

Title	チーグラナータ触媒を用いたポリプロピレンの酸化劣化初期におけるラジカル生成機構の検討
Author(s)	飛田, 泰良
Citation	
Issue Date	2017-03
Type	Thesis or Dissertation
Text version	ETD
URL	<a href="http://hdl.handle.net/10119/14259">http://hdl.handle.net/10119/14259</a>
Rights	
Description	Supervisor: 寺野 稔, マテリアルサイエンス研究科, 博士

## **Initial oxidative degradation of polypropylene through radical formation during polymerization**

Taira TOBITA

1440010

Polypropylene (PP) has been widely used in various industrial fields because of its wide variety of characteristics. However, the oxidative degradation of PP easily proceeds, which leads to poor mechanical properties and limits its long-term applications. While the degradation of PP has been well studied in terms of reaction intermediates and structural factors that influence the rate of degradation, the origin of initial radicals has been long overlooked despite the fact that their presence triggers the auto-oxidation. The objective of this dissertation is to enhance an innovative technology for the low-additive stabilization or for more high stability of PP, investigation of the origin of initial radical during polymerization was performed. In addition, to extend the stability of PP by progress control of the initial oxidative degradation, a radical trapping approach with nitroxide compounds as a radical scavenger was also performed.

In chapter 2, the impacts of polymerization parameters on the lifetime of as-synthesized PP reactor powder were investigated. Propylene polymerization conditions were varied and the OIT of the obtained polymers were analyzed by CL analysis. All results which the impacts of polymerization parameters on the lifetime of polymer were laid in the same correlation line between polymerization yield and OIT. PP powder obtained at high yield conditions exhibited shorter lifetime than polymer obtained at low yield conditions, regardless the lower concentration of catalyst residues. These results suggested that initial radicals were already formed in polymerization. Polypropylene produced under a higher yield condition exhibited a shorter lifetime with a larger amount of oxidative products after air exposure, suggesting the presence of a larger amount of initial radicals. The addition of a nitroxide radical trapping agent drastically enhanced the stability of as-synthesized polymer by passivating the initially formed radicals. Different experimentation approaches revealed that initial radicals are plausibly formed in polymerization.

In chapter 3, in order to prove the presence of initial radicals and stabilize as-synthesized PP, a radical trapping strategy using nitroxide radical trapping agent was applied. It was found that the lifetime of as-synthesized PP significantly increased in the presence of nitroxide trapping agent (TEMPO), indicating the suppression of peroxy radical formation by grafting of TEMPO to initial radicals. It was also showed that these factors which can mislead the results were removed by polymer washing and catalyst extraction. PP produced at higher polymerization yield showed the higher lifetime improvement and the higher amount of TEMPO was required to reach the maximum lifetime. Using a calibration curve synthesized with PP and BPEA, quantitative determination with profluorescence nitroxide (PFN) in polymer by fluorescence spectrophotometer was performed, the result of the concentration of PFN in PP functionalized with PFN was proved the the presence of initial radicals in PP. From these results, the presence of initial radicals were successfully proved and stabilized as-synthesized PP by a radical trapping strategy using nitroxide radical trapping agent.

In this dissertation, the investigation of the origin of initial radical during polymerization was performed. These results showed a the possibility of enhancing an innovative technology for the new stabilization strategy and applications by functionalization was provided.

**KEYWORD:** polypropylene / Ziegler-Natta catalyst / oxidative degradation / radical trapping agent / TEMPO / initial radicals