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Initiation of oxidative degradation in polypropylene reactor powder produced by Ziegler-Natta catalyst

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ABSTRACT

The oxidative degradation of polypropylene reactor powder was studied to clarify the origin of initial radicals that trigger auto-oxidation. Polymerization conditions were found to have direct impacts on the stability of as-synthesized polymer irrespective of catalyst residues and polymer structures. 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.

1. Introduction

Despite being one of the most versatile and widely used plastics, the susceptibility to oxidative degradation is one of the biggest shortfalls of polypropylene (PP). Generally, the oxidative degradation of PP follows a so-called auto-oxidation mechanism [1–3], which is initiated by the formation of radicals on tertiary carbon atoms. Once the radicals are formed, they spontaneously react with atmospheric oxygen to produce peroxy radicals before splitting into hydroperoxides and new radicals through the abstraction of hydrogen atoms from proximate tertiary carbons. The decomposition of hydroperoxides results in a decrease of the molecular weight from macromolecular chain scission, leaving acetyl groups and radicals at the chain ends of the fragments. In this way, the concentration of radicals increases exponentially to accelerate the degradation of PP.

A combination of stabilizers is added during pelletizing and additionally on-site to synergistically interrupt the auto-oxidation cycle: hindered phenol- and hindered amine-based stabilizers scavenge radicals, while phosphate- and thioether-based stabilizers decompose hydroperoxides. Accordingly, the PP lifetime can be extended by optimizing the amount and the combination of stabilizers for each specific purpose [4]. Further, a variety of new stabilizers have been developed to improve the stabilizing efficiency per addition [5]. Nonetheless, increasing trends for an environmental conservation require even a longer lifetime of PP for improved recyclability and an innovative stabilization technology that can omit an energetically demanding pelletization process. An in-reactor stabilization technology, which adds “passivated” stabilizers in olefin polymerization, is such a potential technology [6,7].

In order to develop an innovative stabilization technology, an understanding on how auto-oxidation initiates and promotes is essential. A number of researches have been focused to elucidate a mechanistic aspect of the auto-oxidative degradation such as the identification of reaction intermediates, products, and related reaction pathways in the auto-oxidation cycle [8–10], the influence of catalyst residues or inorganic fillers [11,12], and the influence of polymer primary/higher-order structures on the polymer degradation [13–15]. These efforts enriched the understanding on how the degradation progresses and spreads, but the answer on how the degradation initiates has not yet reached a consensus in spite of the fact that initially formed radicals trigger the auto-oxidation cycle. While the oxidative degradation of unstabilized PP easily initiates and progresses under heat, a longstanding controversy lies in the too high C—H dissociation energy (at least 410 kJ/mol for a tertiary carbon of PP) compared with available thermal energy [16]. A potential explanation for this controversy is a catalytic role of transition metal (*e.g.* Ti) that exists as a catalyst residue. However,

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recent studies have raised some clues for the origin of the initial radical. For example, Freund et al. and Cavallo et al. suggested a radical nature of a titanium halide and alkylaluminum system (*i.e.* Ziegler-Natta catalyst) [17,18]. Moreover, Malikova et al. reported an enhancement of PP lifetime when as-synthesized powder was heated under inert atmosphere [19]. In combination with the possibility of a local high temperature induced by exothermicity of polymerization [20], the above findings can raise a hypothesis that initial radicals may be formed during polymerization.

In this work, the oxidative degradation of PP reactor powder was investigated with an attention to the possibility of the initial radical formation during polymerization. It was found that the lifetime of as-synthesized powder was dominated by certain polymerization conditions, *i.e.* "how it was synthesized", rather than the concentration of catalyst residues and the polymer structures. The formation of peroxo species was detected when as-synthesized PP powder was exposed to air under mild condition without heating. Finally, we showed that the addition of a radical trapping agent can drastically enhance the lifetime of as-synthesized PP by passivating the initially formed radicals. All of these results suggested the initiation of degradation in polymerization.

2. Experiments

2.1. Materials

Propylene of research grade was donated by Japan Polypropylene Corporation and used without further purification. Triethylaluminum (TEA, donated by Tosoh Finechem Corporation), tri-*iso*-butylaluminum (TIBA, donated by Tosoh Finechem Corporation) and tri-*n*-octylaluminum (TNOA, Sigma-Aldrich Corporation) were used after diluting in heptane. *n*-Heptane and acetone were dried over 4A molecular sieve followed by N_2 bubbling prior to use. Cyclohexylmethyldimethoxysilane (CMDMS) was purified by distillation under reduced pressure. 2,2,6,6-tetramethylpiperidine 1-oxyl free radical (TEMPO, Sigma-Aldrich Corporation. LLC.) was used after diluting in heptane. A $TiCl_4$/di-*iso*-butylphthalate (DBP)/$MgCl_2$ catalyst was prepared using a spherical $Mg(OEt)_2$ precursor according to literature [21]. The Ti and DBP contents were measured as 3.4 wt% and 12 wt%, respectively.

2.2. Propylene polymerization

A series of propylene slurry polymerization were conducted using a $TiCl_4$/DBP/$MgCl_2$ catalyst. 400 mL of heptane as polymerization medium was introduced to a 1 L stainless steel reactor equipped with a mechanical stirrer rotating at 350 rpm. After propylene saturation at 0.3 MPa for 20 min, specified amounts of an alkylaluminum activator and CMDMS (an external donor) were added, where the Al/Si molar ratio was kept at 4.7. Thereafter, a specified amount of the catalyst was injected to the reactor to initiate polymerization at a desired temperature. Followed by the termination of polymerization with the addition of acetone, the slurry was transferred to a receiving flask kept under N_2 and as-synthesized powder was washed with 200 mL of heptane for three times followed by vacuum drying at room temperature. The obtained polymer was stored in dark under N_2 and controlled temperature. It must be noted that all of the procedures were carefully conducted under N_2 atmosphere in order to prevent the intrusion of air.

Table 1 summarizes all polymerization conditions employed in this study. The standard polymerization condition was as followed: polymerization time = 60 min, polymerization temperature = 30 °C, catalyst amount = 15 mg, type of activator = TEA, activator concentration = 5.0 mmol/L, and without the addition of H_2. In Runs 2–5, polymerization was conducted at the same condition as the standard except the fact that the polymerization time was varied from 20 to 100 min. The influences of the polymerization temperature (Runs 1,6–9), the activator concentration (Runs 1,12–15), the type of activator (Runs 1,16,17), and the catalyst amount (Runs 1,18–20) were also examined systematically. In Runs 8,10,11, 0–10 mmol of H_2 as a chain transfer agent was added before the catalyst injection, while the other conditions were kept at the standard one.

2.3. Treatment with TEMPO

Assuming the radical formation in polymerization, a radical trapping agent, TEMPO, was added to as-synthesized PP powder. After polymerization at 60 °C (Run 8), the slurry was transferred to a receiving flask without contacting to air and washed with 200 mL of heptane for three times to remove the alkylaluminum activator and external donor. Subsequently, 2.0 mmol of TEMPO dissolved in 2.0 mL of heptane was added and the polymer slurry was stirred for 12 h in dark at room temperature under N_2 atmosphere. Thereafter, PP powder was thoroughly washed with heptane in order to completely remove ungrafted TEMPO and dried in *vacuo* at room temperature. A comparable sample was also prepared in the same way except the fact that PP powder was once exposed to dry air at room temperature before the addition of TEMPO.

2.4. Chemiluminescence measurement

The detection of chemiluminescence (CL) that arises from the decomposition of peroxo species is known as one of the most sensitive methods to identify the oxidative degradation of PP. In CL measurements, PP powder can be held in a constant-temperature oven under dry air flow or under N_2. The former is utilized to measure the oxidative induction time (OIT), which is defined as the period till the auto-oxidative degradation initiates, while the latter is utilized to estimate the amount of peroxo species present in a polymer sample [22,23]. The CL measurements were conducted using a CL analyzer (CLA-ID-HS, Tohoku Electronic Industrial Co., Ltd.). In the case of the OIT measurement, 10 mg of a powder sample was filled in an aluminum pan under N_2 to minimize the exposure to air. The sample pan was transferred to a CL analyzer and held at 110 °C or 130 °C under dry air with the flow rate of 100 mL/min. As for the detection of peroxo species, the sample preparation was done in a similar way except the fact that the sample pan filled with PP powder was pre-exposed to dry air at room temperature for 10 min before the CL measurement at 150 °C under N_2 flow at the flow rate of 100 mL/min.

2.5. Polymer characterization

The molecular weight of PP was determined by a high-temperature gel permeation chromatography (HP-GPC, Malvern Instruments Ltd. Viscotek HT GPC module 350) equipped with polystyrene gel columns (Shodex GPC UT-806M and GPC UT-G) at 140 °C using *o*-dichlorobenzene as a solvent. The meso pentad (*mmmm*) and the concentration of unsaturated terminal groups were respectively measured by ^{13}C and ^{1}H NMR (Bruker 400 MHz) at 120 °C using 1,2,4-trichlorobenzene as a diluent and 1,1,2,2-tetrachloroethane-d_2 as an internal lock and reference.

3. Results and discussions

In seeking a possibility of the initial radical formation during