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Dependence of tacticity distribution in thermal oxidative degradation of polypropylene

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Summary

Thermal oxidative degradation behavior of two kinds of polypropylene (PP) with different tacticity distribution was investigated based on the data obtained by NMR, temperature rising elution fractionation (TREF) and thermogravimetric analysis (TGA). Although these PPs have similar molecular weights and tacticity, the behavior of degradation was considerably different. The differences were found to be due to the tacticity distribution by TREF measurement. In order to investigate the effect of tacticity distribution on the degradation in more detail, the more stable PP having a broad tacticity distribution was divided into four kinds of tacticity fraction by TREF, and each of degradation behavior was investigated by TGA. The results indicated that the rate of degradation systematically depended on the tacticity. The higher stability of PP with the broader tacticity distribution would be originated from the abstraction reaction of tertiary hydrogen, which was the rate-determining step in PP degradation reaction.

Introduction

Polypropylene (PP) has been widely applied for the commercial products such as the form of fibers and films. However, the degradation of PP proceeds easily by stimulation such as elevated temperature and sunlight [1-8], causing the materials to become embrittlement. The PP degradation chemistry has been very extensively studied and has long been recognized as a free-radical chain reaction [9], which leads to polymer chain to scission. The addition of stabilizers has been widely used to suppress the radical reaction. However, it is difficult to maintain the long-term performance of stabilizers because of volatility [10-12]. In order to suppress the radical reaction during long-term use, the modification of PP itself will be required.

In our previous studies [13,14], the effect of tacticity on thermal oxidative degradation of PP was examined using highly isotactic, syndiotactic and atactic PPs, resulting that the degree of oxidation of isotactic PP was the severest. On the basis of this result, it was concluded that the tacticity affects the radical reaction in the degradation. However, the relationship between the tacticity and the rate of degradation has been not systematically clear yet. To study the dependence of tacticity will be required to prepare a highly stable PP against degradation.

By development of polymerization catalyst technology in recent years [15-18], it is possible to control the PP's molecular characteristics such as molecular weight and tacticity distribution. Moreover, there is a new fractionation technique, which called temperature rising elution fractionation (TREF). Even PP having a broad tacticity distribution such as stereo block PP can be correctly divided into each of an inherent tacticity fraction using TREF [19]. By the catalyst technology and TREF, the dependence of tacticity in degradation will be evaluated correctly.

In this study, with aim of clarifying the dependence of tacticity in PP degradation, thermal oxidative degradation behavior of two kinds of polypropylene (PP) with different tacticity distribution was investigated, and the difference was studied by TREF and thermogravimetric analysis (TGA) in detail.

Experimental

Materials

Propylene of research grade (donated by Chisso Corp.), anhydrous $MgCl_2$ and $TiCl_3$ (donated by Toho Titanium Co.,Ltd.), nitrogen (purchased from Uno Sanso Co.), and triethylaluminium (TEA) (donated by Tosoh Finechem Co.) were used without further purification. TEA was used as a toluene solution. Toluene was purified by passing through a molecular sieves 13X column.

Catalyst preparation

In order to obtain PP with different tacticity distribution, two kinds of $TiCl_3$-based Ziegler catalyst were used. The catalyst denoted "dry ground" was prepared by grinding $MgCl_2$ and $TiCl_3$ by a 1.2L stainless steel vibration mill pot with 55 balls (25mm diameter) under nitrogen atmosphere for 30 hours at room temperature, whereas one denoted "wet ground" was done by grinding $MgCl_2$ and $TiCl_3$ with heptane solvent under the same condition. Ti contents of each catalyst were the same (0.05mmol-Ti/g-cat). The catalysts were used as toluene slurry.

Polymerization

The PPs denoted "PP1" and "PP2" were synthesized using dry ground $TiCl_3/MgCl_2$ - triethylaluminium (TEA) and wet ground $TiCl_3/MgCl_2$-diethylaluminiumchloride (DEAC) catalyst systems, respectively. Polymerizations were performed at Al/Ti molar ratio of 2 or 3 at 30 °C for 30 minutes in toluene as a solvent. Pretreatment to the catalyst was carried out with DEAC at 30 °C for 10 minutes when PP2 was synthesized. In order to remove catalyst residues, PP1 and PP2 were reprecipitated from a boiling xylene solution into methanol.

Thermal oxidative degradation in the solid

Thermal oxidative degradation was performed at 130 °C for 10-120 minutes in air. The heater (Senshu SSC-9300, as shown in Figure 1) was used for examination. No additional antioxidant was used in all cases. The PP samples were dried in vacuo at 60 °C for 3 hours. Then 5mg of each PP in a small vial was allowed to stand in a heater. In the heater, the vial was covered with a heating jacket to achieve effective heat transfer to the samples.

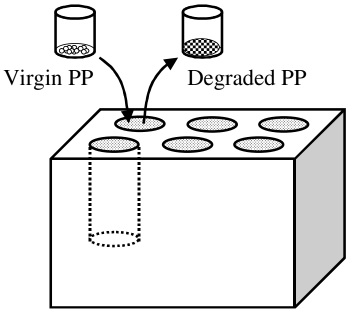

Figure 1. An apparatus for thermal oxidative degradation of PP

GPC characterization of PP

After the thermal oxidative degradation, the degraded PP in the small vial was dissolved in 5ml of o-dichlorobenzene containing 2,6-di-t-butyl-p-cresol as an antioxidant, and the obtained PP solution was directly measured by GPC [13,14]. In the meantime, degraded PP solution was sucked up to the small vial and dried with N_2 flow. Then it was dissolved in 5ml of o-dichlorobenzene (ODCB) containing antioxidant. The molecular weight of PP sample was determined by GPC (Senshu, SSC-7100) with styrene-divinylbenzene gel columns (SHODEX, HT-806M) at 140 °C using o-dichlorobenzene as a solvent.

^{13}C-NMR measurement of PP

The primary structure was determined by ^{13}C-NMR measurement using a Varian Gemini-300 spectrometer at 120 °C on 20% (w/v) solution in hexachloro-1,3-butadiene. 1,1,2,2-tetrachloroethane-d_2 was added as an internal lock and used as an internal chemical shift reference.

TREF analysis of PPs

The tacticity distribution of PP was determined by temperature rising elution fractionation (TREF: Senshu, SSC-7300) with ODCB as an extraction solvent, which contains same antioxidant. A fraction column packed with Chromos orb (bought from Celite Corp.) with 10mm diameter and 30cm in length was used for the TREF characterization. About 70mg of each PP sample was dissolved in 10ml of ODCB at 140 °C, and a part of the solution (ca.6ml) was passed through the fraction column, which was slowly cooled down at 6.7 °C/h from 140 °C to 20 °C simultaneously. Elution of the deposited PP with ODCB at a flow rate of 150ml/h was first carried out at 20 °C for 30 minutes to obtain the ODCB-soluble fraction, and then the column was heated at 16 °C /h up to 140 °C. The eluted PP solution was analyzed by a refractive index detector to obtain the TREF diagram. Moreover, tacticity fractions of the polymer with increasing crystallinity were then eluted with ODCB at temperatures increasing stepwise. Extraction took place over temperatures ranging from 20 °C to 140 °C divided into 5 steps (20, 60, 90, 106 and 140 °C). Polymer was eluted during 90 minutes at every step after the temperature had stabilized for 30 minutes. Tacticity fractions were then collected and precipitated in methanol.

Thermal analysis of PP

The decrease in weight of PP was analyzed by thermogravimetric analysis (TGA, METTER TG50) at 130 °C for 40 hours under air.

Results and discussion

As shown in Table 1, PP samples having roughly equal average tacticity and molecular weight are synthesized. Thermal oxidative degradation of these samples is performed at 130 °C in air atmosphere.

Table 1. Tacticities and molecular weights of synthesized PP samples

Sample	mmmm [1)] (mol%)	$\overline{\text{Mn}}$ [2)]
PP1	47	0.7×10^4
PP2	40	1.0×10^4

1) Measured by ^{13}C-NMR. 2) Measured by GPC.

Figure 2 shows that changes in ratio of molecular weight ($M_{n,t}/M_{n,0}$) of PPs during thermal oxidative degradation.

In our previous reports [13, 14], the degradation of isotactic PP was found to proceed vigorously as compared with atactic PP. However, the decrease in $M_{n,t}/M_{n,0}$ of PP2 is considerably faster than that of PP1 regardless of the almost same tacticity. In addition, each tacticity after degradation is considerably different as shown in Table 2.

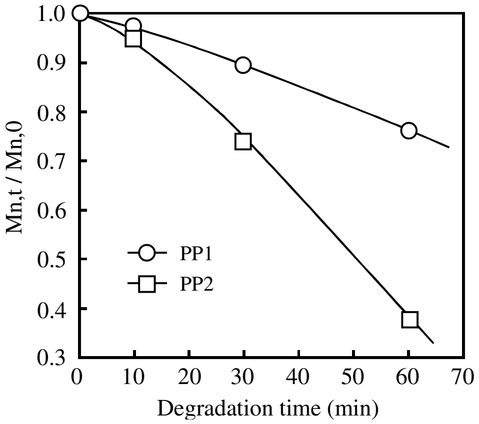

Figure 2. Changes in ratio of molecular weight ($M_{n,t}/M_{n,0}$) of PPs during thermal oxidative degradation: $M_{n,t}$= number average molecular weight in a degradation time (t), $M_{n,0}$= original number average molecular

Table 2. Tacticities of PPs before and after thermal degradation

Sample	mmmm (mol%) [1)] Before	mmmm (mol%) [1)] After
PP1	47	45
PP2	40	30

1) Measured by ^{13}C-NMR.

Figure 3 shows the TREF diagrams of PP1 and PP2, corresponding to the intensity of each fraction against the elution temperature. TREF elution temperature increases in accordance with a concomitant increase of tacticity. Thus, TREF diagram qualitatively reflects the tacticity distribution [20]. The TREF diagram of PP1 does not exhibit a distinct peak, and that of PP2 does a sharp one, suggesting that the difference between degradation behavior will be ascribed to the tacticity distribution. In addition, these are the TREF diagrams of insoluble parts at 20 °C. The weight fractions of soluble parts in PP1 and PP2 were 52 and 60 wt%, respectively.

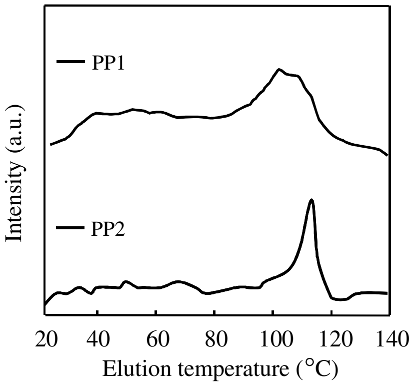

Figure 3. TREF diagrams of PPs (PP1 and PP2)

Figure 4 shows the TREF diagrams of PP1 and PP2 before and after thermal oxidative degradation. The sharp peak in PP2 is shifted to a lower elution temperature by the degradation. In addition, although the change in TREF diagram of PP1 is not so remarkable after thermal oxidative degradation, the shift of the peak at the higher elution temperature can be seen as well as PP2. As shown in Table 2, the fall of tacticity of PP2 is confirmed by ^{13}C-NMR measurement. These results imply that a higher isotactic fraction is selectively degraded.

In order to clarify the dependence of tacticity in thermal oxidative degradation, PP1 having the broad tacticity distribution is divided into five kinds of tacticity fraction by TREF (see Figure 5).

The tacticity of each fraction is shown in Table 3. The degradation behavior of these fractions is studied by TGA. According to Girois *et al.*, weight change of PP sample displays multi-stages with advance of degradation. A period of constant weight, namely induction period, is initially seen, and then the weight is increasing by oxidation. Beyond a maximum, weight loss increases with volatilized component, and finally mass balance becomes negative.

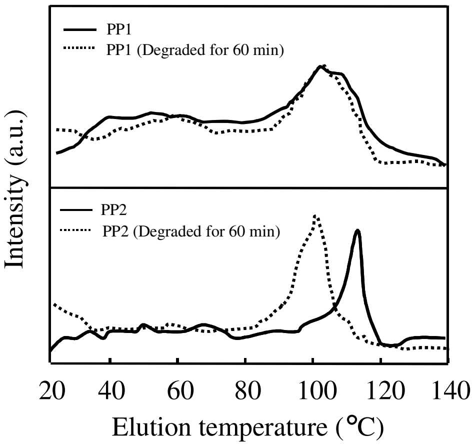

Figure 4. TREF diagrams of PPs before and after thermal oxidative degradation. The thermal oxidative degradation was carried out at 130 °C for 1h in the air

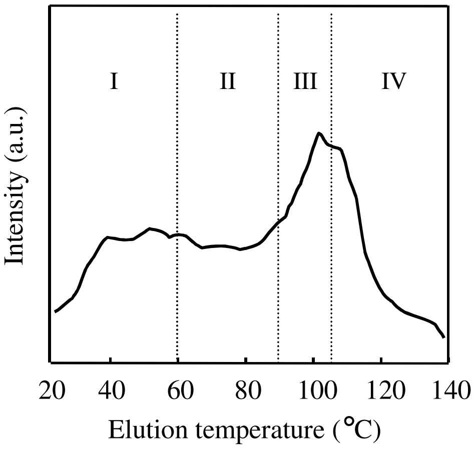

Figure 5. Determination of PP fractions temperature from TREF result of PP1

Table 3. Characteristics of PP1 fractions

Fractions	Range of elution temperature (°C)	mmmm[1)] (mol%)	$\overline{Mn}$[2)]	Weight ratio (wt%)
0	20	25	0.6×10^4	52
I	20-60	52	1.1×10^4	17
II	60-90	76	1.8×10^4	12
III	90-106	87	2.5×10^4	9
IV	106-140	91	7.4×10^4	10

1) Measured by ^{13}C-NMR. 2) Measured by GPC.

As shown in Figure 6, the weights of fractions denoted “II, III, and IV” are changing to the multi-stages with degradation time. In the cases of fractions “0 and I” with lower tacticities, the weight changes are just in the induction period stage in this degradation time. It appears that the advance of degradation is slower as tacticity becomes lower.

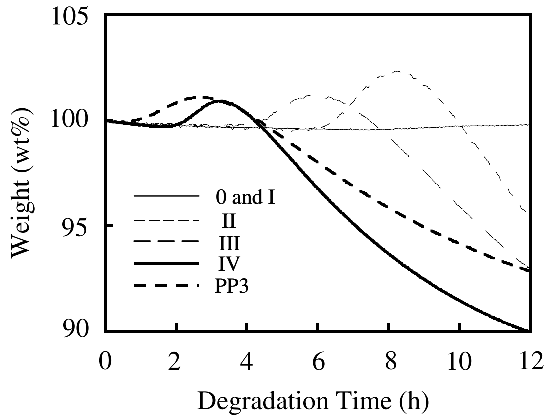

Figure 6. Thermogravimetric analysis results of PP1 fractions and PP3

In the case of the remarkable difference of molecular weight, e.g. fraction 0 and IV, the difference may affect the advance of degradation. In the case of slight difference of molecular weight such as fraction I-III, however, the difference is hardly thought to affect it. In order to remove the parameter of the difference of molecular weight, the effect of tacticity on the degradation is studied using “PP3” with $\overline{M}_n = 1.8\times10^4$ and mmmm=93. The PP3 was supplied from Toho Catalyst Co., Ltd. and was used after sufficient purification. The molecular weight is the same as that of II fraction, and the tacticity is the highest in comparison with the fractions (see Table 3). As shown in Figure 6, the advance of degradation is obviously the most rapid. This result demonstrates that the rate of thermal oxidative degradation depends on the tacticity.

Weight ratio of PP2 fractions is summarized in Table 4. PP2 mainly consists of 0 and IV fractions. The IV fraction has highest tacticity and molecular weight, and the 0 fraction does lowest them. It appears that the molecular weight and tacticity of PP2

Table 4. Characteristics of PP2 fractions

Fractions	Range of elution temperature (°C)	Weight ratio (wt%)
0	20	60
I	20-60	9
II	60-90	7
III	90-106	6
IV	106-140	18

rapidly change because of selective degradation of IV fraction. Apparently the difference between degradation behavior of PP1 and PP2 is originated from their tacticity distributions.

Oxidative degradation of PP is believed to propagate by a free radical chain reaction [9]. The formation of alkyl radical by the dissociation of tertiary C-H bond firstly occurs. The reaction of this alkyl radical with oxygen leads to the production of peroxy radical, which propagates the chain reaction by intramolecular tertiary C-H abstraction from PP. The abstraction reactions produce hydroperoxides, which are responsible for the autocatalytic nature of the oxidation. In the case of meso sequence, the peroxy radical and the tertiary C-H are located on the same side, resulting that the abstraction of tertiary hydrogen easily occurs. Whereas, in the case of racemo sequence, the abstraction of tertiary hydrogen hardly occurs due to the steric hindrance of methyl group, in which the peroxy radical and tertiary C-H are mutually located on the contrary side. Therefore, the rate of thermal oxidative degradation will increase systematically with the increase in tacticity. Although a more detailed study is required, the abstraction of tertiary hydrogen is thought to be the rate-determining step in PP degradation reaction.

Conclusion

Dependence of tacticity distribution in PP degradation was investigated by two kinds of PP with different tacticity distribution. Although these PPs have similar molecular weights and tacticity, the behavior of degradation was considerably different. The PP having a higher degradation resistance was divided into five kinds of tacticity fraction by TREF, and each of degradation behavior was investigated by TGA. The results indicated that the rate of degradation systematically depended on the tacticity, suggesting that the higher stability was originated from the abstraction reaction of tertiary hydrogen, which was the rate-determining step in PP degradation reaction.

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