

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	http://hdl.handle.net/10119/14259
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**

by

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Submitted to

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March 2017

Preface

The present dissertation is the result of the studies under the direction of Professor Dr. Minoru Terano during 2015-2017. The purpose of this dissertation is a basis of the oxidative degradation mechanism of polypropylene materials. The fundamentals in the polypropylene chemistry related to degradation and stabilization is presented as a general introduction in the first chapter. Chapter 2 shows the approach for initial oxidative degradation of polypropylene materials by the examination of the effects of the polymerization conditions on the lifetime of polypropylene. Chapter 3 shows the radical trapping strategy using nitroxide radical scavenger to prove the initial radical formation during propylene polymerization and stabilized as-synthesized PP. The last chapter summarizes the conclusive items of this dissertation.

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Chapter 1

General Introduction

1.1. Polypropylene

1.1.1. Background

Polypropylene (PP) is one of the commodity plastics for industrial sections. Because it has characterized by excellent moldability, mechanical properties, chemical resistance, lightweight and inexpensively. In addition, PP is one of the plastic materials which can be reused and recycled due to simple molecular structure of PP consisting of carbon and hydrogen. On this account, the productive capacity of PP based materials in world has increased steadily. Ministry of Economy, Trade and Industry reported that productive capacity of PP based materials in world was 106.9 million tons in the end of 2010 [1]. Especially, the productive capacity of PP in some Asian countries, which had achieved a remarkable level of economic growth such as China and India, was projected to increase a 4-6% annual growth rate [2]. As has been noted, production volume of PP is expected to increase in world. Moreover, from viewpoint of environmental problems and issues of the recent years, as an alternative to the expensive and/or high environmental impact material, expansion of the use region of PP has been desired. From this kind of circumstance, PP based materials has been well studied. Currently, PP based material has been improved by the improved performance of PP resins which serve as the base of PP such as improvements in the

performance of polymerization process, and advancements in compound technology of inorganic fillers [3]. As a consequence, PP based materials has still attracted a lot of attention and is studied well.

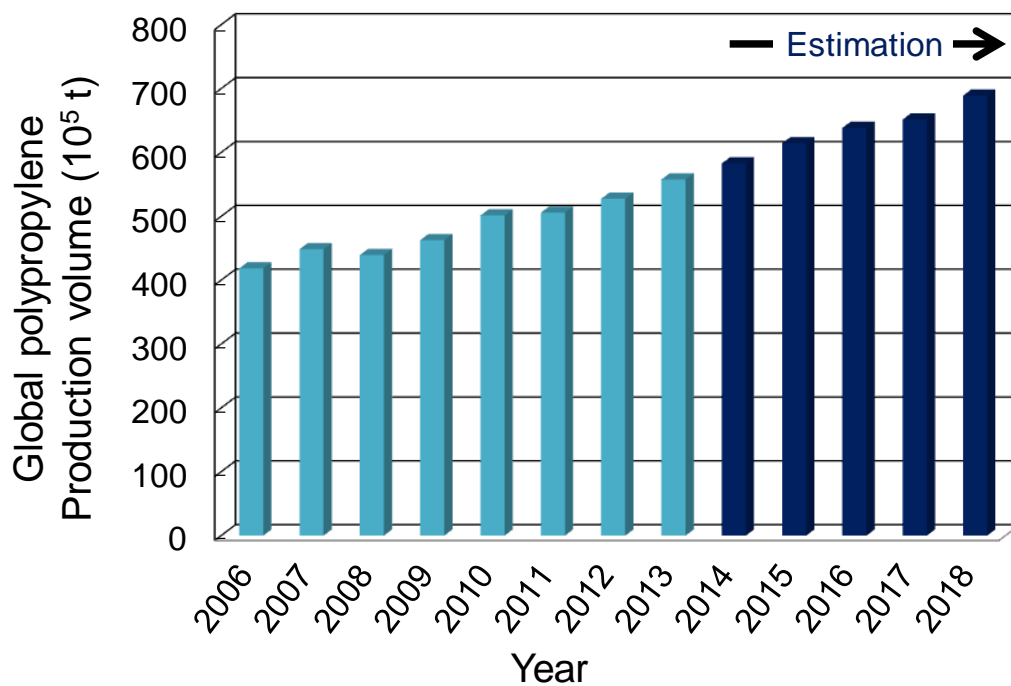


Figure 1.1 Global polypropylene production and the future trends [4].

Most of PP is produced by Ziegler-Natta catalysts in industrial manufacturing, because PP synthesized by Ziegler-Natta catalysts is cheaper and able to show broad range of mechanical properties. Mechanical properties of PP homopolymer are depended not only molecular weight and molecular weight distribution but also

stereoregularity. The properties of PP were dominated by the repeating units of the carbons in terms of meso (*m*) and racemo (*r*). The structures completely composed of *m*, *r* and random sequences are defined as isotactic, syndiotactic and atactic, respectively (Figure 1.2). In the industrial fields, isotactic PP is produced the most in the world, and it is showed the relatively high crystallinity from 40 to 70 %. Even to this day, research on scientific and industrial approach for PP such as the structure, processing and mechanical properties has been carried out.

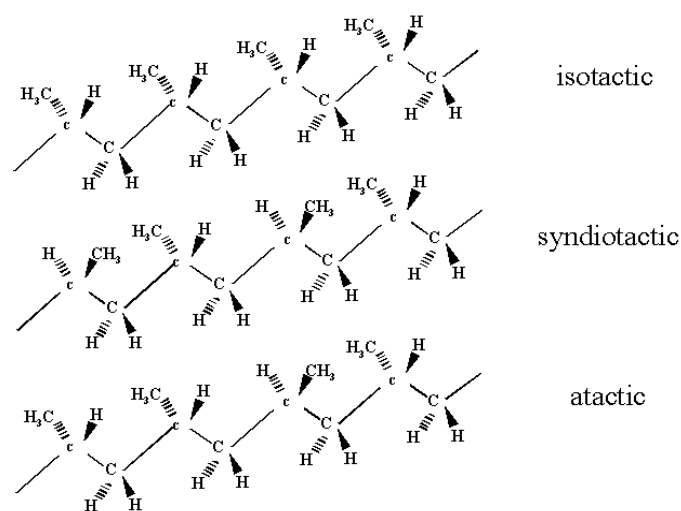


Figure 1.2. The type of PP stereoregularity

1.1.3. Ziegler Natta catalyst

Ziegler-Natta catalyst is a one of industrial catalyst for polyolefin manufacturing. Especially, this catalyst is used for 99% of PP production in industry. From the following importance of PP in the world, this catalyst comes to have very important role of industrial field. Ziegler-Natta catalyst in the early generation showed low productivities and stereo-specificity. Thus, both separation of the atactic PP fraction and removal of the catalyst residues were required, increasing the complexity and cost of the production process [5] . Until now, many research about Ziegler-Natta catalyst in scientific and industrial had been performed. At the present time, by the investigation regarding research directed toward research in external and internal donor such as aromatic mono ester compound and development of $MgCl_2$ supported Ziegler-Natta catalyst with alkylaluminum as an activator, PP production process with Ziegler-Natta catalyst was revolutionary developed, which showed high stereoregularity and low catalyst residues.

1.2. Degradation and stabilization of polymer

1.2.1. Background

Degradation of materials is generally defined that the material unable to provide quality or strength for practical use though reducing the property of material gradually undergo physical and chemical interaction in various environments. Especially, the degradation of polymeric material shows that the polymer unable to provide physical and chemical property for practical use though gradual reducing the molecular weight in various environments such as light heat [6].

The factors of polymeric material degradation are roughly divided into the external factors from natural environments and the structural factors from primarily and higher-order structure. External factors of polymeric material degradation are these factors which come from natural environments in practical usage such as heat, light, radiation, mechanical interaction, chemicals interaction, moisture, microorganisms and so on. In addition, the presence or absence of oxygen strongly effects the degradation phenomenon of polymer due to easily proceeds of the oxidative reaction with oxygen molecule. On the other hands, structural factors of polymeric material degradation are these factors constituting the molecular or atom in polymer and higher-order structure such as functional group, stereoregularity, hydrophobicity, unsaturation group, catalyst

residues, crystallinity and so on. Degradation of the polymer materials is extremely complicated, because these degradation phenomenon are proceeded reciprocally and intricately under natural environments [7].

PP is also one of the polymeric material that easily undergoes oxidative degradation, which leads to deterioration of mechanical properties. Degradation of PP constitute the topic of an enormous number of publications, because of their significant importance in practical use and scientific relevance.

1.2.2. Degradation of Polypropylene

Development of the art of stabilization and degradation into a science book took place rapidly after Hoffman reported in 1861 that degradation of natural rubber was accompanied by absorption of oxygen [8]. This report triggered the development of the research on the degradation mechanism of polymer. The degradation of PP basically resulted from the variation of primary structure by the chemical reaction of polymer chain and the variation higher-order structure of macromolecule. Besides, the degradation of PP is, same as low molecular, progress while the reaction with disconnection of polymer main chain, desorption and substitution of atom or molecules. However, in the case of polymer such as PP, these reaction is heterogeneous reaction

from the microscopic point of view, because of the influence of stereoregularity of primary and higher-order structure such as stereoregularity, presence of catalyst residues and distribution of the crystal region (Figure 1.3.) [9]. Additionally, it is said that few amount of double bond and branched structure, traces of metal from the catalyst residue are involved in the degradation process [10].

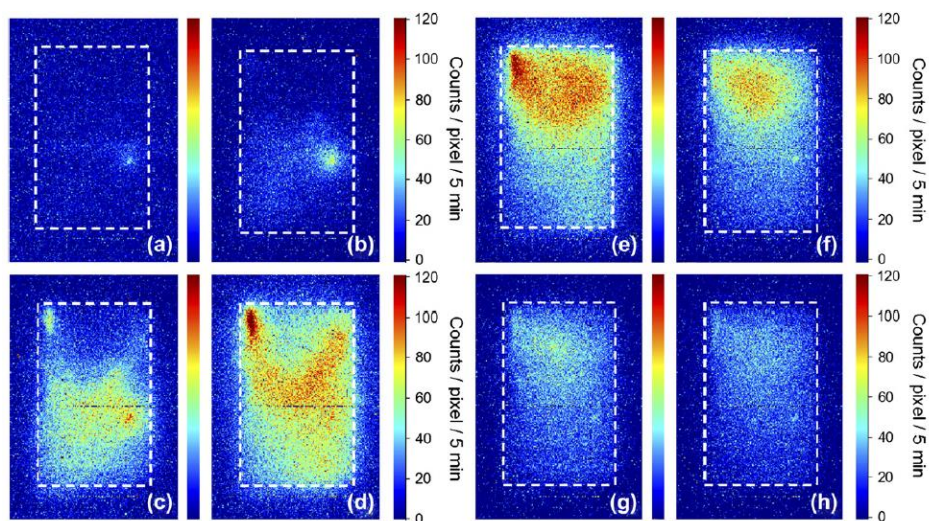


Figure 1.3. Time-resolved CL images of PP during heterogeneous oxidative degradation at 150 °C. (a) 5 min; (b) 10 min; (c) 15 min; (d) 20 min [11] .

The progress of oxidative degradation of PP in the presence of oxygen is easily proceed, due to high reactivity of oxygen molecular with active-site of reaction on the main chain. Generally, the oxidation is preceded according to the auto-oxidative degradation mechanism (Scheme 1.1).

It was said that the auto-oxidative degradation is initiated when alkyl radicals are formed on carbon atoms (Scheme 1. 4. (A)). Especially, the oxidative degradation of PP is easily proceed compared with polyethylene due to the presence of carbon atom in polymer main chain. Once the radicals are formed, they react with oxygen and produce peroxide radicals (Scheme 1. 4. (B)). Because of low bond dissociation energy of oxygen-oxygen bonds, produced hydroperoxide easily desorption and re-generate new radicals (Scheme 1. 4. (D, E)). In addition, alkoxy radicals not only generate (Scheme 1. 4. (F)) but also cause chain scission (Scheme 1. 4. (H)) . Therefore, the progress of oxidative degradation of PP was accelerated. Besides, oxidation infection to spread from the oxidation region to the region easily oxidized and unoxidized [12]. The physical and chemical properties of PP were descend from the higher-order structure, though the molecular structures. Thus, the reducing the molecular weight though the chain scission strongly effects on the properties. Hence, because of not only the change of primary structure but also the change of high-order structure such as reducing the crystallinity, it causes low mechanical properties, yellowing and cracking [13].

Chain initiation



Chain propagation and branching



Chain break



Scheme 1.1. Auto-oxidative degradation mechanism

A number of researches have been well studied the degradation of PP. The focus of these studies was mainly based on issues such as i) the identification of reaction intermediates, products, and related reaction pathways in the auto-oxidation cycle [14-16], ii) the evaluation of influences of catalyst residuals or inorganic fillers on the lifetime of the polymer [17,18], iii) the understanding of the spatial distribution of the degradation aimed at establishing relationships between polymer primary or higher-order structures and the lifetime [19-21], and so on.

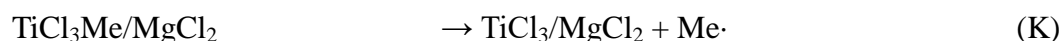
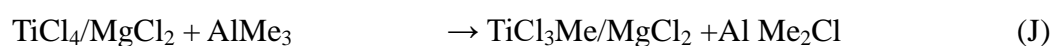
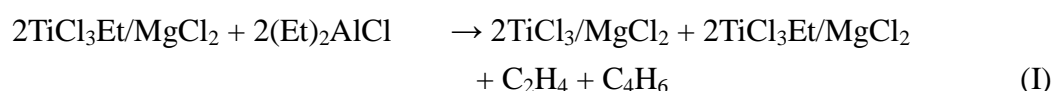
As has been noted that the oxidation mechanism of PP has been studied by many researchers. These studies were essential for fulfilling the understanding of how the degradation of PP progresses and spreads from an academic point of view.

1.2.3. Origin of oxidative degradation

Generally, the initial reaction of degradation has been started from alkyl radical reaction which is produced through hydrogen desorption at tertiary carbon, and then polymer oxidation proceeds according to the ‘auto-oxidative degradation mechanism’. While the oxidative degradation of PP easily progresses and spreads under heat and light, a longstanding controversy lies in the too high C-H dissociation energy (at least 410 kJ/mol for ternary carbon of PP) compared with available thermal and light energies. Moreover, it is necessary to form initial radicals by only thermal or light which the light in the ultraviolet region that is not included in the sunlight ,or the high temperatures for decomposition of (about 400 °C or more). Therefore, initial radicals formation was caused by the effects of error structures and metal compound (such as few amount of double bond, vinyl end group, and/or catalyst residue) which worked as an active-site of degradation under high temperature during the molding process.

Recently, Malicova *et. al.* reported that heating reactor powder of PP in nitrogen atmosphere greatly enhances its lifetime [22]. That report enabled us to reach an idea that “radical may be formed during polymerization”. They reported that heating reactor powder of polypropylene in an ambient atmosphere greatly enhances its

lifetime, which has enabled us to reach an idea that “radicals may be formed during polymerization”. It may be possible that a local high temperature, induced by exothermicity of reaction prominently played a role in the initial radical formation during polymerization. Kosek *et al.* was reported that temperature inside growing polymer particles can shoot much beyond the melting temperature within 10 s if the full activity is reached in dynamic simulation [23]. Moreover, Freund and Cavallo suggested a radical nature of reaction pathways associated with alkyl aluminum compounds [24,25]. There is a reaction of (H-K) is expected that these reactions research by Freund and Cavallo.



So, there is a reaction of (J) is expected.



No report that $\text{AlEt}_3\text{Cl}\cdot$ has not been observed during polymerization, it was possibility

that the reaction of (J) was also occur same as (H, I) since activation occurs at low Ti catalyst supported ratio. There was a possibility that the initial radicals occurs during polymerization by the presence of AlEt_3Cl in polymerization. Thus, initiation of polymerization by alkylation raises the possibility of initial radical formation during polymerization.

As has been noted that the oxidation mechanism of PP has been studied by many researchers. However, these studies were mainly focus to enrich the understanding of how the degradation of PP progresses and spreads, in spite of the fact that the degradation accelerates from initially formed radicals. If this could become clear, it can be expected to extract much information regarding the radical generation mechanism and measures to control it.

1.2.4. Stabilization of Polypropylene

The oxidative degradation of PP easily proceeds, which leads to poor mechanical properties and limits its long-term applications. The most frequently way to suppress a progress of oxidative deterioration is the addition of stabilizer. antioxidants are generally mixed with PP by extrusion to slow or inhibit the oxidation process. PP is exposed to shear rates and high temperatures during the extrusion

process which cause destructive reactions, causing a combination of mechanical and chemical thermal degradation.

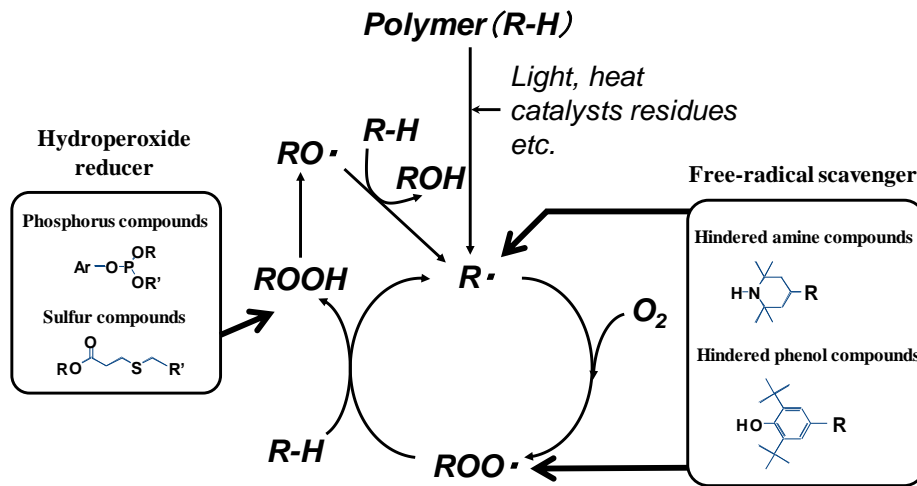


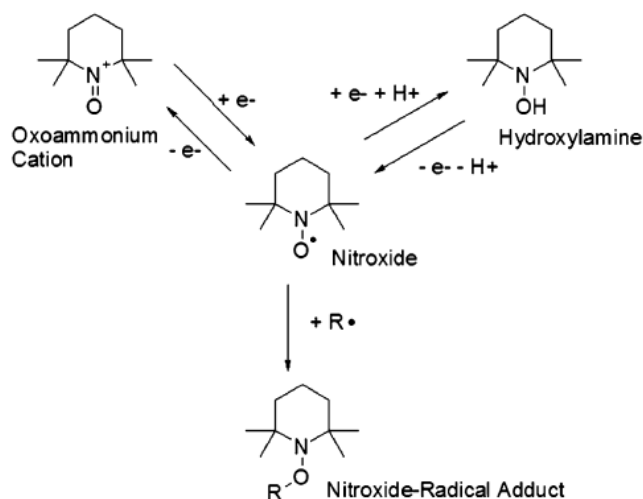
Figure 1.4. The auto-oxidative degradation of PP and the effects of antioxidants

However, it is well known that the PP lifetime in finished product depends on the amount of stabilizer and their performance. High amount of stabilizer causes lower mechanical properties and stabilizer bleeding. This has enhanced the necessity of an innovative technology for low-additive or even additive-free stabilization, not only for the reuse and recycle of PP but also for applications with inorganic fillers or under severe environmental conditions.

1.3. Nitroxide free radical compounds

1.3.1. Background

2,2,6,6-tetramethylpiperidine 1-oxyl free radical (TEMPO) is one of the stable nitroxide free radicals. Possible reactions of nitroxides in biological systems was showed in Scheme 1.2. [26]. The methyl groups limit access to reactive substances though via preventing radical-radical dismutation and quenching the radical species, then these confer stability to the nitroxide radicals [27]. In the case of their use as co-agent, nitroxide be covalently anchored onto the backbone of Carbon-centered radicals to form an alkoxyamine.

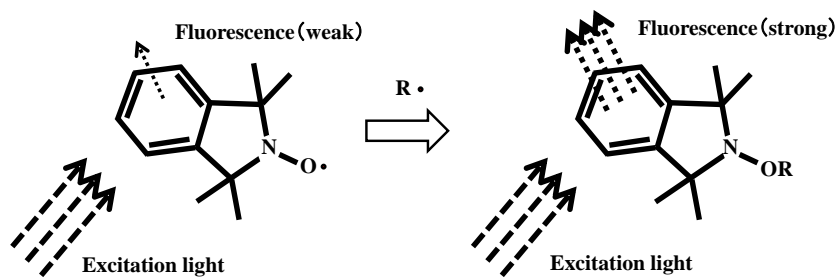


Scheme 1.2. Biological systems of TEMPO [28]

1.3.2. Nitroxide free radical compounds with Polypropylene

TEMPO has been widely used in various applications by functionalization with PP [29,30]. For example, Miwa *et al.* reported that it was successfully controlled the molecular weight of grafted styrene which polymerized in molten state with TEMPO use as co-agent [31]. Recently, George *et al.* reported that the profluorescent nitroxide (PFN) could be used as a probe for the radical-mediated degradation of stabilized polypropylene [32-34]. PFN have a fluorophore covalently anchored to a paramagnetic nitroxide. The nitroxide radical acts to quench the fluorescence of the fluorophore. On the other hand, the nitroxide radical is removed by radical-radical coupling, the fluorescence is restored.

Thus, the presence of the PFN can actor as integrating sensors for radical formation in auto oxidative degradation by turning on and off the fluorescence (Figure 1.7) [35]. Therefore, it suggested that profluorescent nitroxide has the potentials to trap and prove initial radicals formed during polymerization.



Scheme 1.7. The reaction scheme model of profluorescent nitroxide

1.4. Objective

PP has been widely used in various industrial fields because of its wide variety of characteristics. However, the susceptibility to oxidative degradation is one of the biggest shortfalls of it. A number of researches have been well studied the degradation of PP. whereas, the origin of initial radical has never been clarified. In this work, we have paid attention towards the initial radical formation during polymerization.

The objective is to enhance an innovative technology for more high stability of PP, investigation of the origin of initial radical formed 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 was performed.

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Chapter 2

Initial radical formation during propylene polymerization by Ziegler-Natta catalyst

2.1. 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, 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, Malicova *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 peroxy 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.

2.2. Experiments

2.2.1. Materials

Propylene of research grade was donated by Japan Polypropylene Corporation and used without further purification. Triethylaluminum (TEA, donated by Tosoh Finechem Co.), tri-*iso*-butylaluminum (TIBA, donated by Tosoh Finechem Co.) and tri-*n*-octylaluminum (TNOA, Sigma-Aldrich Co.) were used after diluting in heptane. *n*-Heptane and acetone were dried over 4A molecular sieve followed by N₂ 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 Co. LLC.) was used after diluting in heptane. A TiCl₄/*di-iso*-butylphthalate (DBP)/MgCl₂ 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.

2.2.2. Propylene polymerization

A series of propylene slurry polymerization were conducted using a TiCl₄/DBP/MgCl₂ 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 N₂ 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 N₂ and controlled temperature. It must be noted that all of the procedures were carefully conducted under N₂ atmosphere in order to prevent the intrusion of air.

Table 2.1 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 H₂. 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 H₂ as a chain transfer agent

was added before the catalyst injection, while the other conditions were kept at the standard one.

Table 2.1. Summary of polymerization conditions and results

Run	Polym. time (min)	Polym. temp. (°C)	H ₂ conc. (mmol/L)	AlR ₃ conc. (mmol/L)	AlR ₃ type	Cat. amount (mg)	Yield (g)	OIT ^a (h)	<i>mmmm</i> ^b (mol%)	Vinyl end group ^b (mol%)	Ti residue in PP ^c (ppm)	<i>M_w</i> ^d	<i>M_w</i> / <i>M_n</i> ^d
1	60	30	0	5.0	TEA	15	1.7±0.5	8.3±1.0	90			1.1 × 10 ⁵	6.4
2	20						0.9	13					
3	40						1.7	12					
4	80	30	0	5.0	TEA	15	2.7	8.4					
5	100						3.3	7.2					
6		0					0.7	15	87		160	8.6 × 10 ⁴	5.5
7		10					0.9	14					
8	60	60	0	5.0	TEA	15	5.2	4.6	90	0.2	20		
9		80					2.2	5.1	91			8.5 × 10 ⁴	6.3
10			0.12				13	2.7		0.2			
11	60	60	0.25	5.0	TEA	15	17	2.4	90	0.1			
12				1.3			2.6	9.2					
13				2.5			2.5	8.4					
14	60	30	0	10	TEA	15	3.5	7.4					
15				20			3.8	6.2					
16					TIBA		1.3	14					
17	60	30	0	5.0	TNOA	15	0.6	17					
18						5	0.9	9.3					
19	60	30	0	5.0	TEA	30	5.3	9.4					
20						60	11	9.2					

^aOxidative induction time (OIT) was determined by chemiluminescence measurements at 110°C under dry air; ^bDetermined by ¹H and ¹³C NMR; ^cDetermined by X-ray fluorescence; ^dDetermined by high-temperature gel permeation chromatography (HT-GPC)

2.2.3. 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 N₂ 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.

2.2.4. Chemiluminescence measurement

The detection of chemiluminescence (CL) that arises from the decomposition of peroxy 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 N₂. 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 peroxy 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 N₂ 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 peroxy 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 N₂ flow at the flow rate of 100 mL/min.

2.2.5. 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 ¹³C and ¹H NMR (Bruker 400 MHz) at 120°C using 1,2,4-trichlorobenzene as a diluent and

1,1,2,2-tetrachloroethane-d₂ as an internal lock and reference.

2.3. Results and discussions

In seeking a possibility of the initial radical formation during polymerization, a first potential choice of examination is to observe the stability of as-synthesized PP as a function of polymerization conditions. However, one should pay special attention, since there are several factors that could impact the stability of as-synthesized PP besides the formation of initial radicals, such as

- i) Catalyst residues, especially Ti, are known to have a great impact in accelerating the oxidative degradation [24,25]. The concentration of catalyst residues contained in polymer has an inverse relationship with the polymer yield. By changing polymerization conditions, the concentration of catalyst residues also varies unless the polymerization is performed at a constant polymer yield per g-catalyst.
- ii) Unsaturated groups such as vinyl and vinylidene at the chain ends, which are formed as a consequence of chain transfer reactions during propylene polymerization [26,27], were reported to negatively affect the stability of PP [28-31]. Considering the dissociation energy of C-H bond, an allylic carbon

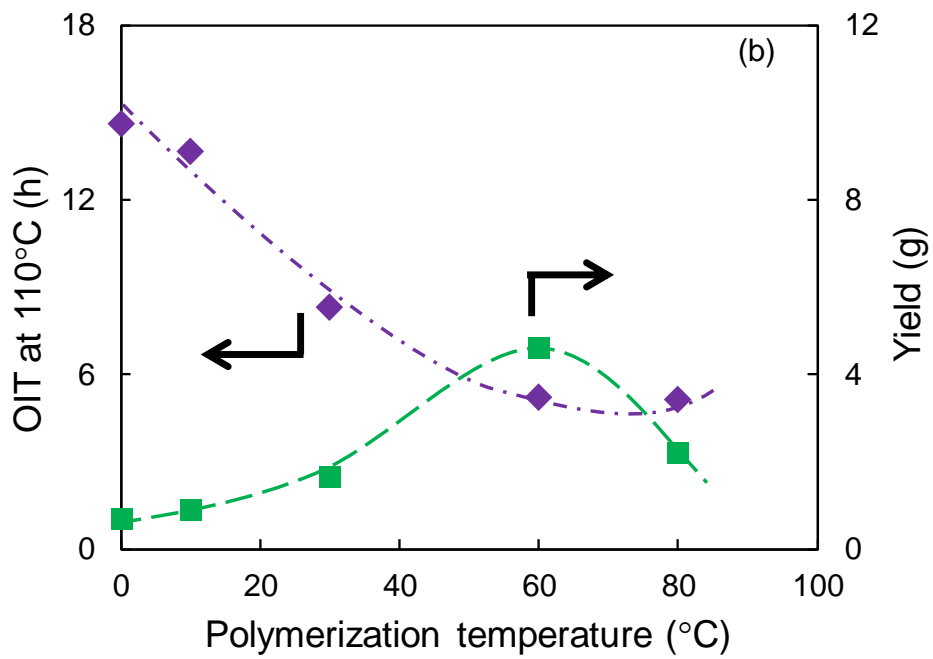
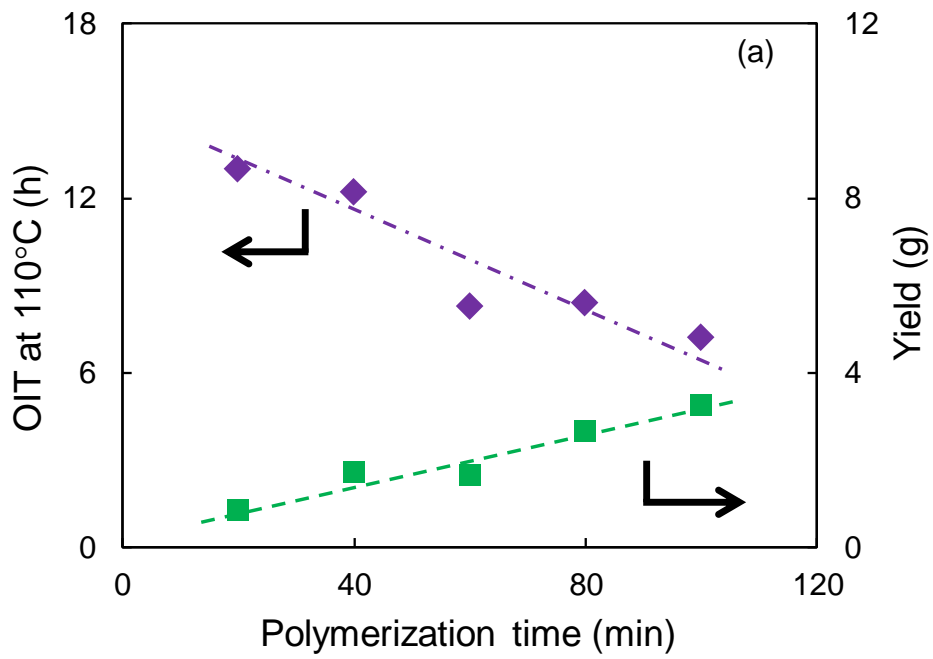
has a lower dissociation energy than that of a tertiary carbon, thus being more prone to undergo the hydrogen abstraction.

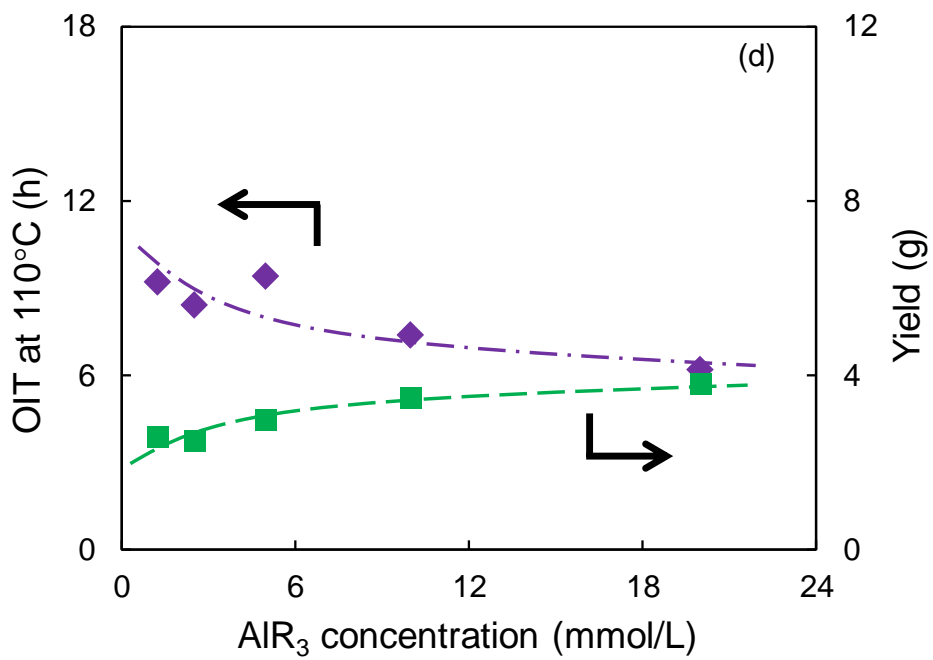
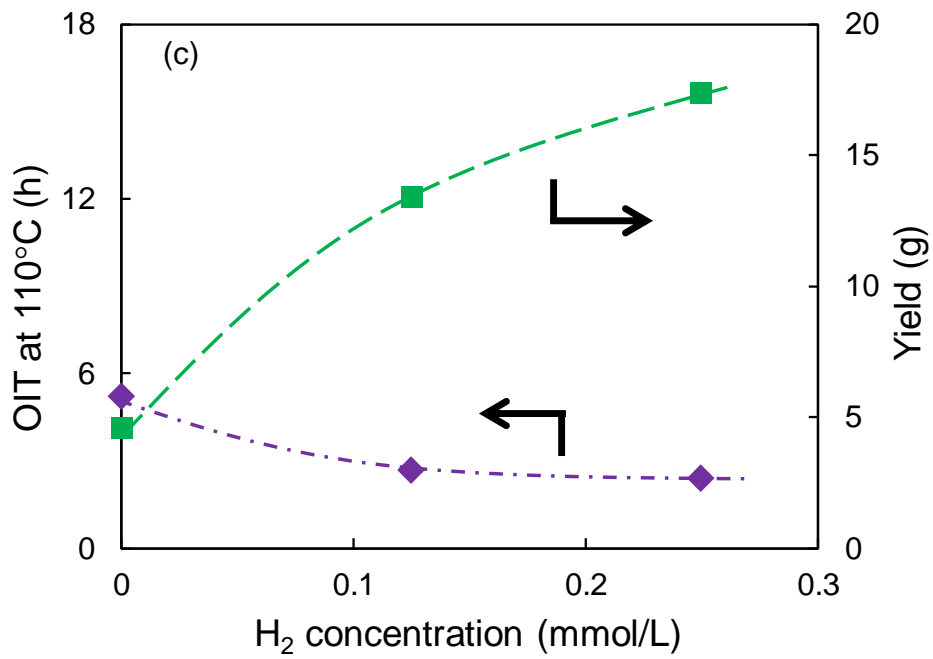
- iii) PP with lower isotacticity is known to have a longer lifetime [32,33]. It was reported that atactic and syndiotactic PP were much more stable than isotactic PP [34].
- iv) A lower molecular weight and lower crystallinity shorten the PP lifetime by an increase of oxygen permeability [35]. Gómez-Elvira *et al.* and Suzuki *et al.* found that the oxygen diffusion was restricted with the increase in the tacticity and crystallinity, resulting in slower oxidation [36].

For the sake of comparisons, the above mentioned factors must be controlled by conducting polymerization in an appropriate range of conditions to produce PP with similar primary structures. Typical polymerization conditions such as polymerization time, polymerization temperature, the concentration of H₂, the type and concentration of activator and the amount of the catalyst were varied. The stability of as-synthesized PP was evaluated as OIT. It must be noted that all of the procedures from polymerization to the OIT measurement were strictly conducted under N₂ atmosphere to make sure that as-synthesized powder never experienced thermal history and to prevent the effects of light, atmospheric oxygen and moisture on the lifetime of PP.

Table 2.1 summarizes all of the polymerization conditions and the polymerization results along with the OIT values at 110°C under dry air. In addition, relationships of various polymerization conditions with OIT and the polymer yield are plotted in Figure 2.1. Inspecting all the relationships, a clear inverse correlation was found between the yield and OIT. For instance, the polymer yield developed linearly to the polymerization time, thus diluting catalyst residues in the formed polymer. Nonetheless, OIT decreased along the polymerization time (Figure 2.1a). The polymer yield increased with the increase of temperature and reached the maximum value at around 60°C, thus giving the minimum concentration of catalyst residues at the same temperature (Figure 2.1b). However, OIT showed the lowest value at this point with an anti-proportional relation with the yield along the plot. H₂ is the most widely employed chain transfer agent in catalyzed olefin polymerization. The primary purpose of the H₂ addition is at the molecular weight regulation, while the other two consequences may have more important roles in terms of the polymer stability: i) the chain transfer to H₂ produces saturated end groups (typically *i*Bu- and *n*Bu-) [37] to reduce the fraction of unsaturated end groups (see Runs 8,10,11 in Table 2.1), and ii) as can be widely recognized for higher generation of Ziegler-Natta catalysts [38], the addition of H₂ significantly promoted the polymerization yield (Figure 2.1c), in which

the concentration of catalyst residues in polymer powder is accordingly diluted. In spite of these positive aspects of H_2 , the increase of the yield by the addition of H_2 was found to persist an inverse relation with OIT. In the case of an alkylaluminum activator, the increase of the activator concentration (Figure 2.1d) and the decrease of alkyl chain length (Figure 1e) increased the polymer yield, while inverse relations between the polymer yield and OIT were again evident. Only an exceptional relation was found for the variation of the catalyst amount (Figure 2.1f). By increasing the amount of the catalyst, the yield proportionally increased in a way that the microstructure of PP and the concentration of catalyst residues in the resultant powder were unaffected. In this case, OIT was not affected by the yield. On the other hand, we speculated that the initial radical formation might arise from the catalysis itself. In this light, the relationships between the polymer yield and OIT obtained in Figure 2.1 a-f was interpreted again based on the yield normalized by the catalyst amount (g-PP/g-Cat.).





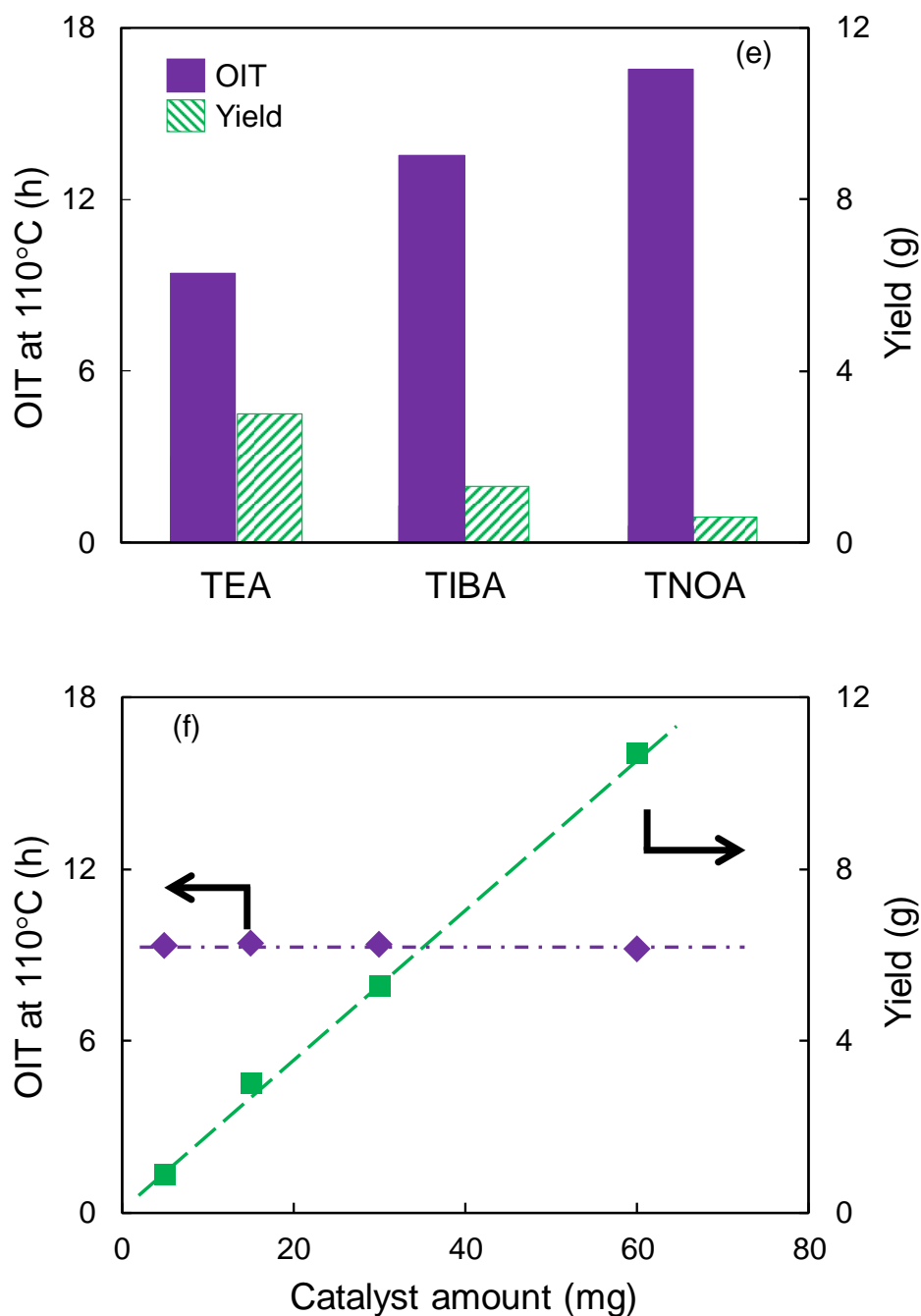


Figure 2.1. Influences of polymerization conditions on the oxidative induction time (OIT) and the polymer yield: a) polymerization time (Runs 1-5), b) polymerization temperature (Runs 1,6-9), c) H₂ concentration (Runs 8,10,11), d) activator concentration (Runs 1,12-15), e) activator type (Runs 1,16,17), and f) catalyst amount (Runs 1,18-20).

The polymerization condition was listed in Table 2.1. The OIT values were determined based on CL measurements at 110°C under dry air flow with the flow rate of 100 mL/min.

In Figure 2.2, all the relationships between the normalized yield and an inverse of OIT were compiled in a single curve, where the inverse of OIT tended to monotonically increase along the polymer yield. The utmost two points in the presence of H₂ showed slight deviation in curvature, which might be attributed to too short OIT at the measured temperature. It must be pointed out that OIT was predominantly determined by the yield in polymerization, rather than the difference in polymer structures such as the molecular weight and unsaturated chain end content. From this fact, two scenarios were considered: i) catalyst residues stabilized as-synthesized polymer, and ii) initial radicals were formed in polymerization. For the former scenario, catalyst residues can exhibit both of the positive and negative effects on the polymer stability [39-42]. It was reported that in the local area where the amount of catalyst residues was high, transition metal ion scavenged the peroxy and carbon-centered radicals to form non-radical products [39]. At the same time, migratable and more reactive radical species can be also generated through the

hydroperoxide decomposition. This negative effect of catalyst residues is well-recognized in the literature [40-42].

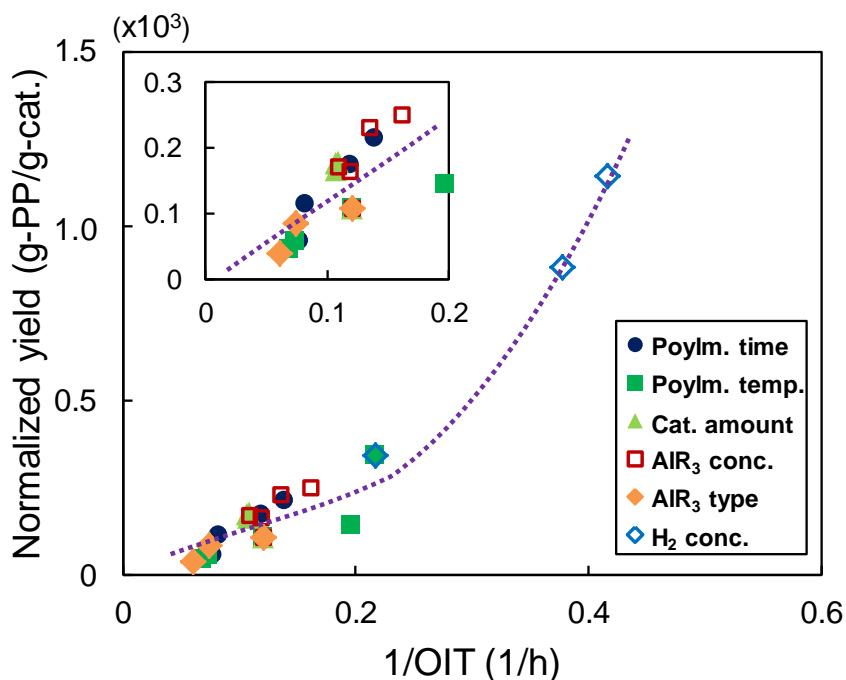


Figure 2.2. Relationship between the inverse of OIT and the polymer yield normalized by the catalyst amount. The data points were collected from Figure 2.1a-f.

The latter scenario is in one part based on the heat generation from an exothermic nature of polymerization (the heat of reaction of 100 kJ/mol) [43]. It was simulated that the temperature inside a polymer/catalyst particle can raise to nearly 400°C in the first few seconds of polymerization [20]. This temperature shooting in the initial stage of polymerization is much closer to the temperature required for the

bond dissociation and it is in fact dependent on the polymerization activity. Moreover, it was reported that the catalyst activation pathway by alkylaluminum involves the formation of radical species [18]. Hence, the second scenario supposes that initial radicals are formed during polymerization with the aid of alkylaluminum and/or heat accumulated within polymer particles: A higher yield is related to the stronger activation and heat generation, leading to more radical formation.

In order to confirm the presence of initial radicals during polymerization, we have further applied two strategies: the detection of oxidative products produced from initial radicals, and radical trapping by TEMPO, a nitroxide free radical. In the first strategy, when initial radicals are formed on tertiary carbons of PP, they spontaneously react with O₂ under ambient temperature to form peroxy products, which can be directly quantified from the CL intensity generated from its thermal decomposition under N₂ [44,45]. Accordingly, PP powder samples obtained at different polymerization temperature (Runs 1,6,8) were exposed to dry air for 10 min at room temperature prior to the CL measurement at 150°C under N₂ flow. The peroxy species that are formed during the pre-exposure are decomposed at an elevated temperature to emit CL (while N₂ atmosphere prevents the formation of additional peroxy species). Figure 2.3 shows that all the three samples emitted CL, supporting that initial radicals were already

present in as-synthesized PP powder. The intensities were in the order of PP-60°C > PP-30°C > PP-0°C, thereby agreeing well with an inverse order of their stability. PP-60°C, which has the lowest OIT value, exhibited the largest amount of peroxy species, *i.e.* the largest amount of initial radicals might be formed under the highest yield condition.

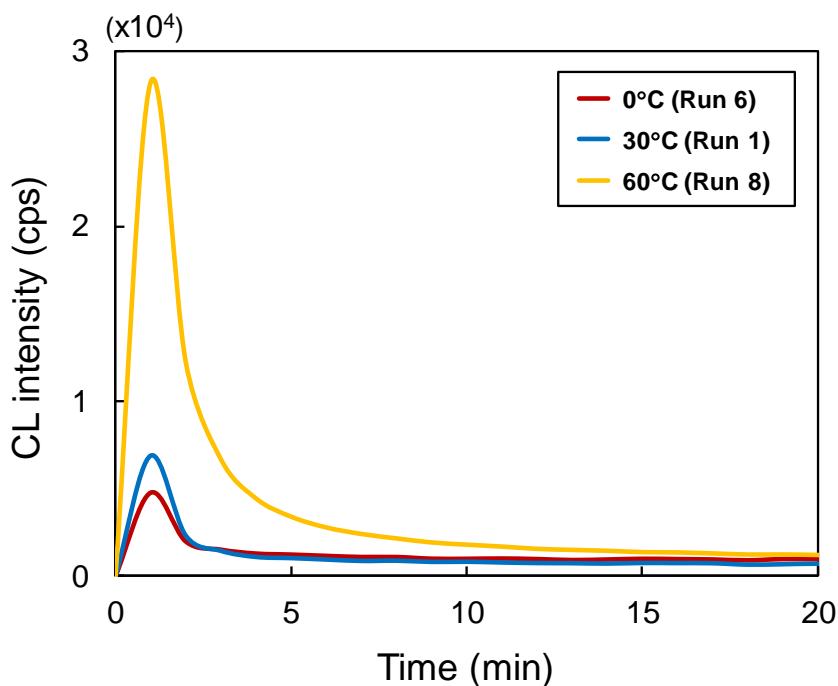


Figure 2.3. CL from air-exposed PP measured at 150°C under N₂, where PP powder was exposed to a dry air flow for 10 min at room temperature before the measurement. The CL emission corresponds to the decomposition of peroxy species present in a sample.

TEMPO is one of the stable nitroxide free radicals that has been used as a

polymer stabilizer and a chain inhibitor in radical polymerization [46-48]. TEMPO reacts with carbon-centered radicals to form alkoxyamine before decomposition into non-radical products [49]. If carbon-centered radicals were present in as-synthesized PP, they would be trapped with TEMPO and stabilized to provide PP with a longer lifetime. Likewise, PP powder synthesized at 60°C was treated with TEMPO strictly under N₂ as described in the experimental section before the OIT measurement at 130°C under dry air flow (denoted as PP/TEMPO). It was found that OIT dramatically increased more than 10 times by the addition of TEMPO as compared to its original lifetime (Figure 2.4). In comparison, the TEMPO treatment was performed using the same PP sample but after exposing to air (denoted as PP(exposed)/TEMPO). The result showed no stabilization effect by the addition of TEMPO after the exposure. Since the reaction between nitroxide radicals and peroxy radicals is thermodynamically unfavorable due to an instability of trioxide products [50], these results strongly suggested that carbon-centered radicals exist in as-synthesized PP as initial radicals, which can be captured by TEMPO if not exposed to air.

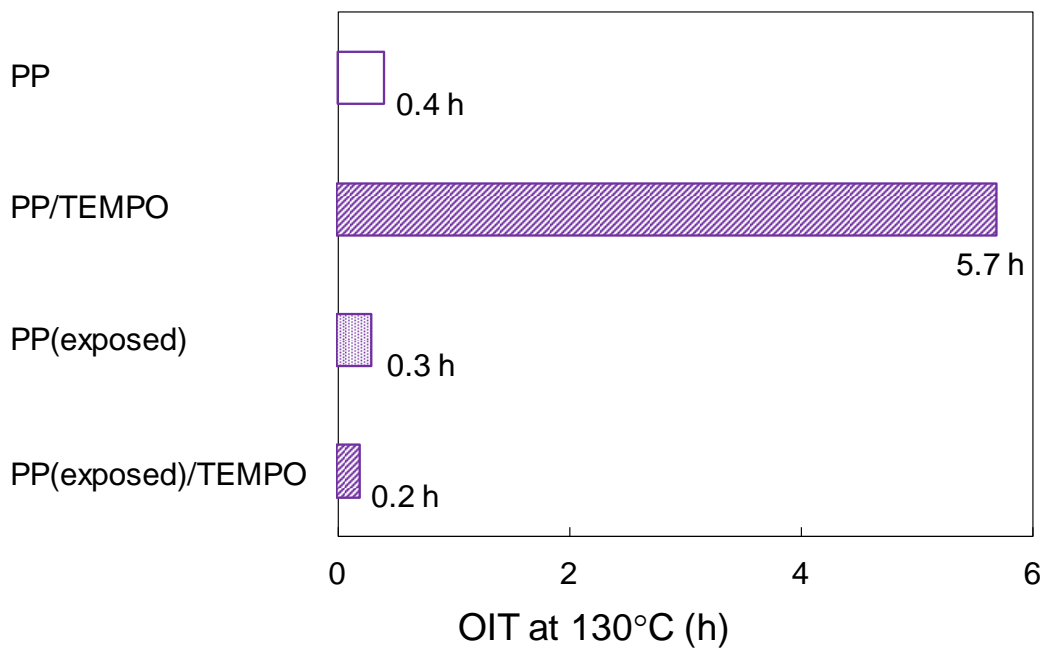


Figure 2.4. Influence of the addition of TEMPO on the stability of PP powder. OIT was evaluated at 130°C under dry air. Significant stabilization was attained when the PP powder was immediately contacted with TEMPO after the polymerization, which was not the case when the PP powder was once exposed to air before contacting with TEMPO.

The results of these experimental approaches suggested that initial radicals are already formed during polymerization. Polymer produced at a higher yield condition exhibits a shorter lifetime irrespective of other factors due to the formation of more initial radicals. Although the mechanism for the initial radical formation has not yet been clarified, it is believed that heat accumulation inside polymer particles and a

radical nature of the catalyst system are involved. In addition, it was demonstrated that initially formed radicals could be successfully trapped using a radical trapping agent, thus providing PP powder with a longer lifetime.

2.4. Conclusions

Various experimental approaches were utilized in this study for clarifying the origin of initial radicals for the oxidative degradation of PP. Polymerization conditions were found to have a direct impact on the stability of as-synthesized PP. For instance, PP produced under a higher yield condition exhibited a shorter lifetime irrespective of a lower concentration of catalyst residues. The CL analysis under N₂ revealed that as-synthesized PP spontaneously formed peroxy species through air exposure even at ambient temperature. The amount of the formed peroxy species was correlated with the lifetime of PP powder. The addition of TEMPO, as a carbon-centered radical trapping agent, drastically enhanced the stability of as-synthesized PP, while the same treatment never gave a stabilization effect if polymer was once exposed to air. This fact evidentially supported the existence of initial radicals in as-synthesized PP, in which the treatment with TEMPO passivated them and prevented the further chain reaction. These results obtained from our various approaches coincided well and led to

a strong suggestion that initial radicals are already formed during polymerization.

Although the mechanism for the initial radical formation has not yet been clarified, its understanding can be regarded as to be a critical target in establishing a more effective or even additive-free stabilization technology.

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Chapter 3

***Stabilization of polypropylene using
radical trapping agent for initial
radicals formed in polymerization***

3.1. Introduction

Polyolefins, especially polypropylene (PP), have been 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 the compounding technologies to impart particular 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 according to a 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 abstract of hydrogen atoms from proximate tertiary carbons and cleaved into a 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 to deteriorate polymer properties and shorten the lifetime.

A common way to suppress a 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 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 overglanced 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 as-synthesized reactor powder. In order to establish a new scheme of a stabilization technology, one the most effective ways is to stabilize these initially formed radicals.

Recently, George *et al.* reported that the profluorescent nitroxide (PFN) could be used as a probe for the radical-mediated degradation of stabilized polypropylene [20,21]. 2,2,6,6-tetramethylpiperidine 1-oxyl free radical (TEMPO) is one of the stable nitroxide free radicals and has been widely used in various applications by functionalization [22,23]. Nitroxyl free radicals can couple with C-centred radical species as in the case of their use as co-agent. If they bear specific functionalities, these can be covalently anchored, by nitroxide grafting, onto the backbone of Carbon-centered radicals. Therefore, it suggested that nitroxide has the potentials to prove initial radicals formed

during polymerization and enhance an innovative technology for high stability.

In this contribution, a radical trapping strategy was applied to prove the presence of initial radicals and to extend the lifetime of PP reactor powder. A nitroxide free radical, namely 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. In addition, the result of a radical trapping strategy using PFN showed that the initially formed radicals could be successfully trapped using PFN, thus providing reactor powder with fluorescence emission of polymers functionalized with PFN. These results suggested that the initial radical was formed during polymerization and the radical trapping by nitroxide compounds could potentially suppress the oxidative degradation by preventing the new radical formation.

3.2. Experiments

3.2.1. 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), di-*iso*-butylphthalate (DBP) were used as received. 9,10-bis(phenylethynyl)anthracene (BPEA, Sigma-Aldrich Co. LLC.) was used as received. 1.9-(1,1,3,3-tetramethylisindolin-2-yloxy)-5-ethynyl-10-(phenylethynyl) anthracene (PFN) which was donated by Laboratory of Prof. Steven E. Bottle, Science and Engineering Faculty, Queensland university of technology, was used as the profluorescent nitroxides.

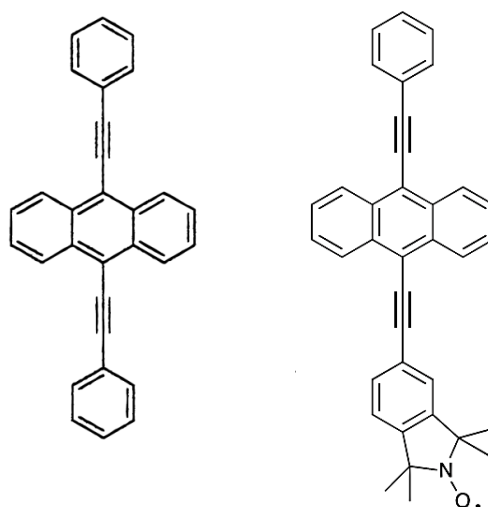


Figure 3.1. Chemical structures, Left; 9,10-Bis(phenylethynyl)anthracene (BPEA) and Right; 9-(1,1,3,3-tetramethylisoindolin-2-yl)oxy-10-(phenylethynyl)anthracene (PFN)

3.2.2. Catalyst synthesis

A $\text{TiCl}_4/\text{DBP}/\text{MgCl}_2$ catalyst was prepared based on a patent [24] using a spherical $\text{Mg}(\text{OEt})_2$ precursor. The titanium and DBP contents were respectively measured as 3.4 wt% and 12 wt%.

3.2.3. Propylene polymerization

400 mL of heptane as polymerization solvent was introduced to a 1 L stainless steel reactor under N_2 . 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 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 the alkylaluminum and external donor residues. The resultant PP powder was dried in vacuo at room temperature and stored in dark under N₂ blanking.

3.2.4. Synthesis of PP grafted nitroxide trapping agent

A radical trapping strategy using nitroxide trapping agent was applied to prove the presence of initial radicals. First, the polymer slurry was transferred into a round bottom flask under N₂ atmosphere after polymerization,. 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 to remove free TEMPO before drying in vacuo at room temperature. The sample was denoted as PP/TEMPO. To remove the influence of the 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 contacting with TEMPO. The other steps were kept the same as for the preparation of

PP/TEMPO.

Finally, to prove the formation of initial radicals during polymerization, examine the quantitative determination of radicals formed during polymerization using profluorescence nitroxides was investigated. Synthesis of PP grafted PFN followed same scheme with PP-g-TEMPO. It must be noted that all of the procedures were carefully conducted under nitrogen in order to prevent the intrusion of oxygen.

3.2.5. Removal of TEMPO-grafted catalyst residues

TEMPO, which was grafted to non-initial radicals such as catalyst residues, was removed to clarify the impact of stabilization only through the initial radical trapping. 0.1 g of PP-g-TEMPO powder was stirred in 100 mL of acetone for 1 h to allow the dissolution of catalyst residues and simultaneously removal of TEMPO-grafted 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 for better washing efficiency. The samples were denoted as PP-g-TEMPO (MeOH) and PP-g-TEMPO (Acetone), respectively. For the PP-g-PFN washed, synthesis of PP grafted PFN followed same scheme with PP-g-TEMPO washed. Thereafter, the slurry

was dried under vacuum at room temperature.

3.2.6. Chemiluminescence measurement

Chemiluminescence (CL) analysis is one of the most sensitive methods to estimate of the oxidation stability by detecting the light emitted from the decomposition of peroxide species. The oxidative induction time (OIT) of 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 Corporation), where 10 mg of a powder sample was held at 130°C or 110°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.

3.2.7. 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.

3.2.8. Fluorescence spectrophotometer

Fluorescence spectra were collected with a Varian Cary Eclipse fluorescence spectrophotometer. For measurements on polymer samples, 2 mg of sample were put on aluminum pans and excited at an angle of 45° to the surface. Emission was recorded from the back face of the sample to limit interference from scattered and reflected exciting light. For the determination of quantitatively the concentration of radicals in the polymer, synthesized standard polymer for calibration curve of fluorescence spectrophotometer were conducted. Specified amounts of BPEA in a 10 µL of chloroform added to the 2.0 mg of PP polymerized at 60°C without using nitroxide. Then, the polymer was dried in air.

3.3. Results and discussions

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 (Figure 3.2.). 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 relation between polymer yield and OIT persisted in a series of experiments and led to a strong suggestion that radicals are already formed during polymerization in deep relation with the catalyst activation pathway 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.

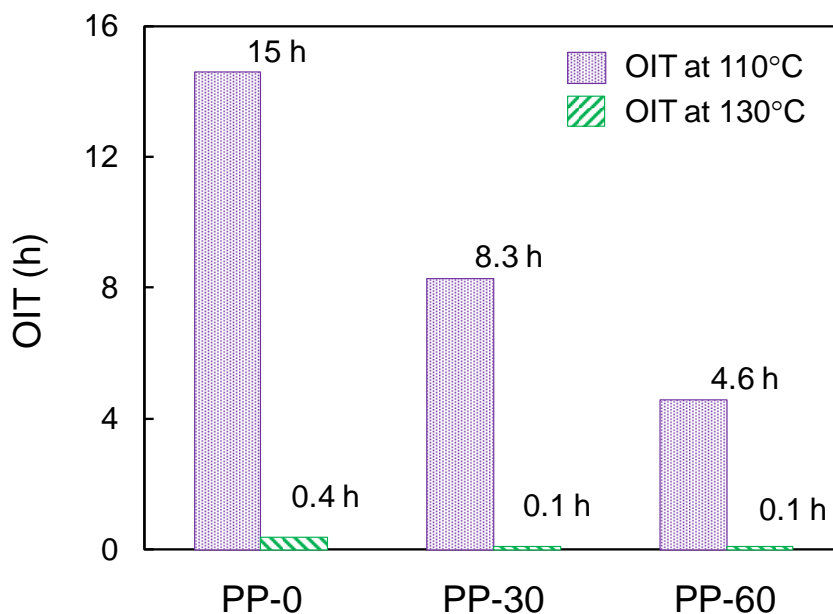


Figure 3.2. Influences polymerization temperature on the polymer yield and the oxidative induction time (OIT) for obtained PP powder polymerized at 0°C, 30°C and 60°C. The OIT values were determined based on CL measurements at 110°C or 130°C under dry air flow with the flow rate of 100 mL/min.

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 delocalized 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 (Figure 3.3.) [25]. If carbon-centered radicals

were presented in as-synthesized PP as initial radicals, they would be stabilized on contact with TEMPO.

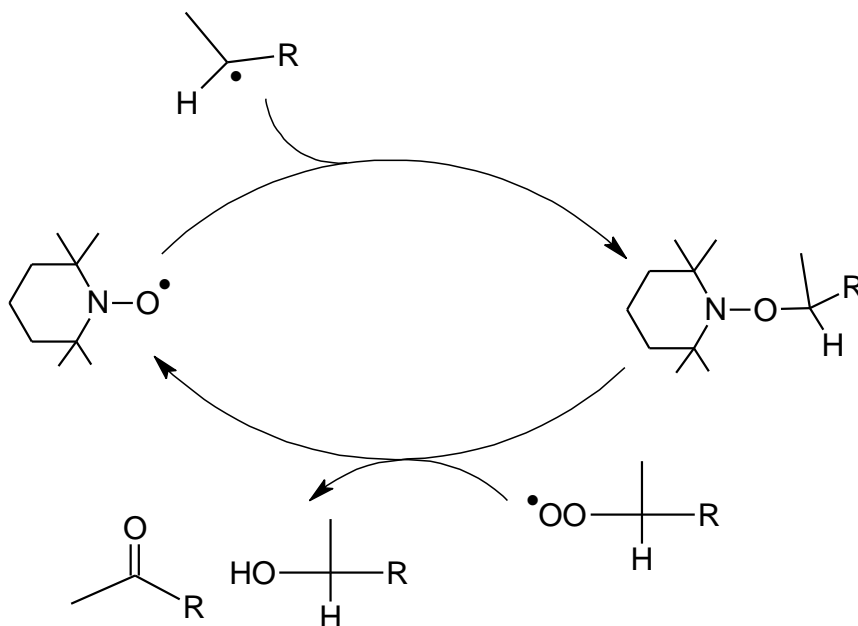


Figure 3.3. Simplified mechanism of nitroxide radical trapping

In 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 (Figure 3.4a). As a comparative sample, as-synthesized PP produced at 60°C was once exposed to air for 10

min followed by contacting with the same amount of TEMPO. However, no improvement of the stability was observed as indicated by a similar OIT value between PP-air-TEMPO and the original PP powder (Figure 3.4b). 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. 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 (Figure 3.4a). Thus, it was plausibly 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.

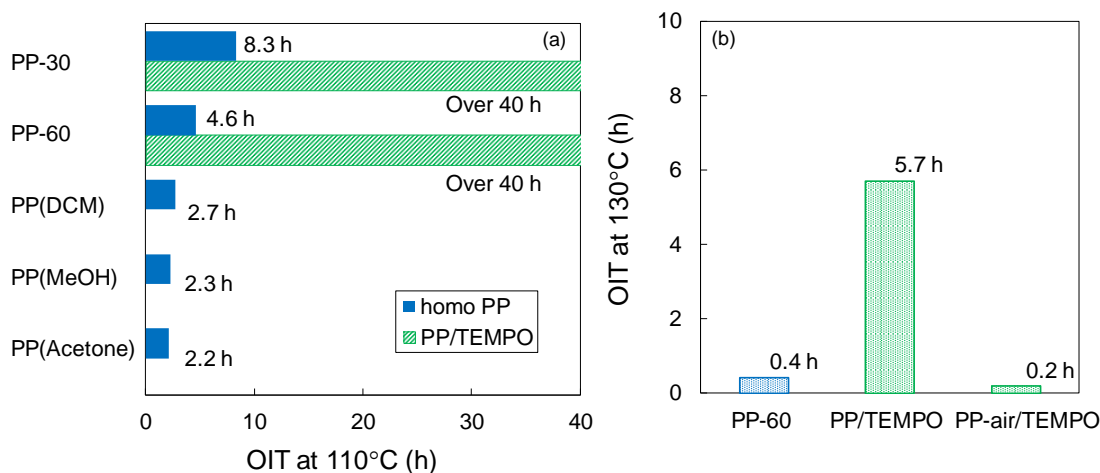


Figure 3.4. The stability of as-synthesized PP powder: a) OIT of PP powder produced at 30°C and 60°C in the absence and presence of TEMPO treatment and OIT of PP powder produced at 60°C after the removal of catalyst residues by various washing methods; b) The stabilization effect of TEMPO for as-synthesized PP and air-exposed PP produced at 60°C.

The influence of TEMPO addition amount on the stability of as-synthesized PP produced at 60°C was investigated. Figure 3.5 shows that OIT increased monotonically with the increase of TEMPO addition amount before reaching the plateau. It was notable that the higher amount of TEMPO was required to reach the maximum stability in the case that TEMPO was immediately added to the polymer slurry without the removal of alkylaluminum and external donor residues (PP/TEMPO). The

introduction of washing process after polymerization reduced the required amount of TEMPO about 10 times to reach a similar level of OIT (PP-*g*-TEMPO). Potapov *et al.* performed the ESR studies and reported that TEMPO did not react with alkylaluminum at room temperature [25]. 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 [26] and alkylaluminium chloride [27], 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.

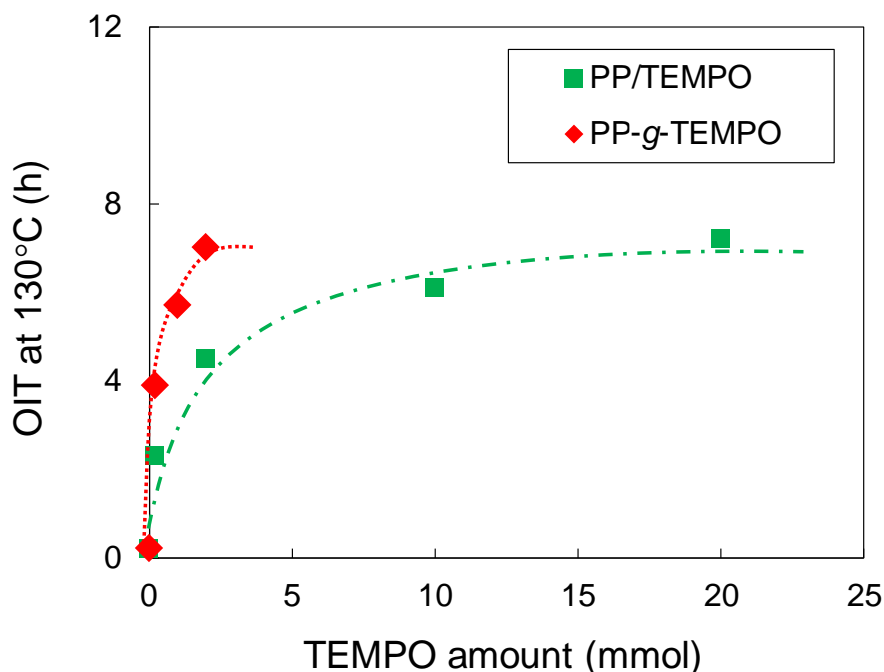


Figure 3.5. Influence of the amount of TEMPO added on the stability of as-synthesized

PP. The addition of TEMPO before and after washing polymerization slurry. PP powder was polymerized at 60°C. The OIT values were determined based on CL measurements at 130°C under dry air flow with the flow rate of 100 mL/min.

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 and remain in polymer [28]. In order to completely remove free TEMPO as well as catalyst-grafted TEMPO, PP-g-TEMPO was additionally washed with acetone. Figure 3.6. shows ESR spectra of PP-g-TEMPO before and after the second washing with acetone. It was found that unwashed PP-g-TEMPO exhibited a strong signal of 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. Figure 3.7 shows the OIT values of PP-g-TEMPO after the acetone washing. It can be clearly seen that the stabilization effect in the presence of TEMPO persisted even after the complete removal of free TEMPO.

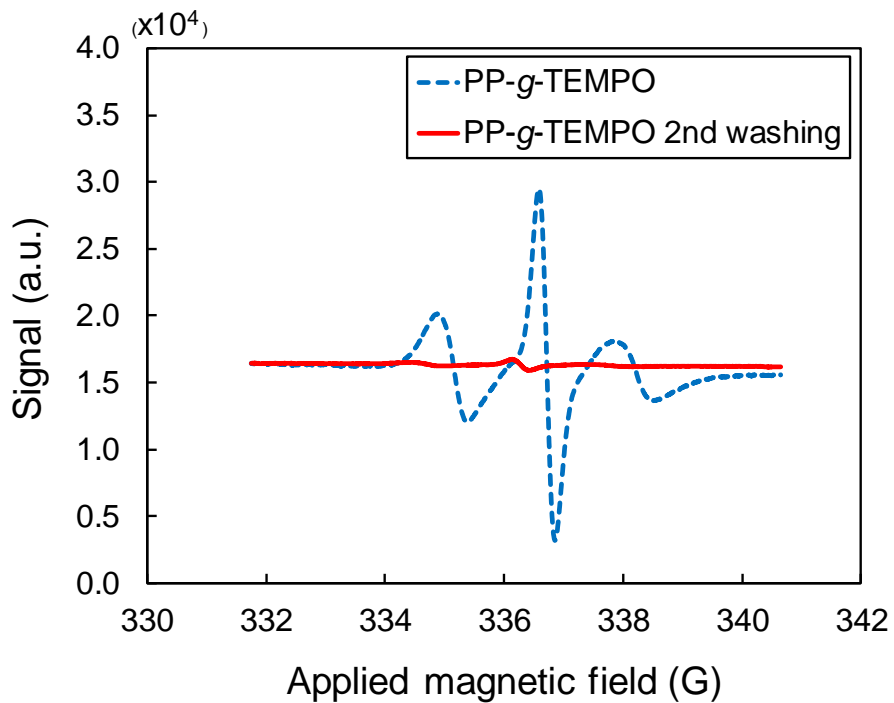


Figure 3.6. ESR spectra of PP/TEMPO powder before and after washing by stirring and filtrating 2 times with acetone. 3.0 mg of PP-g-TEMPO samples were measured at room temperature under air.

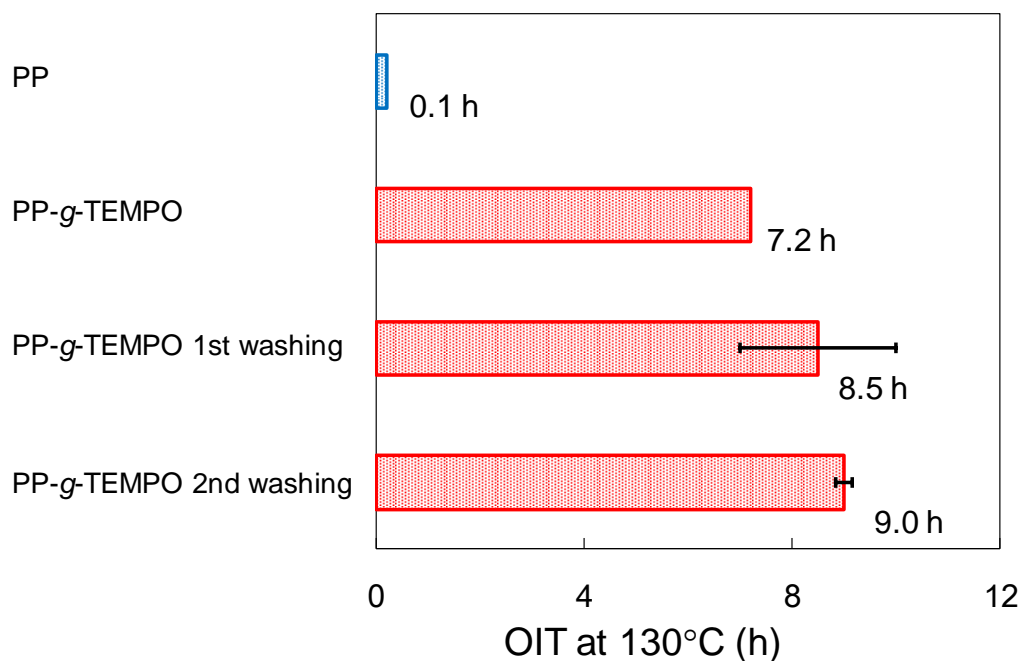


Figure 3.7. Effects of the number of washing time on the lifetime of PP-g-TEMPO.

The amount of additional TEMPO for PP-g-TEMPO was 2 mmol. 0.1 g of PP-g-TEMPO was stirred with 100 mL of acetone, then the slurry was filtrated and dried several times.

In Figure 3.8, the washing efficient was further improved by applying soxhlet extraction at room temperature. It can be seen that both of acetone and methanol solvents gave a similar OIT throughout the course of extraction time, indicating a similar efficiency of washing. It should be noted that the same washing procedure using acetone was applied to remove catalyst residues. Nonetheless, it never led to the improvement of PP stability (see Figure 3.4). Likewise, the improvement of PP

stability likely originated from the stabilization of initial radicals rather than the effect of catalyst residues. These results suggested that initial radicals, which might already formed during polymerization, could successfully trapping using nitoxide radical trapping agent, thus providing as-synthesized PP with a longer lifetime.

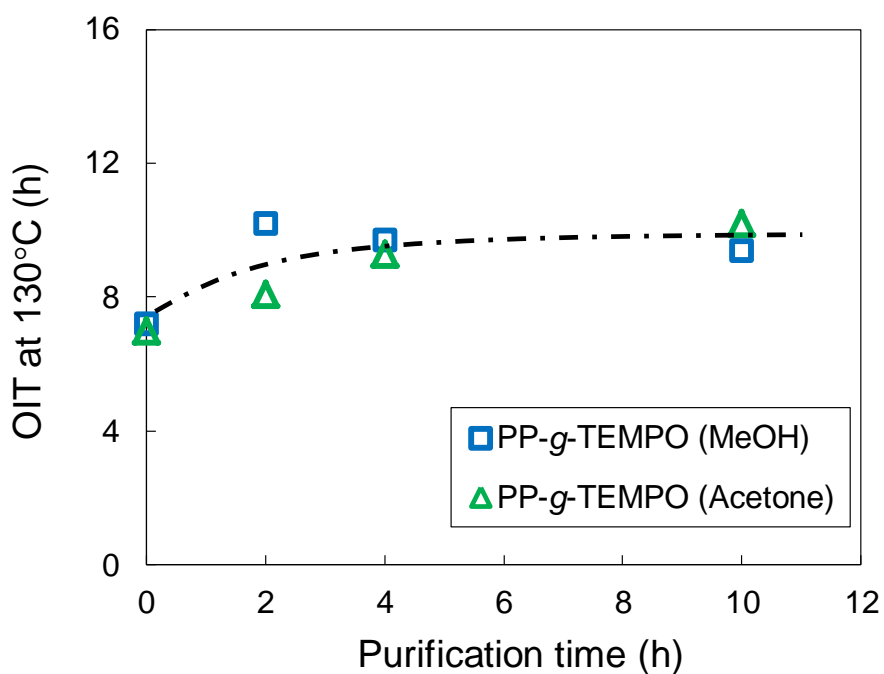


Figure 3.8. Dependence of the lifetime of PP-g-TEMPO on Purification time and different soxleht extraction solvents at room temperature. Soxhlet extraction with methanol or acetone was performed under N₂ atmosphere. PP powder was polymerized at 60°C. The OIT values were determined based on CL measurements at 130°C under dry air flow with the flow rate of 100 mL/min.

Our previous results was suggested that that as-synthesized PP powder obtained at a high temperature offered polymer with shorter lifetime, indicating initial radical formed during polymerization. If this hypothesis was correct, the radical trapping strategy for the PP produced at higher polymerization yield should be showed the higher stabilization effect, indicated that more TEMPO could be grafted. Therefore, in order to investigate the effects of polymerization temperature on PP stability, polymerization temperature and amount of TEMPO were varied (Figure 3.9). PP produced at higher polymerization yield showed the higher lifetime and the higher amount of TEMPO was required to reach the maximum lifetime. This result indicated that more TEMPO could be grafted, leading to higher stabilization effect. In other words, more initial radicals were formed at high yield conditions and served as graftable sites for TEMPO. From these results, the initially formed radicals could be successfully trapped with TEMPO, thus providing polymer with longer lifetime.

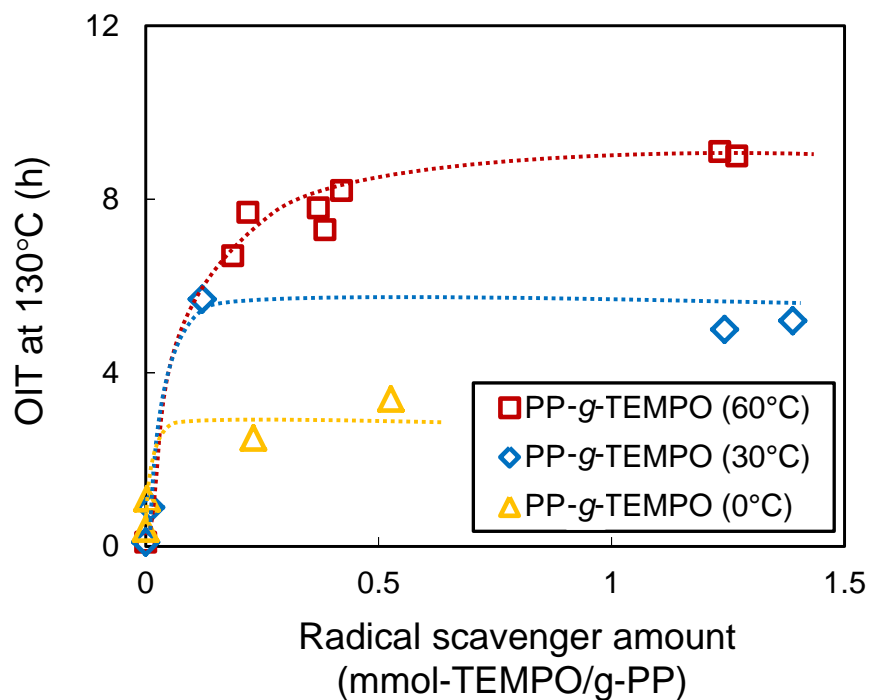


Figure 3.9. The correlation between the amount of TEMPO and the lifetime of PP the polymerized at different polymerization temperature. The OIT values were determined based on CL measurements at 130°C under dry air flow with the flow rate of 100 mL/min.

PFN is the one of the useful tool for an oxidative environment sensor because of its sensitivity [20,21]. PFN is comprised a sterically hindered nitroxyl radical with its attached fluorophore. Fluorescence from a PFN is seen no emission initially due to quenched by spin-orbit coupling. Scavenging of a polymer C-center radical by the nitroxide radical of PFN to form the non-radical product (alkoxyamine) reduces the

quenching, then fluorescence is seen with intensity proportional to the radicals. Therefore, it suggested that PFN is possible to prove the formation of initial radicals during polymerization by the quantitative determination of the radicals.

In order to quantitatively determine the existence radicals in polymer using PFN, polymer characterization by fluorescence spectroscopy was investigated. The results were shown in Figure 3.10. Fluorescence emission of PP without PFN did not show any peaks and fluorescence emission of PP functionalized with PFN showed the same peak at 515 nm and 485 nm from benzene and anthracene in PFN, respectively.). However, the peaks at 515 nm showed same intensity with 485 nm, in spite of different ratios of molecule in PFN. In addition, compared with previous paper reported by Fairfull-Smith, the result showed the different shape of the peaks [29]. It was thought that the reasons for this were heterogeneous dispersion of PFNs and/or much amount of radicals in polymer which caused sifting and broadening of the peaks. Thus, PP functionalized with PFN was washed by chloroform several times (PP-g-PFN washed). Fluorescence emission of the PP-g-PFN showed the sharpness of the peak with previous paper was shown, indicating the initially formed radicals could be successfully trapped with PFN. Using a calibration curve synthesized with PP and BPEA, quantitative determination of PFN in polymer by fluorescence spectrophotometer was performed.

The results of the concentration of PFN in PP-g-PFN was 1.5 nmol-PBEA/kg-PP. The result showed that the initially formed radicals could be successfully trapped using PFN, thus providing PP powder with fluorescence emission of polymers functionalized with PFN. However, it should be noted that the concentration of radicals initially formed radicals in polymer was not necessarily accurate, because of the possibility of low efficiently performing of impregnation and dispersion depending on particle size and density. At least, it was showed that the radicals forming during polymerization could successfully trap and proved the presence of radicals by PFN.

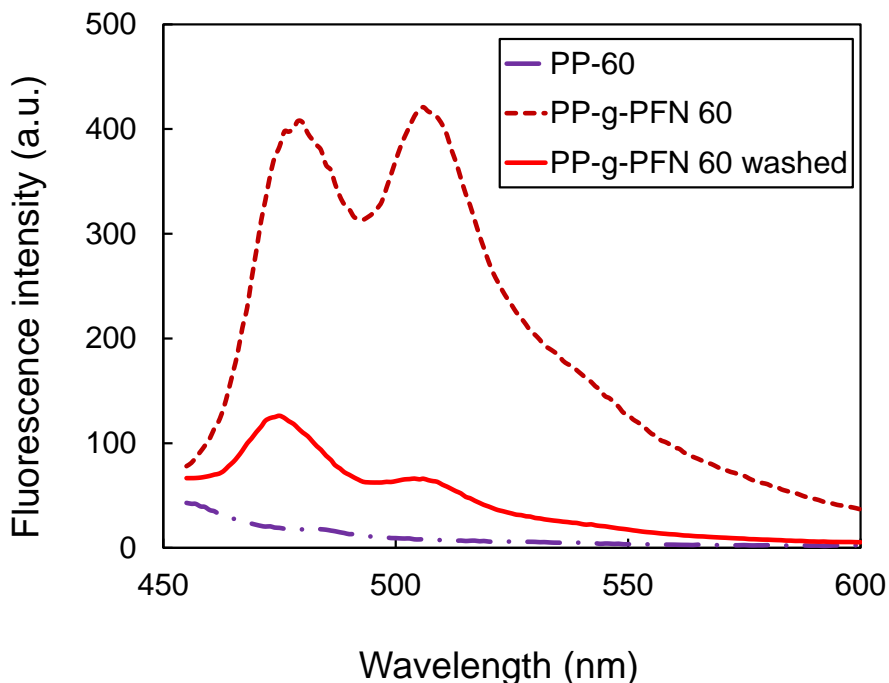


Figure 3.10. The fluorescence intensity of PP, PP functionalized PFN polymerized at 60°C. After catalyst extraction by Soxhlet extraction at room temperature, PP/PFN was washed by chloroform (PP-g-PFN).

In this work, to prove the presence of initial radicals and stabilize as-synthesized PP, a radical trapping strategy using nitroxide radical trapping agent was applied. In addition, to prove the formation of initial radicals during polymerization, examine the quantitative determination or identify the existence radicals in polymer using PFN was also investigated. It was found that the OIT significantly increased in the presence of

TEMPO, indicating the suppression of peroxy radical formation by grafting of TEMPO to initial radicals. These results suggested that the initial radical was formed during polymerization and the radical trapping by nitroxide compounds could potentially suppress the oxidative degradation by preventing the new radical formation. From these results, the initially formed radicals could be successfully trapped with TEMPO, thus providing polymer with longer lifetime. In addition, the result of a radical trapping strategy using PFN showed that the initially formed radicals could be successfully trapped using PFN, thus providing PP powder with fluorescence emission of polymers functionalized with PFN.

3.4. Conclusions

In this work, to prove the presence of initial radicals and stabilize as-synthesized PP, a radical trapping strategy using TEMPO agent was applied. It was found that the the lifetime of as-synthesized PP significantly increased in the presence of TEMPO, indicating the suppression of peroxy radical formation by grafting of TEMPO to initial radicals. These factors which can mislead the results were removed by polymer washing and catalyst extraction. PP polymerization temperature indicating different concentration of initial radical and amount of TEMPO were varied. The results

showed that PP produced at higher polymerization yield showed the higher lifetime improvement and the higher amount of TEMPO was required to reach the maximum lifetime.

Finally, to quantitatively determine the existence of initial radicals in polymer, a radical trapping strategy with using PFN and characterization by fluorescence spectroscopy were investigated. Fluorescence emission of the PP-g-PFN showed the sharpness peak. Using a calibration curve, quantitative determination of PFN in polymer by fluorescence spectrophotometer was performed. The results showed 1.5 nmol-PBEA/kg-PP. The result showed that the initially formed radicals could be successfully trapped using PFN, thus providing PP powder with fluorescence emission of polymers functionalized with PFN. A simple way to synthesis high stability PP was realized by initial radical trapping approach. This is the first reports to prove directly the presence of initial radical formed during polymerization.

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Chapter 4

General conclusion

4.1 General Summary

This dissertation discussed the origin of radical formation during polymerization for Ziegler-Natta polypropylene (PP) on the oxidative degradation and radical trapping approach using its reaction was investigated.

In Chapter 1, history and development, degradation and stabilization of polypropylene, study for nitroxide free radical compounds with as-synthesized PP powder were introduced based on the objectives of this dissertation.

In chapter 2, the impacts of polymerization parameters on the lifetime of as-synthesized PP powder were systematically investigated. Propylene polymerizations under various conditions were conducted using industrial Ziegler-Natta catalyst and the lifetime of obtained PP was analyzed by chemiluminescence (CL) analysis. It was found that as-synthesized PP powder obtained at a low temperature offered polymer with longer lifetime in spite of a lower polymer yield, *i.e.* a higher concentration of the catalyst residue. Similarly, a short polymerization time offered polymer with longer lifetime even though the concentration of catalyst residue in polymer was higher. The increase of TEA and H₂ concentration resulted in the increase of polymer yield, which simultaneously resulted in the decrease of the lifetime of PP. Although, low catalyst residue was expected in polymer obtained at high yield,

the lifetime of polymer was found to inversely proportional to the polymerization yield rather than the catalyst residue. From this result, it was surprisingly found that the lifetime of PP was dominated by polymerization conditions such as the polymer yield per g-catalyst, rather than the polymer structure such as the concentration of catalyst residues and molecular weight. A comparison between the lifetime of PP powder pre-exposed to dry air and the area of initial intensity in CL measurement under inert atmosphere was performed. It was found that the amount of radicals, which formed during polymerization, was determined by polymerization conditions such as the polymer yield per g-catalyst, because the PP powder produced the higher polymerization temperature which having the lower lifetime showed the higher amount of peroxide in the PP powder. In addition, a radical trapping strategy with nitoxide radical scavenger for the PP powder to trap the radical in the PP chain also performed. It was suggested that that the initial radicals might be formed during polymerization process due to the result that the lifetime of PP became surprisingly high by the addition of nitoxide radical scavenger which could graft only the Carbon-centered radicals. It suggested that the alkylation of active sites by alkyl aluminum compounds and/or a local high temperature might play a role in the initial radical formation during polymerization. The mechanism of initial radical formation has been still unclear.

However, it is most important that we have ascertained the facts that the initial radical was more initially than previously thought, that is, already presented after polymerization process.

In chapter 3, to prove the presence of initial radicals and stabilize as-synthesized PP, a radical trapping strategy using nitroxide radical trapping agent was applied. In addition, to prove the formation of initial radicals during polymerization, examine the quantitative determination or identity the existence radicals in polymer using profluorescence nitroxides (PFN) was also investigated. 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. These factors which can mislead the results were removed by polymer washing and catalyst extraction. Polymerization temperature indicating different concentration of initial radical and amount of TEMPO were varied. The results showed that PP produced at higher polymerization yield showed the higher lifetime improvement and the higher amount of TEMPO was required to reach the maximum lifetime. The results of a radical trapping strategy using PFN showed that fluorescence emission of the PP functionalized with PFN showed the sharpness peak. Using a calibration curve synthesized with PP and BPEA, quantitative determination of

PFN in polymer by fluorescence spectrophotometer was performed, the result of the concentration of PFN in PP functionalized with PFN was 1.5 nmol-PBEA/kg-PP. From these results, the presence of initial radicals were successfully provided by a radical trapping strategy using nitroxide radical trapping agent. In addition, this approach provided high stability PP. A simple way to synthesis high stability PP was realized by initial radical trapping approach.

4.2 Conclusions

PP has been widely used in various industrial fields because of its wide variety of characteristics. However, the susceptibility to oxidative degradation is one of the biggest shortfalls of it. A number of researches have been well studied the degradation of PP. whereas, the origin of initial radical has never been clarified. In this work, we have paid attention towards the initial radical formation during polymerization. The objective of this study was 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 performed.

The impact of polymerization parameters on the lifetime of PP powder suggested that the initial radicals were already initiated during polymerization. A radical trapping approach with TEMPO and PFN as a radical scavenger showed that the initially formed radicals could be successfully trapped using nitroxide radical trapping agent, thus providing PP powder with longer lifetime.

Technological improvements though advancements in compound technology also has been carried out actively, such as PP base inorganic filler composite, controlling high-order structure by melt processing and resin additives. Especially, the addition of stabilizer is assumed an important role for the elongation to limit of long-term applications. Thus, this has enhanced the necessity of an innovative technology for low-additive stabilization, not only for the reuse and recycle of PP but also for applications with inorganic fillers or under severe environmental conditions. The results of this study has a potential technology for the technological improvements for the elongation to limit of long-term applications such as new reactor stabilization technology in olefin polymerization. In addition, this radical trapping strategy also has a potential technology for the applications by functionalization without degradation.

In this study, by the investigation of the origin of initial radical during polymerization, the possibility of enhancing an innovative technology for the new

stabilization strategy and applications by functionalization was provided.

Achievements

Original Article

Taira Tobita, Patchanee Chammingkwan, Minoru Terano and Toshiaki Taniike

“Initiation of oxidative degradation in polypropylene reactor powder produced by Ziegler-Natta catalyst” *Polym. Degrad. Stab.* **2017**, *137*, 131-137.

Taira Tobita, Patchanee Chammingkwan, Toshiaki Taniike and Minoru Terano

“Stabilization of polypropylene reactor powder produced by Ziegler-Natta catalyst through passivation of initially formed radicals” *Curr. Trends Polymer Sci.* **2017**, *17*, 51-57.

International conference

“Effects of Cocatalyst for Oxidative Degradation of Polypropylene” *International Symposium for Green-Innovation Polymers*, Ishikawa, Japan, March 2014.

“Influence of polymerization conditions and cocatalyst structure on polypropylene stability” *248th American Chemical Society National Meeting and Exposition*, San Francisco, USA, August 2014.

“Effects of polymerization conditions and radical trapping agent on initial oxidative degradation of polypropylene” *10th International Symposium on Weatherability*, Gunma, Japan, July 2015.

“Inhibitions of initial oxidative degradation of polypropylene using nitroxide radical trapping agent” *Asian Polyolefin Workshop 2015 and World Polyolefin Congress 2015*, Tokyo, Japan, November 2015.

“Investigation of initial radical formation leading to degradation of polypropylene”
6th International Conference on Polyolefin Characterization, Shanghai, China, November 2016.

Domestic conference

“重合時に用いる助触媒がポリプロピレンの酸化劣化に及ぼす影響”

マテリアルライフ学会 第19回春季研究発表会、東京、2014年、2月

“触媒と助触媒の反応生成物がポリプロピレンの初期酸化劣化に及ぼす影響”

マテリアルライフ学会 第25回研究発表会・特別講演会、東京、2014年、7月

“ラジカルトラップ剤を用いたポリプロピレン初期酸化劣化反応の抑制”

マテリアルライフ学会 第19回春季研究発表会、東京、2015年、2月

“ニトロキシド化合物によるポリプロピレン初期酸化劣化の抑制”

第65回高分子学会年次大会、兵庫、2016年、5月

“ラジカル補足剤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”

マテリアルライフ学会 第26回研究発表会・特別講演会、滋賀、2016年、7月

“初期ラジカル生成に着目したポリプロピレンの劣化開始機構の解明”

第65回高分子学会討論会、神奈川、2016年、9月

“ニトロキシドラジカル捕捉剤を用いたポリプロピレンの初期酸化劣化反応の抑制”

マテリアルライフ学会 第21回春季研究発表会、神奈川、2017年、2月

Award

“ラジカルトラップ剤を用いたポリプロピレン初期酸化劣化反応の抑制”

マテリアルライフ学会 第19回春季研究発表会、東京、2015年、2月

研究奨励賞 受賞

“ニトロキシド化合物によるポリプロピレン初期酸化劣化の抑制”

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第65回高分子学会討論会、神奈川、2016年、9月

優秀ポスター賞 受賞

Acknowledgments

I would like to express my sincere gratitude to Professor Dr. Minoru Terano for his excellent guidance and encouragement. This work would never have been performed without his great help.

I also wish to express my gratitude to Professor Dr. S. E. Bottle and Professor Dr. G. A. George, Queensland University of Technology in Australia for their kind guidance in my minor research theme.

I deeply appreciate Associate Professor Dr. Toshiaki Taniike and Assistant Professor Dr. Patchanee Chammingkwan for their quite valuable comments and suggestions. I also deeply appreciate colleagues in Terano and Taniike Laboratory for their kind encouragement and support.

I would like to express my gratitude to Mr. Takeshi Nagai, Ms. Supawadee Poonpong, Mr. Goond Hongmanee, Ms. Mingkwan Wannaborn, Mr. Ashutosh Thakur, and Ms. Bulbul Maira. I would never have challenged getting Ph.D. and have concentrated on my research without their kind encouragement.

I am grateful to Toho Titanium Co., Ltd., Mitsui Chemical Co., Ltd., Mitsubishi Chemical Co., Ltd., and Tosoh Finechem Co., for their constant support.

Finally, I am grateful to my parents, Etsuko and Etsuo, brother Akihiro and Yousuke, friend Tomoko for their great support and kindness.

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**Quantitative determination of radicals forming during
polymerization in polypropylene using profluorescence
nitroxides**

**reported by
Taira Tobita**

Submitted to

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【Introduction】

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. Generally, the oxidation is preceded according to the auto-oxidative degradation mechanism. Once the radical is formed, it reacts with oxygen to make peroxide radical and re-generate new radicals. The oxidation mechanism of PP has been studied by many researchers^{1,2}. However, the mechanism of initial radical formation still remains unclear.

In our previous works, we have paid attention towards the initial radical formation during polymerization. Some of experimental results was surprisingly suggested that the degradation already occurred during polymerization. In addition, a radical trapping strategy using 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO) showed that the initially formed radicals could be successfully trapped using nitroxide radical trapping agent, thus providing reactor powder with longer lifetime.

Recently, S. E. Bottle and G. A. George *et al.* reported that the profluorescent nitroxide (PFN) could be used as a probe for the radical-mediated degradation of stabilized polypropylene³⁻⁶. Fluorescence from a PFN, comprising a sterically

hindered nitroxyl radical with its attached fluorophore is initially quenched by spin-orbit coupling so no emission is seen. Scavenging of a polymer C-center radical by the PFN to form the non-radical product (alkoxy amine) reduces the quenching so fluorescence is then seen with intensity proportional to the radicals^{7,8}. Therefore, it suggested that PFN is possible to prove the formation of initial radicals during polymerization by the quantitative determination of the radicals.

In this report, to prove the formation of initial radicals during polymerization, examine the quantitative determination of radicals formed during polymerization using profluorescence nitroxides was investigated.

The results showed that the initially formed radicals could be successfully trapped using PFN, thus providing reactor powder with fluorescence emission of polymers functionalized with PFN. However, an accurate quantitative determination of radicals in polymer could not evaluate, because of low efficiently performing impregnation and dispersion, indicating small particle size and low density. At least, it was showed that the radicals forming during polymerization could trap by profluorescence nitroxide successfully.

【Experimental】

<Materials>

Propylene of research grade was donated by Japan Polypropylene Co., Ltd. and used without further purification. n-heptane was dried over 4A molecular sieve followed by N₂ bubbling for 2 h prior to use. Triethylaluminum (TEA, donated by Tosoh Finechem. Co.) was used after dilution in n-heptane. Cyclohexylmethyldimethox -silane (CMDMS) was purified by distillation under reduced pressure. 9,10-bis(phenylethynyl)anthracene (BPEA, Sigma–Aldrich Co. LLC.) was used as received. 1.9-(1,1,3,3-tetramethylisoindolin-2-yloxy)-5-ethynyl)-10-(phenylethynyl) anthracene (PFN) which was donated by Laboratory of Prof. Steven E. Bottle, Science and Engineering Faculty, Queensland university of technology was used as the profluorescent nitroxides.

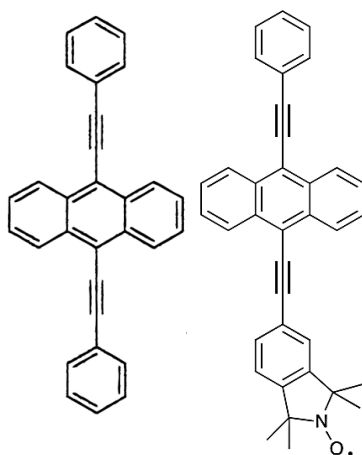


Figure 1. Chemical structures, Left; 9,10-Bis(phenylethynyl)anthracene (BPEA) and Right; 9,10-Bis(phenylethynyl) anthracene (BPEA, Left.), 9-(1,1,3,3-tetramethyl isoindolin-2-yl)ethynyl-10-(phenylethynyl) anthracene (PFN)

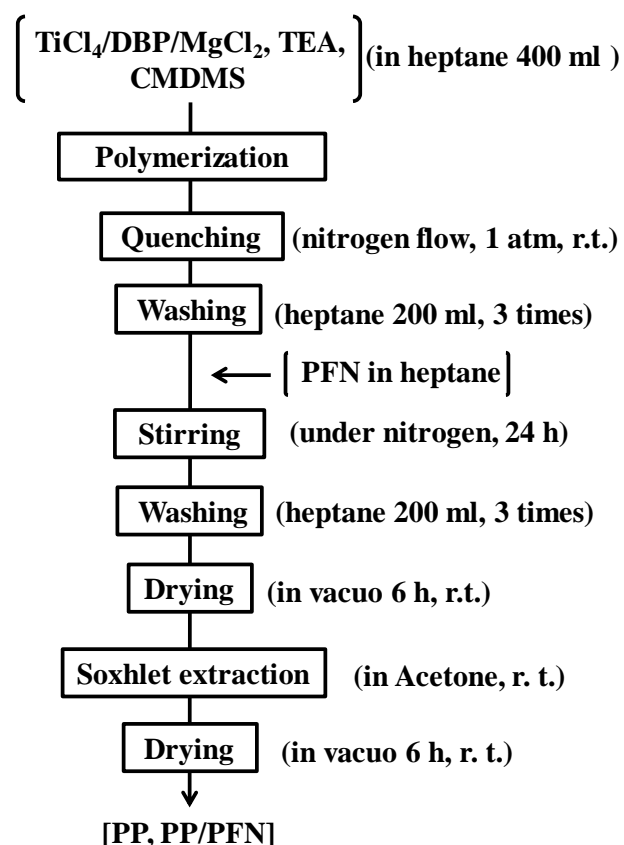
<Experimental method>

- Catalyst synthesis

A $\text{TiCl}_4/\text{Di-}i\text{-butylphthalate}/\text{MgCl}_2$ catalyst was prepared using spherical $\text{Mg}(\text{OEt})_2$ particles (donated by Toho Titanium Co., Ltd.) according to literature⁹. The Ti and the di-iso-butylphthalate content were measured as 3.4 wt.-% and 12wt.-%, respectively.

- Synthesis of PP reactor powder

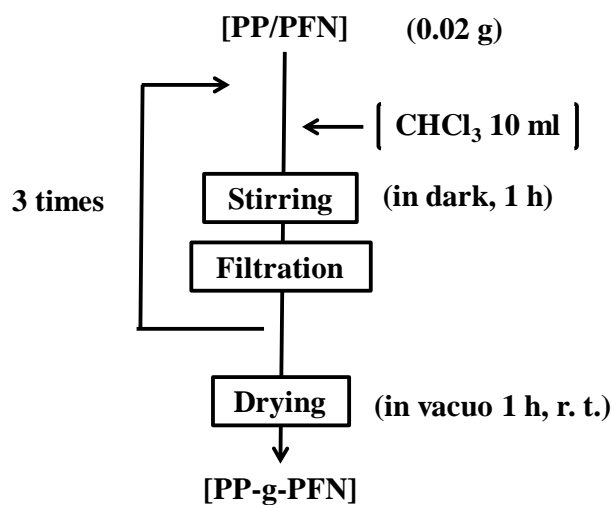
PP reactor powder was synthesized in slurry phase polymerization using industrial Ziegler-Natta catalyst. 400 mL of heptane as solvent was introduced to a 1 L stainless steel reactor. After propylene saturation at 0.3 MPa, 2 mmol of TEA as activator and 0.4 mmol of CMDMS as an external donor were added. Thereafter, 15 mg of the catalyst was injected to the reactor to initiate polymerization. The polymerization was conducted at 0, 30 and 60°C under the total pressure of 0.3 MPa for 60 min. After polymerization, the slurry was washed by heptane to remove Al compounds and external donor. Then the polymerization slurry was quenched by several amount of PFN. Thereafter, the slurry was stirred 24 h and subsequently washed with heptane and dried under vacuo at room temperature. In addition, to remove catalyst residues, soxhlet extraction at room temperature 4 h under each reactor powders was performed. It must be noted that all of the procedures were carefully conducted under nitrogen in order to prevent the intrusion of oxygen.



Scheme 1. Sample preparation of PP, and PP-g-PFN

- Polymer washing by stirring and filtering

To remove ungrafted nitroxides from PP, examination of washing effects with some solvents were investigated. After stirring for 1 h in solvent in the dark, the slurry was filtered. The washing was performed 3 times for each sample. Thereafter, the slurry was dried under vacuum at room temperature.



Scheme 2. Polymer washing procedure

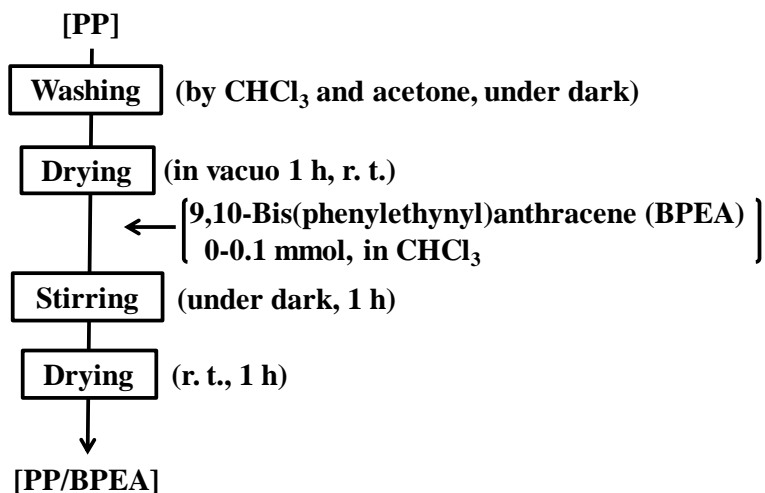
- Synthesized standard polymer samples for calibration curve of electron paramagnetic resonance

In order to determinate quantitatively the concentration of radicals in the polymer, synthesized standard solvents for calibration curve of electron paramagnetic resonance were conducted. Specified amounts of TEMPO in CHCl_3 were prepared and measured by EPR. EPR measurements were conducted under air on several gains (10, 30 and 900).

- Synthesized standard polymer samples for calibration curve of fluorescence spectrophotometer

In order to determinate quantitatively the concentration of radicals in the

polymer, synthesized standard polymer for calibration curve of fluorescence spectrophotometer were conducted. Specified amounts of BPEA in a 10 μ L CHCl_3 add to the 2.0 mg of PP polymerized at 60°C without nitroxide. Then, the polymer was dried in air.



Scheme 4. Synthesized the standard polymer for fluorescence spectrophotometer

<Characterizations>

- Chemiluminescence analysis

The chemiluminescence (CL) measurements were conducted using a CL analyzer (CLA-ID-HS, Tohoku Electronic Industrial Co., Ltd.), where 10 mg of a powder sample was held at 110 or 130°C under dry air flow at 100 ml/min. The

oxidative induction time (OIT) was determined from experimental records of CL intensity-time.

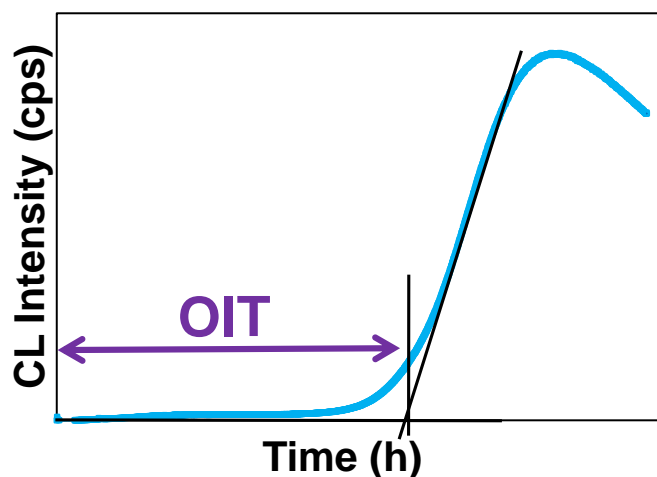


Figure 2. Oxidative induction time for CL curve under air

- Fluorescence spectrophotometer

Fluorescence spectra were collected with a Varian Cary Eclipse fluorescence spectrophotometer. For measurements on polymer samples, 2 mg of sample were put on aluminum pans and excited at an angle of 45° to the surface. Emission was recorded from the back face of the sample to limit interference from scattered and reflected exciting light.

- EPR measurement

Continuous wave EPR measurements were performed using Magnettech, MiniScope MS 400. 3.1 mg of polymer samples were prepared in 50 μm of Sample tube. Then, continuous waves were measured at room temperature under air.

【Results and Discussion】

Table 1 summarizes all of the polymerization conditions employed in this study. It was noted that “Nitroxide concentration” was the condition during impregnation method. In this report, the PP polymerized at 0, 30 and 60°C were used for synthesis of polymers functionalized with PFN. Because our previous results showed that polymerized PP powder obtained at a higher temperature offered polymer with shorter lifetime, indicating more radicals can be formed.

Table 1. Polymer information and results of stability

Run	Sample	Polymerization temperature (°C)	Cold soxhlet extraction	CHCl ₃ washing	OIT at 110°C (h)	OIT at 130°C (h)	Nitroxide concentration (mmol-TEMPO/g-PP)
1	PP-0	0	×	×	15	0.4	-
2	PP-30	30	×	×	8.3	0.1	-
3	PP-60	60	×	×	4.6	0.1	-
4	PP-g-PFN 0	0	○	○	-	-	1.8
5	PP-g-PFN 30	30	○	○	-	-	13
6	PP-g-PFN 60 1st	60	○	○	-	-	27
7	PP-g-PFN 60 2nd	60	○	○	-	-	40

<The results of Polymer characterizations by EPR>

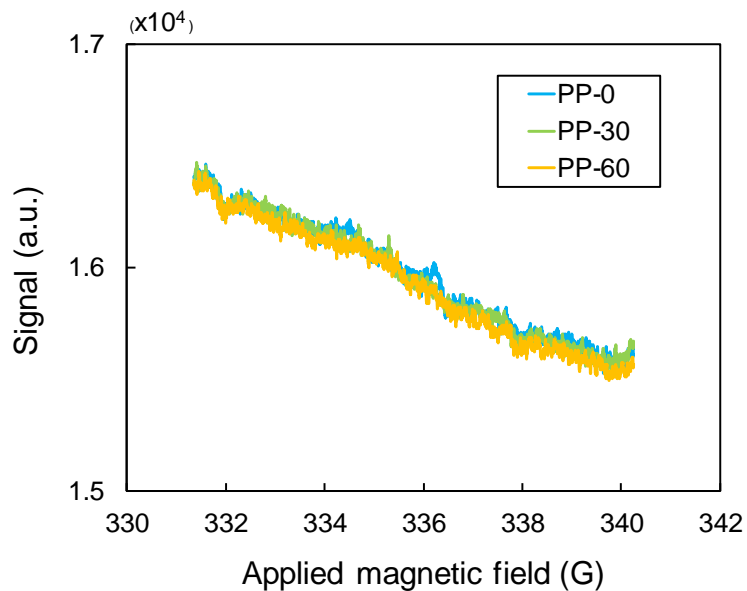
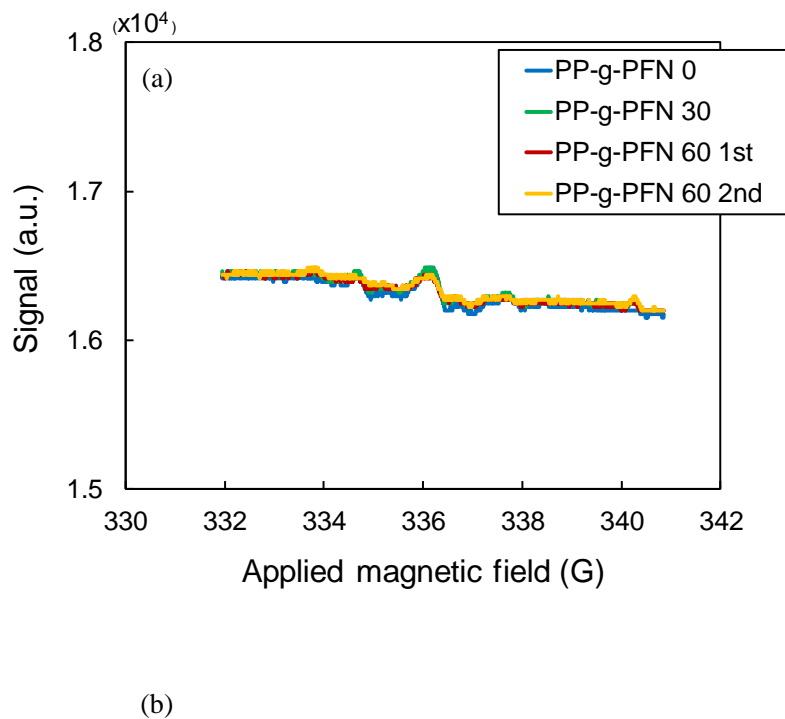


Figure 4. Comparison of polymers without nitroxides and powder EPR spectra



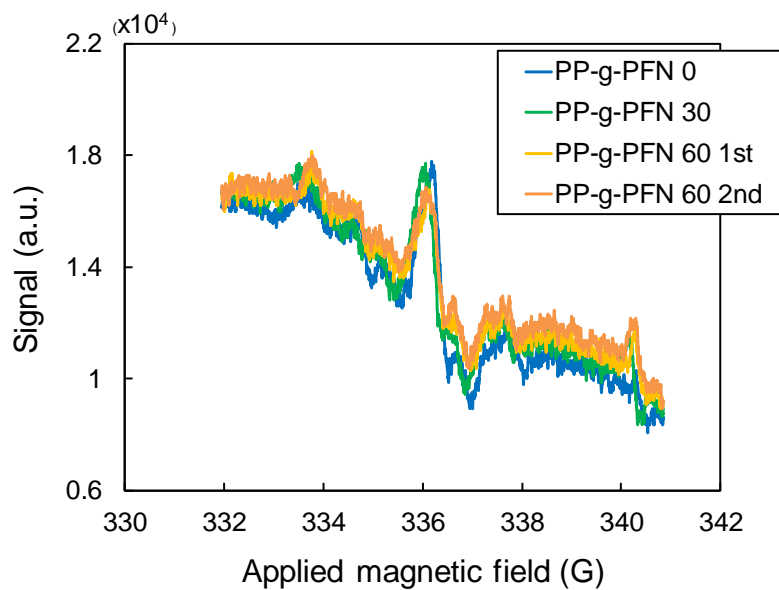


Figure 5. Comparison of polymers functionalized with PFN. a) Gain: 30, b) Gain: 900

In order to confirm the amount of active nitroxides in PP, polymer characterization by EPR was investigated. Results were shown in Figure 4 and 5. EPR spectra of polymers without nitroxides did not show any peaks. EPR spectra of polymers functionalized with PFN showed small peak. It suggests that almost of ungrafted PFN was removed with washing with CHCl_3 .

<The results of Polymer characterizations by fluorescence spectrophotometer>

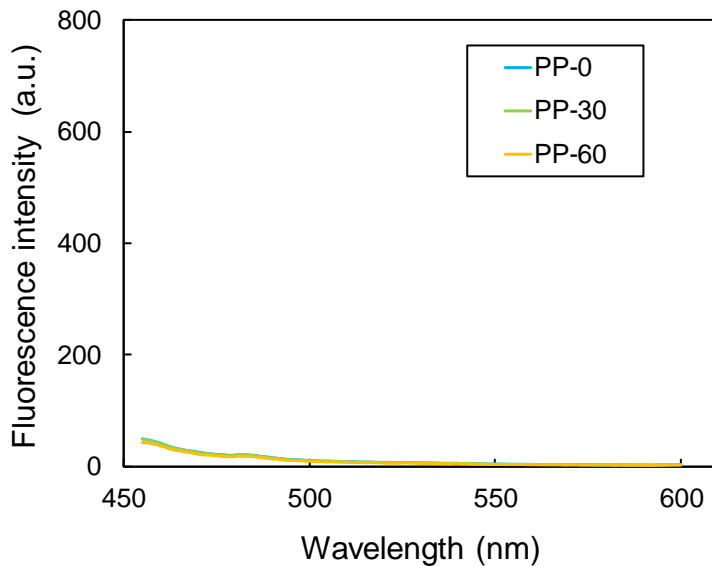


Figure 6. Comparison of fluorescence emission of polymers functionalized without PFN

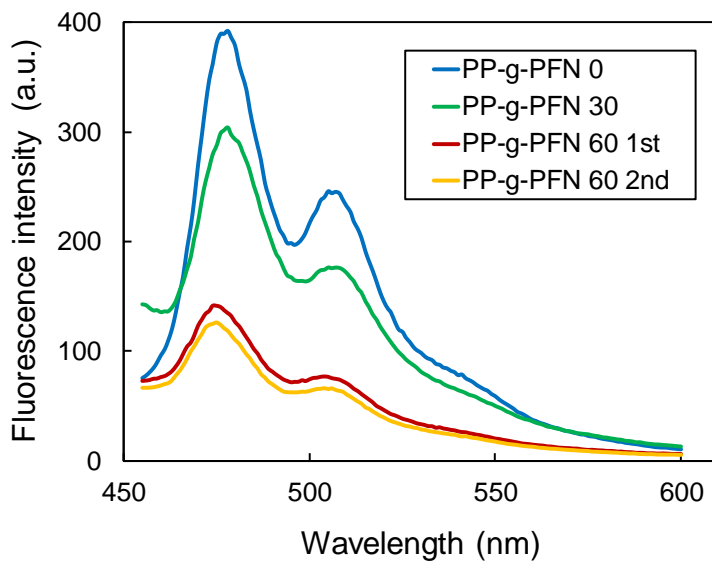


Figure 7. Comparison of fluorescence emission of polymers functionalized

with PFN polymerized different temperature

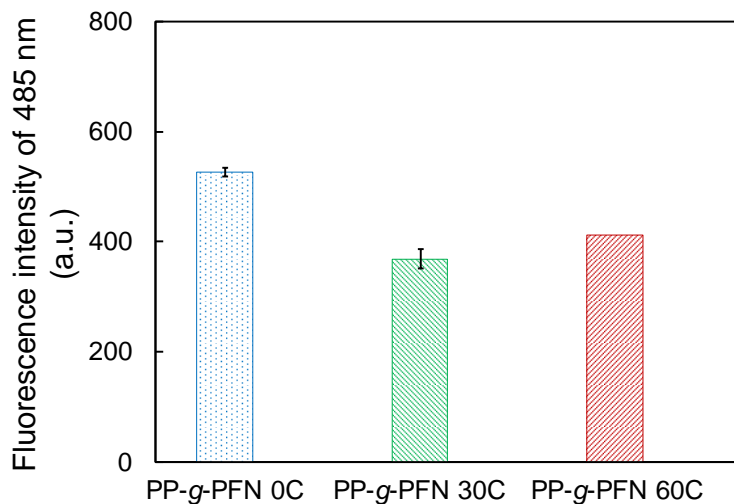


Figure 8. Comparison of 485 nm of fluorescence intensity of polymers functionalized with PFN polymerized different temperature

In order to quantitatively determine the radicals formed during polymerization in polymer using profluorescent nitroxides, polymer characterization by fluorescence spectroscopy was investigated. The results were shown in Figure 6-8. Fluorescence emission of polymers without PFN did not show any peaks (Figure 6). Fluorescence emission of polymers functionalized with PFN showed the same peak (Figure 7). 485 nm and 515 nm of fluorescence intensities originated from PFN, same as the shape of with previous paper reported by K. E. Fairfull-Smith⁷. It was suggested that the initially formed radicals could be successfully trapped using PFN, thus providing

reactor powder with fluorescence emission of polymers functionalized with PFN.

< synthesis of standard polymer samples for calibration curve >

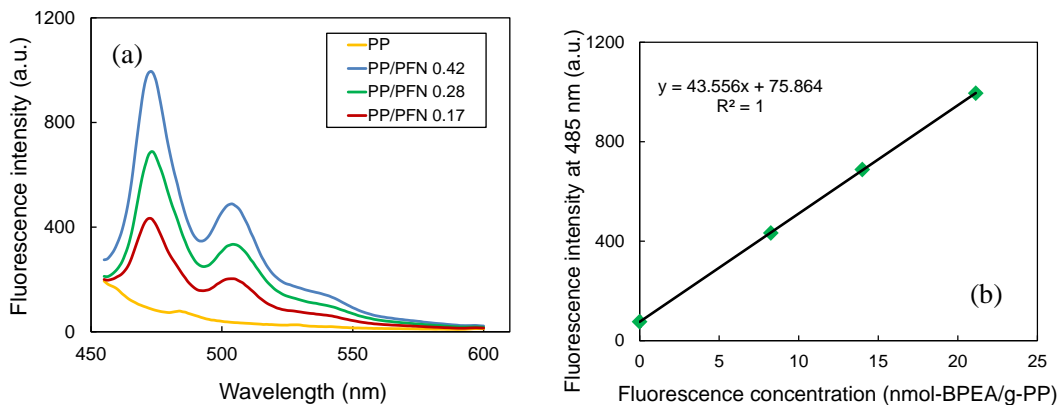


Figure 9. The fluorescence intensity of (a) PP/BPEA and (b) calibration curve at 485 nm

The results of fluorescence for synthesized the standard polymer were shown in Figure 9a. 485 nm and 515 nm of fluorescence intensities originated from BPEA were appeared. Based on the results, a calibration curve was performed to determinate quantitative of the fluorescence in polymer (Figure 9b).

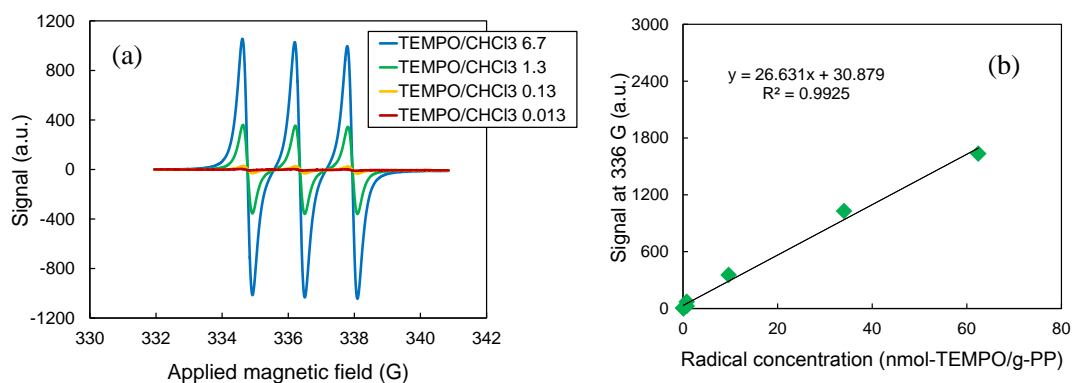


Figure 10. The normalized EPR signals of a) TEMPO/CHCl₃ and b) calibration curve at 336 G

In order to determine quantitatively the radicals in polymer, synthesized the standard sample for calibration curve of EPR were conducted. Specified amounts of TEMPO in CHCl₃ were prepared and measured by EPR. EPR measurements were conducted under air on several gains (10, 30 and 900). The results of EPR signals which synthesized the standard polymer were shown in Figure 10a. 3 peaks originated from TEMPO radicals were appeared. Based on the results, a calibration curve was generated to determine quantitatively of the radicals in polymer using middle peak (Figure 10b).

<Quantitative determination of the radicals in polymer by EPR and fluorescence spectrophotometer>

Table 2. The results of quantitative determination using calibration curves

Run	Sample	Concentration of active nitroxide ($\mu\text{mol-TEMPO/kg-PP}$)	Concentration of PFN (nmol-PBEA/kg-PP)
1	PP-0	-	-
2	PP-30	-	-
3	PP-60	-	-
4	PP-g-PFN 0	n.d.	7.3
5	PP-g-PFN 30	n.d.	5.2
6	PP-g-PFN 60 1st	n.d.	1.5
7	PP-g-PFN 60 2nd	n.d.	1.2

n.d.(not determined): The peak was too small to detect.

Using the results of calibration curves, quantitative determination of the radicals in polymer and PFN in polymer by EPR and fluorescence spectrophotometer was performed. The concentration of active nitroxide should show the concentration of ungrafted PFN in PP. The result showed that the concentration of active radical in PP functionalized with PFN was too small to detect by ESR. It was suggested that almost of ungrafted PFN was washed by CHCl_3 . The concentration of PFN should show the concentration of grafted PFN, indicating PFN can be grafted radicals formed during polymerization. PP produced at lower yield condition showed the highest

concentration of PFN (7.3 nmol-BPEA/kg-PP). In previous results, PP produced at higher polymerization temperature showed the lower lifetime, indicating more nitroxide can be grafted and stabilized. However, the results of polymers functionalized with PFN suggested that PP produced at lower polymerization temperature showed highest concentration of the radicals. It was suggested that the results was caused by low efficiently performing impregnation and dispersion, indicating small particle size and low density.

【Conclusion】

To prove the formation of initial radicals during polymerization, examine the quantitative determination or identity the existence radicals in polymer using fluorescence nitroxides were investigated. EPR spectra of polymers without nitroxides did not show any peaks and EPR spectra of polymers functionalized with PFN showed small peak. It suggests that almost of ungrafted PFN was removed with washing with CHCl_3 . Fluorescence emission of polymers without PFN did not showed any peaks and fluorescence emission of polymers functionalized with PFN showed the same peak. It was suggested that the initially formed radicals could be successfully trapped using PFN. Finally, using the standard polymer, quantitative determination of the radicals in

polymer by EPR and fluorescence spectrophotometer was performed. It was the opposite trend with previous polymer stability (the concentration of initial radicals increased with the increase of polymerization yield, indicating much nitroxides can be grafted with PP). It was suggested that the results was caused by low efficiently performing impregnation and dispersion, indicating small particle size and low density.

At least, it was showed that the radicals forming during polymerization could trap by profluorescence nitroxide successfully.

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Acknowledgments

I would like to express my sincere regards and gratitude to Professor Steven E. Bottle for his invaluable guidance and support. This work would never have been performed without his help.

I would like to extend my special thanks to Dr. John M. Colwell, Dr. Melissa A.L. Nikolic and Dr. Michael for their constant help in my experiments.

I am greatly thankful to all the colleagues of George Laboratory for their biggest support and encouragement.

Finally, I am grateful to Professor Minoru Terano, Associate professor Toshiaki Taniike and Assistant professor Patchanee Chammingkwan.

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