

Chemical Modification of Polypropylene with Peroxide/Pentaerythritol Triacrylate by Reactive Extrusion

XIAOCHUAN WANG, COSTAS TZOGANAKIS,* and GARRY L. REMPEL

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

SYNOPSIS

To explore the possibility of producing branched polypropylene (PP) by a reactive extrusion (REX) process, isotactic PP was reacted with a polyfunctional monomer, pentaerythritol triacrylate (PETA), in the presence of 2,5-dimethyl-2,5(*t*-butylperoxy) hexane peroxide (Lupersol 101). Experiments were carried out in an intermeshing, corotating twin-screw extruder at 200°C using three concentrations of peroxide (200, 600, and 1000 ppm) and four concentrations of PETA (0.64, 1.8, 2.8, and 5.0%, by weight). Shear viscosity and MFI of the whole polymers was found to increase with PETA concentration and decrease with increasing the peroxide concentration at a given PETA concentration. The macrogel amount in the materials produced was determined in refluxing xylene using Soxhlet extraction and at PETA concentrations higher than 1.8 wt % the macrogel content increased with increasing peroxide concentration. No macrogel was detected at low PETA concentrations (<0.64%) at all three peroxide levels, suggesting that low concentrations of PETA and peroxide should be used in order to minimize the formation of macrogels. The xylene soluble portions (sols) of the modified materials were characterized by FTIR and DSC. Generally, the relative intensities A_{1740}/A_{841} in the FTIR spectra increased with increasing PETA incorporated into PP. Two melting peaks (T_{m1} and T_{m2}) were observed in the DSC traces of some of the sols, and the crystallization temperatures (T_c) were higher than those of the virgin and degraded polypropylenes. The DSC behavior of the sols suggests that the modified PPs contain branched and/or lightly crosslinked chain structures. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Commercial isotactic polypropylene (PP) is a partially crystalline polymer with many diversified desirable properties that have made it one of the most widely used thermoplastics since the Ziegler–Natta discovery in 1955. Its performance properties can be further enhanced via postreactor chemical modifications. Current modification techniques for PP involve controlled degradation, crosslinking, functionalization, and branching. Reactive extrusion (REX) processes have been employed in the first three types of modification^{1–3} due to their efficiency and economic advantages.

Although PP has many useful properties, its melt strength is low and it exhibits no strain hardening

behavior in the melt state. This is due to its linear chain structure, which is a direct result of the Ziegler–Natta polymerization method used for its production. Thus, its uses have been limited in applications requiring high melt strength, such as blow molding and thermoforming. The introduction of long-chain branching onto the PP backbone may be one of the alternatives to improve its melt strength shortcoming. There are several possible routes to branching PP. Scheve et al.⁴ achieved this objective by irradiating a solid, high molecular weight, linear PP with high-energy radiation in a nitrogen environment and the irradiated PP was found to exhibit substantial melt strain hardening. However, it is known⁴ that the use of high-energy radiation produces branching confined for the most part to the amorphous phase of the semicrystalline PP, since it is in this region that the segmental mobility and free volume are sufficient for macroradicals formed on irradiation to approach one another and form

* To whom correspondence should be addressed.

branches. In principle, branches can also be introduced onto the polypropylene backbone by post-reactor grafting reactions. Wang et al.⁵ produced model branched PPs by the reaction between a randomly functionalized PP and hexadecylamine, a long-chain alkyl amine which was used as a model molecule for a terminally functionalized PP. It was found that as a result of branching both the zero-shear rate viscosity and storage modulus increased. Another alternative to branching PP may be through the recombination reactions in which PP molecules react with a polyfunctional monomer, having more than two double bonds, in the presence of a peroxide. It is well known that at relatively low concentrations of peroxide the primary radicals generated by the peroxide will abstract preferentially the tertiary hydrogens, forming tertiary polypropylene macroradicals which are unstable and degrade through β -scission reactions. However, addition of a polyfunctional monomer to the above system can convert some of the tertiary macroradicals to the more stable secondary macroradicals which tend to undergo recombination rather than scission. Owing to the randomness of these recombination reactions, polypropylene chains may be extended, branched, or even crosslinked.

For the sake of clarity here, the term "crosslinker" is referred to both polyfunctional monomers and other compounds called coagents, which are all capable of crosslinking PP. "Crosslinking" of polypropylene in our work refers to both branching and a limited degree of crosslinking. These limited crosslinked species are probably highly branched, but still soluble polypropylenes. Because of the use of a polyfunctional monomer, an insoluble homopolymer of the polyfunctional monomer may also be formed simultaneously with the insoluble highly crosslinked polypropylene possibly formed. Thus, the term "macrogel" refers to any insoluble portion of polymers which may consist of insoluble highly crosslinked PP and the homopolymer of the polyfunctional monomer.

Much work has been done on highly crosslinked PP or related polyblends by using polyfunctional monomers^{6,7} or coagents^{8,9} in glass ampules. Recently, using a batch mixer, Thitiratsakul¹⁰ reacted isotactic PP with different polyfunctional monomers or coagents mainly at 175°C in the presence of different peroxides. In this work, peroxides were used at three relatively high concentrations, i.e., 0.1% wt (1000 ppm), 0.5% wt (5000 ppm), and 1.0% wt (10000 ppm). From the torque level during the reactions, pentaerythritol triacrylate (PETA), a polyfunctional monomer, was found to be superior to any other

crosslinkers examined. It was concluded qualitatively by gel permeation chromatography (GPC) that the PP was branched during the reactions. No other properties of either the whole polymers or their sols were studied. Kim and Kim² also crosslinked isotactic PP in a twin-screw extruder at 230°C using four crosslinkers, in the presence of 1,3-bis(*t*-butylperoxyisopropyl)benzene. No separation of gels was performed in this work and the whole products were analyzed in terms of melt flow index (MFI), mechanical properties, and DSC. It was concluded that triacrylates (including PETA) were the most effective among the polyfunctional monomers used.

One of the objectives of our current work was to develop a reactive extrusion process for the modification of commercial linear PP to a branched one while minimizing the degradation and formation of insoluble macrogels, by using relatively low concentrations of PETA and 2,5-dimethyl-2,5(*t*-butylperoxy)hexane (Lupersol 101). Meanwhile, a study of how the chemical modification affects the structure and properties of polymers was carried out, since it is important, in practice, both for choosing the optimal conditions for reactive extrusion as well as for evaluating the potential applications of the modified polymers. In this preliminary study, an unstabilized isotactic PP was used to avoid the possible interference of stabilizers. Both peroxide and PETA were added into the system in a way that ensured a long enough residence time in the extruder. The macrogel amount in the polymers produced was determined by Soxhlet extraction and the sols were studied using FTIR and DSC. Finally, the shear viscosity and MFI of the whole polymers produced were measured with a capillary rheometer.

EXPERIMENTAL

Materials

Additive-free isotactic polypropylene powder (KY6100) was supplied by Shell Canada. The MFI of this PP was 3 when measured with 1.0% wt Irganox 1010. 2,5-Dimethyl-2,5(*t*-butylperoxy)hexane peroxide (Lupersol 101) was obtained from Elf Atochem North America, Inc., and pentaerythritol triacrylate (PETA), containing 100 ppm hydroquinone monomethyl ether as an inhibitor, was obtained from Aldrich Co. Both the peroxide and PETA were used as received.

Reactive Extrusion

Reactive extrusion experiments were carried out in a Leistritz LSM 30.34 twin-screw extruder (10 barrel

zones plus a die) which was equipped with a Ktron LWFD5-200 loss-in-weight solids feeder and vacuum capacity (30 in. Hg vacuum). The feed port temperature was kept low (70°C) by water cooling and the rest of the zones were controlled at 200°C. A vent port (in zone 9) was used to remove volatile species such as solvent and unreacted materials. The throughput and screw speed were 1.4 kg/h and 60 rpm, respectively. The intermeshing, corotating screw configuration used is shown in Figure 1.

Before the reactive extrusion runs, the PP powder was mixed with a peroxide master batch to obtain the desired peroxide concentrations. Three peroxide concentrations (200, 600, and 1000 ppm) were used. PETA was dissolved in acetone at the concentration of 20% wt. During the runs, the PETA solution was injected into the extruder at the feed port using an FMI (Fluid Metering Inc., Oyster Bay, NY) metering pump. The precision of the injection rates was around $\pm 1\%$ of the setpoint.

Measurements

Flow properties of the whole polymers produced were measured using a Kayeness Galaxy V capillary rheometer. The melt flow index (MFI) was measured at 230°C using a load of 2.16 kg according to the ASTM D-1238-86T standard. The steady-state shear viscosity was measured at 230°C using a die of $L/D = 40$ ($D = 0.02$ in.) and the Rabinowitsch correction was applied to the data.

The amount of the insoluble portion (macrogel) in the samples was determined by Soxhlet extraction in refluxing xylene, containing 0.1 wt % of hydroquinone as antioxidant, for 48 h. The soluble portions (sols) were dissolved in xylene and precipitated in acetone. This procedure was repeated three times. The purified sols were dried under vacuum at 60°C for 24 h and consecutively used for other measurements.

FTIR spectra of the previously purified sols were obtained using a Nicolet 520 FTIR spectrometer. Samples were dissolved in chlorobenzene and then cast onto NaCl disks. Films were formed by drying at about 60°C under vacuum for 24 h and then they were stored in a desiccator over phosphorus pentoxide.

Thermal analysis of the purified sols was carried out with a TA Instruments thermoanalyzer equipped with a 2920 differential scanning calorimetric (DSC) cell under a helium environment. The DSC was calibrated with indium as a standard and no stabilizer was added to all the samples measured. Specimens were scanned from -60 to 200°C held at 200°C for

3 min, then cooled to 40°C. The heating and cooling rates were 20°C/min and the same sample weight (4.12 mg) was used throughout the DSC experiments. For all the experiments, the first heating/cooling cycle was used to condition the samples and, hence, only the data of the second cycle are reported here. The information obtained from the DSC runs consists of (1) the heat of fusion (ΔH_m); (2) the melting temperature (T_m) and the melting range which is represented by the half-width of the melting peak (qualitative information only); and (3) the crystallization temperature (T_c).

RESULTS AND DISCUSSION

Flow Curve

Degradation reactions in PP are generally explained by the fragmentation of tertiary alkyl macroradicals, while the crosslinking, branching, and extension reactions can be explained by the recombination of secondary alkyl macroradicals that have a lesser tendency to degrade.^{1,4,6} The addition of a polyfunctional monomer can stabilize tertiary macroradicals against scission by assisting the formation of secondary macroradicals which can subsequently lead to recombination reactions. The resulting chain extension, branching, and/or crosslinking reactions increase the molecular weight and, hence, increase the viscosity of the polymer melt. Thus, at a given peroxide concentration, materials produced using PETA should exhibit enhanced melt viscosities compared to the degraded PP (0% PETA). This behavior can be observed in the shear viscosity data presented in Figure 2. It can be seen that generally the shear viscosity increases with PETA concentration and decreases with increasing peroxide concentration. In Figure 2(a) (200 ppm peroxide level series), it can be observed that, at 1.8 and 5.0% PETA concentrations, the viscosity of the materials produced is higher than that of the virgin PP. This suggests that the recombination/chain extension/branching reactions are significantly more important than is the chain scission reaction that tends to reduce the viscosity. Another observation is that, regardless of the peroxide concentration, the Newtonian plateau is shifted to lower shear rates as the PETA level is increased.

Melt Flow Index

The effect of PETA concentration on the MFI is shown in Figure 3 and it is consistent with the pre-

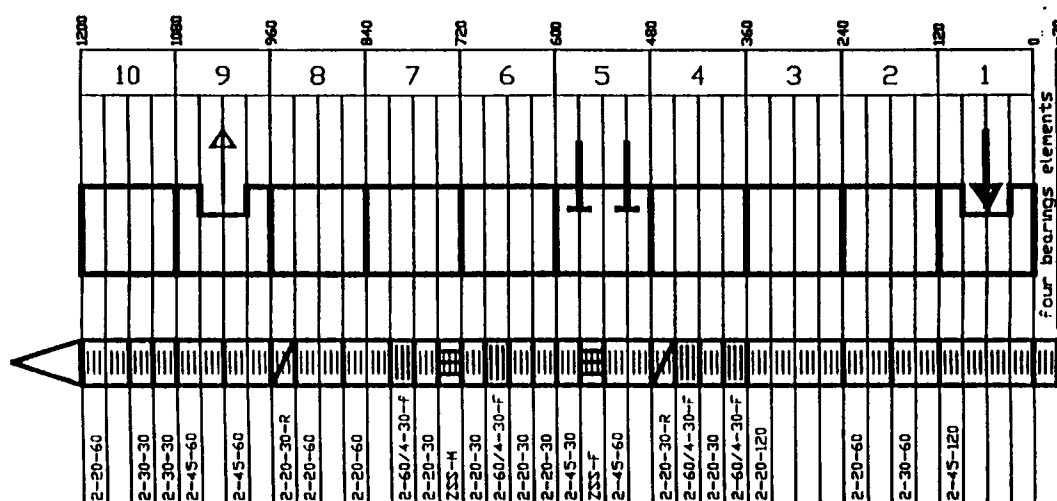


Figure 1 Twin-screw extruder configuration.

viously presented shear viscosity data. As expected, the MFI decreases when PETA is added to the system for any peroxide concentration. However, PETA seems to have no significant effect on MFI at high concentration levels. This may be attributed to increased PETA grafting reactions and higher consumption of primary peroxide radicals in the PETA homopolymerization.

Gel Content

Gel content data are summarized in Table I. As mentioned before, PETA molecules can form an insoluble homopolymer gel and, hence, the insoluble content should be regarded as a mixture of highly crosslinked PP and PETA homopolymer macrogels which are rather difficult to separate experimentally. It can be observed that, overall, no significant macrogel amount was formed for the concentration ranges used in this study. It is also interesting to note that there is no evidence of any macrogel formation at the low PETA concentration (0.64%) regardless of the peroxide level. The onset of macrogel formation seems to occur at progressively lower PETA levels as the peroxide concentration employed is increased, and for a given PETA concentration higher than 0.64%, the macrogel amount increases with increasing peroxide content. These results suggest that to minimize the formation of macrogel low concentrations of PETA and peroxide should be used in a reactive extrusion process.

FTIR Analysis of the Sols

Similar FTIR spectra were obtained for the sols produced at all three peroxide levels and only the

ones at 200 ppm peroxide level are shown in Figure 4. For all the samples reacted with PETA, there are bands at around 1740 cm^{-1} which are due to the stretching vibration of the carbonyl group of the ester in the PETA molecule and the intensity of this band seems to increase with PETA concentration. The band at 841 cm^{-1} is due to the characteristic absorption peak of the C—CH₃ vibration in the PP backbone and it can be used as an internal reference band. The relative intensity of these two bands (A_{1740}/A_{841}) is shown in Figure 5 as a function of the PETA concentration used, and it can serve as an indication of the extent of the recombination reactions. It should be noted, however, that there are two possible existing forms of the PETA units on the PP backbone which can contribute to this relative intensity. These include the grafted PETA units (either monomeric or polymeric) and the PETA units incorporated due to recombination reactions such as chain extension, branching, or crosslinking.

In Figure 5, it can be observed that, generally, A_{1740}/A_{841} increases with PETA concentration at all peroxide levels, suggesting that more PETA would favor the reactions between PP and PETA. Obviously, the recombination reactions would be enhanced as indicated earlier from the viscosity and MFI data. It appears that for PETA concentrations lower than or equal to 2.8% wt the peroxide concentration does not affect significantly this relative intensity and, therefore, the amount of PETA incorporated into the PP chain. Within this range, the relationship between A_{1740}/A_{841} and PETA concentration seems to be linear. At higher PETA concentrations (greater than 2.8%) and for 200 ppm

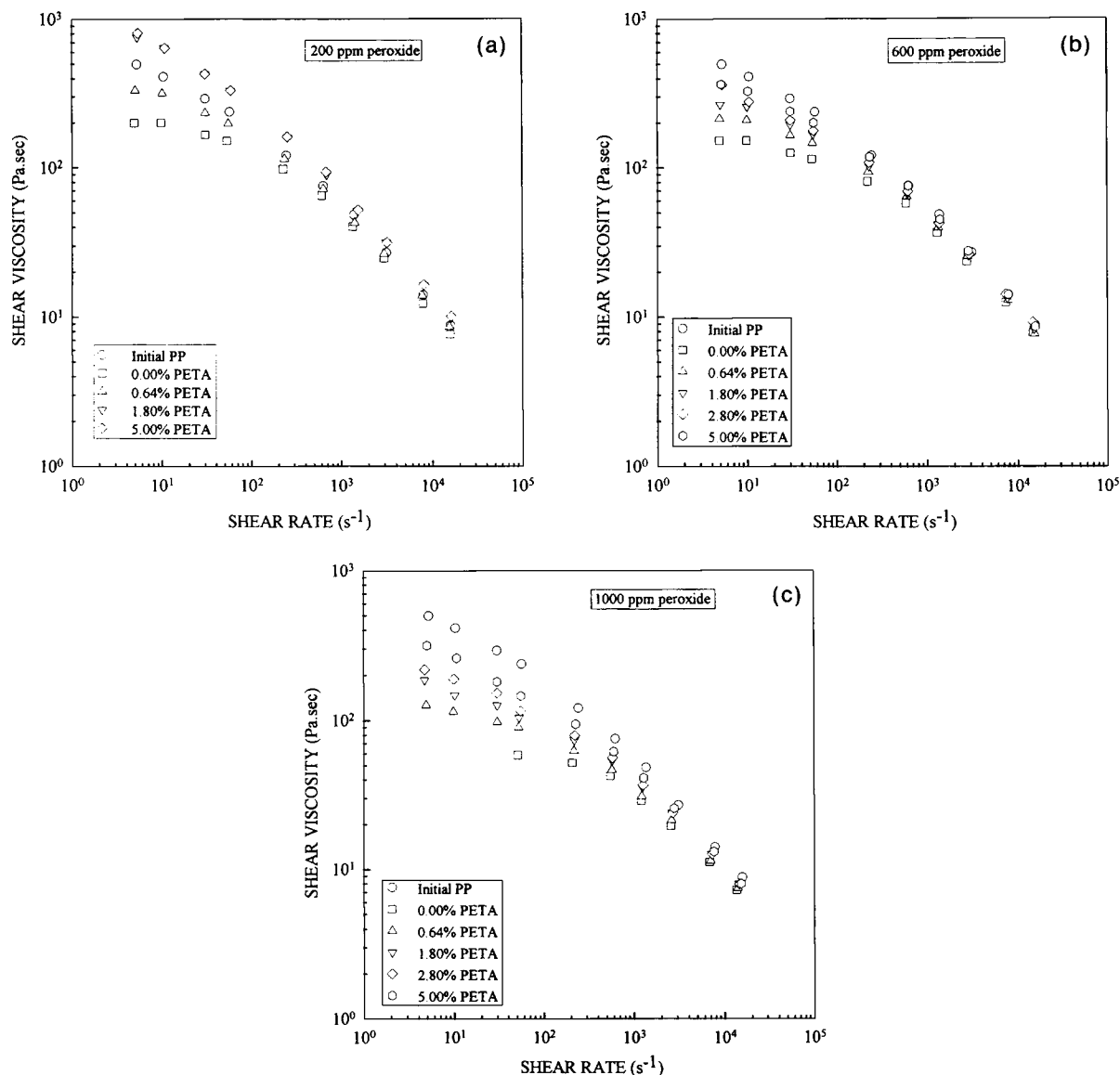


Figure 2 Effect of the PETA and peroxide concentrations on the shear viscosities of the whole polymers: (a) 200 ppm peroxide; (b) 600 ppm peroxide; (c) 1000 ppm peroxide.

peroxide, the relative intensity appears to level off. This can be attributed to an increased consumption of primary peroxide radicals by the excess PETA rather than by PP chains, thus stabilizing the amount of the PP macroradicals generated and therefore the amount of PETA incorporated into PP. For the 600 and 1000 ppm peroxide cases, the system appears not to be saturated with PETA yet, and as a result, increasing PETA concentration leads to higher value of relative intensity and, therefore, more PETA incorporated into PP. It should be pointed out that at 5% PETA a reversal of effects between the 600 and 1000 ppm cases is observed, which suggests that the effect of peroxide level on

the PETA amount incorporated into PP is not monotonic. This further indicates that under certain conditions (600 ppm peroxide) the reaction between PP macroradicals and PETA is favored over the PETA homopolymerization.

DSC Analysis of the Sols

In the present system, degradation, recombination, and grafting reactions may take place simultaneously. These reactions will result in changes of the following molecular factors: (1) molecular weight and its distribution; and (2) chain irregularity due to branching/crosslinking, grafting of PETA, and/

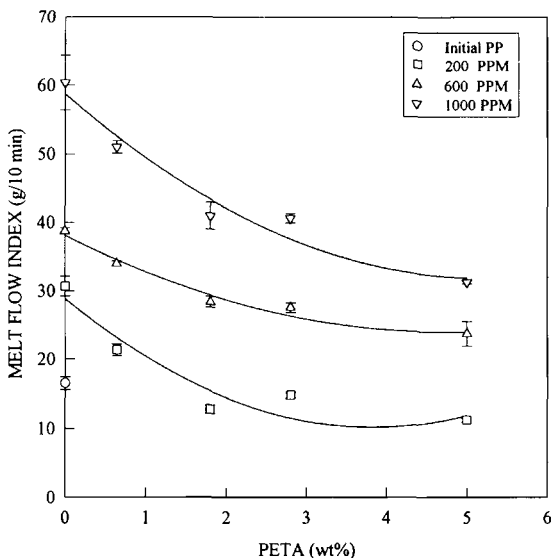


Figure 3 Effect of the PETA and peroxide concentration on the melt flow index (MFI) of the whole polymers.

or binding of peroxide radicals to the polymer chain. All these microstructural differences will affect the crystallization behavior of the sols of the modified PPs. Generally, for a given polymer and at a given crystallization temperature, the degree of crystallinity depends on the molecular weight and the structural regularity of the chain.¹¹ For homopolymers, at higher molecular weights and, hence, melt viscosities, the ease of crystallization decreases and thus the final extent of crystallization is reduced. Thus, the level of crystallinity is relatively high at the lower molecular weights and then decreases monotonically with increasing molecular weights until a limiting value is reached. The level of crystallinity, which can be reflected by the heat of fusion ΔH_m , is further reduced by the introduction of non-crystallizing structural units into the chains, such as branching. Meanwhile, T_m will also decrease due to the introduction of chain defects (chain ends,

Table I Gel Content Measurements

PETA Concentration (Wt %)	Gel Content (Wt %)		
	200 ppm ^a	600 ppm ^a	1000 ppm ^a
0.00	0.00	0.00	0.00
0.64	0.00	0.00	0.00
1.80	0.00	0.20	0.56
2.80	0.05	0.83	1.00
5.00	0.55	1.13	2.54

^a Peroxide concentration.

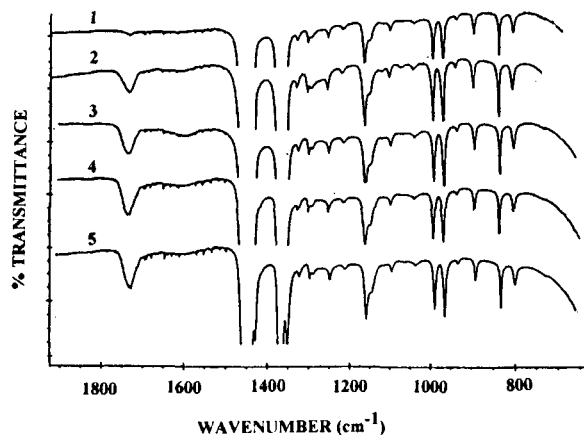


Figure 4 FTIR spectra (600–2000 cm^{-1}) of the sols at different PETA concentrations (200 ppm peroxide): (1) 0.0% PETA; (2) 0.64% PETA; (3) 1.8% PETA; (4) 2.8% PETA; (5) 5.0% PETA.

crosslinks, branching points, and nonisotactic sequences), which would act as a second component in the system. For example, the T_m of branched PE is significantly less than that of its linear counterpart and its melting range is broader.

Before performing the DSC measurements on the sols of the PETA/peroxide-modified PPs, the effects of branching on the crystallization behavior of model branched PPs prepared elsewhere⁵ was examined by DSC and only the results are briefly reported here, as it is believed that they are helpful in understanding the DSC curves of the sols in this work. In the

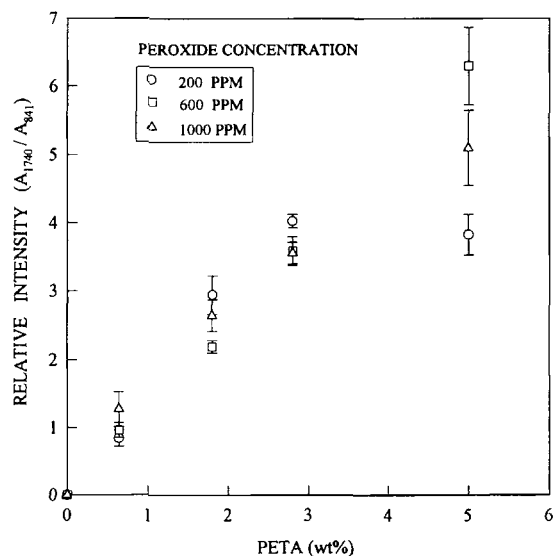


Figure 5 Effect of the PETA concentration on the relative intensity of the bands at 1740 and 841 cm^{-1} in the FTIR spectra of the sols.

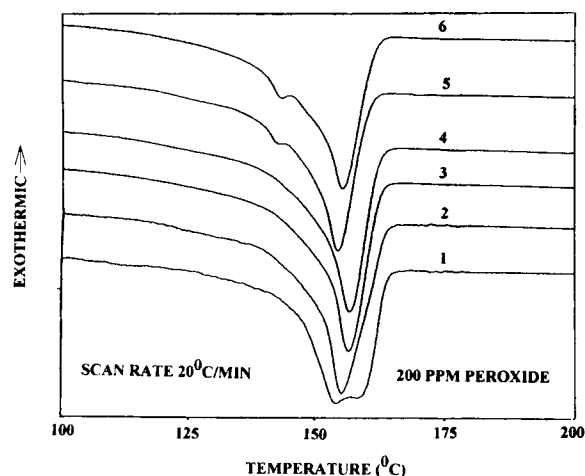


Figure 6 Effect of the PETA concentration on the DSC melting endotherms of the sols at 200 ppm peroxide: (1) virgin PP; (2) 0.00%; (3) 0.64%; (4) 1.80%; (5) 2.80%; (6) 5.00%.

model branched PP work,⁵ a single melting peak and a small shoulder were found for the relatively linear virgin polymer. However, two sharp melting peaks (T_{m1} designated as the higher melting peak, and T_{m2} , the lower melting peak) were observed in the thermograms for all model branched PPs. Only one single crystallization peak (T_c) was observed for the linear virgin polymer and the model branched PPs. It was found that the T_{m1} and ΔH_m of the branched PPs were slightly lower than those of the linear virgin polymer, which is consistent with theoretical considerations. In this model system, the occurrence of T_{m2} should be due to the alkyl branches introduced and T_{m2} seemed to decrease with the amount of the branches introduced. The T_c of the branched PPs are found to be lower than those of the relatively linear virgin polymer, in agreement with similar observations by Borsig et al.⁷

Melting Temperature (T_m) and Heat of Fusion (ΔH_m)

Figures 6–8 show the DSC melting endotherms of the sols of the samples prepared at 200, 600, and 1000 ppm peroxide levels and the data are summarized in Table II. In Figure 6, curve 1 is the DSC trace of initial PP, in which a doublet melting endotherm is observed at 154.45 and 158.50°C. This situation is probably because of the coexistence of the α - and β -form crystals. A similar observation was also made by Jacoby et al.¹² on their roll-milled virgin isotactic PP, although no nucleating agent for β -form crystals was added. A main melting peak (T_{m1}) and a lower small melting peak (T_{m2}) are also

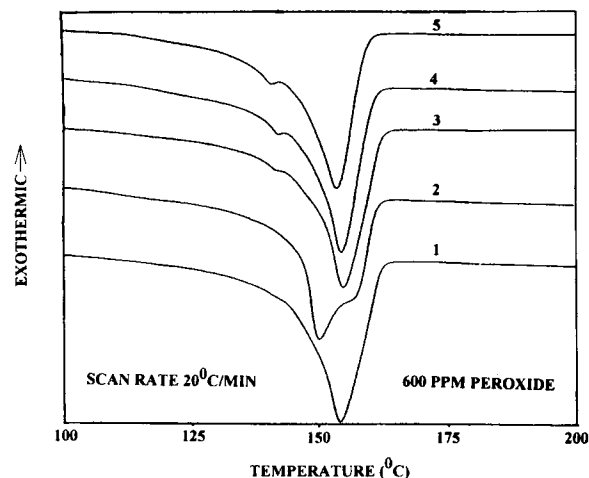


Figure 7 Effect of the PETA concentration on the DSC melting endotherms of the sols at 600 ppm peroxide: (1) 0.00%; (2) 0.64%; (3) 1.80%; (4) 2.80%; (5) 5.00%.

observed in most of the DSC traces. Increasing the peroxide concentration causes the appearance of T_{m2} at lower PETA concentrations. For example, T_{m2} begins to appear at 2.8% of PETA in the 200 ppm peroxide series (Fig. 6), at 1.8% PETA in the 600 ppm series (Fig. 7), and at 0.64% for the 1000 ppm series (Fig. 8). The presence of T_{m2} cannot be attributed to the possibly grafted PETA homopolymer chains since they are not crystallizable as indicated from DSC scans of PETA homopolymer prepared in ampule experiments. The presence of multiple melting peaks, rather, suggests the presence of multiple molecular structures/architectures. This is in

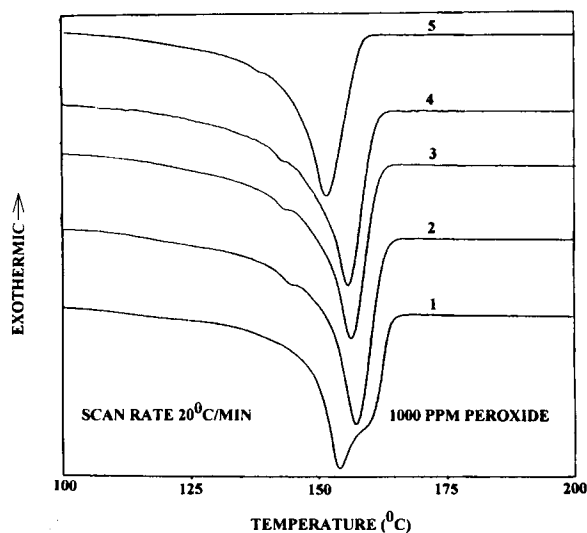


Figure 8 Effect of the PETA concentration on the DSC melting endotherms of the sols at 1000 ppm peroxide: (1) 0.00%; (2) 0.64%; (3) 1.80%; (4) 2.80%; (5) 5.00%.

Table II Effects of PETA and Peroxide Concentrations on the Thermal Behavior

PETA Concn (Wt %)	200 ppm			600 ppm			1000 ppm		
	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)
0.00	155.75	—	96.68	154.34	—	95.49	154.51	—	95.75
0.64	157.16	—	97.44	151.15	—	94.08	157.88	145.75	99.05
1.80	157.16	—	91.29	154.70	141.64	96.30	156.60	144.05	97.51
2.80	157.56	143.60	91.29	154.98	142.60	95.34	156.16	143.41	96.38
5.00	155.64	143.45	93.14	154.00	141.50	93.45	151.81	—	92.19
Virgin PP	158.50	154.45 ^a	95.54						

^a The T_{m2} of virgin PP was detected as the main melting peak by the DSC built-in program. However, the T_{m1} 's of all the other samples were detected as the main melting peaks by DSC.

agreement with similar melting characteristics observed for branched LDPE and the sols of crosslinked LDPE.¹³ However, the branched PP species in this work may not be simply branched polymers such as our model branched PPs,⁵ but rather intermolecularly crosslinked and/or branched ones due to the molecular structure of the PETA used.

In Table II, for the 200 and 1000 ppm peroxide series, ΔH_m and T_{m1} seems to increase initially with PETA concentration, reach a maxima at relatively low PETA concentrations, and then decrease. The sols from 600 ppm peroxide series seem to behave differently. In this series, ΔH_m and T_{m1} initially pass through a minimum, next increase, and then remain relatively constant. Kim and Kim² reported similar thermal behavior on the modified PPs crosslinked by PETA. However, the multiple melting behavior and the presence of a maximum in the change of T_{m1} in terms of the PETA concentration were not reported in their work. In the study of the branched PPs produced by the irradiation method, DeNicola et al.¹⁴ also found that at the same TREF elution temperatures the T_m for the irradiated PP appears to be either higher or lower than that of the base linear PP. The increase in T_{m1} is contrary to the observations on our simple branched polymers.⁵ It has been proposed² that the increase in T_m is attributed to the improved packing of polymer chains into a crystalline structure by a few crosslinking points which can properly restrict the flow of the melt. Although this is possible, some other factors may also cause the changes in T_{m1} : (i) the change in the structure and size of the crystals because of the modified chain structures such as crosslinking/branching; and (ii) the reduction in the melting entropy ΔS_m as a result of chemical crosslinking/branching of the chains. With intermolecular crosslinking, the conformational entropy of a polymer

melt decreases.^{13,15} Therefore, the ΔS_m becomes smaller, and for the crosslinked PPs, the elevation of the temperature $T_m = \Delta H_m/\Delta S_m$ can be expected if ΔH_m is not changed very much. The modified chain structure may also lower the enthalpy of fusion ΔH_m , especially at the higher PETA concentrations where the crosslinking density of PP chains may be very high and, hence, reduces the mobility of the chain. If the ΔH_m is reduced too much, it will finally result in a decrease in T_m despite the decrease in ΔS_m . Finally, it is found from the observed DSC thermograms that the half-widths (used to represent the melting range ΔT_m) of some of the sols of the modified PPs are narrower than those of the virgin PP and degraded PPs. This might be due to the change in the dispersion of the lamella thicknesses caused by the crosslinks since ΔT_m is usually related to the dispersion of the lamella thicknesses.¹⁶ The complicated situation in T_{m1} and T_{m2} implies that the sols of the modified polypropylenes should not be a single species of simple branched polypropylene, but possibly a combination of linear, branched, or even lightly crosslinked.

Crystallization Temperature (T_c)

When the specimens were cooled at a rate of 20°C/min, only one peak was observed in the crystallization endotherms of the virgin PP, degraded PPs, and all the sols of the modified PP. This suggests a co-crystallization process between a large range of different molecular structures in the sols of the modified materials. In Figure 9, the crystallization temperature T_c of the virgin PP and the sols is plotted as a function of PETA amount at all three peroxide levels used. The observed T_c is about 106.5°C for our virgin linear PP, which is in agreement with literature values.¹⁴ Generally, T_c seems to increase

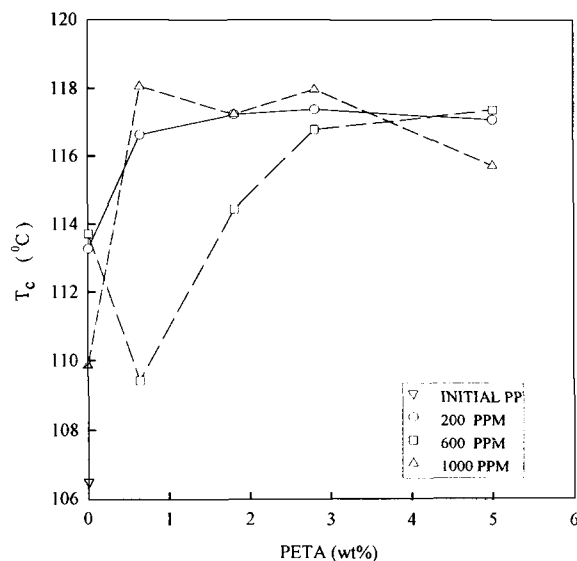


Figure 9 Effect of the PETA and peroxide concentration on the crystallization temperatures (T_c) of the sols.

and to subsequently level off at 200 and 1000 ppm peroxide concentrations. However, in the 600 ppm peroxide series, T_c decreases at low PETA levels before recovering and leveling off at higher PETA values. It is also noted that almost all the sols from the materials modified with PETA have higher T_c than that of the virgin PP or the corresponding degraded PPs (0% PETA). The crystallization exotherm T_c is an indication of the bulk crystallization rate. The higher the T_c , the faster the polymers crystallize. Hence, the sols from the modified PPs must have higher crystallization rates than their linear chain species under the present crystallization conditions. Since the sols must have higher molecular weights than their linear counterparts as indicated by the viscosity/MFI measurements in this work and data from the literature,¹⁰ they are supposed to crystallize slower than the linear counterparts if the sols only have linear chain structures. This is supported by noting that the degraded PPs without PETA have higher T_c 's than the virgin PP, suggesting the faster crystallization of the degraded PPs, and this result is in agreement with the study of Chen et al.¹⁷ Philips and Kao^{18,19} noted that the introduction of a small number of crosslinks considerably increases the nucleation density of crosslinked low-density branched polyethylene and that the sol crystallizes much more rapidly than does the uncrosslinked polymer. DeNicola et al.¹⁴ also found that the T_c of the irradiated PP (branched PP) was always higher than that of the linear PP at the same TREF elution temperature and the nucleation density of the ir-

radiated PP was much higher than that of the linear precursor. Thus, it could be inferred that the elevation of T_c in our system may be due to the increased nucleation density caused by the branching/crosslinking of the linear PP.

CONCLUDING REMARKS

Branched/crosslinked PP has been produced by a reactive extrusion process using a mixture of a peroxide and pentaerythritol triacrylate (PETA). Measurements of shear viscosity and MFI of the modified PPs indicate an enhancement of viscosity and, therefore, an increase in molecular weight. The amount of macrogel in the modified PP has been found to increase with increasing PETA and peroxide concentrations and it can be minimized by using low concentrations. The amount of PETA incorporated into the base PP has been determined through FTIR measurements and it has been found to increase with increasing PETA concentration at all peroxide levels. Two melting peaks have been observed in the DSC traces of some of the modified materials and, generally, the crystallization temperatures have been higher than those of the virgin and corresponding degraded polypropylenes. Examination of the DCS data suggests that the modified materials have branched and chain extended/crosslinked structures.

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