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Description	Supervisor: Prof. Dr. Minoru Terano, 材料科学研究科, 博士

Investigation of the Mechanism of Thermo-Oxidative Degradation of Polypropylenes with a Variety of Primary Structures

Tomoyuki Hatanaka

*School of Materials Science,
Japan Advanced Institute of Science and Technology*

(Supervised by Prof. Dr. Minoru Terano)

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Abstract

Thermo-oxidative degradation of polypropylene(PP)s with a variety of tacticities was investigated in terms of various degradation factors, such as catalyst residue in the PP and molecular weight of the PP. The key concept of this study was to investigate the influence of individual factors by choosing suitable PP samples and appropriate conditions, where other factors can be negligible. Heat treatment was typically carried out in air at 200 °C for 30 min, where the PP powder was converted into a molten state within several minutes. The catalyst residue and molecular weight had only a slight influence on the thermo-oxidative degradation of isotactic PP (iso-PP). The thermal stabilities of two PPs (iso-PP, atactic PP (ata-PP)) having similar molecular weights were investigated under the same conditions. The degradation of iso-PP was found to proceed significantly, while the degradation behavior was not remarkable in the case of ata-PP. In iso-PP, methyl groups are located on one side of the plane of the carbon-to-carbon main chain, and most of the configurational repeating units have a meso-configuration. Many racemic structures exist in ata-PP. It seems reasonable to assume that the thermo-oxidative degradation is depressed significantly due to the existence of the racemic structure in ata-PP. In order to clarify this assumption, the thermal stability of syndiotactic PP (syn-PP), which is composed of the racemic structure, was investigated under the same conditions. There was no significant difference in the molecular weight of the syn-PP before and after the heat treatments. That is, the thermo-oxidative stability of syn-PP was appreciably higher than those of iso-PP and ata-PP. Thus, it is inferred that the good thermal stability of the syn-PP is mainly due to the presence of the racemic structure in the main chain.

On the basis of the results mentioned above, our feasible reasons for the difference in the stabilities between iso- and syn-PPs are denoted as follows. (1) Because the dissociation energy of the main chain differed between iso- and syn-PPs. (2) Because the scission of the main chain may hardly proceed, because the tertiary hydrogen atom in the syn-PP

is located on the opposite side of the adjacent tertiary hydrogen. With this in mind, the stability of PP with a variety of tacticities was investigated based on the results of theoretical calculations. Molecular dynamics was performed to clarify the former reason; a semiempirical calculation was performed to clarify the latter reason.

The molecular dynamics provides a specific interaction potential for nuclear motion. The molecular dynamics trajectory was computed using version 6.0 of Irix as provided by MSI Corporation. After iso- and syn-PPs having variations in the degree of polymerization were constructed, a force field was set for all polymers. The potential energy was first minimized using a conjugate gradient method. In spite of assuming similar structures between iso- and syn-PPs at 200 °C, the tendencies of the potential energy of these polymers are different. That of the iso-structure is higher than that of the syn-structure. Because the methyl group in the iso-structure is located on the near side of the adjacent methyl group, excess energy is required in order to remove the steric hindrance of the sidechain. Thus, the extra energy is stored in the case of the iso-structure of the polymer compared to that of the syn-structure. This means that the iso-structure has a more unstable structure than does the syn-structure. The correlation between the degree of polymerization of PP and its potential energy was also discussed. The values of the energy tended to increase with the increasing degree of polymerization of iso-PP. On the other hand, the values of the energy were almost the same in syn-PP with variation in the degree of polymerization. These results indicated that the potential energy was independent of the degree of polymerization of syn-PP. Thus it is suggested that the influence of the degree of polymerization is remarkable only in iso-PP.

The semiempirical calculation (MOPAC) provides a good estimation of the heats of atomization using a quantum mechanical treatment with practical chemical parameters. The PM3 method was useful for the simulation of a hydrogen bond, and the Unrestricted-Hartree-Fock method was useful for the radical reaction. The key reaction steps during the oxidative degradation of (R,S)- and (R,R)-2,4-diethylpentanes, which are model compounds of iso- and syn-PPs, were investigated using the semiempirical method, PM3. The following reaction paths were calculated: (I); formation of a peroxy radical by reaction of a tertiary carbon radical with a free oxygen molecule, (II); abstraction of a tertiary hydrogen atom to give hydroperoxide, (III); decomposition of hydroperoxide to produce an alkoxy radical and a tertiary carbon radical, and (IV); formation of a carbonyl group by a main-chain scission reaction. A significant difference in the activation energy between the (R,R)- and (R,S)-2,4-diethylpentanes was observed during the hydrogen atom abstraction step (II), while the other three steps showed little or no energy differences. The tertiary hydrogen atom abstraction and successive reactions were found to predominantly proceed compared with the reaction path including the methylene hydrogen atom abstraction. In the tertiary hydrogen atom abstraction step, the activation energy for the (R,R)-structure was found to be considerably higher than that for the (R,S)-structure. These results meant that the hydrogen atom abstraction only slightly proceeded in syn-PP compared to iso-PP.

Based on the results of the theoretical calculations, it was suggested that both factors affected the difference in the stabilities between iso- and syn-PPs. In order to determine

the most serious factor, the influence of atmosphere was investigated on the dissolved iso- and syn-PPs at 140 °C in *o*-dichlorobenzene. It was clear that iso-PP degrades in the absence of oxygen, while syn-PP did not degrade under the same condition. If the relative stabilities of the carbon-carbon bond in the main chains act predominantly, the degradation behavior of PP should be independent of oxygen. However, the results obtained in this study indicated the profound contribution of oxygen to the relative stabilities of PPs with a variety of tacticities. In a word, this indicates the superiority of the influence of the peroxy radical reactivity, compared with the effect of steric hindrance.

Publication list

- [1] H. Mori, T. Hatanaka, and M. Terano: "Thermal Stability of Syndiotactic Polypropylene" *Macromol. Rapid Commun.* **18**,157 (1997).
- [2] H. Mori, T. Hatanaka, and M. Terano: "Thermo-Oxidative Degradation of Molten State Polypropylenes With a Variety of Tacticity" *Materials Life* **9**,180 (1997).
- [3] T. Hatanaka, H. Mori, and M. Terano: "Study of Thermo-Oxidative Degradation of Molten State Polypropylenes With a Variety of Tacticities" *Polym. Degrad. Stabil.*, *in press*.
- [4] T. Hatanaka, H. Mori, and M. Terano: "Semiempirical Calculation on the Oxidative Degradation of Polypropylene" *Polym. Degrad. Stabil.*, *accepted*.
- [5] T. Hatanaka, A. Tsuruta, H. Mori, and M. Terano: "Atmospheric Influence for Thermal Stability of Polypropylene with a Variety of the Primary Structure" *To be submitted*.
- [6] T. Hatanaka, A. Tsuruta, H. Mori, and M. Terano: "Kinetic Study of Thermo-Oxidative Degradation of Polypropylene with Variety of Primary Structure" *To be submitted*.

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