

# Improvement of the Photostability of Isotactic Polypropylene by the Incorporation of Ethylene

Md. Shamsul Alam,<sup>1</sup> Hisayuki Nakatani,<sup>2</sup> Ben G. S. Goss,<sup>1</sup> Tomohito Ichiki,<sup>1</sup>  
Boping Liu,<sup>1</sup> Minoru Terano<sup>1</sup>

<sup>1</sup>*School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai Tatsunokuchi, Ishikawa 923-1292, Japan*

<sup>2</sup>*Center for New Materials, Japan Advanced Institute of Science and Technology, 1-1 Asahidai Tatsunokuchi, Ishikawa 923-1292, Japan*

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**ABSTRACT:** The effect of the incorporation of ethylene on the photostability of isotactic poly(propylene) (iPP) was studied with the aim of improving the photostability. iPP was prepared with a random ethylene sequence (ethylene-propylene random copolymer, rPP), and the photooxidative degradation behavior was compared with that of homogeneous iPP. Both samples were thermally post-treated under vacuum to ensure the same crystallinity. The degradation behavior was studied by infrared spectroscopy (IR), gel permeation chromatography (GPC), and temperature rising elution fractionation (TREF) measurements. The rates of hydroperoxide and carbonyl formation in the irradiated iPP increased with irradiation time for > 192 h, whereas those in

the irradiated rPP are almost constant after 96 h. The change in molecular weight with the irradiation time showed similar behavior, suggesting that the degradation reaction in the irradiated rPP was suppressed after 96 h. The degradation behavior of rPP was thought to be due to the dissociation of the methyl group, which leads to the termination of degradation. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1863–1867, 2002

**Key words:** isotactic poly(propylene); ethylene-propylene random copolymer; photooxidative degradation; chain scission

## INTRODUCTION

Isotactic polypropylene (iPP) has been widely applied for commercial products in the form of fibers and films. However, iPP, which has tertiary carbon atoms, is known to be very vulnerable to oxidative degradation under the influence of elevated temperature and sunlight.<sup>1–8</sup> The degradation chemistry of iPP has been very extensively studied and has long been recognized as a free radical chain reaction,<sup>9</sup> which leads to polymer chain to scission. It is generally accepted that this chain scission is responsible for degradation in polymer mechanical properties. The addition of stabilizers has been widely used to depress the radical reaction. However, it is difficult to maintain the long-term performance of stabilizers because of volatility.<sup>10–12</sup> To suppress the radical reaction during long-term use, the modification of iPP itself will be required.

In our previous studies,<sup>13,14</sup> the thermooxidative degradation of polypropylene (PP) was examined in terms of stereoregularity. In the molten state, iPP was more oxidized than atactic PP (aPP) and syndiotactic

PP (sPP). On the basis of this understanding, it seems that the modification of primary structure affects the radical reaction. However, in the solid state, the oxidative degradation is also affected by the morphology. The oxidation of semicrystalline polymer is initially confined to the amorphous phase.<sup>5</sup> We found the same degree of photodegradation behavior for iPP with 50% crystallinity and sPP with 28% crystallinity.<sup>15</sup> Based on these contradictory results, the investigation of the photooxidative degradation of iPP as a function of the primary structure by controlling the morphological effects is indispensable for practical applications.

The modification of the primary structure of iPP by copolymerization with ethylene may be an effective method for improving photostability. The introduction of ethylene, which has no tertiary carbon atoms, effectively removes the reactive tertiary carbon atoms from the polymer backbone.

In this study, the photooxidative stability of iPP and ethylene-propylene random copolymer (rPP) with a low ethylene content and the same morphologies were investigated as a function of their primary structure.

## EXPERIMENTAL

### Materials and film preparation conditions

iPP and rPP were supplied from Tosoh Company Ltd. The characteristics of iPP and rPP are summarized in

Correspondence to: M. Terano (terano@jaist.ac.jp).

TABLE I  
Characterization of PP Samples

Sample	Stereoregularity, mmmm%	Ethylene content, mol%	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Crystallinity, vol%
iPP	99	—	271,000	5.7	56.1
rPP	93	5.3	251,000	6.1	56.1

Table I. In this study, samples of iPP and rPP with very close molecular weight distributions were used. To remove catalyst residues and stabilizers, these PPs were stirred overnight in distilled water containing a small amount of ethanol at room temperature. Then, they were reprecipitated from a boiling xylene solution into ethanol.

iPP and rPP were pressed at 483 and 463 K, respectively, under 10 MPa for 6 min, then quenched with ice water. The thickness of the compression molded samples was  $\sim 100 \mu\text{m}$ . The rPP film was subsequently annealed in a vacuum oven at 373 K for 5 h to ensure similar crystallinities.

The volume fraction of crystallinity was determined by the density measurement. Crystallinities of iPP and rPP were approximately equal ( $\sim 56 \text{ vol } \%$ ).

The X-ray diffraction studies of virgin iPP and rPP films showed peaks at  $2\theta$  of 14, 17, 18.5 and 21.5°, corresponding to the (110), (040), (130) and (041) planes (Figure 1), respectively. These results indicate the presence of the stable  $\alpha$ -form (monoclinic) crystal structure.

### Photooxidation method

The photooxidative degradation was carried out using a weather-meter (ATLAS SUNTEST CPS), equipped with xenon lamp, whose wave length range was similar to that of sunlight. The irradiation time was up to 192 h, and the black body panel temperature was maintained at 336 K.

### Measurements

The infrared (IR) spectra were taken with a JASCO FT-IR500 spectrometer with a  $2 \text{ cm}^{-1}$  resolution and 20 scans.

Molecular weight of the sample was determined by gel permeation chromatography (GPC) (Senshu, SSC-

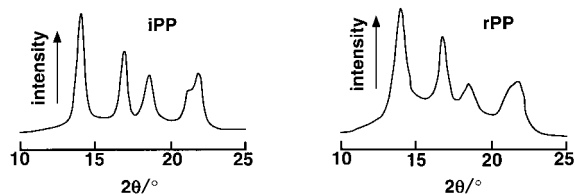


Figure 1 X-ray diffraction pattern of iPP and rPP films.

7100) with polystyrene gel columns (Tosoh, TSK-gel G3000HHR and G5000HHR) at 413 K using *o*-dichlorobenzene as a solvent.

The change of crystalline distribution in the irradiated PP was examined by temperature rising elution fractionation (TREF: Senshu SSC-7300). *o*-Dichlorobenzene was used as a solvent for the measurement at 413 K. The iPP and rPP films used for the TREF analysis were virgin and 192 h irradiated samples.

## RESULTS AND DISCUSSION

The oxidative degradation of PP has been reported to proceed by a free radical chain reactive mechanism to form a carbonyl group ( $\text{C}=\text{O}$ ) via a reaction involving hydroperoxide group ( $\text{ROOH}$ ) formation.<sup>1-9</sup> Therefore, IR spectrometry is a powerful tool for studying the oxidative degradation mechanism of PP. The effect of the incorporation of ethylene on the photooxidative degradation of iPP was investigated by IR spectroscopy. The relationship between the irradiation time and the concentrations of the OH/ROOH and  $\text{C}=\text{O}$  in the irradiated iPP and rPP films is shown in Figure 2. The OH/ROOH absorbing at  $3400 \text{ cm}^{-1}$  has an average molar absorptivity of  $70 \text{ mol L}^{-1} \text{ cm}^{-1}$ ,<sup>8</sup> whereas the  $\text{C}=\text{O}$  absorbing between  $1780$  and  $1700 \text{ cm}^{-1}$  with a maximum at  $1715 \text{ cm}^{-1}$  has that of  $300 \text{ mol L}^{-1} \text{ cm}^{-1}$ .<sup>8</sup> Here, the concentrations were calculated by these molar absorptivities. The OH/ROOH and  $\text{C}=\text{O}$  concentrations in both films increased up to 96 h; however, those of rPP were almost constant over 96 h.

As shown in Figure 3, the molecular weight dependence of irradiation has similar profile to that of the ROOH and  $\text{C}=\text{O}$  concentrations. The GPC curves shift to a lower molecular weight region with significant changes in the shape of the curve up to 96 h. After

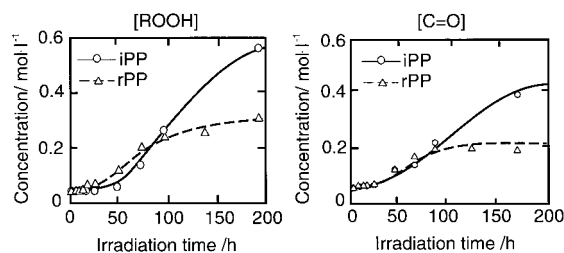
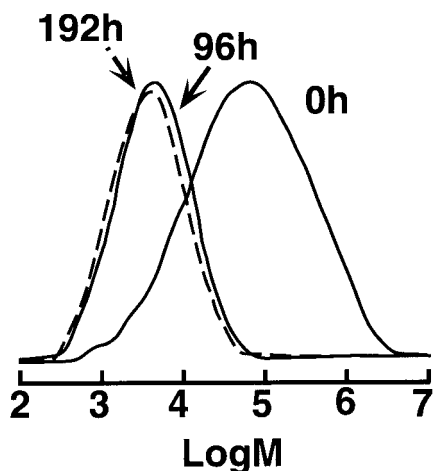


Figure 2 Irradiation time dependence of carbonyl and hydroperoxide concentrations in iPP and rPP films.



**Figure 3** Effect of irradiation time on GPC curves of rPP film.

96 h, the GPC curves do not shift or change with the irradiation time. These results indicate that the rate of photooxidation of rPP is significantly suppressed due to the existence of ethylene unit.

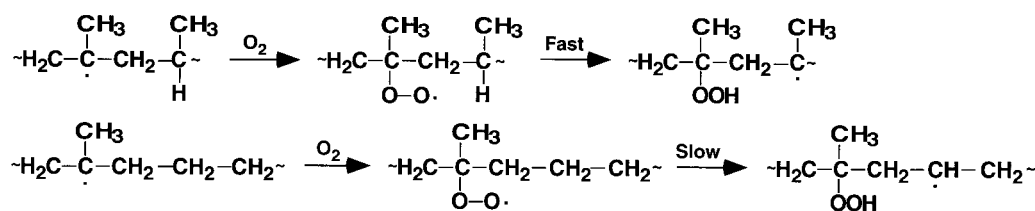
Photooxidative degradation of PP is believed to propagate by a free radical chain reaction.<sup>5</sup> There are two possible mechanisms for the slower decrease of molecular weight of rPP compared with that of iPP. First, it has been frequently shown that PE leads to cross-linking during photooxidation, and therefore an equilibrium may be established between the photo scission of the PP blocks and the cross-linking of the PE blocks. This equilibrium may give a reduced rate of molecular weight change.

The second mechanism, shown in Scheme 1, is for

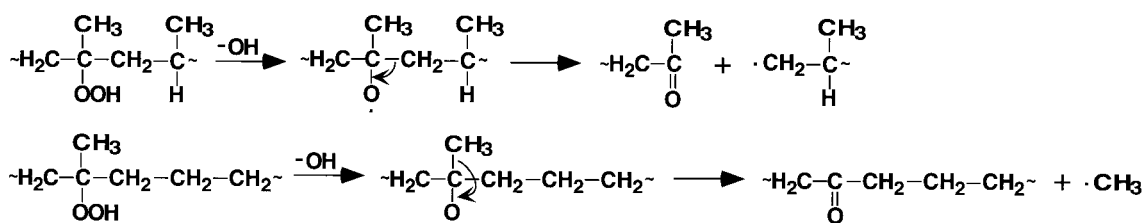
the formation reaction of ROOH in iPP and rPP. The formation of alkyl radical by the dissociation of tertiary C—H bond occurs first. The reaction of this alkyl radical with oxygen leads to the production of the peroxy radical which propagates the chain reaction by intramolecular tertiary C—H abstraction from iPP as well as secondary C—H abstraction from rPP. The abstraction reactions produce the hydroperoxides, which are responsible for the autocatalytic nature of the oxidation. The existence of the secondary C—H in rPP may depress the rate of the chain reaction involving hydroperoxide, leading to a drop in the photooxidation rate. However, the content of ethylene comonomer in this rPP is too low to completely suppress the formation reaction of ROOH.

As another consideration, this difference of the degradation between the iPP and the rPP seems to be due to differences in the decomposition reaction of ROOH. As shown in Scheme 1, the chain scission is known to proceed by two alternative pathways, the main-chain scission or dissociation of methyl group.<sup>4</sup> Main-chain scission gives an end-chain ketone and alkyl radicals in the polymer chain, which leads to the reformation of ROOH. In-chain ketones and methyl radicals are formed from the dissociation of methyl groups from polymer chains. The higher mobility of methyl radicals may cause more frequent association with hydroperoxide or alkoxy radicals. This more frequent association leads to a higher rate of termination than would be expected between the less mobile alkoxy and hydroperoxide groups. To examine the difference in the hydroperoxide decomposition reaction between iPP and rPP, the bond energy of the main chain was

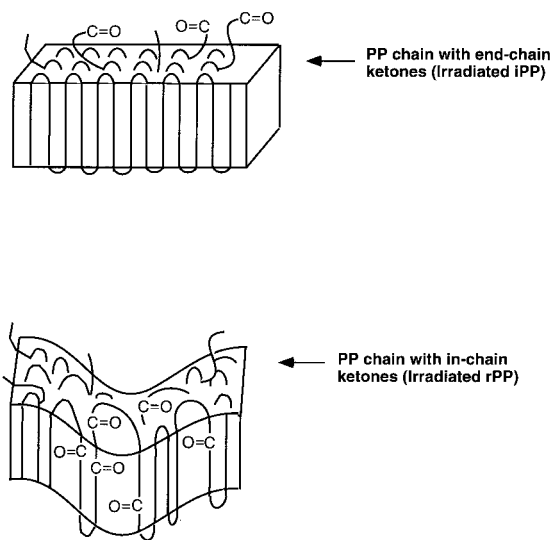
#### Formation of hydroperoxide



#### Decomposition of hydroperoxide



**Scheme 1** Hydroperoxide formation and decomposition in iPP and rPP.



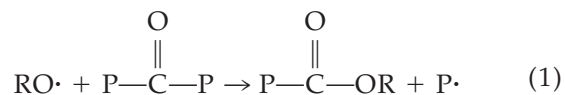
**Figure 4** Schematic models of lamella crystal in recrystallized PPs.

estimated by the MOPAC calculation (Cambridge Soft Corp., Chem 3D Pro Ver. 3.51). The bond energy of rPP was slightly higher than that of iPP (rPP: 190 kJ/mol; iPP: 185 kJ/mol), suggesting that the dissociation of methyl group in rPP may be feasible. Because the degradation mechanism of rPP partially involves the dissociation of the methyl group, the rate of propagation of the radical chain reaction is thought to be gradually suppressed and finally terminated. In addition, main-chain scission by the Norrish type photolysis of ketone groups barely occurs under these degradation conditions because the IR peak of vinyl groups at 909 and 995  $\text{cm}^{-1}$  were not detected in either the irradiated rPP or iPP.

If the decrease of degradation rate is due to the mechanism just mentioned, the in-chain ketone should be present in the irradiated rPP. As seen in Figure 4, when the rPP with in-chain ketones is recrystallized, a partial inclusion of in-chain ketone units in the lamella crystal occurs. This inclusion leads to the disorder of the lamella, suggesting that the recrystallized rPP will have a broader crystalline distribution. The existence of end-chain ketones does not affect the packing of lamella crystals because the end-chain ketones are unable to be included in the lamella crystals. TREF is a useful technique to determine the crystalline distribution in a semicrystalline polymer.<sup>16</sup> Therefore, the existence of in-chain ketones can be confirmed by the change of TREF profiles. The TREF profiles of the iPP and rPP films are shown in Figure 5. The crystalline distribution peaks of the irradiated samples shift to a lower temperature region compared with the virgin samples. The TREF curve for the irradiated iPP does not become broader, indicating the formation of few in-chain ketone units. However, the TREF curve

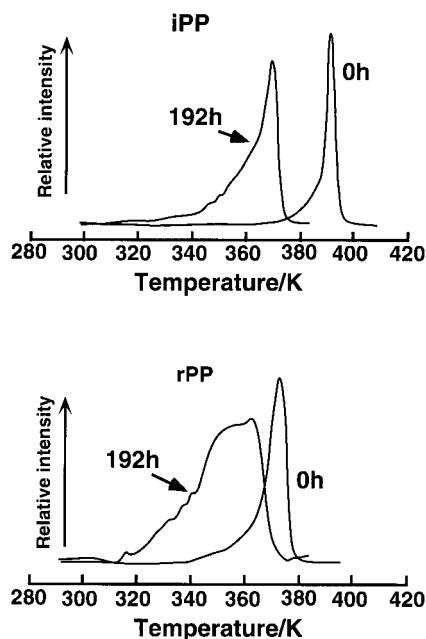
for the irradiated rPP becomes considerably broader. These TREF measurements suggest that in-chain ketone units are formed in irradiated rPP.

It is difficult to detect the existence of in-chain ketones directly by IR measurements because the absorbance band overlaps with that of the end-chain ketone. A secondary reaction of in-chain ketones with alkoxy radicals was proposed by some investigators.<sup>17,18</sup> This reaction causes the formation of ester group following by the reaction.<sup>17</sup> It was proposed that presence of in-chain ketones can be detected by forcing further oxidation to form ester groups and subsequent detection of the esters. It is not possible to quantify the amount of in-chain ketone; however, this method is a simple qualitative test.



R = alkyl; P = polymer chain

The appearance of ester groups is detectable because the in-chain ketone peak position ( $\sim 1735 \text{ cm}^{-1}$ ) is a slightly lower wave number than the ester groups. The formation of ester group occurs at a fairly high degree of degradation. To accelerate the degradation of the irradiated samples, they were placed under vacuum in an oven at 353 K according to the literature.<sup>18</sup> The IR curves of before and after heat treatment of irradiated PPs are shown in Figures 6 and 7. In the case of iPP, the decrease of peak intensity between 1700 and 1780  $\text{cm}^{-1}$  (assigned to acid, ester, and ketone groups) indicates that the heat treatment forms



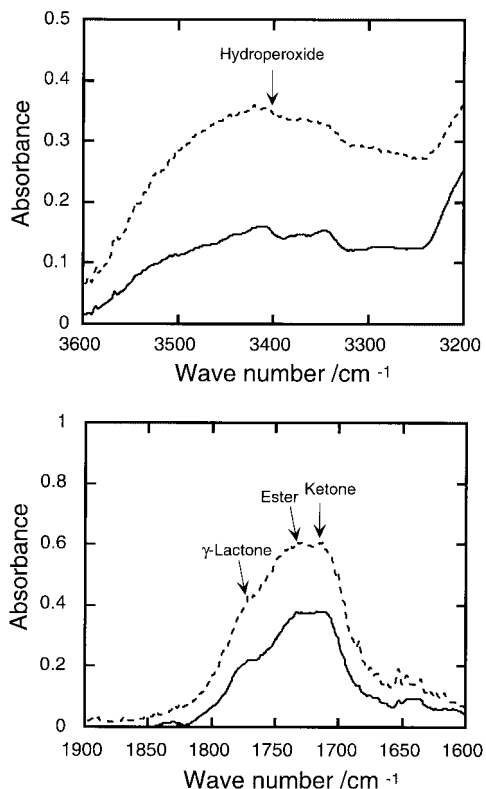
**Figure 5** TREF curves of irradiated and unirradiated PPs.

volatile low molecular weight products. In the case of the rPP, an increase of the peak assigned to ester groups was observed. This increase of ester groups is attributed to the reaction of in-chain ketones with alkoxy radicals that are produced from the additional decomposition of hydroperoxides as a result of the heating. Although the volatilizing of a lower molecular weight part surely exists as well as the case of heating the iPP, the loss of volatilized acid, ester, and ketone groups may be compensated by the new ones being produced from the additional decomposition of hydroperoxides as a result the heating. Because it is difficult to decompose the rPP into a lower weight part compared with the iPP, it is thought that the increase of ester groups with slightly less ketone groups is observed.

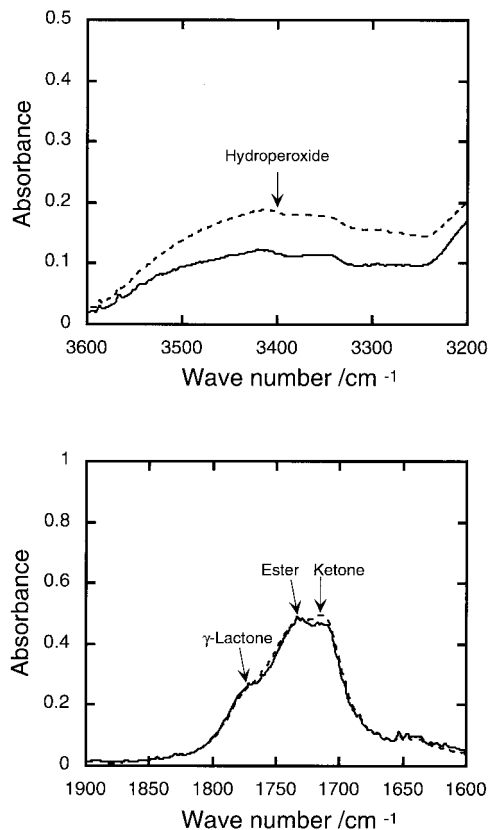
These results support the idea that the introduction of ethylene changes the pathway of chain scission.

### CONCLUSIONS

In this study, the photooxidative stability of rPP with a low ethylene content was investigated as a function of its primary structure using morphology changes to get information about the improvement of the photostability of iPP. At a longer irradiation time, rPP showed a better photostability than iPP. Therefore, the



**Figure 6** IR spectra of before and after heat treatment of irradiated iPP. Key: (---) before; (—) after heat treatment.



**Figure 7** IR spectra of before and after heat treatment of irradiated rPP. Key: (---) before; (—) after heat treatment.

photostability of iPP could be improved by modifying the primary structure, using ethylene as a comonomer.

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