

Note

Study of the thermo-oxidative degradation behavior of isotactic polypropylene with the varying ethylene content

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The thermo-oxidative degradation behavior of isotactic polypropylene is studied as a function of varying ethylene and oxygen concentration effects by means of gel permeation chromatography (GPC) measurement. The thermal stability of three types of isotactic polypropylene viz. iPP, ePP1, ePP2 which contains 0, 0.5, 2.7 wt% of ethylene, respectively having similar average molecular weights and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) is studied in solution at 453 K. Under this condition, the changes of molecular weight and $\overline{M}_w/\overline{M}_n$ in isotactic polypropylene samples are decreased with the increase of ethylene. The rate of degradation has also been increased with the increase of oxygen concentration for each sample. The variation of time effect on changing of GPC curve is also studied. GPC curves are changed preferably by the scission of longer chain in iPP, ePP1 and ePP2 with the increasing degradation time. The results reveal that the thermo-oxidative stability of isotactic polypropylene significantly depends upon the varying ethylene content incorporation.

Keywords: Isotactic polypropylene, ethylene unit incorporation, thermo-oxidative degradation, stability, gel permeation chromatography

Polypropylene (PP) in terms of stereoregular is divided into isotactic PP, syndiotactic PP and atactic PP. Among them, isotactic PP has been widely used in the world as medical goods, fibres, raping films etc¹⁻².

However, isotactic iPP, which has methine protons is very vulnerable to oxidative degradation. The oxidative degradation of isotactic PP is recognized to proceed by radical formation reaction that leads to the scission of the polymer chain, which level is corresponding to the different primary structure of isotactic PP. As a function of isotacticity, the difference in the oxidizability between isotactic PP, syndiotactic PP and atactic PP has been studied to some extent³⁻⁹ and it was concluded that isotactic PP is more susceptible to oxidation. The addition of

stabilizers is widely used to improve the oxidative stability of isotactic PP. However, the stabilizers have the disadvantage of limited retain-ability because of volatility¹⁰. Besides stabilizers, there are also other factors that influence the stability of isotactic PP, such as the ethylene incorporation. Terano *et al.* studied the improvement oxidative stability of isotactic PP by the incorporation of ethylene¹¹⁻¹³.

In this study, the thermo-oxidative degradation of isotactic PP was investigated in terms of varying ethylene and oxygen concentration effects at 453 K in solution. Thus, this method is suitable to discuss the effect of single polymer chain on degradation.

The purpose of this work is to get the information about the influence of varying ethylene concentration effects in degradation of isotactic PP.

Experimental Section

Materials

Isotactic polypropylene containing varying ethylene content 0, 0.5, 2.7 wt%, respectively are named as iPP, ePP1 and ePP2 produced by MgCl_2 -supported Ziegler catalyst were supplied from Chisso Co., Ltd. In order to remove any unfavorable catalyst residues and stabilizers, these samples were stirred overnight in distilled water containing a small amount of ethanol at room temp. Then, they were reprecipitated from a boiling xylene solution into ethanol.

Methods

The purified samples were dried *in vacuo* at 333 K for 5 hr. The degradation was carried out in a glass-reactor where 20 mg polymer was dissolved in 20 mL 1, 2, 4-trichlorobenzene at 453 K under the various oxygen concentrations (N_2 : 0%, air: 20%, O_2 : 100%) for 30 min. In the case of the degradation under N_2 , the reactor was evacuated and filled up with N_2 for 45 min. This procedure was done to remove the O_2 absorbed on the polymer. In the case of the degradation under air and/or under pure O_2 , the degradation was performed when the systems were purged by air and/or O_2 using the same apparatus (**Figure 1**).

After the thermo-oxidative degradation, the treated samples in solution were precipitated by ethanol, filtered and dried *in vacuo* at 333 K for 1 hr. No

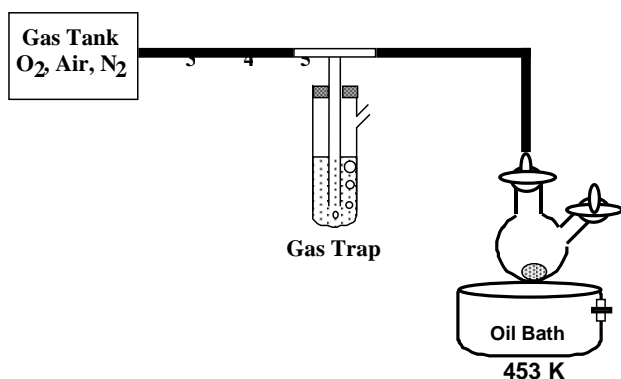


Figure 1—An apparatus for thermal degradation of polypropylenes

additional stabilizer and additive were used during degradation. The degree of degradation was evaluated by the changes of molecular weight and molecular weight distribution (\bar{M}_w/\bar{M}_n) of various isotactic PP samples.

Measurement

Molecular weights and \bar{M}_w/\bar{M}_n of isotactic PP determined by GPC (Senshu, SSC-7100) with polystyrene gel columns (Tosoh, TSK gel G3000HHR and G5000HHR) at 413 K using *o*-di-chlorobenzene containing 2,6-di-*tert*-butyl-*p*-cresol (antioxidant) as a solvent. The calibration curve of the isotactic PP was made with standard polystyrene samples.

The stereoregularity (pentad fraction) of the polymer was determined by ^{13}C NMR measurement using a Varian Gemini-300 spectrometer at 393 K on 20% (w/v) solution in 1,2,4-trichlorobenzene. 10% (v/v) Benzene- d_6 was added as an internal lock, and hexamethyldisiloxane was used as internal chemical shift reference.

The melting temp. of PP sample was determined by differential scanning calorimetry (DSC, METTLER DSC 820). Calorimetry was made in nitrogen flux to avoid thermal degradation. The 10 mg of samples sealed in aluminium pans and heated from 293 K to

463 K at a scanning rate of 10 K/min. Indium was used as the standard for calibrating the temperature axis and the melting temp. at the maximum of the endothermic peak was taken.

All the molecular orbital calculations were performed by the PM3 optimization with UHF calculation, as realized in the MOPAC version 7 program. The key word 'precise' was used to increase by a factor of 100 the criteria for terminating all optimization, both electronic and geometric semi-empirical methods now based on better approximation and implemented on small computers can be very easily used for the investigation of various reaction mechanisms.

Results and Discussion

Isotactic polypropylene is a typical plastic whose properties are profoundly affected by the primary structure as a function of varying ethylene incorporation which the relative stability and degradation behavior of isotactic PP are dependent on. To get the clear image about the effect of varying primary structure on the degradation of isotactic PP; iPP, ePP1 and ePP2 were used in this study after washing. The degradation reaction was performed at 453 K for each sample. Degrading polymer molecules undergo a series of chemical reactions whose effects can be structural modifications such as side-group reaction or elimination or cross-linking. In most cases, bond scissions take place on the polymer main chains to yield radical species that may initiate chain processes, while average molecular weights and molecular weight distribution (\bar{M}_w/\bar{M}_n) change continuously¹⁴. Therefore, average molecular weights and \bar{M}_w/\bar{M}_n changes can reveal fundamental characteristics of the degradation process.

Table I lists the calculated values of number average molecular weight (\bar{M}_n), weight average molecular weight (\bar{M}_w), \bar{M}_w/\bar{M}_n , tacticity

Table I—Sample characteristics of isotactic polypropylenes

Sample	E ^a wt%	\bar{M}_n^b	\bar{M}_w^b	\bar{M}_w/\bar{M}_n^b	Tacticity ^c (mmmm%)	T _m ^d
iPP	0.0	70000	400000	5.7	99	438
ePP1	0.5	71000	390000	5.5	96	433
ePP2	2.7	72500	415000	5.7	92	420

^a Ethylene content (E wt%) in polypropylene per 100 segments.

^b \bar{M}_n , \bar{M}_w and \bar{M}_w/\bar{M}_n were estimated by GPC.

^c Tacticity was determined by ^{13}C NMR spectroscopy.

^d Melting temperature (T_m) determined by DSC.

Table II—Effect of ethylene concentration on degradation of isotactic PP under air at 453K for 30 min

Sample	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
iPP	54000	190000	3.5
ePP1	57000	230000	4.0
ePP2	62000	293000	4.7

(mmmm%) and melting temperature (T_m) for virgin iPP, ePP1 and ePP2 samples by using GPC, NMR and DSC measurements. From this table it is observed that they have almost same average molecular weights and \bar{M}_w/\bar{M}_n values.

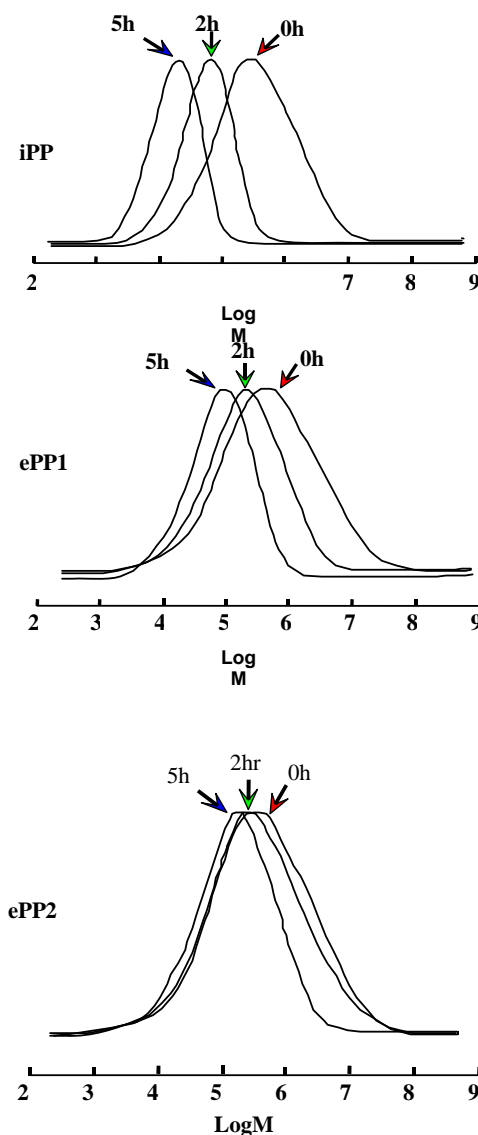
The effect of ethylene concentration on thermo-oxidative degradation of isotactic polypropylenes (iPP, ePP1 and ePP2) is shown in **Table II**. The degradation is carried out in solution under air at 453 K for 30 min. The degree of degradation was evaluated by the changes of \bar{M}_n , \bar{M}_w and \bar{M}_w/\bar{M}_n comparing with the virgin samples. Under this condition, the values of \bar{M}_n , \bar{M}_w and \bar{M}_w/\bar{M}_n were decreased at lower rate with increasing ethylene concentration. This means that the rate of degradation in ePP1 and ePP2 is reduced due to varying ethylene concentration effects compared to iPP.

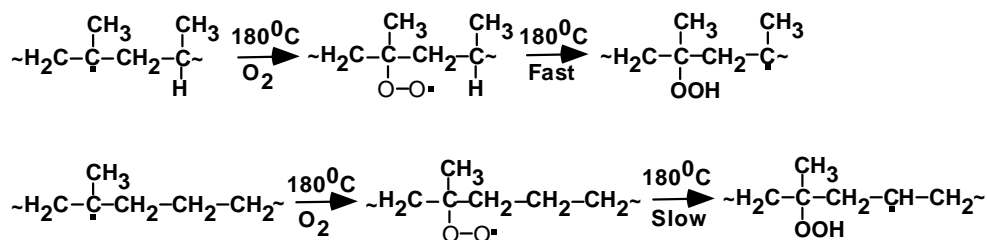
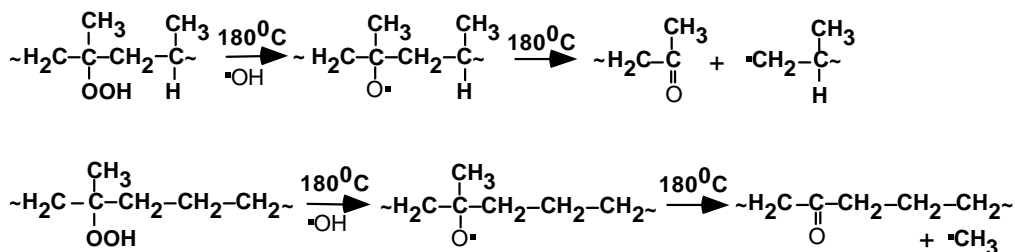
To perform the ethylene concentration effect, the thermo-oxidative degradation behavior of iPP, ePP1 and ePP2 by the treatment in various oxygen atmospheres in solution was investigated at the same time and temperature (**Table III**). It can be seen that decrease in \bar{M}_n , \bar{M}_w and \bar{M}_w/\bar{M}_n of all samples occurs with the increasing oxygen concentration. Under nitrogen, the \bar{M}_n values for all degraded samples kept constant with the \bar{M}_n values of virgin samples. However, the decreasing rate in iPP is higher than those of ePP1 and ePP2. This reveals that the termination reaction rapidly occurs in ePP2 compared to iPP and ePP1.

In general, if the degradation occurs by the chain reaction the GPC curve shifts toward the lower molecular weight side. The GPC curves of iPP, ePP1 and ePP2 are shown in **Figure 2** as a function of degradation time. The curves of degraded samples were analyzed in respect of virgin isotactic polypropylenes. With the increase of degradation time, the curves shifted towards the lower molecular weight side and it is clearly observed that the shape of the curve changes with reduction in width together

Table III—Effect of oxygen concentration on degradation of isotactic PP at 453K for 30 min

Sample	Oxygen concentration (%)	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
iPP	0	70000	400000	5.7
ePP1		71000	390000	5.5
ePP2		72500	415000	5.7
iPP	20	54000	190000	3.5
ePP1		57000	230000	4.0
ePP2		62000	293000	4.7
iPP	100	51000	158000	3.0
ePP1		55500	198000	3.6
ePP2		59000	260000	4.4

**Figure 2**—Effect of time on GPC curves of iP, ePP and ePP2 under O_2 at 453 K in solution

iPP and ePP1 or ePP2**iPP and ePP1 or ePP2****Scheme I**—Hydroperoxide formation and decomposition reactions in iPP and ePP1 or ePP2

with the drastic decrease of the high molecular weight region. However, the shifting and narrowing of the GPC curves of ePP1 and ePP2 are lower than that of iPP. With the continuation of degradation the amount of short chains could be developed.

On the basis of the results the feasible reason for the difference in the stabilities between iPP, ePP1 and ePP2 is considered to be as follows: The oxidative degradation of PP has been reported to proceed by a free radical chain reactive mechanism to form a carbonyl group (C=O) via a reaction involving hydroperoxide group (ROOH) formation¹⁵. In the presence of ethylene unit in ePP1 and ePP2, a significant variation in degradation behavior was observed between iPP, ePP1 and ePP2. There are two possible mechanisms for the slower decrease of molecular weight of ePP1 or ePP2 compared with that of iPP. First, it has been frequently shown that polyethylene (PE) leads to cross-linking during degradation, and therefore an equilibrium may be established between the thermal degradation 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 I**, is for the formation reaction of ROOH in iPP and ePP1 or

ePP2. 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 ePP1 or ePP2. The abstraction reactions produce the hydroperoxides, which are responsible for the autocatalytic nature of the oxidation. The existence of the secondary C-H in ePP1 or ePP2 (sec C-H bond energy: 397KJ/mol>tert C-H bond energy: 368KJ/mol) may depress the rate of the chain reaction involving hydroperoxide, leading to a drop in the degradation rate. However, the content of the ethylene unit in ePP1 or ePP2 is too low to completely suppress the formation reaction of hydroperoxide.

As another consideration, this difference of the degradation between the iPP and ePP1 or ePP2 seems to be due to the differences in the decomposition reaction of ROOH. As shown in **Scheme I**, the chain scission is known to proceed by two alternative pathways, the main chain scission or dissociation of methyl group¹⁶ as side chain scission. 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 as side chain scission from the dissociation of methyl groups. 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. In order to examine the difference in the ROOH decomposition reaction between iPP and ePP1 or ePP2, the bond energy of the main chain was estimated by the MOPAC calculation (Cambridge Soft Corp., Chem 3D Pro Ver. 3.51). The bond energy of ePP1 or ePP2 was found to be slightly higher than that of iPP (iPP: 185 kJ/mol, ePP1 or ePP2: 190 kJ/mol), suggesting that the dissociation of methyl group in ePP1 and ePP2 may be feasible, and main chain scission occurs in iPP due to the lower bond energy. Since the degradation mechanism of ePP1 and ePP2 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.

Conclusion

Thermo-oxidative degradation behavior of dissolved isotactic PP was examined as a function of varying ethylene and oxygen concentration effects. The observation exhibited the different degradation behavior of isotactic PP. The relative stability of polypropylenes decreases in the following order: ePP2>ePP1>iPP. The results demonstrated that the stability of iPP can be improved by the incorporation of varying ethylene content through changing the reaction pathway of degradation.

Acknowledgement

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