be detected. The content of *p*-BT in the copolymer is calculated by the ratio of the integrated peak area at 2.67 ppm to those at 0.8–1.8 ppm and the number of protons each peak represents. The equation is as follows:

$$C_{p\text{-BT}} = \frac{1/2A_{2.67}}{1/6A_{0.8-1.8}} \tag{1}$$

From the calculation based on eq 1, the contents of *p*-BT in PP–BT1, PP–BT2, and PP–BT3 are 0.20, 0.39, and 0.73 mol %, respectively. Additionally, Figure 2 shows the ¹³C NMR spectrum (with an inset of the chemical shift assignments) of PP–BT2; no signal of continuous *p*-BT sequence was observed with about 6600 scans. The CH₂ carbon resonances at 46.6 and 43.9 ppm are assigned to the dyads PP and (*p*-BT)P, respectively, where P denotes propylene unit and *p*-BT denotes *p*-(3-butenyl)toluene unit. Number-average sequence lengths can be determined from the dyad distributions using the following relationships:³⁰

$$\overline{n}_{\rm P} = \frac{[\rm PP] + 1/2[(p-BT)P]}{1/2[(p-BT)P]}$$
(2)

$$\overline{n}_{p\text{-BT}} = \frac{[(p\text{-BT})(p\text{-BT})] + 1/2[(p\text{-BT})P]}{1/2[(p\text{-BT})P]}$$
(3)

In addition, the monomer reactivity ratios $r_{\rm P}$ and $r_{p-\rm BT}$ can be calculated from the ¹³C NMR spectra using the subsequent equations³¹

$$r_{\rm P} = \frac{2[\rm PP]}{[(p-\rm BT)P]X} \tag{4}$$

$$r_{p-BT} = \frac{2[(p-BT)(p-BT)]X}{[(p-BT)P]}$$
 (5)

where *X* is the concentration ratio of propylene and *p*-BT in the feed. The dyad distributions, number-average sequence lengths, and values of reactivity ratios for PP–BT2 are summarized in Table 2. The number-average sequence lengths of P and *p*-BT in PP–BT2 are 249 and 1, respectively.

Figure 3 displays the melting parameters listed in Table 1 as a function of the *p*-BT content of the copolymers. The $T_{\rm m}$ and $\Delta H_{\rm m}$ of PP–BT copolymer decrease linearly as the content of *p*-BT in the copolymer increases. These behaviors result from the rejection of the side groups of the comonomers from the crystal cores, which reduces the length and the concentration of crystal-lizable unit sequences and consequently leads to a reduction of the size and amount of crystals.^{32–34} The subsequent equation, developed by Monrabal et al.³⁵ according to the classic Flory equation, can be applied to describe the dependence of melting temperature of random copolymer on its low comonomer content:

$$T_{\rm m} \simeq T_{\rm m}^0 - \frac{R(T_{\rm m}^0)^2}{\Delta H_{\rm u}} N_2 \tag{6}$$



Figure 1. ¹H NMR spectra of (a) PP–BT2 and (b) a representative PP-g-PB copolymer in o-C₆D₄Cl₂ at 125 °C.



Figure 2. Aliphatic region of 13 C NMR spectrum of PP-BT2 in o-C₆D₄Cl₂ at 125 °C.

where $T_{\rm m}^{0}$ is the melting temperature of homopolymer, $T_{\rm m}$ is the equilibrium melting temperature of the copolymer, R is the gas constant, N_2 is the molar fraction of comonomer incorporated, and $\Delta H_{\rm u}$ is the fusion heat per polymer repeating unit. Therefore, a linear dependence of the observed $T_{\rm m}$ of the obtained PP–BT copolymer on its *p*-BT content, consistent with eq 6, implies the random distribution of *p*-BT in the copolymer.

3.2. Synthesis of PP-*g*-EBR Graft Copolymers. Scheme 1 also illustrates the reaction process for the synthesis of PP-*g*-EBR copolymers. The graft copolymers were obtained through three further steps. In the first step, the above-obtained PP–BT2 copolymer was lithiated by *sec*-BuLi/TMEDA to obtain stable benzylic anions. Then the obtained lithiated polymer was washed with hexane for several times. Because of the insolubility of the PP–BT2 copolymer in hexane at room temperature, the excess *sec*-BuLi could be removed completely from the lithiated polymer. In the second step, the benzylic anions effectively initiated anionic polymerization of 1,3-butadiene in cyclohexane with a living manner at 30 °C. All the PP–BT2 backbone. Although

Table 2. Dyad Distributions, Number-Average Sequence Lengths, and Values of Reactivity Ratios for PP-BT2 Copolymer

(<i>p</i> -BT)(<i>p</i> -BT)	(<i>p</i> -BT)P	РР	¯n _p	$\overline{n}_{p-\mathrm{BT}}$	$r_{\rm P}$	$r_{p-\mathrm{BT}}$
0	0.008	0.992	249	1	3.08	-
					1	
170	_				100	
160	* *	ΔH _m	.		80	
်ပ 150	-	*		*		
⊢ [∎]				_	(B/r	
140	- m				40	
	0.0 0.2	2 0.4	4 0	.6 0	.8	
	р-В	i conten	t (mol%))		

Figure 3. Dependences of $T_{\rm m}$ and $\Delta H_{\rm m}$ of the PP-BT copolymers on their *p*-BT contents.

the PP-BT2 backbone is not soluble in cyclohexane, most of the p-CH₃ groups had to be located in the amorphous phase and were readily accessible for the lithiation reaction.²⁶ Therefore, in most parts, the lithiation reaction and the subsequent graft-from polymerization of 1,3-butadiene were not hindered by the heterogeneous reaction conditions due to the swelling of the amorphous phase. The branch density of PP-g-PB copolymer can be controlled by regulating the efficiency of lithiation reaction of PP-BT2 backbones. Because the graft-from polymerization of 1,3-butadiene was a living anionic polymerization, it is reasonable to assume that each benzylic anion produced one PB branch and each branch had a similar length.²⁶ In order to obtain PP-g-PB copolymers with variable branch lengths, the graft-from polymerizations of 1,3-butadiene were carried out at different concentrations and with different polymerization times due to the living character of anionic polymerization. Finally, a hydrogenation reaction was done to produce PP-g-EBR copolymers.

Figure 1b shows a representative ¹H NMR spectrum of the PP-g-PB copolymer (sample 6 in Table 3). In addition to three major chemical shifts corresponding to the PP backbone, there are several new chemical shifts corresponding to the PB side chains. The coexistence of 1,2- and 1,4-microstructures are demonstrated in chemical shifts at 5.01 ppm corresponding to two external olefinic protons (=CH₂), at 5.65 ppm corresponding to internal protons (-CH=) in the 1,2-structure, and at 5.47 ppm corresponding to internal protons (-CH=) in the 1,4-structure. The signals between 1.95 and 2.45 ppm correspond to the allylic (-CH-C=C) protons in the PB side chains generated by the 1,2-insertion of 1,3-butadiene. The chemical shift of aliphatic protons $(-CH_2-C-C=C)$, generated by the 1,2-insertion of 1,3-butadiene and located at about 1.35 ppm, is immerged in that of PP backbone, but its integrated peak area is equal to that of 5.01 ppm. The content of PB side chains in PP-g-PB graft copolymer and the molar ratio of 1,2 and 1,4 microstructures of PB side chains can be determined by the relative integrated peak areas of 0.8 to 1.8, 5.01, and 5.47 ppm and the number of protons each peak represents.

	reaction con	nditions ^a			structure o	f PB (mol %) ^f			
sample	$PP^{-}Li^{+}(g)^{b}$	BD $(g)^c$	yield (g) ^d	BD in branched polymer (mol %) e	1,2	1,4	$\mathrm{GE}^{g}\left(\% ight)$	branch density ^h	branch length ⁱ
1	2.0	10.4	2.05	2.5	77.7	22.3	25.9	5.07	1450
2	2.0	8.3	2.02	0.9	77.9	22.1	6.0	1.17	2180
3	2.0	7.0	2.15	6.1	79.7	20.3	22.9	4.49	4030
4	2.0	9.8	2.30	11.3	77.3	22.7	38.1	7.46	4760
5	2.0	6.9	2.10	3.6	76.6	23.4	9.1	1.78	5880
6	2.0	8.6	2.62	20.1	78.8	21.2	60.8	11.9	5930
7	2.0	6.8	2.75	23.7	77.4	22.6	38.4	7.51	11600
8	2.0	9.6	3.20	32.5	79.2	20.8	59.2	11.6	11700
9	2.0	6.3	2.64	20.6	77.8	22.2	20.6	4.04	18000
10	2.0	9.6	3.55	38.0	77.0	23.0	31.5	6.17	27800
11	2.0	6.8	2.40	13.8	76.9	23.1	6.1	1.19	37800

Table 3. Polymerization Conditions and Main Results of the ¹H NMR Characterization of PP-g-PB Copolymers

^{*a*} Solvent: cyclohexane, 90 mL; reaction temperature: 30 °C. ^{*b*} Starting PP–BT2 copolymer (containing 0.39 mol % of *p*-BT). ^{*c*} BD denotes 1, 3-butadiene. ^{*d*} Weight of the resulting PP-*g*-PB copolymer. ^{*c*} Mol % of 1,3-butadiene in PP-*g*-PB, calculated by ¹H NMR spectra. ^{*f*} Mol % of 1,2 and 1,4 structure in PB branch, calculated by ¹H NMR spectra. ^{*g*} Grafting efficiency, calculated by ¹H NMR spectra. ^{*h*} Average number of branches per 10 000 carbons in the PP backbones, calculated by ¹H NMR spectra. ^{*i*} Average molecular weight of the EBR branches, calculated by ¹H NMR spectra.

The equations are as follows:

BD mol % =
$$\frac{1/2A_{5.01} + 1/2A_{5.47}}{1/2A_{5.01} + 1/2A_{5.47} + 1/6(A_{0.8-1.8} - A_{5.01})}$$
(7)

1, 2-structure of PB mol % =
$$\frac{1/2A_{5.01}}{1/2A_{5.01} + 1/2A_{5.47}}$$
 (8)

BD in eq 7 denotes 1,3-butadiene. The percentage of 1,2-addition of 1,3-butadiene in all the graft-from polymerizations was about 80 (see Table 3). The reason for this phenomenon must have been the presence of the polar chelating agent TMEDA at the Li⁺ active site.²⁶ From the comparison of ¹H NMR spectra of the PP-g-PB copolymer and the backbone PP-BT2 copolymer (see Figure 1), the increase of the relative intensity of the peak at 2.67 ppm corresponding to φ -CH₂ can be observed due to the partial conversion of φ -CH₃ to φ -CH₂ in *p*-BT units during the lithiation reaction. As a consequence, the branch density (defined as the average number of branches per 10 000 carbons in the PP backbone) and the grafting efficiency can be calculated by the subsequent equations:

branch density =
$$\left[\frac{1/2A_{2.67}}{1/6(A_{0.8-1.8} - A_{5.01})} (PP-g-PB) - \frac{1/2A_{2.67}}{1/6A_{0.8-1.8}} (PP-BT2) \right] \times \frac{10000}{2}$$
(9)

grafting efficiency =
$$\left[(\text{branch density}) \times \frac{2}{10000} \right] \\ / \left[\frac{1/2A_{2.67}}{1/6A_{0.8-1.8}} (\text{PP}-\text{BT2}) \right] \times 100\%$$
(10)

Figure 4 shows a typical ¹H NMR spectrum of the PP-g-EBR copolymer (sample PP208-11.9g-EBR5.93 in Table 4). A complete hydrogenation of PB side chains in PP-g-PB copolymers



Figure 4. ¹H NMR spectrum of a representative PP-*g*-EBR copolymer in o-C₆D₄Cl₂ at 125 °C.

was observed due to the disappearance of chemical shifts at 5.01, 5.47, and 5.65 ppm and the increased intensity of chemical shifts between 0.8 and 1.8 ppm.

The branch length (defined as the average molecular weight of the corresponding EBR branches) of the corresponding PP-*g*-EBR copolymer can be determined using the following equation:

EBR branch length =
$$\frac{1/2A_{5.01} + 1/2A_{5.47}}{1/6(A_{0.8-1.8} - A_{5.01})} (PP-g-PB)$$
$$/\left[(branch density) \times \frac{2}{10000} \right] \times 56$$
(11)

All the calculated results based on the eqs 7-11 are collected in Table 3. Upon inspecting Table 3, one can note that the PP-g-EBR copolymers containing the same backbones differ in average length and in average density of the EBR branches. In particular, by comparing the samples 5 and 6, one can observe that their branch lengths are nearly the same, but their branch densities are quite different. The same can be noted for the samples 7 and 8.

sample	$M_{\rm w}^{\ a}$ (kg/mol)	$\mathrm{PDI}^{a}\left(M_{\mathrm{w}}/M_{\mathrm{n}}\right)$	EBR content (wt %)	$T_{c}^{b}(^{\circ}C)$	$T_{\rm m}^{\ b} (^{\circ}{\rm C})$	$\Delta {H_{\rm m}}^b \left({\rm J}/{\rm g} \right)$	$X_{c}^{c}(\%)$	$\eta^{*}_{0.01\mathrm{Hz}}(10^{3}\mathrm{Pa}\!\cdot\!s)$	n^d
PP-BT2	208	1.84	0.0	92.5	142.2	72.2	100	3.1	0.853
PP208-5.07g-EBR1.45	n.m. ^e	n.m.	3.3	106.5	142.5	74.6	107	13.6	0.733
PP208-1.17g-EBR2.18	n.m.	n.m.	1.2	106.1	142.5	74.2	105	33.9	0.643
PP208-4.49g-EBR4.03	252	1.97	7.9	104.6	142.4	68.5	103	47.5	0.608
PP208-7.46g-EBR4.76	333	2.76	14.5	104.8	141.5	64.7	105	80	0.530
PP208-1.78g-EBR5.88	n.m.	n.m.	4.7	106.8	142.9	72.9	106	100	0.527
PP208-11.9g-EBR5.93	289	2.35	24.1	103.6	142.4	59.5	108	187	0.428
PP208-7.51g-EBR11.6	448	2.44	27.9	102.1	141.4	53.2	102	201	0.417
PP208-11.6g-EBR11.7	n.m.	n.m.	36.4	101.6	140.7	45.9	100	262	0.398
PP208-4.04g-EBR18.0	367	2.37	24.4	103.5	141.7	57.9	106	228	0.403
PP208-6.17g-EBR27.8	534	2.64	40.9	97.1	139.4	42.4	99	402	0.391
PP208-1.19g-EBR37.8	230	1.88	17.6	104.5	142.0	65.2	109	107	0.501

Table 4. Summary of Characterization Results by SEC-TALLS, DSC, and Rheology Measurements for PP-BT2 and PP-g-EBR Copolymers

^{*a*} Measured by SEC with light scattering detector. ^{*b*} Determined by DSC measurements. ^{*c*} Relative crystallinity of PP segment (%) = $[\Delta H_{PP-g-EBR}/(\Delta H_{PP-BT2} \times \text{weight fraction of PP in the PP-g-EBR copolymer})] \times 100$. ^{*d*} Power-law exponent. ^{*c*} n.m. = not measured.



Figure 5. Molecular weight distributions of linear PP–BT2 and several PP-*g*-EBRs determined by light scattering detector.

On the other hand, the couples of samples 2 and 11, samples 4 and 7, and that of samples 6 and 8 are almost identical in the branch densities, but their EBR branch lengths are distinctly different.

3.3. Characterization of PP-*g*-EBR by SEC with Triple Detectors. Triple detection SEC can determine the absolute molecular weight, radius of gyration (R_g) and intrinsic viscosity ([η]) simultaneously. Therefore, branched polymers can be characterized with this technique by direct application of the Zimm–Stockmayer approach.^{36,37} A branched chain has lower R_g and [η] than its linear counterpart with the same molecular weight. The double-logarithmic plot of [η] versus M_w , generally referred to as the Mark–Houwink plot, can be used to qualitatively describe the LCB distribution across the molecular weight distribution.

Figure 5 shows molecular weight distribution curves of linear PP–BT2 and PP-g-EBR samples (determined by light scattering detector). Compared to the linear copolymer PP–BT2, molecular weights of PP-g-EBR samples were larger due to the introduction of LCBs onto PP–BT2 backbones, and molecular weight distributions were broadened slightly. The polydispersity indices, M_w/M_n , of all the resulting PP-g-EBRs remained below 3. The absolute molecular weights and molecular weight distributions determined by light scattering are listed in Table 4 (The nomenclature denotes the topology of the graft polymer which is described as PPx-dg-EBRy: The symbol x denotes the M_w of the backbone (kg/mol), d denotes the EBR branch density, and y denotes the EBR branch length (kg/mol).)



Figure 6. Mark–Houwink plots of linear PP–BT2 and several PP-g-EBRs.

Figure 6 shows the Mark—Houwink plots of the linear PP—BT2 and several PP-g-EBR samples. The negative deviation of the slope from linear behavior in all PP-g-EBR plots starts at low molecular weight and gradually increases with the increase of molecular weight, which implies a uniform branch distribution along the PP backbone. As the branch length and the branch density of PP-g-EBRs increase, the negative deviation of $[\eta]$ becomes more pronounced. These results demonstrate that the higher the LCB level in a branched polymer, the larger the negative deviation of $[\eta]$.

3.4. Compatibility of PP Backbones with EBR Branches in **PP-g-EBRs.** Different from a normal LCB polymer, the chemical structures of PP backbone and EBR branch are different. The compatibility between both segments can be investigated by means of DMA. The dependences of storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) on temperature for PP-BT2 and PP208-1.19g-EBR37.8 copolymers, measured by DMA, are shown in Figure 7a,b. Tan δ of PP–BT2 showed an apparent peak at around 8 °C corresponding to glass transition temperature (T_g) of iPP in amorphous phase (Figure 7a). In order to investigate the compatibility between PP-BT2 backbones and EBR branches in PP-g-EBRs, the corresponding PP-BT2/EBR37.5 blend with the same EBR weight fraction as that of PP208-1.19g-EBR37.8 copolymer was prepared by solution mixing in toluene under an argon atmosphere. Herein the EBR37.5 ($M_n = 37.5 \text{ kg/mol}, M_w/M_n = 1.07$) copolymer was an ethylene/1-butene copolymer containing 62.2 mol % of



Figure 7. Dependences of the mechanical storage modulus (E'), loss modulus (E''), and loss tangent $(\tan \delta)$ on temperature for PP–BT2 (a) and PP208-1.19*g*-EBR37.8 (b). (c) Comparison of dependence of loss modulus (E'') on temperature for the two samples and the corresponding PP–BT2/EBR37.5 blend.

1-butene, which was synthesized through two steps: first, the anionic polymerization of 1,3-butadiene was initiated by sec-BuLi/TMEDA (molar ratio: 1/5); then, the obtained PB (the content of 1,2-structure in the PB is 76.7 mol %) was hydrogenated by *p*-toluenesulfohydrazide and tripropylamine. Since the EBR37.5 copolymer is too viscous to be formed into a permanent shape, its T_g could not be characterized by DMA. The T_{g} of EBR37.5 copolymer was about -46 °C, determined by DSC measurement. Furthermore, DSC results confirmed that the EBR37.5 copolymer was fully amorphous and rubbery. As seen in Figure 7c, the only single $T_{\rm g}$ of PP–BT2/EBR37.5 blend (around -15 °C) was located between the T_{gs} of PP–BT2 and EBR37.5 copolymers. The T_g of PP208-1.19g-EBR37.8 was the same as that of the PP-BT2/EBR37.5 blend. It should be noticed that the molecular weight and molecular structure of EBR37.5 are almost identical with the branches of PP208-1.19g-EBR37.8 copolymer. These results suggest that the EBR copolymer containing 62.2 mol % of 1-butene is miscible with the amorphous part of iPP, consistent with the results reported by Yamaguchi et al.³⁸ Therefore, the amorphous parts of PP-BT2 backbones are miscible with EBR branches in the PP-g-EBRs studied in this work.

3.5. Effects of Branching Parameters on the Rheology. The influences of branching parameters (branch length and branch density) on the complex viscosity (η^*) and storage



Figure 8. (a) Complex viscosity and (b) storage modulus vs angular frequency for the linear PP–BT2, PP-g-EBR (PP208-1.19g-EBR37.8), and PP–BT2/EBR37.5 blend at 180 °C.

modulus (G') as defined in eq 12 were investigated.

$$\eta^* = \left[\left(\frac{G'}{\omega} \right)^2 + \left(\frac{G''}{\omega} \right)^2 \right]^{1/2} \tag{12}$$

3.5.1. Comparison of Rheological Behaviors of PP-g-EBR and PP-BT2/EBR Blend with the Same Composition. Figure 8 shows the η^* versus angular frequency (ω) and G' versus ω at 180 °C for the linear PP-BT2, PP208-1.19g-EBR37.8, and PP-BT2/ EBR37.5 blend. Although the molecular weight and molecular structure of EBR37.5 are almost identical with the branches of PP208-1.19g-EBR37.8 copolymer, the rheological behavior of PP208-1.19g-EBR37.8 is totally different from that of PP-BT2/ EBR37.5 blend. For linear PP–BT2, the η^* becomes independent of the frequency at low shear frequencies, in accordance with the characteristic behavior of a viscoelastic material in the Newtonian region. Compared to PP-BT2, the addition of EBR37.5 into PP–BT2 leads to a slight reduction of η^* and G', but the changing of η^* exhibits a similar trend. However, the introduction of EBR LCBs onto the PP-BT2 backbone significantly enhances the η^* and G' at low shear frequencies and leads to more prominent shear-thinning phenomenon. The above results show that the presence of EBR LCBs on the PP backbone strongly changes the rheological behavior. The influences of branching parameters on the rheology were detailedly studied in the following sections.

3.5.2. Effect of Branch Length on the Rheology. Figures 9–11 show the η^* versus ω , G' versus ω , and G' versus loss modulus (G'') at 180 °C for the linear PP–BT2 and several PP-g-EBR samples gathered in groups of nearly identical branch densities around 1.2, 7.5, and 11.6, respectively. We attempt to fit the viscosity data by the Cross equation³⁹ written as follows:

$$\eta^*(\omega) = \frac{\eta_0}{1 + (\lambda \omega)^{\alpha}} \tag{13}$$

where η_0 is the zero-shear viscosity, λ is a relaxation time which inversely accounts for the onset of shear-thinning region, and α is



Figure 9. (a) Complex viscosity vs angular frequency, (b) storage modulus vs angular frequency, and (c) storage modulus vs loss modulus for the linear PP–BT2 and PP-*g*-EBR samples (PP208-1.17*g*-EBR2.18 and PP208-1.19*g*-EBR37.8) at 180 °C.

a shear-thinning index. Nevertheless, for all the PP-g-EBR samples, a continuous shear-thinning region can be observed in almost all the frequency range measured, without any symptom of leveling off at low shear frequencies due to their remarkable long relaxation times. Therefore, the value of η_0 can hardly be related to the Newtonian viscosity of the general linear viscoelastic model. In order to correlate the rheological properties with topological structure of PP-g-EBR, we approximated η_0 with the η^* obtained at the frequency of 0.01 Hz. This parameter is listed in Table 4. Moreover, the viscosity data at high shear frequencies were fitted by eq 14 to quantify the shear-thinning behavior:

$$\eta^* = m\omega^{n-1} \tag{14}$$

where *m* is the consistency and *n* is the power-law exponent, which indicates the degree of non-Newtonian behavior. The more pronounced the shear-thinning phenomenon, the smaller the value of *n*. The power-law exponents for all the samples at 180 $^{\circ}$ C are also included in Table 4.

As shown in Figure 9a, the η_0 of PP208-1.17g-EBR2.18 sample is much higher than that of PP-BT2, meaning that the EBR branch with the length of 2.18 kg/mol is long enough to enhance η_0 . Comparing PP208-1.17g-EBR2.18 with PP208-1.19g-EBR37.8, both having nearly the same branch density but



Figure 10. (a) Complex viscosity vs angular frequency, (b) storage modulus vs angular frequency, and (c) storage modulus vs loss modulus for the linear PP–BT2 and PP-g-EBR samples (PP208-7.46g-EBR4.76 and PP208-7.51g-EBR11.6) at 180 °C.

different branch lengths, the value of η_0 increases from 3.39×10^4 Pa·s (PP208-1.17*g*-EBR2.18) to 1.07×10^5 Pa·s (PP208-1.19*g*-EBR37.8). This shows that the increase of branch length enhances the η_0 of PP-*g*-EBR sample. It can also be seen that increasing the branch length remarkably strengthen the shear-thinning behavior. The *n* of PP-*g*-EBR sample decreases with the increase of branch length. Similar results can be observed in Figures 10a and 11a. Samples PP208-7.46*g*-EBR4.76 and PP208-7.51*g*-EBR11.6 possess a similar branch density, but their branch lengths are 4.76 and 11.6 kg/mol, respectively. The η_0 value of PP208-7.51*g*-EBR11.6 is as 2.5 times that of PP208-7.46*g*-EBR4.76 sample. Furthermore, the η_0 value of PP208-11.9*g*-EBR5.93 sample.

Besides η_0 , the G' is also very sensitive to the presence of LCBs. Figures 9b–11b show the G' versus ω for the linear PP–BT2 and several PP-g-EBR samples at 180 °C. The linear PP–BT2 showed a representative behavior of a viscoelastic material in the terminal region. At low shear frequencies, G' of PP–BT2 is proportional to ω^2 . PP-g-EBR samples exhibited much higher G' at low shear frequencies, and the terminal slopes of G' were all less than 2 ascribed to their longer relaxation times. The G' of PP-g-EBR samples with the same branch density increased as the branch length increased.

(a)^{10'}





PP-BT2

PP208-11.9g-EBR5.93

PP208-11.6g-EBR11.7

Figure 11. (a) Complex viscosity vs angular frequency, (b) storage modulus vs angular frequency, and (c) storage modulus vs loss modulus for the linear PP–BT2 and PP-g-EBR samples (PP208-11.9g-EBR5.93 and PP208-11.6g-EBR11.7) at 180 °C.

The nonterminal behaviors of the PP-g-EBR samples can also be illustrated in the Han plot (log $G' - \log G''$, Figures 9c-11c). The Han plot has been proven to be a useful tool to investigate the effects of LCB and polydispersity on rheological properties, ^{5,8,23,40,41} and this plot is independent of molecular weight, only a very weak function of temperature, for high molecular weight polymer melts with narrow molecular weight distributions, just like the case of PP-g-EBR copolymers. As shown in Figures 9c-11c, the Han plot of PP-BT2 is almost a straight line, and its formula is $\log G' = -2.79 + 1.59 \log G''$, implying that the structure of PP-BT2 is linear. However, an upshift from the linear sample PP-BT2 is observed for PP-g-EBR samples at low shear frequencies, indicating that a long relaxation mechanism occurred in these samples. Furthermore, as the branch length of PP-g-EBR samples with almost the same branch density increased, the up-deviation became more prominent, implying that the contribution of LCB to the elasticity is more than that to the viscosity in the PP-g-EBR samples.

3.5.3. Effect of Branch Density on the Rheology. Figures 12 and 13 show the η^* versus ω , G' versus ω , and G' versus G'' at 180 °C for the linear PP–BT2 and several PP-g-EBR samples collected in groups of nearly the same branch lengths around 5.9 and 11.6 kg/mol, respectively. The sample PP208-11.9g-EBR5.93 with higher branch density exhibited a higher η_0 (1.87 × 10⁵ Pa·s for PP208-11.9g-EBR5.93 and 1.0 × 10⁵ Pa·s



Figure 12. (a) Complex viscosity vs angular frequency, (b) storage modulus vs angular frequency, and (c) storage modulus vs loss modulus for the linear PP–BT2 and PP-g-EBR samples (PP208-1.78g-EBR5.88 and PP208-11.9g-EBR5.93) at 180 °C.

for PP208-1.78g-EBR5.88), more distinct shear-thinning behavior, higher storage modulus at low shear frequencies, and more pronounced upshift from linear PP—BT2 in the Han plot than the PP208-1.78g-EBR5.88 sample. Similar results can also be obtained from the comparison between PP208-11.6g-EBR11.7 and PP208-7.51g-EBR11.6. Therefore, the rheological properties of PP-g-EBR samples having the same branch length can be adjusted through changing the branch density.

3.5.4. Comparison of the Effects of Branch Length and Branch Density on the Rheology. From the aforementioned experimental results, a conclusion can be drawn that increasing the branch length and the branch density of PP-g-EBR samples both lead to a considerable change of rheological properties. However, the comparison of the effects of the two branching parameters on the rheology was seldom made, which was ascribed to the difficulty of preparing LCBPP samples with well-defined molecular structures. Figure 14 shows the η^* as a function of ω at 180 °C for linear PP–BT2 and several PP-g-EBR samples with various branch densities and branch lengths. The branch density of PP208-1.78g-EBR5.88 is about 40% of that of PP208-4.49g-EBR4.03, and the branch length of the former is only as 1.46 times as that of the latter, whereas the former exhibits a higher value of η_0 . A similar phenomenon can also be observed by comparing PP208-1.17g-EBR2.18 with PP208-5.07g-EBR1.45. These experimental results reveal that branch length



Figure 13. (a) Complex viscosity vs angular frequency, (b) storage modulus vs angular frequency, and (c) storage modulus vs loss modulus for the linear PP–BT2 and PP-g-EBR samples (PP208-7.51g-EBR11.6 and PP208-11.6g-EBR11.7) at 180 °C.

contributes more to the increase of η_0 than branch density does in PP-g-EBRs. Further evidence can be obtained from Figure 14b, in which the three PP-g-EBR samples (PP208-11.9g-EBR5.93, PP208-7.51g-EBR11.6, and PP208-4.04g-EBR18.0) possess a similar EBR content (about 20 mol %) but differ in the branch densities and branch lengths. From the comparison among the three samples, one can notice that the sample with longer branch length exhibited a larger value of η_0 (2.28 × 10⁵ Pa · s for PP208-4.04g-EBR18.0, 2.01 × 10⁵ Pa · s for PP208-7.51g-EBR11.6, and 1.87 × 10⁵ Pa · s for PP208-11.9g-EBR5.93). Therefore, we can conclude that the branch length has more significant influence on rheological properties of the PP-g-EBR samples compared to the branch density.

The η_0 as a function of M_w is a very sensitive indicator to detect even low level of LCB.^{42,43} For linear polymer, the η_0 is independent of its molecular weight distribution, which is an important precondition for the interpretation of the influence of LCB structure on the complex viscosity in the linear regime.⁴⁴ The dependence of η_0 on M_w for PP-g-EBR samples at 180 °C is shown in Figure 15. The relationship for the linear PP can be described by log $\eta_0 = -15.4 + 3.5 \log M_w$ at 180 °C.¹¹ A considerably increased η_0 compared to the linear PP with the same M_w is observed for all the PP-g-EBR samples due to the formation of additional entanglements by their comblike LCBs.

3.5.5. Van Gurp–Palmen Analysis. Loss angle, δ (tan $\delta = G''/G'$), is another versatile tool for getting insight into the molecular



Figure 14. Complex viscosity vs angular frequency for the linear PP– BT2 and several PP-g-EBR samples with different branch densities and branch lengths at 180 °C.



Figure 15. Zero-shear viscosity (η_0) vs weight-average molecular weight $(M_{w,LS})$ for PP-g-EBR copolymers at 180 °C. The arrows imply that the actual η_0 is higher than the plotted value $\eta^*_{0.01 \text{ Hz}}$.



Figure 16. vGP plots of the linear PP–BT2 and several PP-g-EBR samples at 180 $^{\circ}$ C (vGP plots for the other PP-g-EBRs were omitted for clarity).

structure, having the advantage of without demanding normalization with respect to the molecular weight.^{45,46} The δ plotted as a function of the absolute value of complex modulus ($|G^*|$) is the



Figure 17. DSC cooling curves (a) and heating curves (b) of linear PP–BT2 and several PP-*g*-EBRs (DSC curves for the other PP-*g*-EBRs were omitted for clarity).

so-called vGP plot proposed by Van Gurp and Palmen.⁴⁷ Trinkle et al. applied vGP plot to characterize polydispersity of linear polymers⁴⁸ and classify long chain branched polymers by their topology.⁴⁹

Figure 16 shows the vGP plots of the linear PP-BT2 and several PP-g-EBR samples. It is known that materials are almost completely viscous when the δ terminal value is close to 90° and almost completely elastic when the δ terminal value is close to 0°. The δ terminal value of linear PP-BT2 is close to 90°, demonstrating that this sample is nearly totally viscous. The sample PP208-5.07g-EBR1.45 possessed relatively high branch density but showed similar behavior to that of PP-BT2, as its EBR branches were not long enough to dramatically influence the rheological properties. However, other PP-g-EBR samples exhibited remarkably reduced terminal values of δ compared to linear PP-BT2. Hence, the elasticity of PP-g-EBR sample is much higher than that of linear PP-BT2, and the elasticity enhances with the increase of branch length and branch density. Furthermore, we can observe that the increase of branch density and branch length also changes the shape of vGP plot due to the added long-time relaxation mechanism in the viscoelastic behavior. For the samples of PP208-7.46g-EBR4.76, PP208-7.51g-EBR11.6, PP208-4.04g-EBR18.0, and PP208-11.6g-EBR11.7 with relatively high branch densities and branch lengths, a plateau of their vGP plots started to appear and tended to become more prominent with the increase of branch density and branch length. This interesting phenomenon is also noticed in other LCB polyolefins.^{41,43,50,51} The presence of a plateau in vGP plot showed that these PP-g-EBR samples exhibited a physical gel-like behavior.52

3.6. Effect of EBR Branches on Crystallization of PP Backbones in PP-g-EBRs. The influence of LCB on melt behavior was also reflected in the transition from melt state to solid state, i.e., crystallization process. The nonisothermal crystallization process was analyzed by means of DSC. Figure 17 shows the DSC curves of linear PP-BT2 and PP-g-EBR samples, and the results are summarized in Table 4. The crystallization temperatures of PP-g-EBRs are higher than that of linear PP-BT2

copolymer, suggesting that crystallization rate enhances and the supercooling degree needed for crystallization decreases due to the introduction of EBR LCBs onto the PP backbones. It is very interesting to notice that the crystallization temperature increases with the enhancement of branch length and branch density when the PP-g-EBR samples contain a low level of LCB, among which PP208-1.78g-EBR5.88 exhibits the highest crystallization temperature. However, further elevating the LCB level result in the reduction of crystallization temperature. The crystallization process from melt state during DSC measurements was a phase transition process without shear field. According to the rheological data, the η_0 of PP-g-EBRs was much higher than that of PP-BT2 due to the formation of additional entanglements. The entangled state of polymer chains influences the crystallization process since the rearrangement of chains is necessary to chain folding and perfection. The high viscosity is unfavorable to disentanglement of the chains in polymer melt during crystallization. The above results indicate that, on one hand, the amorphous EBR LCBs perform the function of heterogeneous nucleation to facilitate the crystallization of PP backbone in the PP-g-EBR; on the other hand, the mobility and reptation ability of PP chains are restrained by the LCBs, which hinders the crystallization process.

In addition, the melting temperatures of all the samples listed in Table 4 are around 142 °C. The similarity of melting temperatures between PP-g-EBR copolymers and PP-BT2 copolymer suggests that the thickness of lamellae is almost independent of the content of EBR branches. Though $\Delta H_{\rm m}$ values of the resulting PP-g-EBRs gradually decreased with increasing the content of EBR branches, the relative crystallinity (calculated by the $\Delta H_{\rm m}$ of the PP-g-EBR sample divided by the $\Delta H_{\rm m}$ of the PP-BT2 copolymer and the weight fraction of PP in the PP-g-EBR sample),⁵³ which can be used to estimate the crystallinity of the PP part in the PP-g-EBR samples compared to PP-BT2 copolymer, is nearly constant. This result demonstrates that EBR branches grafted onto the PP backbone have no enormous influence on the crystallinity of PP backbone at least within 40.9 wt % of EBR content, which is in good accordance with the results previously reported by Yamaguchi et al.³⁸

4. CONCLUSIONS

A series of PP-*g*-EBR graft copolymers with controlled branch densities and branch lengths were prepared. Structure—property relationships of PP-*g*-EBR graft copolymers were systematically investigated. The resultant LCBPP consisted of an iPP backbone and EBR LCBs. The branch density of PP-*g*-EBR copolymer can be controlled by tuning the efficiency of lithiation reaction of PP—BT2 backbones. On the other hand, the living 1,3-butadiene polymerization step allows the regulation of branch length through controlling the feed amount of 1,3-butadiene and the reaction time.

The DMA measurements demonstrated that the amorphous EBR LCBs were miscible with the PP–BT2 backbones. Characterization using SEC with triple detectors indicated that EBR LCBs were distributed uniformly along the PP chains. The increase of branch length and branch density both reduced the slope of the Mark–Houwink plot in the high molecular weight range. Moreover, increasing the branch length and branch density both lead to increased η_0 , more pronounced shear-thinning behavior, elevated value of storage modulus at low shear frequencies, and more significant upshift deviation from

linear behavior in the Han plot. Branch length contributes more to the improvement of rheological properties than branch density does. The vGP analysis showed that PP-g-EBRs exhibited lower loss angle compared to the linear counterpart, indicating the enhancement of elasticity. The shape of vGP plot also changed with the increase of branch length and branch density. A plateau began to appear when the branching level exceeded a certain degree, which became more prominent with the further increase of branch length and branch density. DSC results showed that crystallization temperatures of PP-g-EBRs were higher than that of linear PP-BT2. Interestingly, the crystallization temperature of PP-g-EBR increased with the enhancement of branch length and branch density; however, when the LCB level exceeded a certain degree, further elevating the LCB level would reduce the crystallization temperature. This result indicates that, on one hand, the amorphous EBR LCBs can act as heterogeneous nucleating agent to accelerate the crystallization of PP; on the other hand, the mobility and reptation ability of PP chains are restrained by the LCBs, which hinders the crystallization process. Future work will be focused on the relationships between molecular structure and foaming behavior of PP-g-EBRs.

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REFERENCES

- (1) Small, P. A. Adv. Polym. Sci. 1975, 18, 1–31.
- (2) Santamaria, A. Mater. Chem. Phys. 1985, 12, 1–28.
- (3) Gahleitner, M. Prog. Polym. Sci. 2001, 26, 895–944.
- (4) Graebling, D. Macromolecules 2002, 35, 4602–4610.
- (5) Tian, J. H.; Yu, W.; Zhou, C. X. Polymer 2006, 47, 7962-7969.
- (6) Parent, J. S.; Bodsworth, A.; Sengupta, S. S.; Kontopoulou, M.;
- Chaudhary, B. I.; Poche, D.; Cousteaux, S. *Polymer* **2009**, *50*, 85–94. (7) El Mabrouk, K.; Parent, J. S.; Chaudhary, B. I.; Cong, R. J. *Polymer* **2009**, *50*, 5390–5397.
- (8) Li, S. Z.; Xiao, M. M.; Wei, D. F.; Xiao, H. N.; Hu, F. Z.; Zheng, A. N. *Polymer* **2009**, *50*, 6121–6128.
- (9) Zhang, Z. J.; Xing, H. P.; Qiu, J.; Jiang, Z. W.; Yu, H. O.; Du, X. H.; Wang, Y. H.; Ma, L.; Tang, T. *Polymer* **2010**, *51*, 1593–1598.
- (10) Yoshii, F.; Makuuchi, K.; Kikukawa, S.; Tanaka, T.; Saitoh, J.; Koyama, K. J. Appl. Polym. Sci. **1996**, 60, 617–623.
- (11) Auhl, D.; Stange, J.; Munstedt, H.; Krause, B.; Voigt, D.; Lederer, A.; Lappan, U.; Lunkwitz, K. *Macromolecules* **2004**, *37*, 9465–9472.

(12) Krause, B.; Stephan, M.; Volkland, S.; Voigt, D.; Haussler, L.; Dorschner, H. J. Appl. Polym. Sci. 2006, 99, 260–265.

(13) Weng, W. Q.; Hu, W. G.; Dekmezian, A. H.; Ruff, C. J. *Macromolecules* **2002**, *35*, 3838–3843.

(14) Ye, Z. B.; Zhu, S. P. J. Polym. Sci., Part A: Polym. Chem. 2003, 41 1152–1159.

(15) Shiono, T.; Azad, S. M.; Ikeda, T. Macromolecules 1999, 32, 5723-5727.

(16) Weng, W. Q.; Markel, E. J.; Dekmezian, A. H. Macromol. Rapid Commun. 2001, 22, 1488–1492.

- (17) Kolodka, E.; Wang, W. J.; Zhu, S. P.; Hamielec, A. E. *Macro-molecules* **2002**, *35*, 10062–10070.
- (18) Cherian, A. E.; Lobkovsky, E. B.; Coates, G. W. Macromolecules 2005, 38, 6259–6268.
- (19) Naga, N.; Shiono, T.; Ikeda, T. Macromolecules **1999**, 32 1348–1355.
- (20) Kim, I.; Shin, Y. S.; Lee, J. K. J. Polym. Sci., Part A: Polym. Chem. 2000, 38, 1590–1598.

(21) Agarwal, P. K.; Somani, R. H.; Weng, W. Q.; Mehta, A.; Yang, L.; Ran, S. F.; Liu, L. Z.; Hsiao, B. S. *Macromolecules* **2003**, *36*, 5226–5235.

- (22) Paavola, S.; Saarinen, T.; Lofgren, B.; Pitkanen, P. *Polymer* **2004** *45*, 2099–2110.
- (23) Ye, Z. B.; AlObaidi, F.; Zhu, S. P. Ind. Eng. Chem. Res. 2004, 43, 2860–2870.
- (24) Lu, B.; Chung, T. C. Macromolecules 1999, 32, 8678-8680.

(25) Langston, J. A.; Colby, R. H.; Chung, T. C. M.; Shimizu, F.; Suzuki, T.; Aoki, M. *Macromolecules* **2007**, *40*, 2712–2720.

- (26) Lu, H. L.; Chung, T. C. J. Polym. Sci., Part A: Polym. Chem. 1999, 37, 4176–4183.
- (27) Lu, H. L.; Hong, S.; Chung, T. C. J. Polym. Sci., Part A: Polym. Chem. 1999, 37, 2795–2802.
- (28) Chung, T. C.; Dong, J. Y. J. Am. Chem. Soc. 2001, 123, 4871–4876.
- (29) Wu, C. H.; Li, H. Y.; Feng, Y. Q.; Hu, Y. L. Polym. Int. 2007, 56, 711-717.
 - (30) Randall, J. C. Macromolecules 1978, 11, 592-597.
 - (31) Uozumi, T.; Soga, K. Makromol. Chem. 1992, 193, 823-831.
- (32) Alamo, R. G.; Mandelkern, L. Macromolecules 1991, 24 6480-6493.

(33) Simanke, A. G.; Galland, G. B.; Freitas, L.; da Jornada, J. A. H.; Quijada, R.; Mauler, R. S. *Polymer* **1999**, *40*, 5489–5495.

- (34) Villar, M. A.; Failla, M. D.; Quijada, R.; Mauler, R. S.; Valles, E. M.; Galland, G. B.; Quinzani, L. M. *Polymer* **2001**, *42*, 9269–9279.
- (35) Monrabal, B.; Blanco, J.; Nieto, J.; Soares, J. B. P. J. Polym. Sci., Part A: Polym. Chem. 1999, 37, 89–93.
- (36) Zimm, B. H.; Stockmayer, W. H. J. Chem. Phys. 1949, 17 1301-1314.
 - (37) Zimm, B. H.; Kilb, R. W. J. Polym. Sci. 1959, 37, 19-42.
- (38) Yamaguchi, M.; Miyata, H.; Nitta, K. H. J. Appl. Polym. Sci. 1996, 62, 87-97.
 - (39) Cross, M. M. J. Colloid Sci. 1965, 20, 417–437.
- (40) Vega, J. F.; Santamaria, A.; Munoz-Escalona, A.; Lafuente, P. *Macromolecules* **1998**, *31*, 3639–3647.
- (41) Wang, W. J.; Ye, Z. B.; Fan, H.; Li, B. G.; Zhu, S. P. Polymer 2004, 45, 5497–5504.
 - (42) Janzen, J.; Colby, R. H. J. Mol. Struct. 1999, 485-486, 569-584.
- (43) Malmberg, A.; Gabriel, C.; Steffl, T.; Munstedt, H.; Lofgren, B. *Macromolecules* **2002**, 35, 1038–1048.
 - (44) Gabriel, C.; Munstedt, H. Rheol. Acta 2002, 41, 232-244.
- (45) Lohse, D. J.; Milner, S. T.; Fetters, L. J.; Xenidou, M.; Hadjichristidis, N.; Mendelson, R. A.; Garcia-Franco, C. A.; Lyon, M. K. *Macromolecules* **2002**, *35*, 3066–3075.

(46) Stadler, F. J.; Piel, C.; Klimke, K.; Kaschta, J.; Parkinson, M.; Wilhelm, M.; Kaminsky, W.; Munstedt, H. *Macromolecules* **2006**, 39, 1474–1482.

(47) Van Gurp, M.; Palmen, J. Rheol. Bull. 1998, 67, 5-8.

(48) Trinkle, S.; Friedrich, C. Rheol. Acta 2001, 40, 322-328.

(49) Trinkle, S.; Walter, P.; Friedrich, C. Rheol. Acta 2002, 41 103-113.

(50) Wood-Adams, P. M.; Dealy, J. M.; deGroot, A. W.; Redwine, O. D. *Macromolecules* **2000**, 33, 7489–7499.

(51) Robertson, C. G.; Garcia-Franco, C. A.; Srinivas, S. J. Polym. Sci., Part B: Polym. Phys. 2004, 42, 1671–1684.

(52) Garcia-Franco, C. A.; Srinivas, S.; Lohse, D. J.; Brant, P. *Macromolecules* **2001**, *34*, 3115–3117.

(53) Chung, T. C.; Rhubright, D. Macromolecules 1994, 27, 1313–1319.