

Stabilization of polypropylene reactor powder produced by Ziegler-Natta catalyst through passivation of initially formed radicals

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ABSTRACT

A radical trapping strategy using a nitroxide free radical was employed to extend the lifetime of polypropylene (PP) reactor powder. It was found that the addition of a radical trapping agent drastically enhanced the stability of PP reactor powder as long as as-synthesized PP was treated with a radical trapping agent before air exposure. These results suggested that the reactor powder was stabilized through the passivation of carbon-centered radicals present as initial radicals. The stabilization of initially formed radicals prevented the chain reactions from proceeding, thus proving the effectiveness of the new stabilization scheme.

KEYWORDS: polypropylene, Ziegler-Natta catalyst, oxidative degradation, radical trapping, TEMPO, initial radical

1. INTRODUCTION

Polyolefins, especially polypropylene (PP), are widely used in many industrial fields due to their wide range of properties and good cost-performance benefits. Various innovative technologies have been developed to improve polymer properties, which are regarded as a key factor for the continuous success in the market expansion. Until now, advanced polymerization processes and catalyst technologies are revolutionary developed to produce high

stereoregularity polymer with high productivity [1, 2]. Inorganic fillers are incorporated through compounding technologies to impart specific properties for specific applications [3, 4]. However, the usability of polyolefins with the improved performance and functionality can be only realized if their properties remain unchanged throughout the service time.

It is known that PP is susceptible to degradation *via* the so-called auto-oxidation mechanism [5, 6]. Starting from an abstraction of hydrogen atoms from tertiary carbons of PP backbone, alkyl radicals are formed and simultaneously react with atmospheric oxygen to form peroxy radicals. The peroxy radicals are stabilized by an abstraction of hydrogen atoms from proximate tertiary carbons and cleaved into hydroperoxides and new radicals. The decomposition of hydroperoxides results in macromolecular chain scission, generating acetyl groups and radicals at the chain ends of two fragments. Once the auto-oxidation cycle starts, the degradation of PP is accelerated, which deteriorates the polymer properties and shortens the lifetime.

A common way to suppress the progress of the oxidative deterioration is to disrupt the auto-oxidation cycle by the addition of stabilizers. For example, hindered phenol- and hindered amine-based stabilizers are effectively used to scavenge radicals, while phosphate- and thioether-based stabilizers are utilized to decompose hydroperoxides [7, 8]. Accordingly, two or more stabilizers are often

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combined in a synergistic way to decelerate the degradation [9], in which the lifetime of PP in finished products is determined by the efficiency and the retention time of stabilizers in PP. On the other hand, an excessive addition of stabilizers can give undesirable effects, such as blooming, fogging and discoloration [10, 11]. For applications in composites with inorganic fillers, stabilizers can migrate to the surface of hydrophilic fillers, thus reducing the stabilization efficiency and mechanical properties [12, 13]. These drawbacks have raised the necessity of an innovative technology for a low-additive or even additive-free stabilization.

While the degradation of PP has been well studied in terms of reaction intermediates and structural factors that influence the rate of degradation [14-18], the origin of initial radicals has been long overlooked despite the fact that their presence triggers the auto-oxidation cycle. Recently, we reported that the lifetime of PP reactor powder produced using a Ziegler-Natta catalyst was dominated by certain polymerization conditions, *i.e.* “how it was synthesized”, rather than the concentration of catalyst residues and the primary structures of polymer [19]. For instance, polymerization at a lower yield condition necessarily offered reactor powder with a longer lifetime in spite of a higher concentration of catalyst residues. These results suggested that initial radicals are plausibly formed during polymerization and their existence is responsible for the stability of the as-synthesized reactor powder. In order to establish a new scheme of a stabilization technology, one of the most effective ways is to stabilize these initially formed radicals.

In this study, a radical trapping strategy was applied to extend the lifetime of PP reactor powder. A nitroxide free radical, namely 2,2,6,6-tetramethylpiperidine 1-oxyl free radical (TEMPO), was utilized as a radical scavenger. TEMPO can couple with a carbon-centered radical to form a non-radical alkoxy amine product, thus preventing the propagation of initial radicals. We found that the addition of a radical trapping agent drastically enhanced the lifetime of as-synthesized PP, thus proving an effectiveness of the new stabilization scheme.

2. MATERIALS AND METHODS

2.1. Materials

n-Heptane, dichloromethane (DCM), methanol (MeOH) and acetone of research grade were purchased from Wako Pure Chemical Industries, Ltd. and used after passing through a column of 4A molecular sieve followed by N₂ bubbling. Propylene of polymerization grade (donated by Japan Polypropylene Co.) was used as received. Triethylaluminum (TEA, donated by Tosoh Finechem Co.) was used after diluting in heptane. Cyclohexylmethyldimethoxysilane (CMDMS) was purified by distillation under reduced pressure prior to use. 2,2,6,6-Tetramethylpiperidine-1-oxyl free radical (TEMPO, Sigma-Aldrich Co. LLC.), titanium tetrachloride (TiCl₄) and di-*iso*-butylphthalate (DBP) were used as received.

2.2. Catalyst synthesis

A TiCl₄/DBP/MgCl₂ catalyst was prepared based on a patent [20] using a spherical magnesium ethoxide precursor. The titanium and DBP contents were measured as 3.4 wt% and 12 wt%, respectively.

2.3. Propylene polymerization

400 mL of heptane as a polymerization solvent was introduced to a 1 L stainless steel reactor under N₂. After propylene saturation at 0.3 MPa for 30 min, 2.0 mmol of TEA as an activator and 0.4 mmol of CMDMS as an external donor were added. Thereafter, 15 mg of the catalyst was injected to the reactor to start polymerization. The polymerization was conducted at 30 °C and 60 °C under the total pressure of 0.3 MPa. After 60 min of polymerization, the slurry was transferred to a round bottom flask and repetitively washed with heptane under N₂ to remove alkylaluminum and external donor residues. As-synthesized PP powder was dried *in vacuo* at room temperature and stored in dark under N₂ blanking. All procedures and powder handling were carefully conducted under N₂ atmosphere to prevent an exposure of as-synthesized PP powder to air.

2.4. Stabilization of as-synthesized PP using a nitroxide radical trapping agent

After polymerization, the polymer slurry was transferred into a round bottom flask under N₂

atmosphere. A desired amount of TEMPO was added to the flask and the polymer slurry was left stirring for 24 h at room temperature. Thereafter, PP powder was repetitively washed with heptane and dried *in vacuo* at room temperature. The sample was denoted as PP/TEMPO. In order to remove the influence of alkylaluminum activator and external donor residues, another set of samples (denoted as PP-g-TEMPO) was also prepared by applying the repetitive washing of the polymer slurry with heptane prior to contact with TEMPO. The other steps were kept the same as for the preparation of PP/TEMPO.

2.5. Removal of free TEMPO and non-initial radical-grafted TEMPO

Free TEMPO solidified in the pores of PP powder and TEMPO which was grafted to non-initial radicals such as catalyst residues were removed to eliminate the influence of free TEMPO and non-initial radical-grafted TEMPO on the stability of PP. 0.1 g of PP-g-TEMPO powder was stirred in 100 mL of acetone for 1 h to dissolve solidified TEMPO and to allow the dissolution of catalyst residues. Subsequently, the polymer slurry was filtrated and dried under ambient condition (denoted as PP-g-TEMPO washing). In addition, the soxhlet extraction at room temperature with methanol and acetone was performed under N₂ atmosphere to improve the washing efficiency. The samples were denoted as PP-g-TEMPO (MeOH) and PP-g-TEMPO (Acetone), respectively.

2.6. Chemiluminescence analysis

Chemiluminescence (CL) analysis is one of the most sensitive methods to estimate the oxidation stability of a polymer by detecting the light emitted from the decomposition of peroxide species. The oxidative induction time (OIT) of a polymer, which is defined as the period till the auto-oxidative degradation initiates, can be measured in a constant-temperature oven under dry air flow. The CL measurements were conducted using a CL analyzer (CLA-ID-HS, Tohoku Electronic Industrial Co.), where 10 mg of a powder sample was held at 110 °C or 130 °C under dry air flow at the flow rate of 100 mL/min. The OIT value was determined from experimental records of CL intensity-time.

2.7. Electron paramagnetic resonance measurement

The presence of free TEMPO in PP reactor powder was observed by an X-band electron paramagnetic

resonance (EPR) spectroscopy. EPR spectra were recorded on a Magnetech, MiniScope MS 400. 3.0 mg of a powder sample was filled in a 50 μ L sample tube. The continuous waves were measured at 25 °C under air.

3. RESULTS AND DISCUSSION

In order to establish a more effective stabilization technology, an understanding of the origin of initial radicals that trigger the auto-oxidative degradation of PP is essential. In our previous work, the impact of polymerization conditions (such as polymerization temperature, polymerization time, alkylaluminum concentrations, and so on) on the lifetime of as-synthesized PP powder was investigated [19]. Surprisingly, the results revealed that the lifetime of reactor powder was dominated by polymerization conditions rather than the concentration of catalyst residue and the primary structures of polymer. Briefly, Ziegler-Natta propylene polymerization at a lower temperature offered reactor powder with a longer lifetime in spite of a lower polymer yield. The elongation of the polymerization time shortened the lifetime of reactor powder even though it lowered the concentration of catalyst residues in the product. Such an inverse relationship between polymer yield and OIT persisted in a series of experiments and led to a strong suggestion that radicals are already formed during polymerization with the aid of alkylaluminum and/or heat accumulated in the polymer particles. The dependence of polymerization conditions on the stability of as-synthesized PP, which has experienced neither thermal history nor air exposure, suggested that the initially formed radicals are responsible for the stability of as-synthesized PP.

It is well known that initial radicals trigger the auto-oxidation cycle and their chain reactions generate more radicals in an exponential way. The best way to improve the stability of PP is to passivate these initially formed radicals. A nitroxide radical with free electron delocalised over the N-O bond, such as TEMPO, is known to scavenge reactive alkyl radicals *via* an addition reaction to form alkoxyamine before decomposing into non-radical products (Fig.1) [21-23]. If carbon-centered radicals were presented in as-synthesized PP as initial radicals, they would be stabilized on contact with TEMPO.

In an attempt to improve the stability of PP through the passivation of initially formed radicals,

polymerization slurry was immediately quenched in the presence of TEMPO. It was found that the polymer stability drastically increased with the addition of TEMPO. In particular, the OIT values exceeded 40 h at the measured temperature of 110 °C for both of the PP samples synthesized at 30 °C and 60 °C (Fig. 2a). As a comparative sample, as-synthesized PP produced at 60 °C was once exposed to air for 10 min followed by contact with the same amount of TEMPO. However, no improvement in the stability was observed as indicated by a similar OIT value between PP-air-TEMPO and the original

PP powder (Fig. 2b). It should be noted that the OIT measurements were conducted at a higher temperature in this case to reduce the measurement time. These results indicated that TEMPO could be grafted only to carbon-centered radicals to endow the stabilization effect. The exposure of as-synthesized powder to air converted these initially formed radicals into oxidative species, thus disallowing the grafting with TEMPO due to an instability of reaction products [24, 25]. The influence of catalyst residues on the polymer stability was also examined by applying various washing methods to PP reactor powder produced at 60 °C. However, the results showed that the polymer stability hardly improved after the removal of catalyst residues by washing with MeOH, DCM, or even with acetone using soxhlet extraction at room temperature for 4 h (Fig. 2a). Thus, it is plausible that initial radicals that were formed during polymerization depict a greater impact on the stability of as-synthesized PP than the catalyst residues and the improvement of the polymer stability could be effectively done through the passivation of these initial radicals.

The influence of the amount of TEMPO added on the stability of as-synthesized PP produced at 60 °C was investigated. Fig. 3 shows that OIT increased monotonically with the increase in the amount of TEMPO added before reaching the plateau

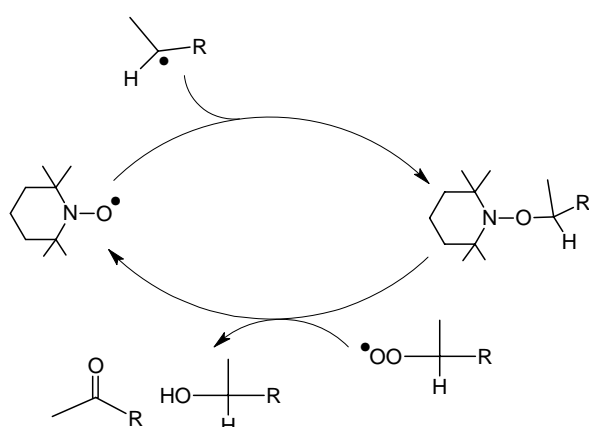


Fig. 1. Simplified mechanism of nitroxide radical scavenging.

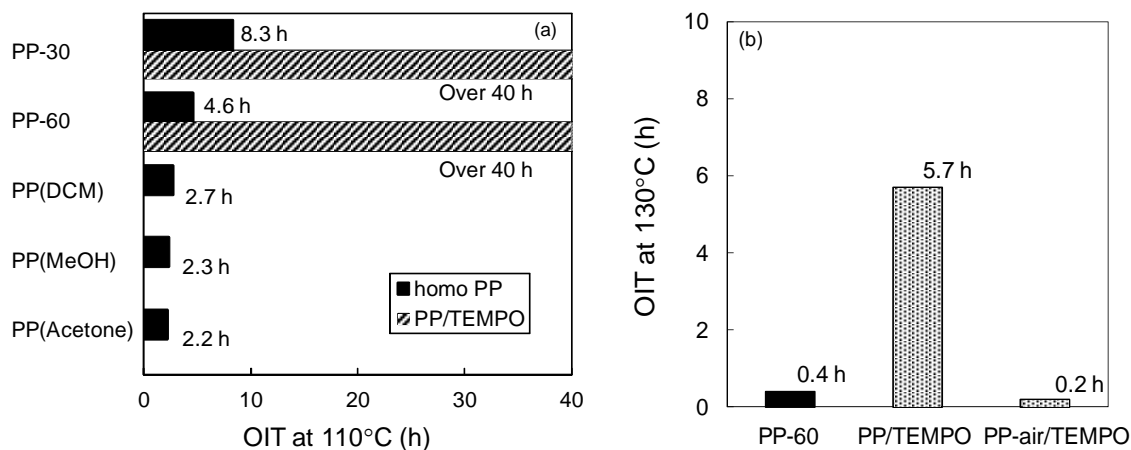


Fig. 2. The stability of as-synthesized PP powder: a) OIT of PP powder produced at 30 °C and 60 °C in the absence and presence of TEMPO treatment and OIT of PP powder produced at 60 °C after the removal of catalyst residues by various washing methods; b) The stabilization effect of TEMPO for as-synthesized PP and air-exposed PP produced at 60 °C.

(PP/TEMPO). The introduction of washing process after polymerization reduced the amount of TEMPO required to reach the similar level of OIT by about 10 times (PP-*g*-TEMPO). Potapov *et al.* performed the electron paramagnetic resonance (EPR) studies and reported that TEMPO did not react with alkylaluminum at room temperature [26]. However, the scavenging of impurities (such as moisture) contained in the polymerization solvent and the alkylation of a $\text{TiCl}_4/\text{MgCl}_2$ Ziegler-Natta catalyst by alkylaluminum lead to the formation of aluminium alkoxide [27] and alkylaluminium chloride [28], respectively, which might therefore

interact with TEMPO through the acid-base pair. Thus, it is reasonable that a considerable portion of TEMPO was consumed by polymerization residues.

Since TEMPO can be used to stabilize PP against degradation, the presence of free TEMPO molecules inside PP reactor powder could potentially bias the validity of stabilization through the initial radical trapping. Furthermore, TEMPO could also interact with acidic sites of $\text{TiCl}_4/\text{MgCl}_2$ Ziegler-Natta catalysts [29] and remain in the polymer. In order to completely remove free TEMPO as well as non-initial radical-grafted TEMPO, PP-*g*-TEMPO was repetitively washed with acetone. Fig. 4 shows

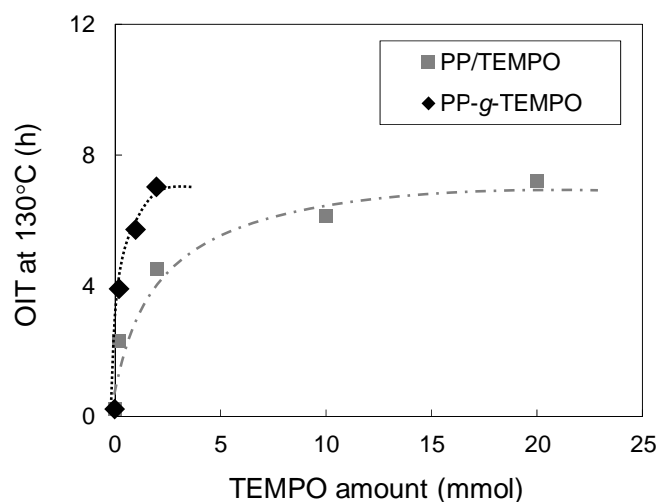


Fig. 3. Influence of the amount of TEMPO added on the stability of as-synthesized PP.

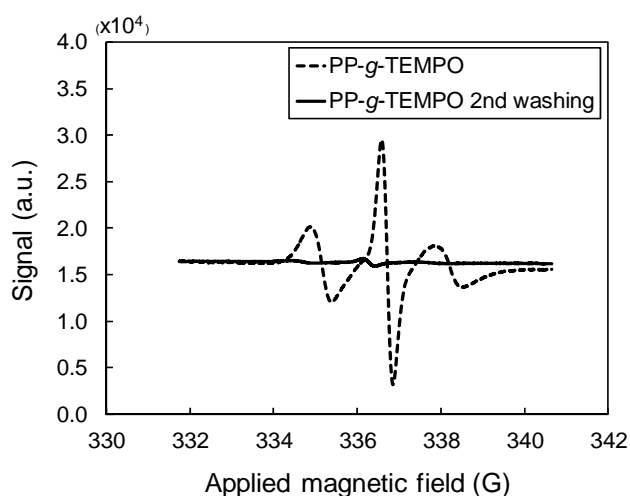


Fig. 4. EPR spectra of PP-*g*-TEMPO powder before and after washing with acetone.

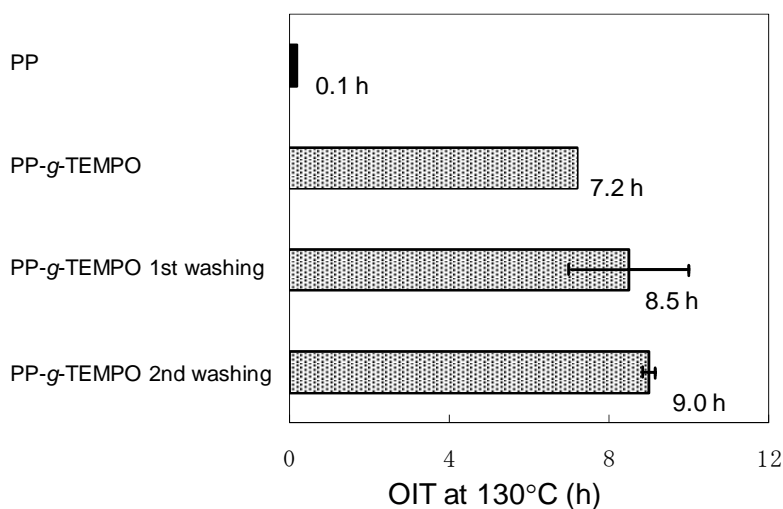


Fig. 5. Influence of free TEMPO removal by acetone washing on the stability of PP-g-TEMPO.

EPR spectra of PP-g-TEMPO before and after the second washing with acetone. It was found that the unwashed PP-g-TEMPO sample exhibited a strong signal corresponding to free TEMPO in the solid form. A signal corresponding to catalyst-grafted TEMPO was not observed in this case probably due to a trace amount. After the second acetone washing, free TEMPO was completely removed from the reactor powder as indicated by the absence of the EPR signal. Fig. 5 shows the OIT values of PP-g-TEMPO after the acetone washing. It can be seen that the stabilization effect in the presence of TEMPO persisted even after the complete removal of free TEMPO. These results clearly indicated that the stabilization effect did not originate from the free TEMPO remaining in the polymer samples.

In Fig. 6, the washing efficiency was further improved by applying the soxhlet extraction at room temperature. It can be seen that both acetone and methanol gave a similar OIT throughout the course of extraction time, indicating a similar efficiency of washing. It should be noted that the same soxhlet extraction using acetone was also applied to PP reactor powder to remove catalyst residues. Nonetheless, it never led to the improvement of PP stability (see Fig. 2a, PP(Acetone)). Likewise, the improvement of PP stability likely originated from the stabilization of initial radicals by TEMPO rather than the removal of catalyst residues. These results suggested that initial radicals could be

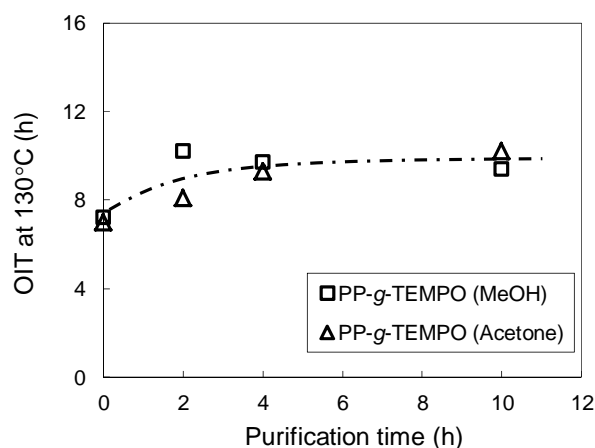


Fig. 6. Influence of soxhlet extraction time using methanol and acetone on the stability of PP-g-TEMPO.

successfully trapped and stabilized by a nitroxide radical trapping agent, thus providing as-synthesized PP with a longer lifetime.

4. CONCLUSION

A radical trapping strategy using a nitroxide free radical, TEMPO, was employed in this work to stabilize PP reactor powder. We found that the addition of TEMPO to as-synthesized PP powder significantly extended its lifetime. The same treatment never gave the stabilization effect if PP reactor powder was once exposed to air. Various washing methods were applied to completely remove

free TEMPO entrapped in the pores of the reactor powder. However, the stabilization effect from TEMPO treatment persisted, suggesting that the stabilization occurred through the trapping of carbon-centered radicals present in as-synthesized PP. Our results demonstrated that the passivation of initially formed radicals to prevent their chain reactions was an effective way to extend the lifetime of PP.

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CONFLICT OF INTEREST STATEMENT

The corresponding author had full access to all the data in the study and had the final responsibility in the decision to submit the manuscript for publication.

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