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The preparation and rheology characterization of long chain branching polypropylene

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Abstract

In order to study the rheological behavior of long chain branching (LCB) polypropylene (PP), linear polypropylene was modified by melt grafting reaction in the presence of 2,5-dimethyl-2,5(*tert*-butylperoxy) hexane peroxide and pentaerythritol triacrylate (PETA) in mixer. The transient torque curves and Fourier transformed infrared spectroscopy (FTIR) results indicated that macroradical recombination reactions took place and PETA had been grafted onto PP backbone. Various rheological plots including viscosity curve, storage modulus, loss angle, Han plot, Cole–Cole plot were used to distinguish LCB PP from linear PP. On the other hand, to quantify the LCB level in modified PPs, a new method was suggested on the basis of macromolecular dynamics models. The results showed that the level of LCB was in the range of 0.025–0.38/10^4 C . Moreover, the length of the branched chains and the content of the branched component increase with PETA concentration. Furthermore, the LCB efficiency of monomer can also be calculated, less than 20% of grafting monomers was used to form branch structure.

Keywords: Polypropylene (PP); Long chain branching (LCB); Rheology

1. Introduction

Isotactic polypropylene (iPP) has become one of the most widely used commercial polymers because it has many desirable and beneficial physical properties such as low density, high melting point and chemical resistance. However, commercial polypropylene is a linear polymer, which has relatively low melt strength and exhibits no strain hardening behavior in the melt state. This limits its use in applications such as thermoforming, foaming and blow molding. Therefore, the preparation and research on high melt strength PP are very active in the past decade [1–5].

One of the effective approaches to achieve the high melt strength PP is to introduce long chain branches (LCB) onto PP backbone. The constrained geometry catalyst (CGC) has been found to be very useful for preparing LCB polyolefin [6–9]. However, this method is often used in laboratory. The other two methods, having been applied in industry, are electron beam irradiation [4,5] and postreactor chemical modifications [1–3]. The former is carried out when PP is in solid state, while the latter is carried out when PP is in melt state. Due to the chemical nature of PP, it has a tendency to undergo β-scission which competes with grafting and crosslinking reaction especially for the latter method. In order to decrease the degradation of PP and improve the degree of branching, various peroxide and polyfunctional monomers had been used to prepare long chain branching PP. Lagendijk et al. [1] investigated the efficiency of peroxydicarbonate (PODIC) with various structures for the LCB modification of PP. All PODIC-modified samples show enhanced strain hardening, and PODIC with non-linear or large linear alkyl groups resulted in the modified PP with the highest degree of branching and the fastest strain hardening. Wang et al. [3] used polyfunctional monomer, pentaerythritol triacrylate (PETA), and 2,5-dimethyl-2,5(*tert*-butylperoxy) hexane peroxide to produce branched PPs and studied their flow curves by capillary rheometer and

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thermal properties. They discussed the effects of the concentration of peroxide and monomer on gel content, and low concentration of PETA and peroxide was suggested to minimize the formation of macrogels. Monomers with different functionality were studied by Yoshii et al. [5], the result showed that relatively shorter chain bifunctional monomers such as 1,4-butanediol diacrylate (BDDA) and 1,6-hexanediol diacrylate (HDDA) are better for improving the melt strength of PP.

Since the melt strength or elongation behaviors of modified PP are strongly related to the level of LCB, it is necessary to determine the level of LCB under different conditions of modification. Generally, three techniques are used to quantify the level of LCB: ^{13}C NMR, multidetector GPC and rheology technique. However, two of the formers fail to detect very low level LCB [10,11]. On the other hand, for NMR, LCB corresponds to chain lengths of six carbon atoms or greater [10], which is different from the definition in terms of rheology. The length necessary for a branch to behave as a long chain branch is $2M_e$ (M_e = molecular weight between entanglements) [4,12–14]. GPC is insensitive to the high molecular weight species in the molecular weight distribution (MWD), whereas the branched species reside at the high molecular weight species, which also makes GPC not a good choice for very low LCB [4,14]. Considering these, rheology technique is very prevalent to detect the existence of LCB although it is an indirect method.

In the past decade, many researchers have investigated LCB polyolefin by rheological method, but most studies focus on PE or model polymers [1,4,15], and only a few literatures are about LCB PP, because LCB PP is difficult to be obtained and the degree of LCB is very low. When PP is modified by peroxide and polyfunctional monomer, the reaction and the product components become very complex. Degradation reaction makes the molecular weight to decrease, grafting reaction introduces short chain branch (SCB) structure, branching reaction introduces LCB structure, and gel will be produced if crosslinking reaction can happen. The complex reactions as well as the complex products make the investigation on LCB PP very difficult.

The main objective of this paper is to prepare LCB PPs by melt grafting reaction in the presence of 2,5-dimethyl-2,5(*tert*-butylperoxy) hexane peroxide and pentaerythritol triacrylate (PETA), and then characterize them by rheological methods. The linear viscoelastic behavior of these samples was investigated by small-amplitude oscillatory shear (SAOS). Various rheological plots were used to differentiate LCB PP qualitatively from linear PP. Moreover, a new way based on macromolecular dynamics models was proposed to quantify LCB in the modified PPs. The branching efficiency of monomer can also be evaluated.

2. Experimental

2.1. Materials

Additive-free isotactic polypropylene powder (401) was supplied by Yangzi Petrochemical Corporation, China. The melt flow index (MFI) is 2.5 g/10 min measured at 2.16 kg and 230 °C. The PP powder was stabilized by the addition of 0.2 wt% Irganox 1010 (Ciba, Switzerland) antioxidant. 2,5-Dimethyl-2,5(*tert*-butylperoxy) hexane peroxide was obtained from Sinopharm Chemical Reagent Co., Ltd, whose half-life time is about 1 min at 180 °C, and pentaerythritol triacrylate (PETA) was obtained from Tianjin Kemao Chemical Reagent Company, China. Both the peroxide and PETA were used as received.

2.2. Sample preparation

Modification of the linear PP took place in a Haake Rheocord90 mixer at 180 °C and 60 rpm for 10 min. The formulations are listed in Table 1. In order to make the additives disperse evenly in PP powder, the peroxide, PETA and Irganox 1010 were dissolved in 10 ml acetone, and then the solution was added into 50 g PP powder. At last, the mixture was stirred for 5 min and placed in ventilating cabinet at room temperature until the acetone volatilized completely.

2.3. Gel determination

The reacted samples were cut into small pieces and packed with filter paper, respectively, and then were Soxhlet extracted in boiling xylene for 24 h. No gel was observed for all samples.

2.4. FTIR spectroscopy

The reacted samples were dissolved in hot xylene at 140 °C, and then the solutions were charged into acetone at room temperature. PP and PP-*g*-PETA precipitated out, while the unreacted PETA monomer and (co)polymerized PETA remained soluble. PP and PP-*g*-PETA were separated by filtration, and then was dried at 60 °C under vacuum for 24 h. The purified samples were pressed into films at 200 °C, 12 MPa. At last the films were analyzed using Paragon 1000 (PerkinElmer, Inc., USA).

2.5. Rheological measurements

A rotational rheometer, Gemini 200HR (Bohlin Instruments, UK), with a parallel-plate geometry (diameter is 25 mm), was used for rheological measurements. Small-amplitude oscillatory shear was performed in the frequency

Table 1
Formulation and abbreviation of samples

Samples	PP powder (g)	Irganox 1010 (g)	Peroxide (g)	PETA (g)
PP	100	0.2	–	–
D0	100	0.2	0.1	–
D1	100	0.2	0.1	0.6
D2	100	0.2	0.1	1.0
D3	100	0.2	0.1	1.5
D4	100	0.2	0.1	2.0
D5	100	0.2	0.1	4.0

range 0.01–100 rad/s at 180 °C. A strain of 1% was used, which was in the linear viscoelastic regime for all samples.

3. Results and discussion

3.1. Reaction in Haake and torque curves

Free-radical grafting in the melt usually goes to completion within less than a few minutes depending mainly on the melting rate and the half-life time of the free-radical generator used [16]. If the residence time (in extruder or mixer) corresponds to 5 half-life times, there will be >97% consumption of the peroxide [17].

To observe clearly, only five transient torque traces of PP, D0, D1, D4, and D5 are shown in Fig. 1. For the plain PP, the torque curve kept nearly horizontal after complete melting. The torque of PP/peroxide (D0) decreased gradually after complete melting, indicating that degradation reaction of PP took place. However, for PP/peroxide/PETA systems, the second peak appeared at about 4–7 min besides the melting peak. Moreover, the second peak became bigger with the increase of PETA concentration, suggesting that branching or cross-linking reactions took place. In fact, no gel was detected for all reacted samples (in Section 2.3). Therefore, the increase of torque, corresponding to the increase of viscosity, can be attributed to the branching reaction of PP chains. In the experiments of Wong and Baker [18], PP was modified by 1,1-di-(*tert*-butylperoxy)-3,3,5-trimethylcyclo-hexane (L231) and glycidyl methacrylate (GMA), the second peak was also observed. As shown in Fig. 1, the second peak occurred only when PETA was used, moreover, the branching reactions took place after PP melted completely and the maximum of the second peak occurred at about 5 min which is just 5 half-life times of the peroxide. The primary radicals decomposed by peroxide are converted to PP macroradicals by abstracting hydrogen very quickly. PP macroradicals are easy to undergo β-scission if no monomer was used, i.e., D0 in our case. When monomer (PETA in our experiments) was used, β-scission was restrained because monomers were grafted onto PP backbone which can stabilize PP macroradicals. Therefore, it can be believed that the branching reaction of PP chains happened between PP macroradicals grafted by monomers (PETA in our experiments), which results in PP molecules with long chain branch.

3.2. FTIR spectroscopy

FTIR spectra of the purified samples are shown in Fig. 2. For all the samples modified with PETA, there are bands at about 1735 cm^{-1} which are due to the stretching vibration of the carbonyl group of the ester in the PETA molecule [3], indicating that PETA was grafted onto the PP backbone. From the FTIR spectra, the carbonyl index (CI) was calculated as follows:

$$\text{CI} = \frac{A_{1735}}{A_{841}} \tag{1}$$

where A_{1735} is the absorbance at 1735 cm^{-1}, characteristic of carbonyl groups of the ester in the PETA molecule; and A_{841} is the absorbance at 841 cm^{-1}, characteristic of the CH_3 groups in the PP backbone. CI is a relative value; in order to achieve the grafting degree, a calibration curve is needed. The blends with known amounts of PETA and PP were prepared in Haake mixer. The calibration curve is presented in Fig. 3. The grafting degree was then calculated and listed in Table 2. It can be seen that the grafting degree increases with the concentration of PETA, suggesting that more PETA would favor grafting reaction and macroradical recombination. The result was in accordance with the analysis of the torque curves.

3.3. Linear viscoelastic properties

Linear viscoelastic properties are very sensitive to the structural change in the materials. It will be demonstrated below from different rheological plots that the radical reactions in

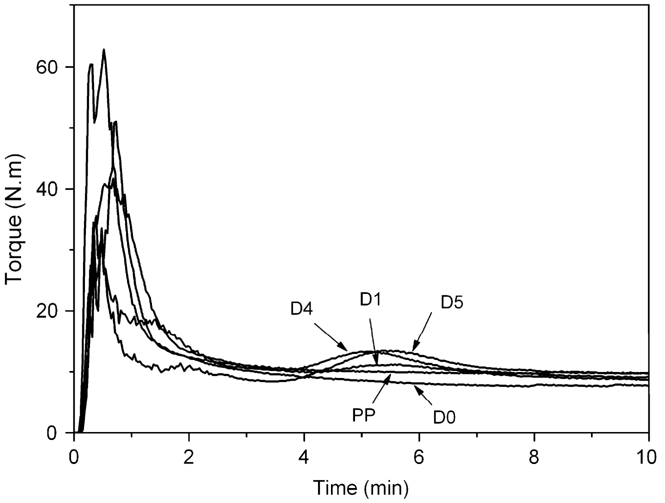

Fig. 1. Transient torque curves of the plain PP and modified PPs at 180 °C.

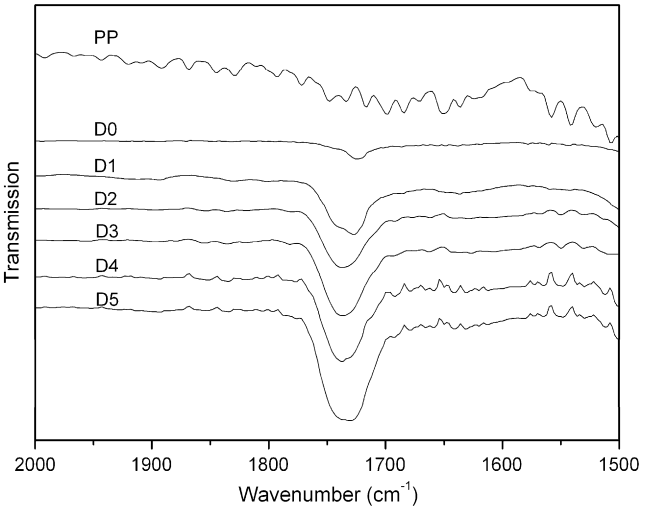

Fig. 2. FTIR spectra (1500–2000 cm^{-1}) of the purified samples.

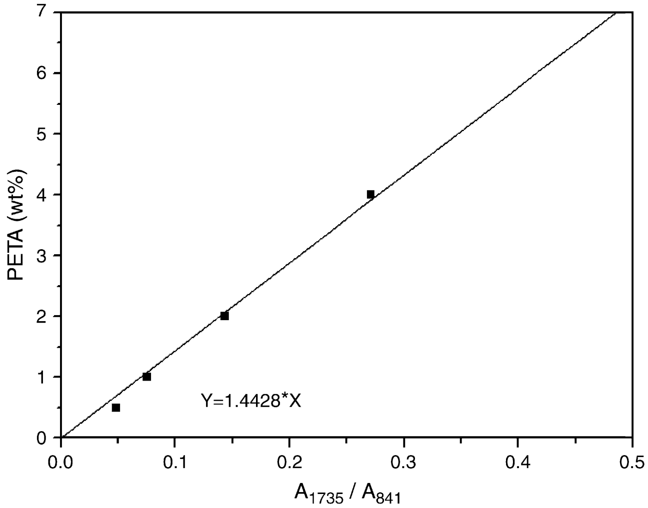

Fig. 3. Calibration curve for the determination of the percentage of reacted PETA in PP-*g*-PETA.

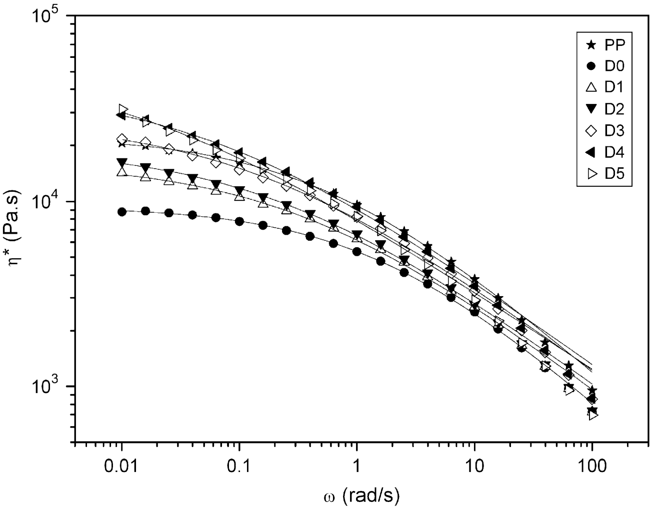

Fig. 4. Complex viscosity vs. angle frequency for the plain PP and modified PPs at 180 °C.

Table 2
Rheological parameters of the plain PP and modified PPs

Sample	Grafting degree (wt%)	η_0 ($\times 10^4$ Pa s)	λ (s)	n	Terminal slope of G'
PP	–	2.00	1.81	0.56	1.73
D0	–	0.88	0.61	0.57	1.80
D1	0.13	1.85	2.78	0.49	1.11
D2	0.18	1.92	4.29	0.48	1.06
D3	0.26	2.74	6.69	0.47	0.96
D4	0.30	3.62	16.11	0.46	0.95
D5	0.55	4.57	71.08	0.43	0.70

PP systems can result in new topological structure with longer relaxation time, which is ascribed to the molecules with long chain branch.

Shear rheology is very sensitive to the topological structure of macromolecules. The presence of very low amounts of LCB can change the zero-shear viscosity (η_0) and the degree of shear thinning, as compared to the linear polymers with similar molecular weight [19]. The complex viscosity curves of the plain PP and modified PPs are shown in Fig. 4. When only peroxide was used (sample D0), complex viscosity decreased severely at low frequency and Newtonian-zone became broader, indicating that there was only degradation reaction and the molecular weight decreased. With the addition of PETA, the complex viscosity curves became higher than that of D0 at low frequency, indicating that the additions of PETA reduced the degradation. Further, the viscosity of PP at low frequency increased gradually when more PETA was used, and the transition from Newtonian-plateau to shear-thinning regime was shifted to lower frequency. The viscosity of the samples can be fitted by the cross equation [12], which is written as

$$\eta^*(\omega) = \frac{\eta_0}{1+(\lambda\omega)^n} \tag{2}$$

where η_0 is the Newtonian viscosity, λ is a relaxation time whose reciprocal accounts for the onset of shear-thinning region and n is a shear-thinning index. These values for the plain PP and modified PP are listed in Table 2. It can be seen that with the addition of PETA, the rheological parameters changed regularly, i.e., η_0 and λ increased and n decreased gradually. The effect of branches on viscosity was clear that there was no evident Newtonian-plateau at low frequency and the shear thinning starts at lower frequency than that of the plain PP and sample D0. Similar result was also obtained by Sugimoto et al. [20]. With 1.5, 2 and 4 wt% PETA concentrations (samples D3–D5), the complex viscosities were higher than that of the plain PP at low frequency, while they were smaller than that of the plain PP at high frequency. These are typical characters of polymers with long chain branching [11].

Besides zero-shear viscosity, the storage modulus and the loss angle are even more sensitive to LCB [11]. In the terminal zone, where only the longest relaxation times contribute to the viscoelastic behavior, G' and G'' of linear polymers follow the well-known frequency dependence [21], i.e., $G' \propto \omega^2$ and $G'' \propto \omega$. The storage modulus (G') of all samples plotted as a function of frequency is shown in Fig. 5. The plain PP and D0 exhibited the typical terminal behavior, indicating that they are linear polymers. The other five samples modified with PETA are deviated from the terminal behavior. With the addition of PETA, G' increased at low frequency and the terminal slope of G' decreased from 1.73 of the plain PP to 0.70 of D5 (Table 2). The non-terminal behavior of D1–D5 suggests that there is a longer relaxation mechanism, which can be ascribed to the long chain branches formed from radical reactions.

It has been shown that the loss angle (δ) is independent of the frequency in a limited frequency range since polymers with LCB have the gel-like rheological behavior [22]. Moreover, with the LCB level increasing, the plateau of δ becomes more evident and the value of δ decreases [11,22,23]. Although this was first obtained from polyethylene and ethylene/1-butene copolymer, Gotsis et al. [24] had made an

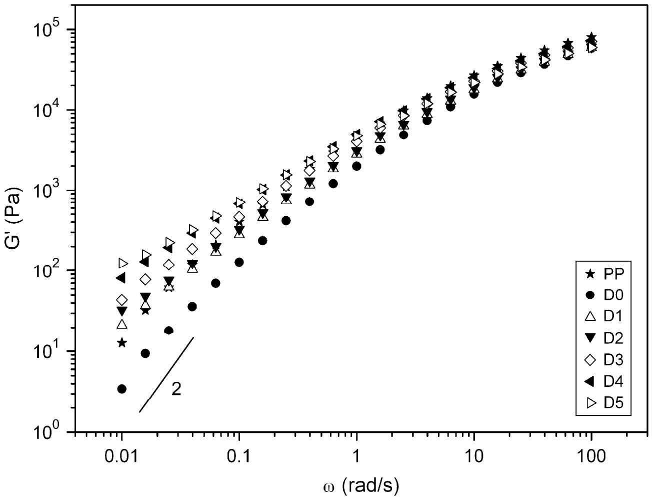

Fig. 5. Storage modulus vs. frequency for the plain PP and modified PPs at 180 °C.

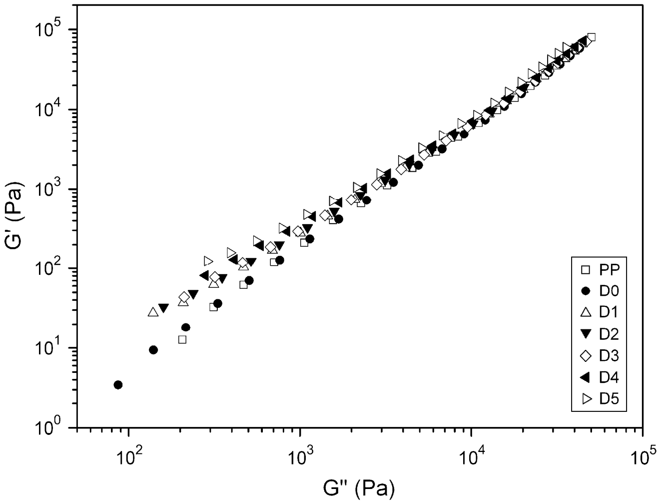

Fig. 7. Han plot of the plain PP and modified PPs at 180 °C.

effort to apply this to LCB PPs modified by myristyl-peroxy-dicarbonate. However, LCB PPs only showed inflection in the curve of the loss angle and no plateau had been found. For our peroxide/PETA reactive systems, similar result was obtained from the tan δ–ω curves shown in Fig. 6. For linear polymers, the plain PP and D0, the curves were ascending with the frequency decreasing, which is a typical terminal behavior of liquid-like material. With the addition of PETA, tan δ decreased quickly at low frequency and showed a plateau. The tan δ decreased continually and the plateau became longer if more PETA was used. This observation is in accordance with the result of Graebling [15], who attributed this to the grafting of long chain branches on the PP skeleton and increasing the terminal relaxation time.

The non-terminal behavior of the modified PPs can also be illustrated in the Han plot (log G'–log G'', Fig. 7) and Cole–Cole plot (η''–η', Fig. 8). The Han plot has been used to investigate order–disorder transitions in block copolymers [25,26], the effect of polydispersity and LCB in polyethylenes [27] and miscibility of polymer blends [28,29]. Han plot is independent of the melt temperature and weight average molecular weight for monodispersed polymers. The Han plots of modified PPs with PETA deviated significantly from the scaling G'–G''^2 of the linear polymer, indicating that a long relaxation mechanism occurred in these samples. This long relaxation process can also be seen in the Cole–Cole plot (Fig. 8). As shown in Fig. 8, the differences of these samples are very clear. For the plain PP and D0, the Cole–Cole plots were close to a semicircle, and the higher the molecular weight was, the bigger the radius was. The curves of D1 and D2 were lower than that of the plain PP and higher than that of D0, indicating that degradation reaction took place, but the degradation degrees were lower than that of D0. Moreover, the curves of D1 and D2 became level at high viscosity corresponding to low frequency. The Cole–Cole plots of D3–D5 were higher than that of the plain PP and showed more evident upturning at high viscosity, indicating that a longer relaxation time appeared.

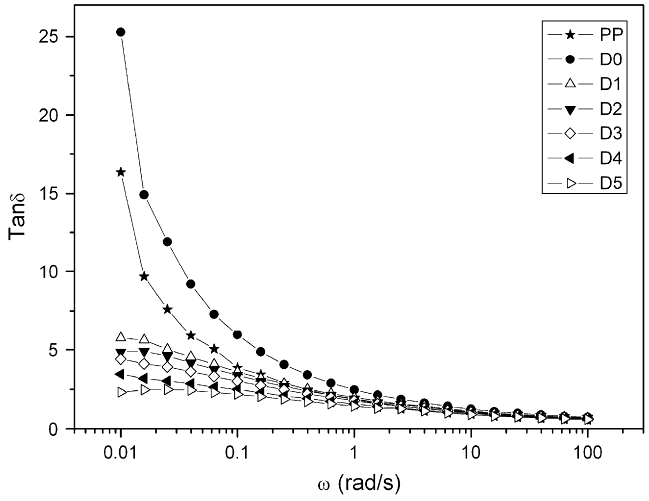

Fig. 6. Tan δ vs. angle frequency for the plain PP and modified PPs at 180 °C.

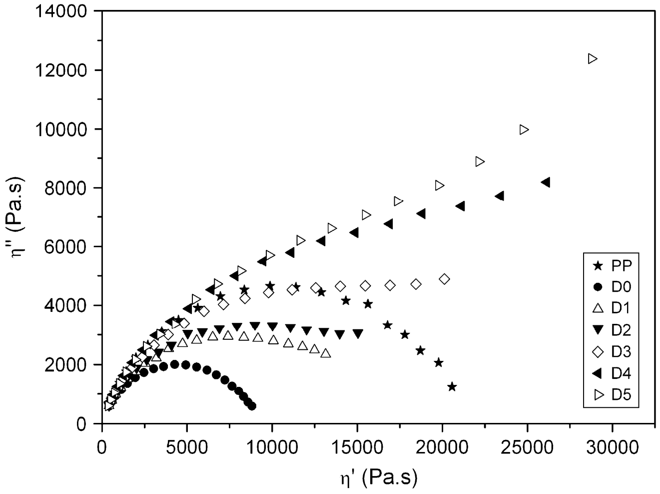

Fig. 8. Cole–Cole plot of the plain PP and modified PPs at 180 °C.

It is clear from all these linear viscoelastic plots that a longer relaxation process appeared in the modified PPs with PETA. It is believed that this longer relaxation process is related to long chain branch that results from the radical reactions in the presence of peroxide and PETA. However, all these plots only proved the existence of long chain branch in a qualitative manner. The exact amount of LCB is hard to be determined directly from linear viscoelastic functions without incorporation of certain theory of macromolecular dynamics.

3.4. Quantitative analysis of LCB

Determination of the level of LCB in polymers is not an easy task, and even more difficult in our system due to the complex reactions that happened during the modifications of PP. Tsenoglou and Gotsis [30] tried to determine the level of LCB in PP modified by peroxydicarbonates (PODICs). They assumed that linear polymer chains break through scission and some of their fragments crosslink with neighbors to form three-arm branched molecules. The product of the radical reactions is a blend of linear molecules and three-arm branched molecules. The weight fraction of branched chains can be expressed as [30]:

$$B_n = \frac{\ln(\eta_{BL}/\eta_L)}{\alpha(M_L/M_C - 1) - 3\ln(M_L/M_C)} \tag{3}$$

here η_{BL} is the zero-shear viscosity of branched and linear blend, η_L and M_L are the zero-shear viscosity and the weight average molecular weight of the linear precursor, and α is an adjustable parameter ($\alpha = 0.42$). M_C is the molecular weight between two successive entanglements and roughly equal to 11.2 kg/mol for PP. In order to get the value of B_n, M_L was calculated from the relationship between zero-shear viscosity and the molecular weight of the linear PP, given as follows:

$$\log \eta_0 = -15.4 + 3.5 \log M_w \tag{4}$$

A very crude approximation has been made when deriving Eq. (3), i.e., the breaking of linear chain happens in the middle which results in the branched chains of arm molecular mass $M_a \approx M_L/2$. This is, in fact, not necessarily true. Moreover, it is clear that Eq. (3) can be used only when η_{BL} is higher than η_L. Therefore, the branching level of D1 and D2 cannot be calculated by Eq. (3) because it has lower zero-shear viscosity than that of the linear precursor. The values of B_n for D3–D5 were predicted by Eq. (3) and listed in Table 3.

A new method is suggested here to determine the LCB level in modified PPs with PETA. The linear chain of PP with initial (weight average) molecular mass M_L can break through β-scission and some fragments recombine to form new molecules. The newly formed molecules can be linear or branched. Therefore, the product of modified PP with PETA is a mixture of linear molecules and branched molecules. Firstly, it is assumed that the linear chain to linear chain transformation does not change the weight average molecular mass of linear chain. This assumption can be validated by the relaxation spectrum of all samples shown in Fig. 9. The relaxation spectrum was calculated from dynamic modulus (G' and G'') data by GENEREG program [31]. The weighted relaxation spectra show that the plain PP and D0 only have one characteristic relaxation time, which is related to the relaxation process of linear molecules. Moreover, the characteristic relaxation time of D0 was smaller than that of the plain PP, indicating that D0 has lower molecular mass than that of the plain PP. For samples modified with PETA, they exhibited an additional longer characteristic relaxation time (τ_B) besides the linear one (τ_L). The longer characteristic relaxation time is ascribed to the relaxation of branched chains. The smaller characteristic relaxation times (τ_L) of D1–D4 samples were very close to the relaxation time in PP sample. This indicates that the linear molecules in D1–D2 samples have comparable molecular mass with the linear molecules in the plain PP. The longer relaxation time (τ_B) of D5, however, was quite long, and larger than the maximum relaxation time that can be determined from our experiments. In the following

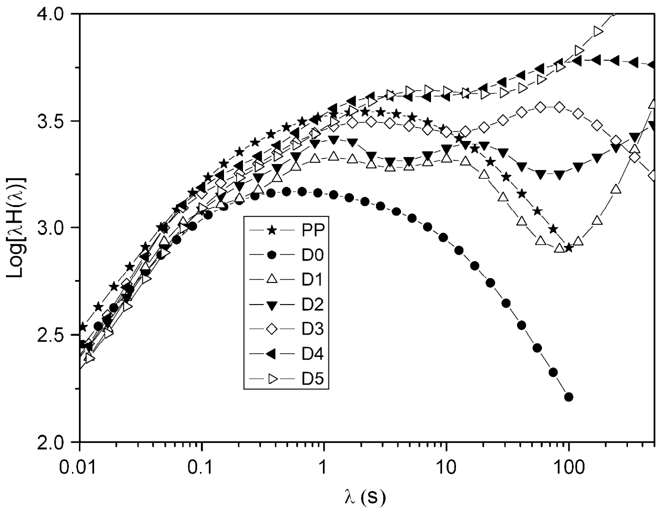

Fig. 9. Weighted relaxation spectrum for the plain PP and modified PPs.

Table 3
Rheological parameters for samples modified with PETA

	B_n	τ_L (s)	τ_B (s)	N	N_a	$\eta_{0,BL}$ ($\times 10^4$ Pa s)	$\eta_{0,L}$ ($\times 10^4$ Pa s)	$\eta_{0,B}$ ($\times 10^4$ Pa s)	x	E_{lcb} (%)
D1	–	2.2	14.2	76	24.9	1.85	2.0	0.41	0.05	2.7
D2	–	2.2	37.0	76	26.5	1.92	2.0	1.00	0.06	2.3
D3	0.07	2.2	130.0	76	28.6	2.74	2.0	3.48	0.56	15.0
D4	0.12	2.2	175.4	76	29.0	3.62	2.0	4.40	0.75	17.5

calculations, the relaxation time τ_B is very important to obtain the branching level. These calculations will not be performed on D5 since it is hard to determine τ_B of D5. The characteristic relaxation times τ_L and τ_B for D1–D4 determined from Fig. 9 are listed in Table 3.

According to the reptation model with contour length fluctuation [32], the relaxation time and the zero-shear viscosity of linear chain can be expressed as:

$$\tau_L = 3\tau^*(a)N^3\left(1-1.47N^{-1/2}\right)^2 \tag{5}$$

$$\eta_{0,L} = \frac{\pi^2 G_N \tau^*(a)}{4}N^3\left(1-1.47N^{-1/2}\right)^3 = \frac{\pi^2 G_N\left(1-1.47N^{-1/2}\right)}{12}\tau_L \tag{6}$$

where $\tau^*(a)$ is the internal equilibration time of each entangle segment, N is the segment number in a linear chain ($=M/M_e$ with M_e the molecular mass between entanglements), G_N is the entanglement plateau modulus. The relaxation time and the zero-shear viscosity of branched chain can be approximated by the Ball–McLeish model [33]:

$$\tau_B = \tau^*(a)\exp\left(\frac{\nu N_a}{3}\right) \tag{7}$$

$$\eta_{0,B} = G_N\tau^*(a)(\nu N_a)^{-1}\exp\left(\frac{\nu N_a}{3}\right) = G_N(\nu N_a)^{-1}\tau_B \tag{8}$$

where N_a is the entanglement segment number in branching chain ($N_a = M_B/M_e$) and ν is a constant ($\nu = 15/8$).

The molecular mass or the length N of linear chain can be calculated from Eq. (4). The length of the branched chain N_a can be calculated by comparing the characteristic relaxation time of branched chain and linear chain:

$$\frac{\tau_B}{\tau_L} = \frac{\exp(\nu N_a)}{3N^3\left(1-1.47N^{-0.5}\right)^2} \tag{9}$$

The calculated N_a is listed in Table 3. It was found that the average length of the branched chain was about 1/3 of the length of the linear chain for D1, and increased with the increasing amount of PETA. This result is completely different from the assumption that has been taken by Tsenoglou and Gotsis [30]. This means that the presumption on the length of the branched chain in such system would cause some errors in evaluating the LCB level.

The zero-shear viscosity of the linear chain, $\eta_{0,L}$, of D1–D4 samples was same as that of the plain PP due to the same length of the linear chains. Zero-shear viscosity of branched component can be calculated as follows:

$$\frac{\eta_{0,B}}{\eta_{0,L}} = \frac{12(\nu N_a)^{-1}\tau_B}{\pi^2\left(1-1.47N^{-0.5}\right)\tau_L} \tag{10}$$

The zero-shear viscosity of branched chains, $\eta_{0,B}$, of D1–D4 samples is also listed in Table 3, which increased quickly with increasing length of the branched chain. Since the samples with LCB can be considered as blends of linear component and branched component, the zero-shear viscosities are assumed to follow a logarithmic mixing rule [34]:

$$\eta_{0,BL} = \eta_{0,L}^{1-x}\eta_{0,B}^{x} \tag{11}$$

here, x is the fraction of the branched chains in all chains.

The total amount of branched chains can be readily obtained from the above equations, and listed in Table 3. Furthermore, it is easy to obtain the fraction of grafted monomer that has been used to form branch structure, i.e., the LCB efficiency of PETA (E_{lcb}),

$$E_{lcb} \approx \frac{x}{\left(x_g/M_{PETA}\right)/\left[\left(1-x_g\right)/M_{PP}\right]} \tag{12}$$

here, x_g is the grafting degree listed in Table 2, M_{PETA} is the molecular mass of PETA ($M_{PETA} = 298$), and M_{PP} is the molecular mass of linear PP, which can be calculated by Eq. (4), the value is 425,000. The calculated data of E_{lcb} are shown in Table 3.

The results show that the length of the branched chains increases with PETA concentration. It can be speculated that the different length of the branched chains is the result of different reaction mechanics. When the concentration of PETA is lower, the grafting reaction follows degradation, so the backbone and branches are both fragment chains. However, with the increasing concentration of PETA, the grafting reaction will happen simultaneously with the chain scission, because there are enough monomers to trap primary macromolecular radicals. Therefore, the majority backbones are the linear precursor, while the branches are fragment chains and their length increase with the concentration of PETA.

The LCB efficiency of monomer also increases with monomer concentration. When the grafting degree increased from 0.13 for D1 to 0.30 for D4, the LCB efficiency of PETA increased quickly from 2.7 for D1 to 17.5 for D4, indicating that more polyfunctional monomer is favored to branching reaction of PP. In general, the LCB level of modified polyolefin detected by NMR or GPC is less than $1/10^4$C [10,11,27,35]. For the kind of PP used in this work, a molecular chain ($M_w = 425{,}000$) includes about 20,000 carbons on the backbone which can be calculated from the molecular weight of PP and repeated units ($2M_w/M_0$). The LCB level is in the range of $0.025–0.38/10^4$C. Therefore, these calculated results are reasonable and acceptable.

4. Conclusions

In this study, LCB PPs were prepared by melt grafting reaction in the presence of peroxide and polyfunctional monomer in mixer. Rheological behaviors of the plain PP and modified PPs were investigated in detail by several rheological plots. Moreover, a new way based on macromolecular dynamics models was proposed to quantify LCB.

The grafting of PETA and the branching of PP could happen when PP was modified with peroxide and PETA in the Haake mixer, which has been verified by the torque curves and FTIR spectra. The formation of branched structure was confirmed by small-amplitude oscillatory shear experiments. Several rheological plots were used to investigate the rheological properties of the plain PP and modified PPs. The rheological properties of LCB PP, such as higher G' at low frequency, plateau in tan $\delta-\omega$ plot, deviating from the scaling $G'-G''^2$ of linear polymer in Han plot, upturning at high viscosity in Cole–Cole plot, are related to the different relaxation mechanism from linear PP.

A new quantitative method was suggested to evaluate the LCB level in the modified PP samples. No presumption has been made on the molecular weight of branched chain. The quantitative analysis results show that the level of LCB is in the range of $0.025-0.38/10^4$C. The length of the branched chains and the content of the branched component increase with PETA concentration. It is speculated that the different length of the branched chains was induced by different reaction mechanism. Furthermore, the LCB efficiency of PETA can also be calculated, and less than 20% of grafting PETA was used to form branched molecules.

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