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New Approaches for the Development of Highly Stable Polypropylene

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Summary: Effects of primary structure on the degradation of polypropylene (PP) were studied using PPs having a variety of tacticities or a random ethylene sequence with the aim of improving the stability of PP. Thermal stabilities of isotactic, atactic and syndiotactic PPs (iPP, aPP and sPP) having similar molecular weights were investigated in terms of stereoregularity under the same conditions. The sPP showed the highest stability, suggesting that the racemic structure of the main chain interferes with the chain reaction of radical species. Moreover, iPP was prepared to evaluate the thermal stability with a random ethylene sequence (ethylene-propylene random copolymer: rPP). The rPP was more stable than iPP. The existence of the ethylene sequence in the main chain was found to be effective in achieving high stability.

Keywords: degradation; polypropylene; primary structure; stereoregularity

Introduction

PP has been widely used for commercial products in the form of fibers and films. However, PP is known to be very vulnerable to oxidative degradation under the influence of elevated temperature and sunlight.[1-8] The PP degradation chemistry has been very extensively studied and has long been recognized as a free-radical chain reaction,[9] which leads to chain scission. It is generally accepted that this 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 performance of stabilizers over a long term because of the volitality.[10-12] In order to suppress the radical reaction during long-term use, the modification of iPP itself may be effective.

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In this study, the thermal degradation of PP was investigated in terms of its primary structure, such as stereoregularity and comonomer incorporation. The key concept of this work is to investigate the influence of primary structure by choosing suitable PP samples and conditions to be able to eliminate other factors. A better understanding of the basic aspects of the decomposition of PP with regard to its primary structure is indispensable for the further development of this area.

Effects of Stereoregularity on Thermal Degradation of PP

The degradation behavior of PP depends on several factors, such as external stimulation, chemical structure of the sample and impurities in the sample. In this study, our attention was focused on stereoregularity. With the aim of clarifying the contribution of the independent factors, the emphasis fell on the choice of suitable PP samples and appropriate conditions to avoid the superimposition of each factor. The resulting information is considered to provide more profound insight into the stability of PPs as well as to contribute to the elucidation of the explicit mechanism of the thermal degradation of PP.

Several criteria for evaluating thermal stability have been proposed.[4] Among them, the most important one is the temperature at which the molecular weight decreases during a certain period. The typical molding temperature in the industrial iPP processing is about 180 °C or higher.[13] Under this condition, the effects of the crystallinity and crystal structure of the sample could be negligible because the applied temperature was higher than the T_ms of PPs (shown in Table I). The effect of stereoregularity on the degradation of PP was investigated in the molten state.

Table I Characteristics of PPs

Sample	$\overline{Mn}$	$\overline{Mw}$ / $\overline{Mn}$	mmmm (%)	T_m (°C)
iPP	50,000	5.0	99	160
aPP	48,000	3.8	23	
sPP	45,000	1.6	>1 (92)[a)]	150

a) rrrr = 92%

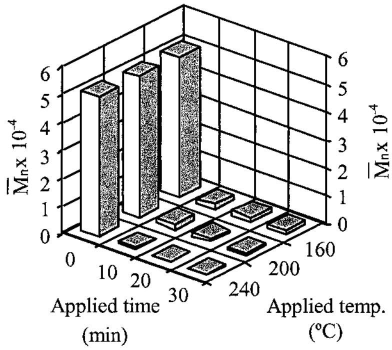

Fig. 1: Thermal degradation of iPP in air.

Recent catalyst technology makes it possible to produce suitable PP samples for the investigation. The dicyclopentadienyl zirconium dichloride-methylaluminoxane (MAO) catalyst system developed by Sinn and Kaminsky was used to produce aPP with high molecular weight.[14, 15] A syndiospecific metallocene catalyst, *i.e.*, isopropyl (cyclopentadienyl-1-fluorenyl) zirconium dichloride-MAO was successfully developed by Ewen[16] to make sPP with very high syndiotacticity (*rrrr* pentad fraction > 90%). iPP prepared by a $MgCl_2$-supported Ziegler catalyst system and aPP and sPP prepared by metallocene catalyst systems were used in this study.

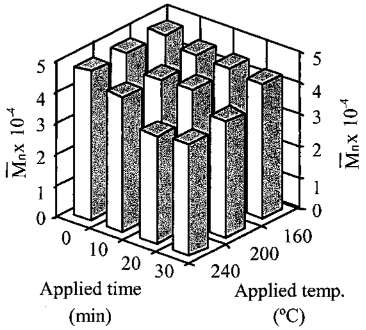

Fig. 2: Thermal degradation of aPP in air.

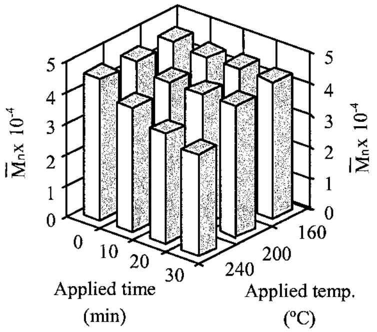

Fig. 3: Thermal degradation of sPP in air.

The molecular weights of these PPs were almost the same as shown in Table I. These PPs were used after the washing treatment. Heat treatments of PPs were carried out at 160-240 °C in air. Hence, the influence of molecular weight, catalyst residues, and crystalline state on the thermal degradation are negligible. The comparison of the thermal degradation of iPP, aPP and sPP was performed in air at 160, 200, and 240 °C. The degradation of iPP was found to proceed significantly (Fig. 1), whereas the degradation behavior was not remarkable in the case of aPP and sPP (Fig. 2 and 3). As can be seen in Fig. 4 (a) and (b), shifts in the GPC profile of the iPP and aPP to lower molecular weights were clearly observed without significant change of shape of the curves and molecular weight distribution after the heat treatment. In iPP, methyl groups are located on one side of the plane of the carbon-to-carbon main chain, and most of the configurational repeating units show meso-dyads. Many racemic structures exist in aPP. It seems reasonable to suppose that the thermal degradation is depressed significantly due to the existence of the racemic structure in aPP. In order to confirm this assumption, the thermal stability of sPP, which is mainly composed of the racemic structure, was investigated under the same conditions. As shown in Fig. 3, there was no significant difference in the $\overline{M}n$ of the sPP before and after the heat treatments, during which iPP was degraded drastically. Furthermore, the shape of the GPC curve of sPP treated at 200 °C for 30 min is almost the same as that of the virgin sPP, as shown in Fig. 4(c). Thus, it was found that the thermal stability of sPP was appreciably higher than either that of iPP and/or aPP. It is inferred that good thermal stability of the sPP is mainly due to the presence of the racemic structure in the main chain.

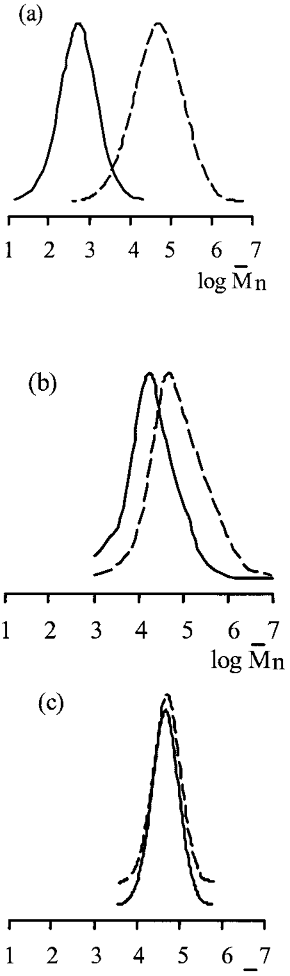

Fig. 4: GPC curves of iPP (a), aPP (b) and sPP (c). The solid lines indicate the results of treated PPS at 200°C for 30 min. The dotted lines indicate the results of virgin PPs.

On the basis of the results obtained, a feasible reason for the difference in the stabilities between iPP and sPP is considered to be as follows. Since the tertiary hydrogen in the sPP is located on the opposite side of the adjacent tertiary hydrogen, the scission of the main chain may hardly proceed even if the radical formation occurs on a tertiary hydrogen. In other words, this indicates that the stereoregularity is a dominant factor in PP degradation due to the reactivity of the peroxide radical. The effect of stereoregularity on thermal degradation of PP was also investigated by means of chemiluminescence, in which the difference in the signals between iPP and sPP was observed.[5]

Effect of Incorporation of Ethylene on Thermal Stability of iPP

Since the introduction of ethylene, which has no tertiary carbon atoms, effectively removes the reactive tertiary carbon atoms from the PP backbone, the modification of the primary structure of iPP by copolymerization with ethylene also seems to be an effective method for improving thermal stability. Therefore, the thermal stability of iPP and ethylene-propylene random copolymer (rPP) with a low ethylene content was investigated as a function of their primary structure.

The characteristics of iPP and rPP are summarized in Table II. In this study, very close molecular weight and molecular weight distribution of iPP and rPP were used.

Table II. Characteristics of iPP and rPP

Sample	$\overline{M}$	$\overline{M}w / \overline{M}$	mmmm	Et cont.[a)] mol
iP	48,000	5.7	99	—
rP	41,00	6.	93	5.3

a) Ethylene content in polypropylene

Fig. 5 showed the heat treatment time dependence of the GPC curves of iPP and rPP. The curve shift between the virgin PP and the degraded one was shown. The curves of both PPs were shifted towards lower molecular weight with the heat treatment time. However, the rate of decrease in the molecular weight of rPP is considerably slower than that of iPP, implying that rPP has a higher thermal stability.

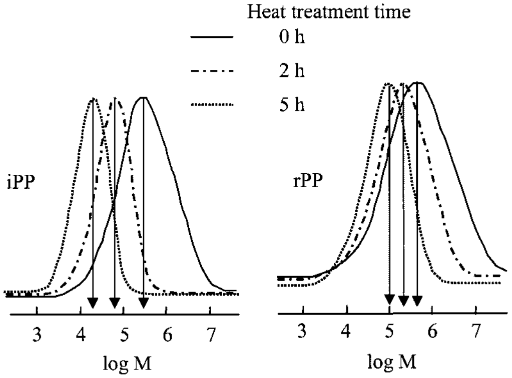

Fig. 5: GPC curves of heat treated PPs at 180 °C in air.

The PP degradation chemistry is believed to propagate by a free radical chain reaction. 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 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 degradation. The existence of the secondary C-H in rPP seems to depress the chain reaction of the hydroperoxide regardless of its low content of ethylene.[8]

Conclusions

In this study, the thermal degradation behavior of PPs with a variety of tacticities and ethylene incorporation was investigated as a function of the primary structure in order to improve the stability of PP. The sPP and rPP showed better stability compared to iPP.

The stability of PP was found to be greatly improved by the modification of the primary structure, such as stereoregularity and comonomer incorporation.

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