

Rheology and Thermal Behavior of Long Branching Polypropylene Prepared by Reactive Extrusion

Feng-Hua Su, Han-Xiong Huang

Center for Polymer Processing Equipment and Intellectualization, College of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510641, P R China

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ABSTRACT: Long-chain branching polypropylene (LCB-PP) was achieved by reactive extrusion in the presence of bifunctional monomer [1,6-hexanediol diacrylate (HDDA)] and peroxide of dicumyl peroxide (DCP). Influences of HDDA and DCP concentrations on the branching efficiency were comparatively evaluated. Fourier transformed infrared spectroscopy (FTIR) results indicated that the grafting reaction took place, and HDDA has been grafted on PP skeleton. In comparison with initial PP, some modified samples showed lower melt flow index because of a large number of LCB in their skeleton. Several rheology plots were used to investigate the rheological properties of the initial PP and modified PPs, and the rheological

characteristics confirmed the LCB in modified PPs skeleton. DSC results showed that the crystallization temperatures of modified PPs were higher than those of initial PP and degraded PP, suggesting that the modified PPs had long-chain branched structure. The contrastive investigation in the rheology of modified PPs suggested that proper concentrations of HDDA and DCP were more beneficial to producing LCB during reactive extrusion. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2126–2135, 2009

Key words: polypropylene; reactive extrusion; long-chain branching; rheology; thermal properties

INTRODUCTION

Polypropylene (PP) is the fastest growing commodity resin in the polymer world market. It has many desirable and beneficial properties when compared with other thermoplastics, such as high melting point, low density, high tensile modulus, and low cost. Although PP has many useful advantages, commercial PP is produced with Ziegler-Natta or metallocene catalysts resulting in high linear chains and a relatively narrow molecular weight distribution. The linear PP exhibits relative low melt strength and no strain hardening behavior in the melt state. Thus, the uses of commercial PP have been limited in the application requiring high melt strength, such as thermoforming, foaming, and blow molding. As a result, the preparation and research on high melt strength PP are very active in the past decades.^{1–6}

High melt strength PP (HMS-PP) is the commercial term used for long-chain branched PP (LCB-PP). There several possible routes to branching PP. There are some reports on the direct synthesis of LCB-PP using metallocene catalysis.^{7–10} But, this method is often used in laboratory. Electron beam irradiation^{4,11–13} and reactive extrusion process^{1,2,5,6,14,15} can be applied easily in industry for branching PP. The electron beam irradiation causes scission of PP chains, which is followed by some crosslinking, leading to LCB. Scheve et al.¹⁰ achieved the branched PP by irradiating a solid and linear PP with high-energy radiation in a nitrogen environment, and the modified PP exhibited substantial melt strain hardening. Even though most commercial HMS-PP is produced by electron beam irradiation, the method of using reactive extrusion has recently regained interest, as it can be directly applied also by the foam manufacturer on commercial linear PP. Lagendijk et al.⁶ investigated the efficiency of peroxydicarbonate (PODIC) with various structures for LCB modification of PP. They found that all PODIC modified samples show enhanced strain hardening. However, PP has a tendency to undergo beta-scission owing to the nature of it, which competes with grafting and crosslinking reaction during the reactive extrusion process. The use of polyfunctional monomer can decrease the degradation and improve the degree of branching for PP. The polyfunctional monomer under the presence of free radicals can produce more stable macroradical sites, which increase the likelihood of undergoing further reaction due to a decrease of the probability of fragmentation. The structure and composition characteristics of polyfunctional monomer and

Correspondence to: F.-H. Su (fhsu@scut.edu.cn).

peroxide have direct influence on the branching level of modified PP. Yoshii et al.¹² found that relatively shorter chain bifunctional monomers were better for improving the melt strength of PP when compared with the longer chain bifunctional monomers. Legendijk et al.⁶ reported that the PODIC with nonlinear or larger linear alkykl groups resulted in modified PP with the higher degree of branching and the fastest strain hardening. Besides the structure of polyfunctional monomer and peroxide, the concentration of them also greatly affect the branching level of modified PP. Wang et al.² used polyfunctional monomer, pentaerythritol triacrylate (PETA), and 2,5-dimethyl-2,5(*tert*-butylperoxy) hexane peroxide (DTBP) to produce branched PPs and suggested low concentration of PETA and peroxide to minimize the formation of macrogels.

Dynamic rheology is sensitive to the structure and branching information of polyolefin. In the past decade, many researchers have investigated LCB polyolefin by rheological method, but most studies focus on the PE and model polymers. Recently, the rheology was used to characterize the LCB-PP.^{1,3,4,16,17} Yu et al.¹ investigated the rheology characterization of LCB-PP prepared by reactive extrusion. They suggested a new rheology technique to quantify the LCB level for the modified PP. Otaguro et al.¹⁶ investigated the rheological properties of polypropylene irradiated with polyfunctional monomers and found that the branched PP could be achieved when proper content of polyfunctional monomers were mixed with PP before irradiation although the beta-scission of PP occurred. At the same time, the degradation and grafting reaction would result in change of molecular weight and its distribution, and chain irregularity. Besides the rheology, the crystallization and melting behavior had direct relation with the branched structure of PP.^{2,18} Wang et al.² found that the two melting peaks were observed in the DSC traces of the modified PP with PETA and peroxide, and the crystallization temperatures of modified PPs were higher than those of initial PP.

In this study, our efforts focused on the preparation of LCB-PPs by reactive extrusion in the presence of dicumyl peroxide (DCP) and 1, 6-hexanediol diarylate (HDDA). The influences of HDDA and DCP concentrations on the branching degree were comparatively evaluated. The linear viscoelastic behavior of initial PP and modified PPs were evaluated by small-amplitude oscillatory shear. Various rheological plots were used to differentiate LCB-PP from linear PP. The grafted reaction between PP and HDDA was investigated by Fourier transformed infrared spectroscopy (FTIR). Moreover, the melting and crystallization behaviors of modified PPs were investigated.

EXPERIMENTAL

Materials

The isotactic PP (iPP) homopolymer powder (T30S) was supplied by Maoming Petrochemical Corporation, China. The melt flow index (MFI) is 3.49 g/10 min measured at 2.16 kg and 230°C in our experiment. The PP powder was stabilized by the addition of 0.1% Irganox 1010 (Jinhai Albemarle, China) antioxidant. DCP was purchased from Lanzhou Auxiliary Agent Plant, whose half-life time is 10 min at 153°C. Polyfunctional monomer HDDA was purchased from Tianjintianjiao Chemical Co, Ltd., China. Both the peroxide and polyfunctional monomer were used as received.

Sample preparation

To make the additives disperse evenly in PP powder, DCP and HDDA were dissolved in 50 mL acetone, and then the solution was added into 1000 g PP powder during the mixing process with SHR10A high speed mixer. The mixture of linear PP with antioxidant, peroxide, and HDDA in mixer was kept for 10 min. The modification of the linear PP was carried out in TE35 corotating twin-screw extruder after the mixing process. The temperatures of the extruder were maintained at 160, 180, 200, 200, 210, and 210°C from hopper to die. The throughput and the screw speed were 4.8 kg/h and 60 rpm, respectively. During extruding process, a devolatilization zone was placed before the pumping zone close to the die for removing small molecules such as decomposition products of peroxide. Extrudates were cooled in water and then pelletized. The initial PP and modified PP with different concentration of DCP and HDDA were given in Table I.

FTIR analysis

The reacted PPs were added in xylene and then heated to 140°C. The solutions were charged into acetone at room temperature. For reacted PP, the unreacted HDDA monomer and copolymerized HDDA remained soluble, whereas PP and PP-g-HDDA precipitated out. PP and PP-g-HDDA were separated by filtration and then were dried at 80°C under vacuum for 48 h. The purified samples were pressed into film with the same thickness about 0.1 mm and then analyzed using Bruker Tensor 27 FTIR. The initial PP was used as a referer and was treated in the same way for FITR analysis.

Gel determination

The granular reacted PPs obtained from extruder were packed with copper net and then were

TABLE I
Initial and Modified Pps with Different Concentration of DCP and HDDA

Samples	DCP (ppm)	HDDA (phr)
Initial PP (PP0)	0	0
PP1	300	0
PP2	300	1.5
PP3	300	2.0
PP4	300	2.5
PP5	300	3.0
PP6	200	3.0
PP7	400	3.0
PP8	500	3.0
PP9	600	3.0

extracted in the Soxhlet extraction apparatus with xylene for 24 h at 140°C. Basically, no gels were observed in reacted samples.

Melting flow rate measurement

The melting flow properties of the initial and reacted PPs were measured by MFI tester CEAST 7072. The measurements were carried out at 230°C using a load of 2.16 kg according to the GB3682 standard.

Rheological measurement

All rheological experiments were conducted with a Bohlin Gemini 200 Rheometer equipped with a parallel-plate fixture (25-mm diameter). The disc samples were prepared by compression molding with a thickness of 2.0 mm and diameter of 25 mm. The gap between the two parallel plates was maintained at 1.75 mm for all rheological measurements. Small-amplitude oscillatory shear was performed as a function of angular frequency (ω) ranging from 0.01 to 100 rad/s at 190°C. A fixed strain of 1% was used to ensure that measurements were carried out within the linear viscoelastic range of the materials investigated.

Thermal behavior analysis

Thermal behaviors of the initial and modified PPs were investigated by DSC204F1 differential scanning calorimetry from NETZSCH Co., Ltd., Germany. Specimens were heated to 200°C at a rate of 10°C/min and kept for 3 min to eliminate the thermal histories and then cooled down to 25°C at a range of 10°C/min to measure the crystallization temperature. Samples were reheated with the same heating condition to determine the melting temperature.

The level of crystallinity of initial and modified PPs was calculated from the enthalpy of the crystallization as follows:

$$\begin{aligned} \% \text{ Crystallinity} &= \frac{\Delta H_{\text{cr-experiment}} (\text{J/g})}{\Delta H_{100\% \text{ crystallinity}} (\text{J/g})} \times 100 \\ &= \frac{\Delta H_{\text{cr-experiment}} (\text{J/g})}{209 (\text{J/g})} \times 100 \end{aligned}$$

where 209 J/g is the theoretical enthalpy of fusion of 100% crystalline PP.

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR spectra of the initial PP and modified PPs are shown in Figure 1. As shown in Figure 1(a), the bands at 1735 cm^{-1} could be found in all modified PPs with various contents of DCP and HDDA, which was ascribed to the stretching vibration of the carboxyl group of the ester in the HDDA molecule, indicating that HDDA were grafted onto PP skeleton. Moreover, it could be seen that the intensity of this band seemed to increase with increasing HDDA, indicating that more HDDA favored the grafted reaction. From Figure 1(b), it could be found

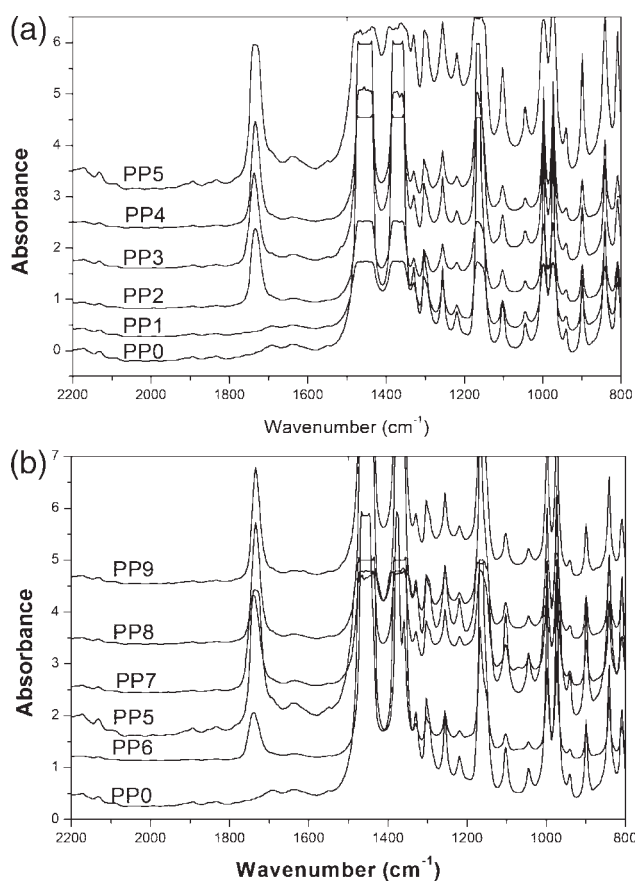


Figure 1 FTIR spectra (800–2200 cm^{-1}) of the initial and modified PPs (a) with increasing HDDA concentration (300 ppm DCP) and (b) with increasing DCP concentration (3.0 phr HDDA).

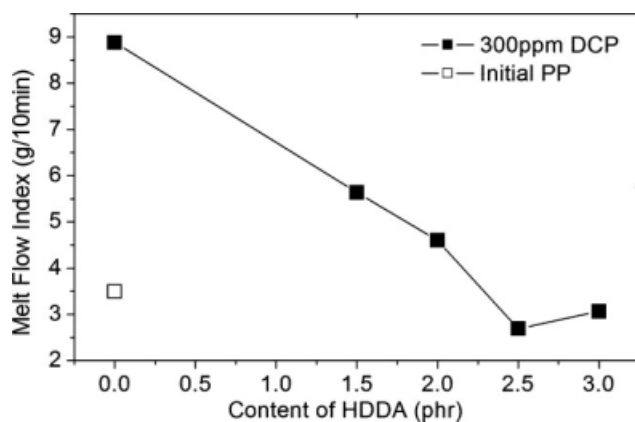


Figure 2 Effect of the HDDA concentration on MFI of the modified PPs (300 ppm DCP).

that the intensity of the bands at 1735 cm^{-1} increased at first and then decreased with increasing DCP. This result suggested that the mass fraction of carboxyl group in modified PPs also had relation with the concentration of DCP. The grafting efficiency was low as low concentration of DCP used in the reacted system; however, the degradation reaction might occur as excessive DCP was added in the system. The FTIR can confirm the grafting reaction but cannot confirm the structure of LCB in modified PPs skeleton. The linear viscoelastic properties are sensitive to the LCB of the polymer, which were discussed in the subsequent section.

Melt flow properties

The influence of the molecular structure on the MFI of polymers has been studied extensively. In case of PP, the samples used have linear chains and similar molecular weight. The melt strength of PP also increases strongly with decreasing MFI. The effects of the concentration of HDDA and DCP on the MFI for modified PPs are shown in Figures 2 and 3, respectively. From Figure 2, it could be seen that MFI of PP1 was much higher than that of the initial PP, indicating that the chain scission process was very severe in no presence of polyfunctional monomer. At the same time, it could be observed that MFI decreased rapidly with increasing HDDA, which might be attributed to the branching reaction between PP and HDDA. MFI of the modified PPs with 300 ppm DCP and 2.5 or 3.0 phr HDDA was lower than that of the initial PP; the reason was that many LBC were grafted in their skeleton. However, HDDA seemed to have no significant effect on MFI at higher concentration level. This might be attributed to the increased HDDA grafting reactions and higher consumption of primary peroxide radicals in HDDA homopolymerization.

As shown in Figure 3, MFI appeared to level off with the increase of DCP concentration up to 400 ppm at fixed HDDA concentration for 3.0 phr. This was attributed to the consumptions of primary peroxide radicals by excessive HDDA, thus stabilizing the amount of HDDA incorporated into PP. However, MFI increased rapidly with the further increase of DCP concentration. With the addition of excessive peroxide (≥ 500 ppm), the amount of monomers was not enough to allow grafting reaction with PP molecules. As a result, degradation reaction could not be prevented, which corresponded to the increased MFI.

Rheology properties

The storage modulus is even more sensitive to LCB structure of PP.^{1,19} The storage modulus G' of modified PPs plotted as a function of frequency ω are shown in Figure 4. As shown in Figure 4(a), it was observed that PP0 and PP1 exhibited the typical terminal behavior, which is owing to the linear chain structure of them. With the addition of HDDA, the modified PPs deviated from the terminal behavior, and G' increased at low frequency and the terminal slope decreased from 1.64 of the initial PP to 0.91 of PP5 with increasing HDDA. As shown in Figure 4(b), with the increasing DCP in system, the behavior of increased G' at low frequency and the decreased terminal slope became unobvious. In general, all modified PPs (PP2–PP8) exhibited the non-terminal behavior, which was attributed to the existence of LCB in their skeleton leading to the longer relaxation mechanism of their chain. However, the G' vs. ω curves are different for modified PPs with the different DCP and HDDA concentration, indicating that the degree of LCB was affected by the concentration of reactant.

Many researchers reported that the presence of LCB in PP skeleton can change the degree of shear

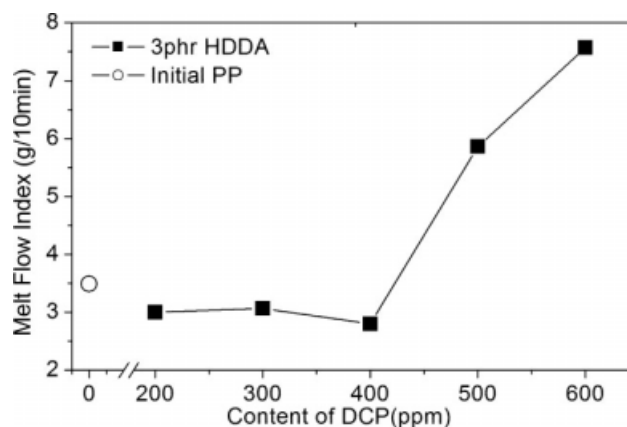


Figure 3 Effect of the DCP concentration on the MFI of the modified PPs (3.0 phr HDDA).

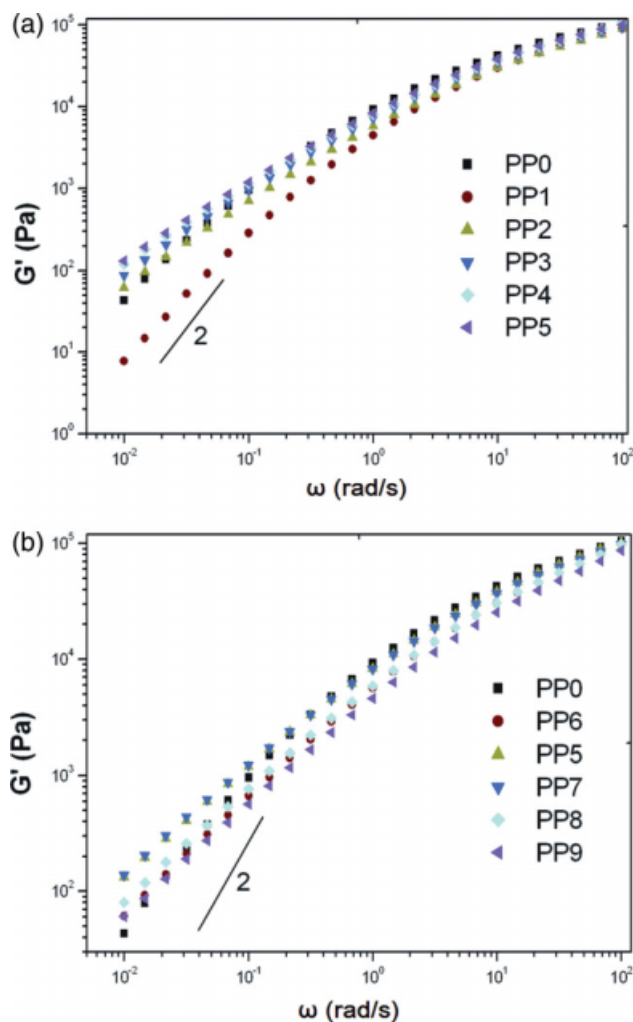


Figure 4 G' vs. ω for initial PP and modified PPs at 190°C (a) with increasing HDDDA concentration (300 ppm DCP) and (b) with increasing DCP concentration (3.0 phr HDDDA). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

thinning in comparison with the linear PP with similar molecular weight.^{1,5,14} It could be seen from Figure 5(a) that the complex viscosity of PP1 decreased severely at low frequency and Newtonian-zone became broader, indicating that there was only degradation reaction. With the addition of HDDDA, the modified PPs exhibited the typical characteristic of shear thinning and the degree of shear thinning increased with increasing HDDDA concentration. The result indicated that the LCB produced as DCP and HDDDA was added in reacted system, and the amount of LCB increased with increasing HDDDA concentration. As shown in Figure 5(b), it could be seen that the degree of shear thinning of modified PPs increased at first and then decreased with increasing DCP concentration. As illustrated earlier, the amount of monomers was not enough to allow grafting reaction with PP molecules and the degra-

mentation reaction became severe as excessive peroxide was added in system.

Besides the behavior of shear thinning and the storage modulus, the loss angle is more sensitive to long chain branched structure of polymer. It is known that the loss angle of the polymers with LCB is independent of the sweep frequency in a limited frequency range. The plateau of the loss angle becomes more evident as more LCB existing in skeleton chain of polymers. Figure 6 showed the $\tan \delta$ vs. ω curves of the initial and modified PPs at 190°C. It could be seen from Figure 6(a) that the curves for PP0 and PP1 were rapidly descending with increasing frequency, which was a typical terminal behavior of liquid-like material, because the polymer chain of them are linear. With the addition of HDDDA, the $\tan \delta$ of modified PPs decreased rapidly with increasing frequency and exhibited a platform at high-frequency regime. Moreover, we could find that the decrease of $\tan \delta$ at low frequency was

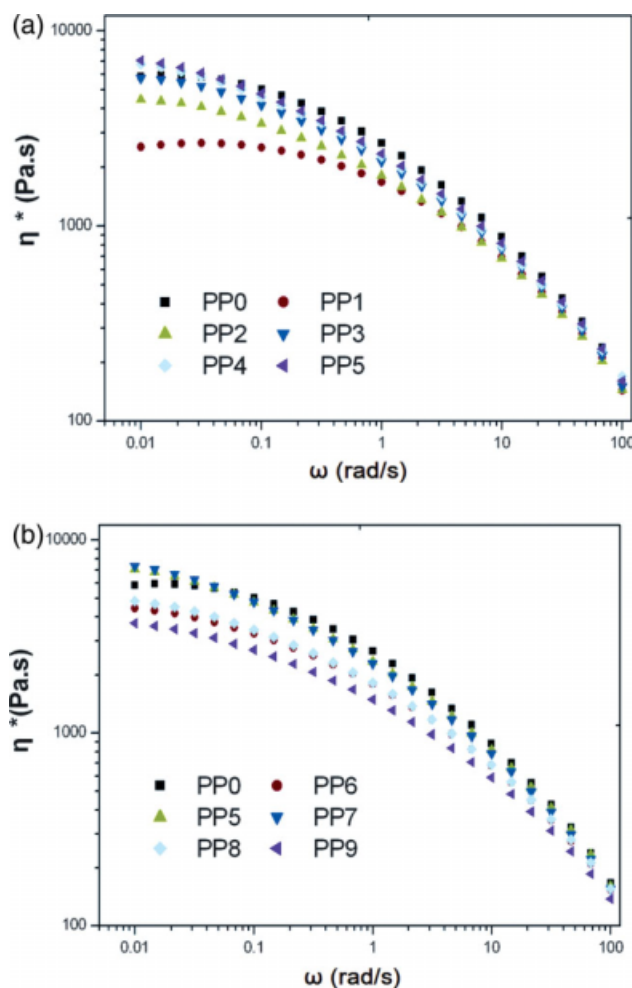


Figure 5 η^* vs. ω for initial PP and modified PPs at 190°C (a) with increasing HDDDA concentration (300 ppm DCP) and (b) with increasing DCP concentration (3.0 phr HDDDA). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

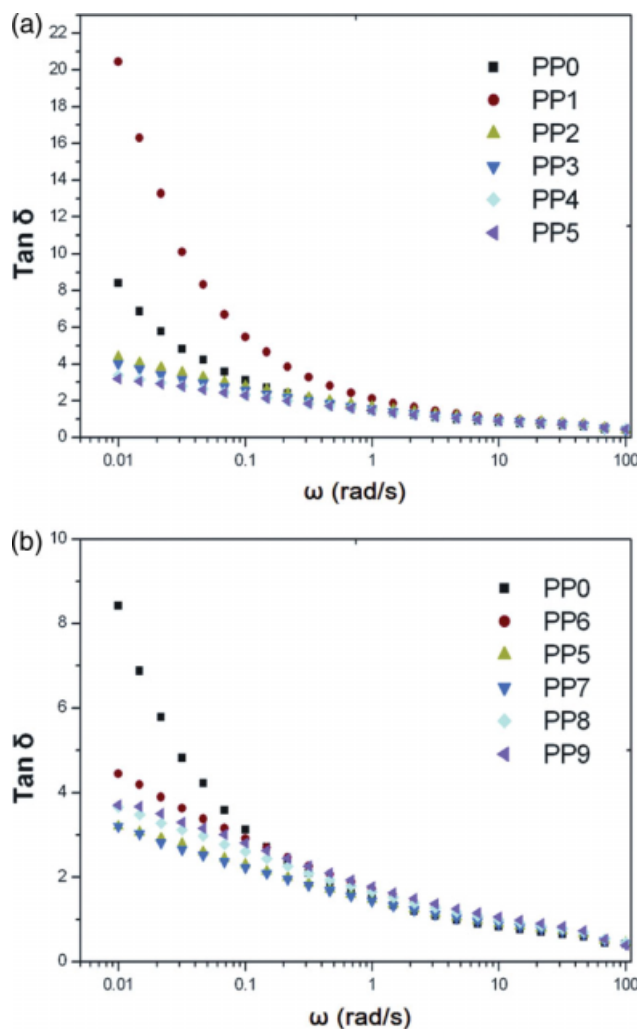


Figure 6 $\tan \delta$ vs. ω for initial PP and modified PPs at 190°C (a) with increasing HDDDA concentration (300 ppm DCP) and (b) with increasing DCP concentration (3.0 phr HDDDA). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

proportional to the HDDDA concentration. The plateau became longer as more HDDDA was used. These results agreed well with the result of Yu¹ and Graebing.³ They attributed the results to the existence of LCB on the PP skeleton that increased the terminal relaxing time. As shown in Figure 6(b), the plateau of $\tan \delta$ vs. ω curve became wider at first and then became narrower with increasing DCP concentration in the system. In fact, the degradation reaction and the branching reaction might occur simultaneously, and the rate of branching depended on the concentration of monomer and peroxide. At low DCP concentration or excessive high DCP concentration, the branching level was low.

Recently, that the LCB structure can be directly suggested with the Van Gorp plot ($\delta - \log G^*$ and $G^* = \sqrt{G'^2 + G''^2}$) has been reported by many researchers.^{4,20,21} Hatzikiriakos²⁰ found that the Van

Gorp curves shifted to smaller value of the phase angle with increasing amount of LCB. The same method was also used in the present work for assessing the existence and the amount of LCB in modified PPs. As shown in Figure 7(a), the Van Gorp plots of modified PPs with different concentrations of HDDDA in the presence of DCP shifted to smaller values of the phase angle in comparison with linear PP (PP0, PP1), indicating that the LCB did exist in their backbone. Meanwhile, it could be found that the shifting degree of Van Gorp plots increased with increasing concentration of HDDDA, suggesting that the amount of LCB increased with increasing HDDDA concentration. It could be found from Figure 7(b) that the shifting degree increased initially and then decreased with increasing DCP concentration, indicating that the amount of LCB

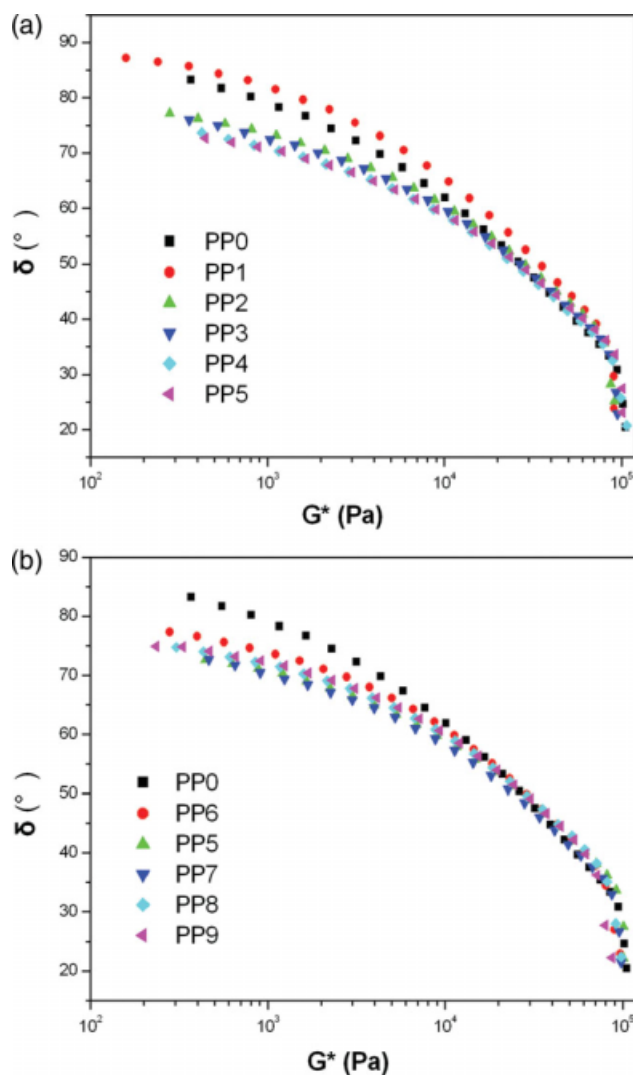


Figure 7 The Van Gorp plot of initial PP and modified PPs (a) with increasing HDDDA concentration at 300 ppm DCP and (b) with increasing DCP concentration at 3.0 phr HDDDA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

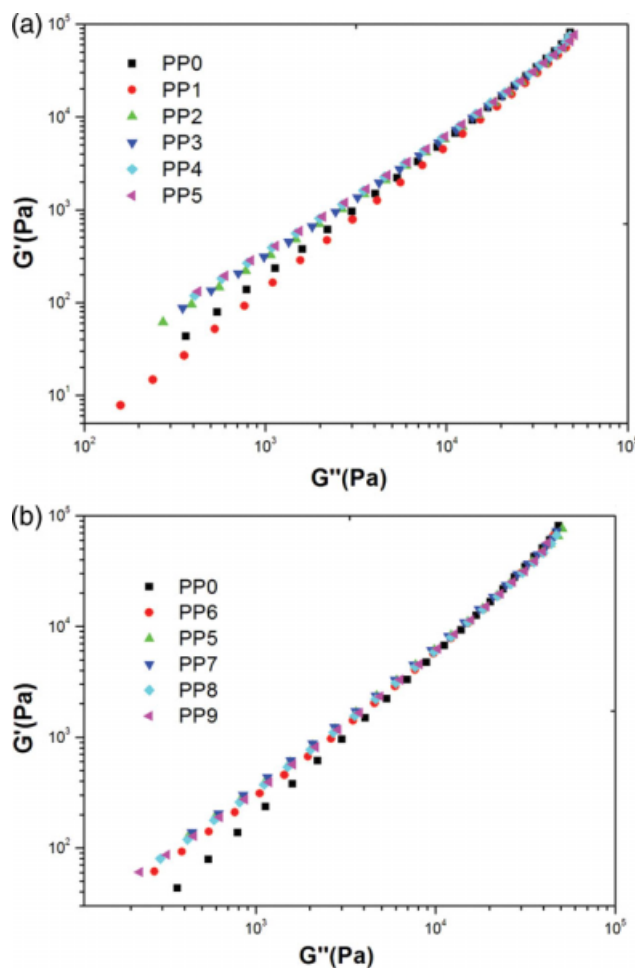


Figure 8 Han plot of the initial PP and modified PPs at 190°C (a) with increasing HDDA concentration (300 ppm DCP) and (b) with increasing DCP concentration (3.0 phr HDDA). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

level increased at first and then decreased with increasing DCP concentration. Summing up the Van Gorp plots of all samples, it could be inferred that the LCB existed in all modified PPs (PP2–PP88), but the amount of LCB were affected by the concentration of DCP and HDDA. In comparison with other modified PPs, PP4, PP5, and PP7, have a large number of LCB, which indicate that proper concentrations of HDDA and DCP were more beneficial to producing long chain branching (LCB) during reactive extrusion.

Han Plot ($\log G' - \log G''$) has been used to study order–disorder transitions in block copolymers, the effect of polydispersity and LCB in polyethylenes²² and the miscibility of polymer blends.²³ To prove the existence of LCB in modified PP skeleton, Han plot of the modified PPs were shown in Figure 8. It can be seen that the Han plots of modified PPs with DCP and HDDA deviated greatly from the linear polymer, indicating a long relaxation mechanism occurred in these samples. It could be observed

from Figure 8(b) that the slope of the curves of modified PPs decreased at first and then increased with increasing DCP concentration, which might be attributable to the decreased branching reaction at low concentration of DCP and the increased degradation reaction at high concentration of DCP.

Besides the Han plot ($\log G' - \log G''$), Cole–Cole plot ($\eta'' - \eta'$), as shown in Figure 9, can also be used to illustrate the long relaxation process. It could be found that the Cole–Cole plots of PP0 and PP1 were close to a semicircle because of their linear chain structure. The curves of PP2 and PP3 were lower than that of initial PP and higher than that of PP1, indicating that the degradation reaction also occurred and the degradation degree of them were lower than that of PP1. As shown in Figure 9(b), it could be seen that the curves of PP6, PP8, and PP9 were lower than that of initial PP, which further confirmed that the branching reaction was not effective at low DCP concentration and excessive DCP led to the degradation reaction. The Cole–Cole plots of PP4, PP5, and PP7 were higher than those of

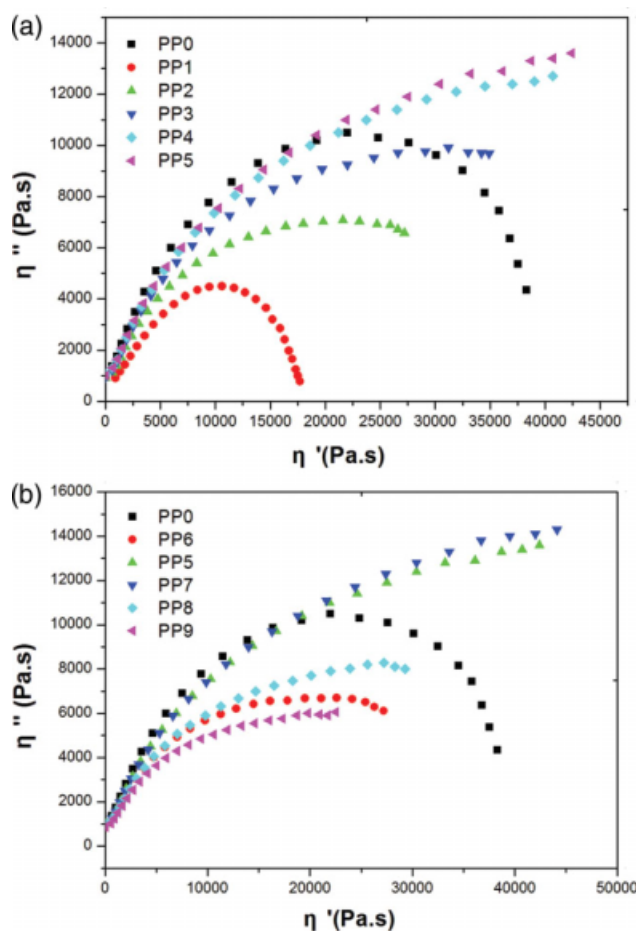


Figure 9 Cole–Cole plot of the plain PP and modified PPs at 190°C (a) with increasing HDDA concentration (300 ppm DCP) and (b) with increasing DCP concentration (3.0 phr HDDA). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
DSC Results of Initial and Modified Pps with Increasing HDDA Concentration (300 ppm DCP)

Sample	ΔH_m (J/g)	T_m (°C)	T_c (peak) (°C)	Crystallization (%)
PP0	107.6	164.0	113.1	51.50
PP1	113.6	163.4	117.7	54.37
PP2	98.34	163.7	122.7	47.05
PP3	111.6	164.0	122.2	53.42
PP4	107.6	164.1	123.2	51.48
PP5	114.0	163.5	124.1	54.54

the initial PP and showed more evident upturn at high viscosity, indicating their skeleton were grafted with a large number of long branching chains which led to a longer relaxation time for them.

In this section, several rheology plots were used to investigate the rheological properties of the initial PP and modified PPs. The rheological properties, such as higher G' at low frequency, plateau in $\tan\delta-\omega$ plot, G^* shifting to smaller values of the phase angle in the Van Gorp plots, deviation from the scaling $G'-G''$ of linear polymer in Han plot, and upturn at high viscosity in Cole-Cole plot, confirmed the existence of LCB in all modified PPs (PP2-PP8) with different concentration of DCP and HDDA. Moreover, the influences of polyfunctional monomer (HDDA) and peroxide (DCP) concentrations on the branching level were comparatively investigated. The results showed that the amount of LCB was affected by the concentration of HDDA and DCP, although all modified PPs had different amount of LCB in their skeleton. Proper concentration of HDDA and DCP in system, such as 300 ppm DCP and 2.5 phr HDDA, 300 ppm DCP, 3.0 phr HDDA, and 400 ppm DCP, and 3.0 phr DCP, was more beneficial to the produce of LCB during reactive extrusion.

Thermal properties

The branching reaction among linear PP, DCP, and HDDA would result in the change of the molecular weight and its distribution, and the chain irregularity. All these microstructure change could affect their thermal properties, especially the crystallization behavior. Table II listed the DSC results for the initial PP and modified PPs with increasing HDDA at fixed DCP concentration of 300 ppm. The corresponding DSC curves are shown in Figure 10. Referring to Table II and Figure 10, the crystalline temperature (T_c) of the LCB-PP were higher than that of initial PP (PP0) and degraded PP (PP1). The crystallization exotherm is an indication of the bulk crystallization rate. The higher the T_c , the faster the polymers crystallize. The higher crystallization temperature and elevated crystallization rate of PP1, when compared to PP0, listed in Table II, were due

to the degradation of linear PP molecular chain induced by DCP. The degradation of linear PP led to the enhanced molecular chain segment's mobility, which favored the diffusion and arrangement of macromolecules into crystal cell; therefore, the crystallization rate was elevated and crystallization temperature increased. With the addition of HDDA, the crystallization temperatures (T_c) of modified PP (PP2-PP5) were higher than that of initial PP0 and degraded PP1. It could be inferred that the branching structure were beneficial to the increase of crystallization temperature and were also responsible for the acceleration of crystallization. The similar results have been reported by other researches.² Meanwhile, it could be seen that the melting enthalpy (ΔH_m) and T_m decreased initially, next increased, and then remained relatively constant. The variation of T_m , ΔH_m , and crystallization rate of modified PPs with increasing HDDA concentration had relations with three factors. First, the branched structure destroyed the structural regularity of the chain, which resulted in the decrease of T_m and ΔH_m . Second, some polar groups such as ester group were grafted on PP skeleton, which resulted

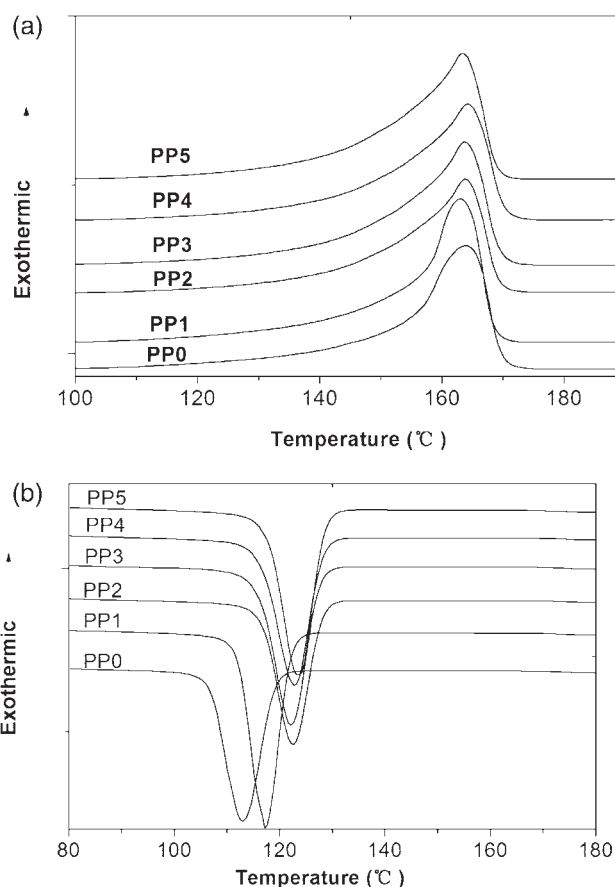


Figure 10 DSC curves of initial and modified PPs with increasing HDDA concentration (3.0 phr DCP). (a) Melting curves. (b) Crystallization curves.

TABLE III
DSC Results of Initial Pp and Modified PPs with Increasing DCP Concentration (3.0 phr HDDA)

Sample	ΔH_m (J/g)	T_m (°C)	T_c (peak) (°C)	Crystallization (%)
PP0	107.6	164.0	113.1	51.50
PP6	111.8	165.2	123.6	53.48
PP5	114.0	163.5	124.1	54.54
PP7	107.9	165.3	122.6	51.64
PP8	115.2	164.7	123.6	55.13
PP9	117.2	164.6	123.6	56.10

in the increase of the ΔH_m . Third, the melting entropy (ΔS_m) was reduced as a result of chemical branching of the chains. Therefore, the melting temperature (T_m) might increased because of the elevation of the temperature $T_m = \Delta H_m / \Delta S_m$ if the ΔH_m was not changed very much. The three factors affected the change of ΔH_m and T_m simultaneously and even oppositely, which resulted in the complicated change of T_m , ΔH_m , and the level of crystallization of the modified PPs with increasing HDDA.

DSC results of initial PP and modified PPs with increasing DCP content at fixed HDDA concentration of 3.0phr were shown in Table III and Figure 11. It could be seen that crystallization temperatures (T_c) of modified PPs with different concentration of DCP were higher than that of initial PP. The T_c increased at first, next decreased, and then remained relatively constant with increasing DCP concentration. When less DCP was added in system, the peroxide radicals were mainly consumed by excess HDDA rather than by PP chain, which resulted in the inefficiency of branching reaction. However, as excessive DCP was used, the system appeared to be not saturated with HDDA, and therefore the degradation reaction might occur. As illustrated above, proper concentration of HDDA and DCP added in system favored the grafted reaction, which would produce a large number of LBC in PP skeleton. Not only the mobility of branched chain in PP skeleton but the mobility of short molecular chain segment, produced by degradation reaction, could increase the T_c of modified PP, which corresponded to the higher T_c of modified PP with different concentration of DCP in comparison with initial PP. The change of T_m , ΔH_m , and the level of crystallization were also very complicated with increasing DCP concentration. These changes of T_m , ΔH_m , and the crystallization degree were due to the changes in the microstructure, the size of the crystals, and the reduction of ΔS_m because of the existence of the branched chain structure. As illustrated earlier, these factors affected the change of T_m , ΔH_m , and the level of crystallization simultaneously and even oppositely, which corresponded to the complicated change of them.

CONCLUSIONS

LCB-PP was prepared by reactive extrusion in the presence of bifunctional monomers HDDA and DCP. Influences of HDDA and DCP concentrations on the branching efficiency were comparatively evaluated. The results suggested that all modified PPs with DCP and HDDA had LCB in their skeleton, and proper concentrations of HDDA and DCP, such as 300 ppm DCP and 2.5 phr HDDA, 300 ppm DCP and 3.0 phr HDDA, and 400 ppm DCP and 3.0 phr DCP, were more beneficial to producing LCB during reactive extrusion process.

FTIR results indicated that the grafting reaction took place and HDDA has been grafted on PP skeleton. Moreover, it was found that more HDDA favored the grafted reaction and macroradical recombination. In cases of some modified PPs, measurement of MFI showed an enhancement of viscosity, and, therefore, indicated the existence of LCB in their skeleton.

The existences of LCB structure in modified PPs were confirmed by small-amplitude oscillatory shear experiments. Several rheology plots were used to investigate the rheological properties of the plain

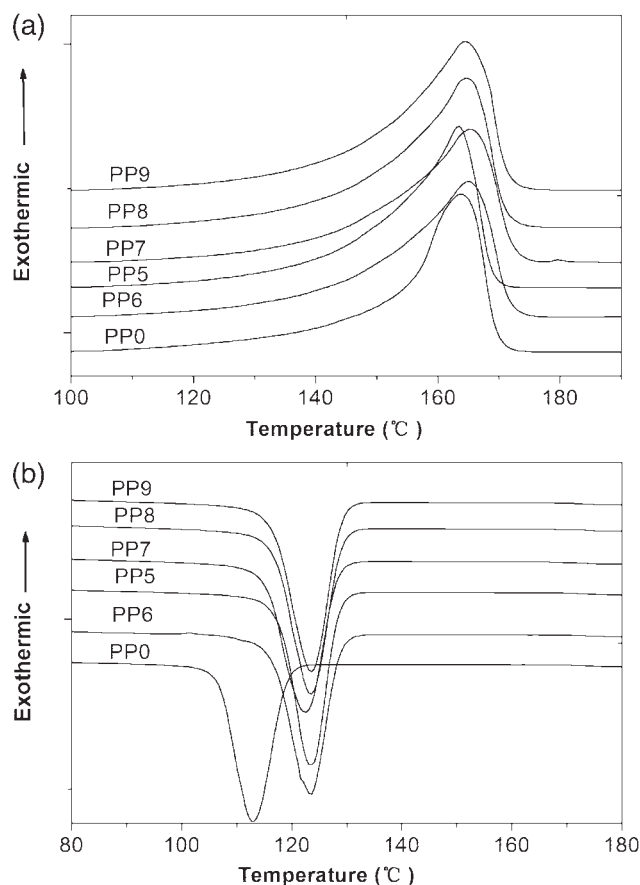


Figure 11 DSC curves of initial and modified PPs with increasing DCP concentration (3.0 phr HDDA). (a) Melting curves. (b) Crystallization curves.

and modified PPs. The rheological characteristics such as higher G' at low frequency, plateau in $\tan\delta-\omega$ plot, G^* shifting to smaller values of the phase angle in the Van Gorp plots, deviating from the scaling $G'-G''$ of linear polymer in Han plot, and upturning at high viscosity in Cole-Cole plot were found in modified PPs, which was due to the different relaxation mechanism of LCB-PP from linear PP.

DSC results showed that the crystallization temperatures of modified PP were higher than those of initial and degraded PP. Examination of the DSC data suggested that the modified PPs had long branched chain. The variation of T_m , ΔH_m and the crystallization degree of modified PPs with the variation of DCP and HDDA concentrations were very complicated, which was attributed to the complex variation in the microstructure, the size of the crystals and the melting entropy (ΔS_m) due to the existence of the LCB.

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