

Influence of isotacticity and its distribution on degradation behavior of polypropylene



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ABSTRACT

The influence of isotacticity and its distribution on the degradation behavior of polypropylene (PP) was examined on a series of PP fractions prepared with the aid of temperature rising elution fractionation technique. It was found that the length of the isotactic sequence predominantly decided the stability of PP fractions, where a faster propagation of oxidation occurred for PP chains with a longer isotactic sequence. Two PP fractions with different tacticity were mixed as the simplest model of polymer to examine the degradation behavior when the primary structure is distributed. It was found that even if two samples have the same average mesopentad, the details of the constituent differentiate their stability, which can be explained as a consequence of infectious degradation spreading.

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1. Introduction

An insight of materials response in their long-term use is essential for materials selection and design. Among thermoplastic polymers, the degradation of polyolefin has gained a special interest due to its interminable growth and expansion into a diversity of industrial sectors. Despite of a relatively high chemical stability and good abrasion resistance, the thermo-oxidative degradation of polyolefin is known to proceed from the pelletization thenceforth through the auto-oxidation [1,2]. Without the aid of stabilizers, the lifetime of polyolefin is too short to be devised in practical applications [3].

Understanding structural factors that are potentially related to the stability of polyolefin is an important target to control its degradation. Following the abstraction of hydrogen from polymer chains, the initially formed macroradicals readily react with atmospheric oxygen to form peroxide radicals, which can further subtract the adjacent hydrogen to form hydroperoxides and new macroradicals [1,2]. Hydroperoxides are regarded as an active intermediate as their decomposition leads to the destruction of polymer chains and the formation of low molecular weight products [4,5]. The rate of hydroperoxide formation depends on the ease

of the subtraction of the adjacent hydrogen by peroxy radicals, which depends on the dissociation energy and the steric hindrance [6,7]. The presence of tertiary carbons in polypropylene (PP) reduces the stability as compared to polyethylene (PE) due to a lower C–H dissociation energy [8,9]. Syndiotactic and atactic PP was reported to possess a higher stability as compared to isotactic PP [10–14], which was ascribed to a higher activation energy for hydrogen subtraction when the neighboring tertiary carbons were aligned in a racemic manner than in an isotactic manner [15]. The inclusion of chemical defects also affects the stability of polyolefin. For example, an interruption of an isotactic sequence of PP by ethylene comonomer, increased the stability of PP [16,17], while the presence of unsaturated chain ends promoted the oxidation [18–20]. Besides the structural factors, it is well accepted that the degradation of polyolefin is a spatially heterogeneous phenomenon. For instance, the destruction is locally initiated at weak areas, often at the proximity of metal contaminants [21,22], and then spreads to neighboring areas especially with lower stability via volatile degradation products [23–26]. In other words, an incidental inclusion of weak areas in the whole polymer infectious accelerates the oxidation of originally stable areas and lowers the stability of the whole polymer. This also holds true for the infectious degradation of two polymers having different original stability when they are brought into contact or even in the vicinity without contact [20,23,27,28]. Considering that polyolefin, especially when produced by a solid catalyst, is a mixture of

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macromolecules with different primary structures (*i.e.* different stability), the infectious degradation among these components would be unavoidable. Hence, it is difficult to individually investigate the influence of structural factors when a primary structure of a virgin polymer is distributed. Furthermore, it was recently reported that polyolefin is subjected to in-reactor degradation, in which the heat of polymerization and alkylaluminum were proposed as the main causes to induce radical formation [29]. Therefore, polymer obtained under different catalytic conditions can possess different stability even though their primary structures are regarded as identical.

In order to minimize undesired effects of the distribution of the primary structure as well as the history of the production, we revisited the influence of the isotacticity on the stability of PP using a series of samples fractionated from a single source of PP. The fractionated samples allowed not only to monitor the degradation of the same polymer with a narrower microstructure distribution, but also to examine how constituents in one polymer affect the lifetime of the whole polymer as a “blend”. We found that the stability of PP fractions was predominantly determined by the average length of their isotactic sequence. However, when two fractions with different tacticity were blended, the stability of the blend was not anymore decided by the average length of the isotactic sequence. Rather, the infectious interaction between two fractions governed the stability.

2. Experiments

2.1. Materials

Propylene of research grade was donated by Japan Polypropylene Co., Ltd. Anhydrous $MgCl_2$ and $TiCl_3$ were donated by Toho Titanium Co., Ltd. Toluene was purified by passing through a column of molecular sieve 13X followed by N_2 bubbling for 2 h prior to use. Triethylaluminum (TEA, donated by Tosoh Finechem Co.) was used after dilution in toluene. Xylene and *o*-dichlorobenzene (ODCB) were used in the presence of 0.03 wt% of 2,6-di-*tert*-butyl-*p*-cresol (BHT) as an anti-oxidant.

2.2. Catalyst preparation

A $TiCl_3$ -based Ziegler-Natta catalyst was prepared by a co-grinding method and employed in order to obtain PP with a broad tacticity distribution. $MgCl_2$ and $TiCl_3$ were added to a 1.2 L stainless steel vibration mill pot with 55 balls (25 mm diameter) under N_2 atmosphere. The grinding was conducted for 30 h at room temperature. The Ti content of the final catalyst was measured as 0.05 mmol-Ti g-cat⁻¹.

2.3. Polymerization

Propylene polymerization was conducted in a stirred three-neck round bottom flask. After sufficient N_2 replacement, toluene as a polymerization solvent was introduced and saturated with propylene at 30 °C and 1 atm for 30 min. Thereafter, TEA was added and the polymerization was initiated by the injection of the catalyst at the Al/Ti molar ratio of 3. Polymerization was continued at 30 °C and 1 atm for 10 min. The catalyst residue was removed by re-precipitation of polymer from xylene into methanol using the xylene/methanol volume ratio of 1/7. A re-precipitated sample was dried *in vacuo* at 60 °C for 3 h.

2.4. Preparation of PP fractions

The above obtained PP was fractionated based on temperature

rising elution fractionation (TREF, Senshu, SSC-7300) equipped with a Chromosorb packed column (10 mm in diameter and 30 cm in length, Celite Co.). ODCB was used as an eluent. Firstly, the TREF profile of the original PP was acquired: 70 mg of the PP sample was dissolved in 10 mL of ODCB at 140 °C. The solution was charged in the fractionation column, which was slowly cooled down from 140 °C to 20 °C at the cooling rate of 6.7 °C h⁻¹. The elution of precipitated PP was firstly carried out at 20 °C for 30 min to remove ODCB soluble fraction. Thereafter, the column was heated to 140 °C at the heating rate of 12 °C h⁻¹ and the flow rate of 2.5 mL min⁻¹. Next, based on the acquired TREF profile (Fig. 1), the original PP was fractionated into six fractions by a stepwise increment of temperature according to the elution temperature as follows: Fr1 (20–33 °C), Fr2 (33–55 °C), Fr3 (55–74 °C), Fr4 (74–90 °C), Fr5 (90–106 °C), and Fr6 (106–116 °C). All the fractions were re-precipitated using xylene/methanol.

2.5. Characterization

The molecular weight and the molecular weight distribution of PP were measured by gel-permeation chromatography (GPC, Senshu, SSC-9300) equipped with polystyrene gel columns (SHODEX, HT-806M). The measurement was conducted using ODCB as a solvent at 140 °C with the flow rate of 1 mL min⁻¹. The mesopentad (*mmmm*) of PP samples was measured by ¹³C NMR (Varian Gemini-300 Spectrometer, Varian Instruments Ltd.) at 120 °C using hexachloro-1,3-butadiene as a diluent, and 1,1,2,2-tetrachloroethane-d₂ as an internal lock and reference. The accumulation number was set to 7000 with the relaxation time of 5.2 s and the acquisition time of 0.8 s. The melting temperature (T_m) of a PP sample was acquired using differential scanning calorimetry (DSC, Mettler-Toledo DSC 820). T_m was determined from the melting endotherm in the first heating, where the sample was heated up to 200 °C at the heating rate of 20 °C min⁻¹ under the N_2 flow rate of 200 mL min⁻¹.

2.6. Thermal oxidative degradation

Thermal oxidative degradation was performed for each PP fraction at 130–150 °C under dry air flow at the flow rate of 100 mL min⁻¹. A chemiluminescence analyzer (CLA, Parkin CLAD2-HS) was used for an *in-situ* measurement of the thermal degradation. The induction time (t_i) was defined as a period of time without any strong chemiluminescence (CL) signal until the auto-oxidation starts. The oxidation time (t_{ox}) was defined as a period of time from the start of the auto-oxidation until the maximum CL intensity was reached.

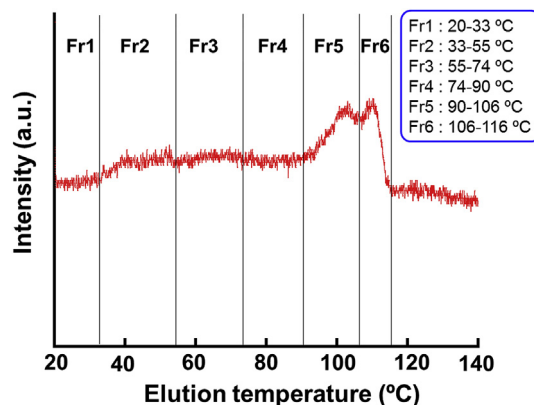


Fig. 1. TREF profile of as-synthesized PP and the fractionation scheme into six fractions.

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