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Peroxide crosslinking of isotactic and syndiotactic polypropylene

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Abstract

Peroxide-induced crosslinking of isotactic (iPP) and syndiotactic (sPP) polypropylene was investigated experimentally. It was found that the two polymers showed similar crosslinking behavior, with iPP having a higher crosslinking efficiency. Our electron spin resonance measurements elucidated that the attack of peroxide radicals on iPP and sPP chains took place at the same position, giving rise to similar spectral hyperfine structures. However, a lower radical concentration was observed in sPP than in iPP with the same peroxide concentration and temperature. This might be caused by steric hindrance to the hydrogen abstraction of peroxide radicals. This low concentration of radicals is believed to be responsible for the lower crosslinking efficiency found with the sPP system. The crosslinking of both polymers was determined by temperature and peroxide type and concentration. The crosslinking kinetics showed that the initial gelation rate increased linearly with the peroxide concentration and temperature. It was also observed that, at high peroxide concentration levels, significant β-scission and other side reactions occurred simultaneously, introducing carbonyl and unsaturated groups to the structure of the polymeric networks. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Isotactic polypropylene; Syndiotactic polypropylene; Peroxide modification

1. Introduction

It has been well established [1–3] that polypropylene (PP) mainly experiences chain scission reactions during peroxide modification, which leads to a decrease in molecular weight and a narrow molecular weight distribution. However, it was also found [4] that this process is often accompanied by branching and crosslinking, though the efficiency is too low to give a measurable level of gel. In the light of the bimolecular characteristics of the crosslinking reaction, large amounts of crosslinked polypropylene could be expected at high peroxide concentrations [5–7].

There have been a number of publications in which the crosslinking of polypropylene initiated by thermal decomposition of peroxide was studied [6–10]. According to these studies, polypropylene can possibly be crosslinked, but the crosslinking process is more complicated than for polyethylene, because of the presence of simultaneous chain scission. The efficiency of crosslinking depends on the decomposition rate of peroxide and the reactivity of the radicals formed. Polyfunctional monomers, such as vinyl silanes [11], diallyl maleate [12,13], triallyl cyanurate [14] and ethers of pentraerythrito [6], have been used to accelerate the crosslinking of polypropylene with peroxide. The mechanism to increase crosslinking efficiency with these coagents has been explained by their ability to react with polypropylene radicals [6,8,15]. The chain scission could be retarded if the new radical located on a coagent molecule is stabilized against fragmentation. The radical thus decays preferably by recombination with another polymer radical, giving rise to crosslinking.

Most of the studies on the peroxide-initiated crosslinking of polypropylene have been limited to isotactic polypropylene (iPP). Little has been reported on the crosslinking behavior of syndiotactic polypropylene (sPP). sPP differs from iPP in chain configuration. It would be expected that the difference in the steroregularity could affect their crosslinking behavior.

In the present research, a comparison between peroxide-induced crosslinking behavior of iPP and sPP was conducted. An attempt was made to explain the difference in crosslinking efficiency, based on electron spin resonance (ESR) measurements. The kinetics of gelation were investigated, and the structural changes of crosslinked polypropylene were also determined.

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2. Experimental

2.1. Materials and preparation

Unstablized iPP (Shell iPP KY6100; M_w 160 000) and sPP (Fina Oil and Chemical, sPP; M_w 150 000) were provided in powder form. The samples were characterized by IR and differential scanning calorimetry (DSC) techniques. The IR spectra of iPP and sPP showed absorption bands characteristic of their chain configurations [16,17]. The melting temperatures were 162.7°C for iPP and 128°C for sPP. Two types of peroxides, t-butyl perbenzoate (TBPB; 98 wt%, Aldrich) and dicumyl peroxide (DCP; Aldrich) were used without further purification. The half-life times of decomposition are 1.8 min (TBPB) and 4.1 min (DCP) at 160°C. Peroxide was first dissolved in acetone and an appropriate amount of the peroxide/acetone solution was added to the powdered PP. Acetone was then evaporated by continuous stirring. After drying in a vacuum oven at room temperature, the peroxide/PP sample was put into a glass ampoule of 5 mm outer diameter (3 mm inner diameter) for crosslinking and ESR measurements.

2.2. Crosslinking

The peroxide crosslinking of iPP and sPP was carried out in an oil bath. The sample ampoules were kept in the bath for 10 half-life times of peroxide decomposition at the given temperature. In the studies of crosslinking kinetics, different reaction intervals were chosen to follow the change of crosslinking extent of samples.

2.3. Gel fraction determination

The crosslinked sample was cut into small pieces and extracted in boiling xylene containing 0.2 wt% of antioxidant for 12 h. The solvent was changed every 3 h. The percentage of the insoluble portion in the initial sample gave the gel fraction. Parallel experiments showed that the values of gel fraction deviated from the average by less than ± 3%.

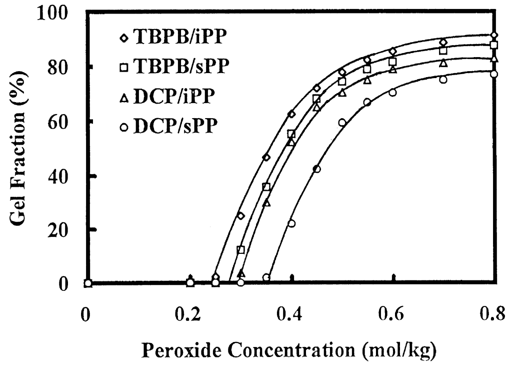


Fig. 1 Dependence of gel fraction on peroxide concentration for the PP/peroxide systems crosslinked at 160°C for 10 half-life times of peroxide decomposition.

2.4. ESR measurements

The ESR measurements were conducted on a Bruker EPR spectrometer (EP072) at the same temperatures as those used in crosslinking. The spectrometer was operated at 2.0 mW power and 100 kHz modulation frequency. The sample ampoule was inserted into the cavity of the instrument. The radical generation and termination were determined by the intensity of ESR signals. All spectra were shown as the first derivative of the absorption intensity. Radical concentration data were obtained by numerical integration of derivative curves and calibration with 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH).

2.5. IR study

Films (100 μm thick) for IR measurements were prepared by pressing samples under a constant load for 18 min at 160°C (same temperature as crosslinking in the oil bath). The films were washed with an excess volume of acetone to remove residue of peroxide for about 72 h, then dried overnight under reduced pressure. The IR spectra were recorded using a Bio-Rad FTS-40 FTIR spectrometer.

3. Results and discussion

Fig. 1 shows the results of gel fraction as a function of the peroxide concentration for the iPP and sPP crosslinking systems. It is observed that both iPP and sPP show similar crosslinking behavior: no gel is formed at low levels of peroxide and the gel fraction increases rapidly with the increase of peroxide concentration after the gel point. At the gel point, insoluble polymers start to appear. It can be seen in the figure that TBPB is more effective than DCP as an initiator for crosslinking for both iPP and sPP.

The results of peroxide crosslinking of PP can be evaluated according to the modified Charlesby–Pinner equation [18]:

$$s+\sqrt{s}=\frac{\mu}{\upsilon}+\frac{1}{\upsilon\bar{P}_{N,0}[\mathrm{I}]_0},$$

where s is the soluble fraction, μ and υ are the probabilities of chain scission and crosslinking, $\bar{P}_{N,0}$ is the number-average chain length of the original polymer, and $[\mathrm{I}]_0$ is the initial peroxide concentration. A plot of $s+\sqrt{s}$ against $1/[\mathrm{I}]_0$ is shown in Fig. 2. The dependence is not linear over the whole range of peroxide concentration. The intercept on the $s+\sqrt{s}$ axis, which is obtained by extrapolating the data to the high peroxide concentration, gives the ratio of the chain scission over crosslinking probabilities. The values of μ/υ are about 0.05–0.1 for TBPB and 0.2–0.3 for DCP. This demonstrates that the crosslinking is dominant at high concentrations of peroxide, and that the crosslinking efficiency of TBPB is higher than that of DCP.

The difference in crosslinking efficiency between the two peroxides can be explained by their decomposition rates [7]. The half-life time of TBPB is much shorter than that of DCP. The faster decomposition rate would cause a higher level of hydrogen abstraction, increasing the radical concentration in the crosslinking system, which favors the recombination of polymer radicals and leads to the increase of crosslinking efficiency.

The comparison between iPP and sPP crosslinking systems reveals that the crosslinking efficiency of sPP is lower than that of iPP. It has been demonstrated [6] that, besides the stationary concentration of polymer radicals, the structure of radicals formed by hydrogen abstraction is a significant factor in determining whether the radicals are terminated by combination or fragmentation. In other words, the crosslinking efficiency depends strongly on the type of polymer radicals involved in the crosslinking process. The mechanism of degradation of PP is generally explained by the β-scission of tertiary alkyl radicals, while the crosslinking of polyethylene is explained by the recombination of secondary alkyl radicals. Although iPP and sPP have the same chemical composition, differences in chain configuration or stereoregularity might influence the attack of peroxide radicals on their polymer chains, and then the reaction process.

In order to find the reasons for the difference in crosslinking efficiency between iPP and sPP, an on-line ESR spectrometer was used under the same crosslinking conditions to investigate the nature of polymer radicals and the molecular processes involved in crosslinking. Fig. 3 shows the ESR spectra recorded during iPP and sPP crosslinking processes. Both ESR spectra have a 24-line hyperfine structure, the same as that observed in an ESR study of peroxide modification of iPP [19]. The latter hyperfine structure was assigned to a mixture of tertiary and secondary alkyl radicals. The ESR spectra kept the same shape except for some changes in the peak intensities during the crosslinking process.

ESR studies of γ-irradiated PP with different stereoregularities (isotactic, syndiotactic and atactic) have been reported by several authors [20–22]. When iPP and sPP were irradiated at − 196°C and measured at room temperature, both polymers showed similar 17-line ESR spectra. It has been concluded [21] that irradiated iPP and sPP contain the same radical species—the tertiary alkyl radicals—but the radicals differ in their steric conformation due to the stereospecificities of the original polymers. The ESR spectra in this work are different from those obtained from irradiated iPP and sPP samples [22,23], with some weak lines in the wings of the spectra. Since the tertiary alkyl radicals are the major radicals involved in the PP modification processes, we believe the two ESR spectra observed in our work are also mainly due to the tertiary alkyl radicals. The discrepancies in the ESR spectra between the present work and previous studies with irradiated PP samples probably lie in the difference in the experimental temperature and the physical state of the polymers.

Fig. 4 shows the results of the polymer radical concentration versus reaction time. It is clear that the polymer radical concentration profile is determined by the type and concentration level of peroxides, reaction time and temperature. At the beginning of the process, peroxide generates primary radicals upon thermal decomposition at an elevated temperature. These primary radicals immediately abstract hydrogen from polymer chains to produce polymer radicals. The higher the level of peroxide used, the higher the concentration of polymer radicals generated. With the increase of radical concentration, the rate of radical termination increases and eventually becomes dominant. The radical

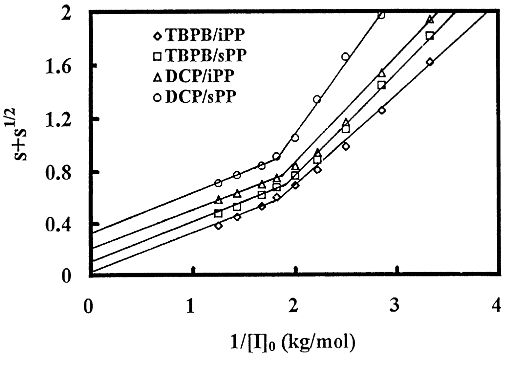


Fig. 2 Charlesby–Pinner plot of gel fraction versus peroxide concentration for the PP/peroxide systems crosslinked at 160°C for 10 half-life times of peroxide decomposition.

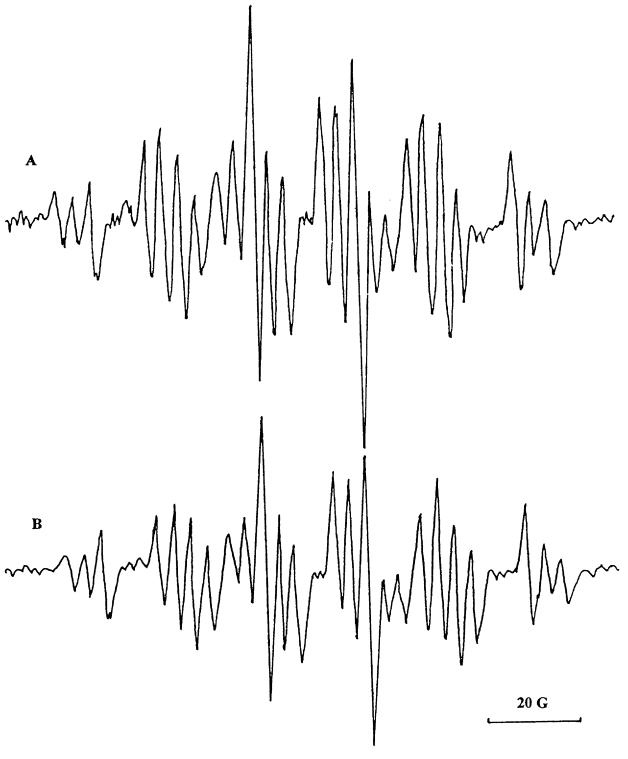


Fig. 3 ESR spectra of iPP and sPP recorded during peroxide crosslinking: (A) TBPB/iPP (0.5 mol kg^{-1}); (B) TBPB/sPP (0.5 mol kg^{-1}) at 160°C.

concentration would then begin to decrease, after a maximum, with reaction time. High temperature could accelerate radical termination, resulting in a sharper maximum in radical concentration–time profile.

The ESR signals from the two crosslinking systems have demonstrated that the attack of primary radicals on iPP and sPP chains took place at the same position, giving rise to the same polymer radicals, i.e. tertiary alkyl radicals. The difference only appeared in the polymer radical concentration. It is seen in Fig. 4 that the polymer radical concentrations in the sPP crosslinking system were lower than those in the corresponding iPP system. This means that the hydrogen abstraction from sPP chains is more difficult than from iPP chains. We believe this is due to the steric effect of PP chains, with sPP imposing more hindrance than iPP to the access of primary radicals. It was the lower radical concentration that caused the lower crosslinking efficiency in the sPP system.

The higher polymer radical concentration using TBPB as the radical initiator rather than DCP (also seen in Fig. 4) justifies the explanation that the faster initiation rate of TBPB led to a higher level of hydrogen abstraction and, consequently, a rise in the crosslinking efficiency.

It has been reported [5,7,10] that temperature is an important parameter influencing the ratio of crosslinking and chain scission of PP. Since the activation energy for β-scission is much higher than that for bimolecular termination, it is expected that lowering the temperature would favor the recombination of polymer radicals. On the other hand, at a lower temperature, the peroxide decomposition rate slows down, resulting in a lower radical concentration, which would have a negative influence on crosslinking.

Fig. 5 shows the dependence of gel fraction on crosslinking temperature for iPP and sPP samples, initiated by DCP and TBPB. As the temperature increases, the gel fraction in the sPP system decreases steadily. This is in agreement with the mechanism discussed above. It is apparent that the inhibition of fragmentation of polymer radicals at lower temperatures is dominant over the negative effect of slowing

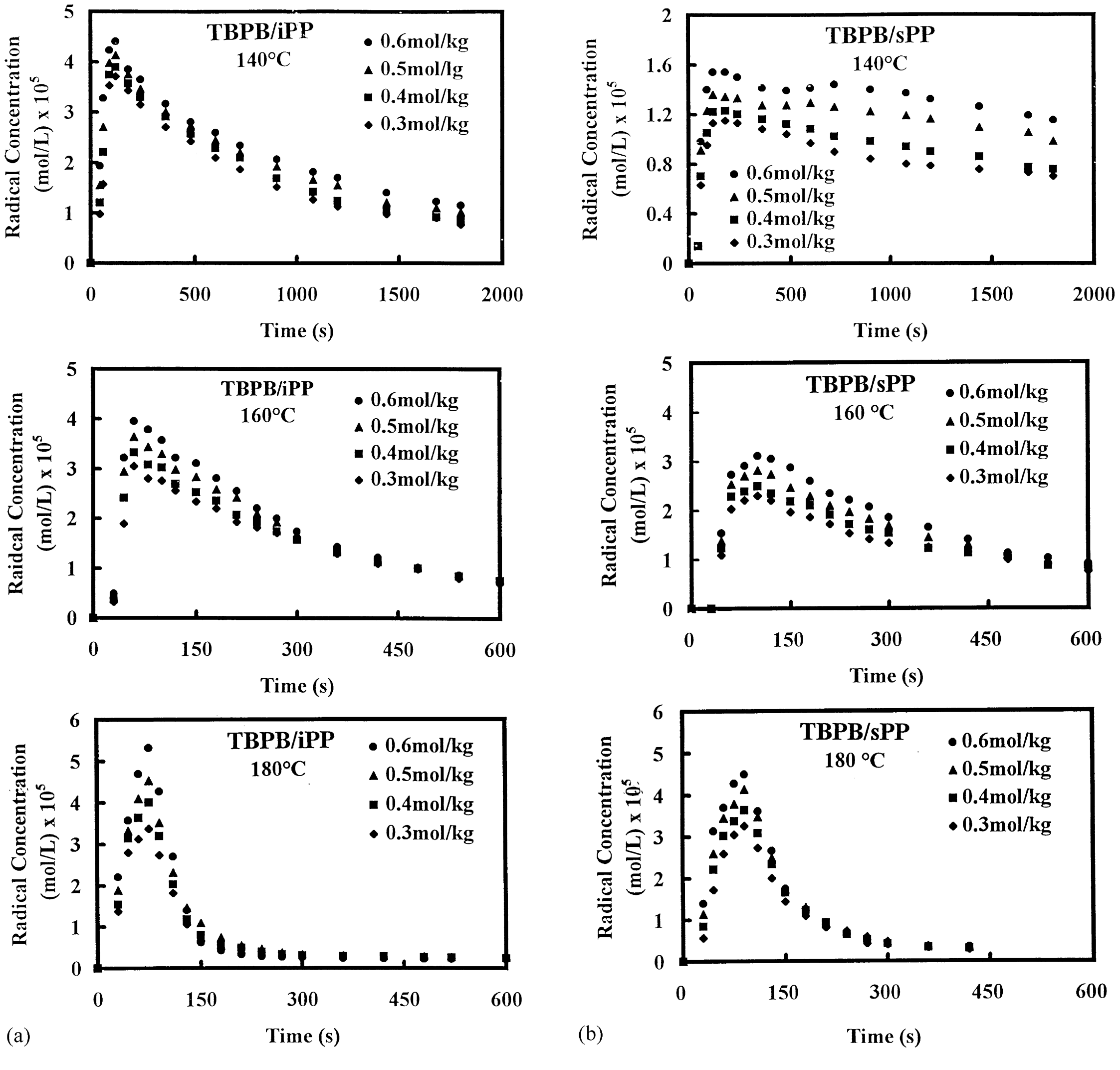
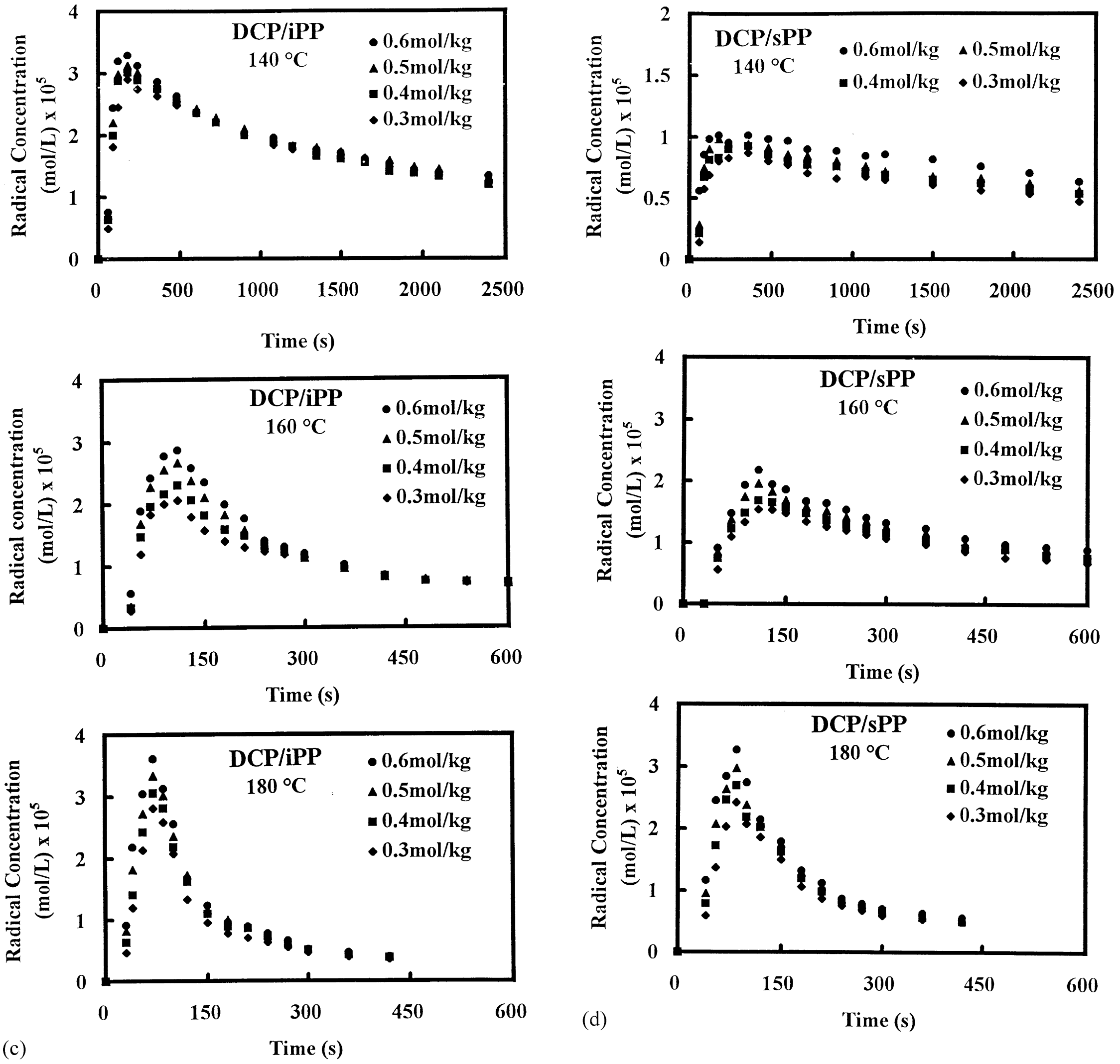


Fig. 4 Variation of polymer radical concentration with reaction time: (a) TBPB/iPP; (b) TBPB/sPP; (c) DCP/iPP; (d) DCP/sPP.



(c)

(d)

Fig. 4 (*continued*).

down the decomposition of peroxide. In the iPP system, the gel fraction passes through a maximum with increase of temperature. The highest amount of gel appears at about 160°C, where the polymer begins to melt. Obviously, the decrease of gel fraction at higher temperatures could be attributed to the accelerating chain scission. At lower temperatures, the decrease of decomposition rate of peroxide would seemingly be responsible for the reduction of crosslinking. However, we believe that the more important reason for this reduction is the reduced mobility of polymer radicals, which makes the diffusion and recombination of polymer radicals in the solid polymer matrix very difficult.

To examine the kinetics of peroxide-induced crosslinking of iPP and sPP, the gel formation was followed for samples with various peroxide concentrations at different temperatures. Fig. 6 shows the variations of gel fraction with reaction time. These curves provide a clear picture of the crosslinking process: after an induction period, which depends mainly on the type and concentration of peroxide, gel was formed and the gel fraction increased very quickly. A high level of gel fraction could be achieved in the early stages of crosslinking at high peroxide levels. The rate of gel formation then slowed down and gradually leveled off. The higher the peroxide concentration used, the faster the gel

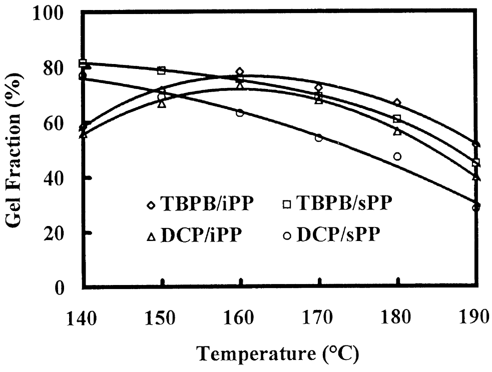


Fig. 5 Effect of temperature on gel fraction of the PP/peroxide systems crosslinked for 10 half-life times of peroxide decomposition at the given temperature: TBPB, 0.45 mol kg^{-1}; DCP, 0.50 mol kg^{-1}.

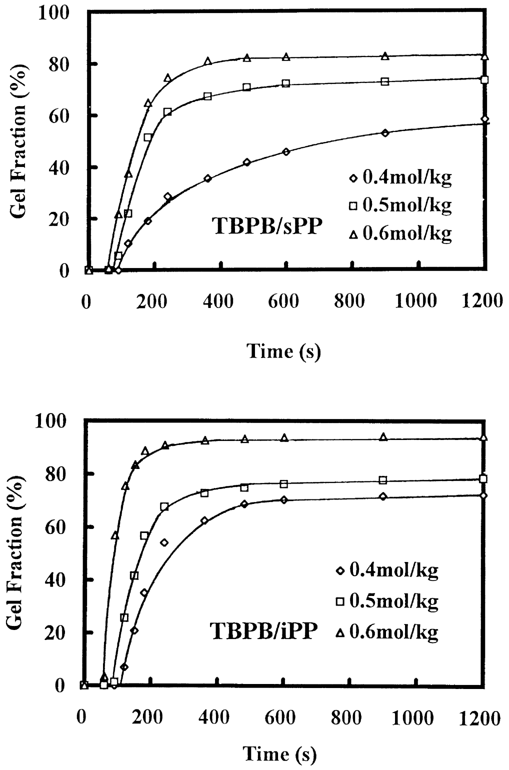


Fig. 6 Variation of gel fraction with reaction of the PP/peroxide systems crosslinked at 160°C.

was formed, and the higher level of gel fraction was reached.

From the initial slopes of gel fraction versus reaction time curves, the gelation rate could be estimated. Fig. 7 shows the gelation rate as a function of the peroxide concentration (crosslinked at 160°C). It can be seen that gelation rates increased linearly with peroxide concentration for all crosslinking systems. This linear relationship suggests first-order kinetics of gelation. The gelation rates for different crosslinking systems follow the order TBPB/iPP > TBPB/sPP > DCP/iPP > DCP/sPP. A linear temperature dependence of the gelation rate is also observed in Fig. 8. It is worth noting that the gelation rate for TBPB/iPP crosslinking at 140°C deviated significantly from linearity due to the diffusion limitations imposed on polymer radicals by the solid-state polymer matrix. The activation energies (E/R) for TBPB/iPP and TBPB/sPP crosslinking systems are 16 120 and 15 350 K^{-1}, respectively. The high activation energy indicates that peroxide crosslinking of PP is sensitive to temperature.

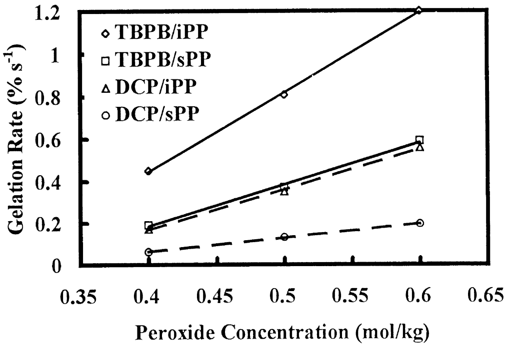


Fig. 7 Dependence of gelation rate on peroxide concentration of the PP/peroxide systems crosslinked at 160°C.

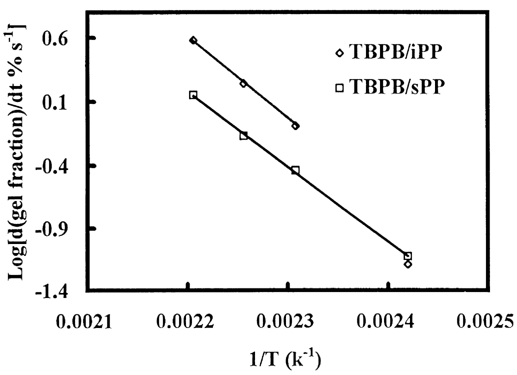


Fig. 8 Dependence of gelation rate on temperature with TBPB (0.50 mol kg^{-1}).

In addition to the crosslinking reaction, β-scission of the PP chain is unavoidable. The decomposition of a large amount of peroxide would also induce some undesirable reactions, such as oxidation. These side reactions more or less affect the structures and thus the properties of the crosslinked products. IR measurements have been made to investigate these structural changes. Fig. 9 shows the IR spectra of crosslinked iPP and sPP samples. Although crosslinked

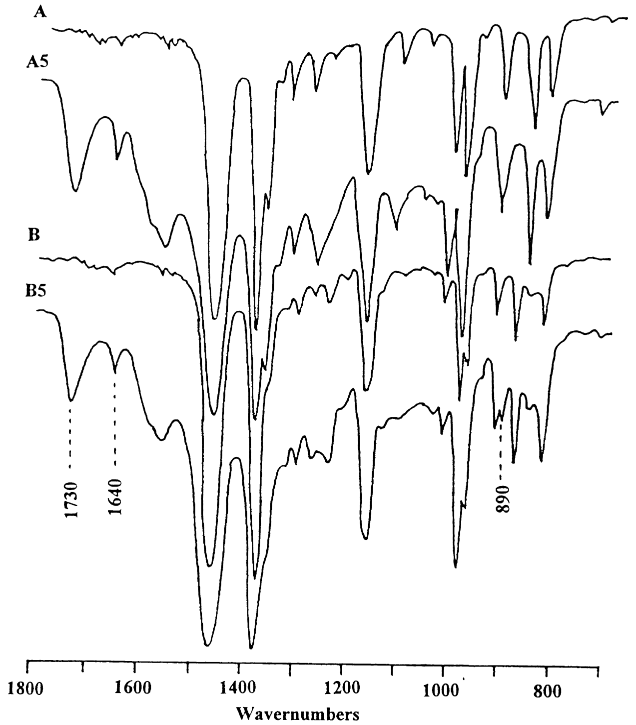


Fig. 9 IR spectra of peroxide-crosslinked polypropylenes: (A) iPP without peroxide; (A5) iPP with TBPB (0.50 mol kg^{-1}); (B) sPP without peroxide; (B5) sPP with TBPB (0.50 mol kg^{-1}).

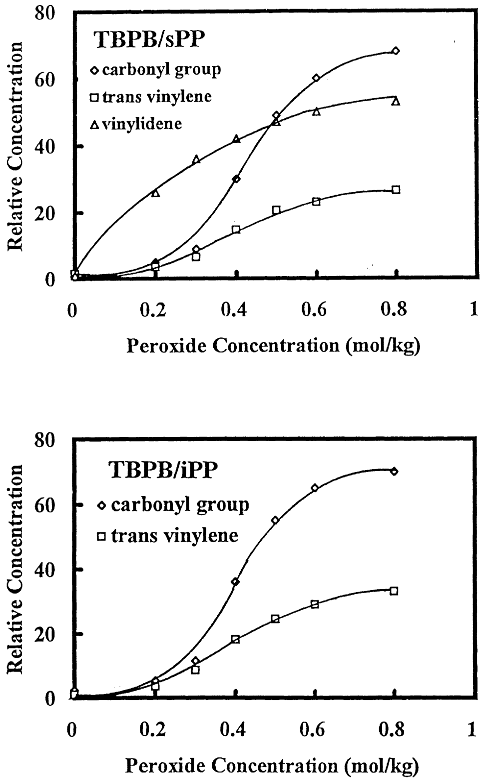
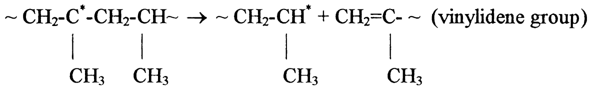


Fig. 10 Variation of relative concentration of carbonyl and unsaturated groups with peroxide concentration reacted at 160°C.

samples retained the characteristic iPP (or sPP) bands, some new peaks appeared, with the absorption at 1730 cm^{-1} attributed to carbonyl groups. This single, distinct band indicates that aldehydes and ketones are the major oxidation products during peroxide crosslinking of PP. At the same time, an absorption from double bonds (*trans*-vinylene) is observed at 1640 cm^{-1}, which originates from the deterioration (degradation) of PP. Besides these bands, an absorption peak of the vinylidene group appeared at 890 cm^{-1} in the crosslinked sPP sample. This group is a typical product of β-scission:



$$\sim CH_2\text{-}\underset{CH_3}{C^{*}}\text{-}CH_2\text{-}\underset{CH_3}{CH}\sim \;\rightarrow\; \sim CH_2\text{-}\underset{CH_3}{CH^{*}} + CH_2\text{=}\underset{CH_3}{C}\text{-}\sim \quad \text{(vinylidene group)}$$

However, this group was not observed in the crosslinked iPP.

The variations of the relative concentrations of carbonyl and unsaturated groups in crosslinked samples with peroxide concentration are shown in Fig. 10. At low peroxide levels, a small amount of carbonyl groups was formed. Starting from the peroxide concentration of 0.3 mol kg^{-1}, the concentration of carbonyl groups increased rapidly, which coincided with the quick formation of a crosslinking network. The relative concentration of *trans*-vinylene groups also showed an increase after the gel point. Contrary to the change of carbonyl and *trans*-vinylene groups, the number of chain-end double bonds (vinylidene groups) increased at low peroxide concentrations, and slowed down when the crosslinking reaction became dominant. It is apparent that large amounts of carbonyl and unsaturated groups were generated, along with the formation of a crosslinking network, at high peroxide levels. It is expected that these groups damage the properties of crosslinked products.

4. Conclusion

The experimental results in the present research support the following conclusions:

1. The ESR spectra demonstrated that the same type of polymer radicals were formed as the peroxide radicals abstracted hydrogens from iPP and sPP chains. It is believed that these polymer radicals were mainly the tertiary alkyl radicals on the PP chains.
2. iPP and sPP showed similar crosslinking behavior. The lower crosslinking efficiency of sPP was attributed to the lower concentration of polymer radicals. This was believed to be caused by the steric hindrance of the sPP chain to hydrogen abstraction. The crosslinking efficiency for both polymers was also determined by the peroxide decomposition rate and reaction temperature.
3. The initial gelation rate increased linearly with the peroxide concentration and followed first-order kinetics. The activation energies (E/R) of gelation for TBPB/iPP and TBPB/sPP were 16 120 and 15 350 K^{-1}, respectively.
4. β-Scission and other side reactions occurred simultaneously with the crosslinking reaction, particularly at high peroxide concentrations, introducing some carbonyl and unsaturated groups into the structure of the polymer chains. These groups would be deleterious to the properties of crosslinked PP products.

Acknowledgements

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