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| Title        | イソタクチックポリプロピレンへのエチレン導入が光及び熱酸化劣化に与える影響   |
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## **Abstract**

**Polypropylene has different tacticity and various crystalline forms which affect its overall performance. According to its stereoregularity, polypropylene (PP) can be divided into isotactic PP (iPP), atactic PP (aPP) and syndiotactic PP (sPP). Among them, iPP has been widely used in the world as medical goods, fibres, rapping films etc.. However, iPP, which has methine protons, is very vulnerable to oxidative degradation under the influence of elevated temperature and light irradiation. The oxidative degradation of iPP 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 iPP, and the effect of varying the primary structure on this radical reaction has not been clarified until now. Therefore, to study on oxidative degradation behavior of iPP as a function of varying primary structure is indispensable. However, it is generally accepted that the chain scission reaction is responsible for degradation in polymer mechanical properties which causes curtailment of useful life. Therefore, to keep the long-term performance of iPP, it must inhibit the radical formation reaction. The addition of stabilizers is widely used to inhibit the radical reaction. However, the stabilizers have the disadvantages of limited long-term application and highly expensive. Therefore, in order to suppress the radical reaction during long-term use as improvement of oxidative stability, the modification of primary structure of iPP itself is required. The result of this investigation will be useful to achieve new information about the oxidation reaction mechanism of iPP and will make possible to improve the oxidative stability. Thus, it can be responded to social requirements.**

**The modification of the primary structure of iPP by the incorporation of ethylene may be an effective method for improving its oxidative stability. The introduction of ethylene effectively reduces the reactive tertiary carbon atoms in the polymer backbone. Therefore, in this investigation, to know the effect of the incorporation of ethylene which changes the primary structure on the oxidative stability of iPP with the aim of improving of the oxidative stability is studied.**

**The iPP incorporated with low content of ethylene as a random manner**

(rPP) still has a semi-crystalline character. Therefore, to investigate the effect of ethylene incorporation in PP as improvement of oxidative stability, iPP and rPP samples were studied in terms of photo and thermal degradation. The degradation behavior was estimated by IR (infrared spectroscopy), GPC (gel permeation chromatography) and TREF (temperature rising elution fractionation) measurements.

The photo-oxidative degradation was carried out in a weather meter. The irradiation time was changed up to 192 h at 336 K. In the solid state, the oxidative degradation is affected by the crystallinity. Therefore, to eliminate the crystallinity effect, thin films of iPP and rPP samples with the same crystallinity and molecular weight distribution (MWD) were used.

The oxidative degradation of PP is regarded to proceed by a free-radical chain mechanism to form a carbonyl group via a reaction involving hydroperoxide group formation.

The hydroperoxide and carbonyl concentrations in irradiated iPP film increased against irradiation time for more than 192 h, whereas those in the irradiated rPP were almost constant over 96 h. Also the molecular weight of irradiated rPP did not change over this time, suggesting that the radical reaction in irradiated rPP was terminated over 96 h.

The thermo-oxidative degradation was carried out in solution at 453 K under the various oxygen concentrations up to 5 h. Thus, this method is suitable to discuss the effect of single polymer chain on degradation. The degree of degradation was evaluated by changing the molecular weight and MWD. The shape of MWD was changed by the scission of longer chain in iPP and rPP with the increasing degradation time and oxygen concentration. However, the chain scission in rPP is lower than in iPP.

These results reveal that the incorporation of ethylene is effective for the depression of iPP degradation rate by changing the pathway of chain scission.

The feasible reasons for the difference in the stability between iPP and rPP samples denoted as follows:

The chain scission reaction is known to proceed by two alternative pathways as main or side chain scission during degradation. The main chain

scission reaction occurred in iPP in respect of lower bond energy in main chain (185 KJ/mol) estimated by the MOPAC calculation (Cambridge Soft Corp., Chem 3D Pro Ver. 3.51) and regarding of higher bond energy (190 KJ/mol) side chain scission proceeded in rPP. End-chain ketone formed in iPP would predominate as a result of chain scission, whereas in-chain ketone in rPP does not involve chain scission. As the end-chain and in-chain ketone formation the difference in the distribution of crystallizability was observed by TREF analysis. The shape of the TREF curve in iPP is maintained, which indicates there are little in-chain ketone units in the polymer chain, whereas the shape of the TREF curve in the rPP is changed, indicating that the in-chain ketone units certainly exist in the polymer chain.

However, it is difficult to directly discriminate the existence of peak location for the in-chain and end-chain ketones by IR measurement because they overlap each other. Heat treatment effect on irradiated samples eliminated this limitation by accelerating the degradation of irradiated samples as a result of different final product formation. In the case of iPP, heat treatment caused low molecular weight products with volatility, whereas in the case of rPP, it caused the formation of ester groups. The arising of ester indicates that rPP is hardly decomposed to low molecular weight products with volatility.

Based on the results obtained in this study, a state-of-the-art designing of tailor-made polypropylenes with ultimate stability can be expected in the near future under persistent effort in this direction.