High-performance polypropylene-based copolymer containing a small amount of reactive functional group

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ABSTRACT

High-performance polypropylene (PP)-based copolymer containing a small amount of reactive functional group was synthesized through copolymerization using a Ziegler-Natta (ZN) catalyst. It was found that a small amount of alkoxysilyl group in the PP chain (comonomer content was under 5.0×10^{-3} mol%) does not deteriorate the base properties of PP such as melting temperature, crystallinity and so on. However, drastic enhancement in the crystallization rate as well as physical properties was observed in the copolymer. It is suggested that these improvements could be attributed to the reaction of functional groups incorporated in the PP chains.

KEYWORDS: polypropylene, copolymer, functional group, Ziegler-Natta catalyst

1. INTRODUCTION

Polypropylene (PP) is the most commonly used commodity plastic with a wide variety of applications in automobile components, electronic parts, packaging film, food containers, etc. PP has excellent characteristics such as good moldability, well-balanced physical properties, low environmental impact, recyclability, and is halogen-free. Therefore, the development of high-performance PP and PP-based materials has been continuously attracting great attention [1-6].

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Functionalization of PP can be an effective approach for the purpose. Functional groups introduced in PP chains are expected to play an important role in improving the physical properties of PP and its copolymer [3-5, 7, 8]. Especially, reactive functional groups are expected to effectively improve PP properties. Chung *et al.* reported that borane groups introduced into PP can be converted to OH, NH_2 or halides [9, 10]. In addition, PP graft copolymers, such as PP-graft-poly(methyl methacrylate), can be prepared *via* radical polymerization by transforming borane functional groups into a living free radical initiator [11, 12].

Vinylalkoxysilane is also a reactive functional group. The hydrolysis and condensation reaction of alkoxysilane advances the crosslinking reaction. Silane grafting of polyolefins is performed by chemical modification using peroxide through melt-mixing with vinylalkoxysilane and polyolefins. Silane-grafted moisture-curable polyethylene has been in wide commercial use since the 1970s, with many papers and patents reporting on the grafting reaction [13-15]. On the other hand, there are only a few reports regarding silane-grafted PP [16]. β-scission and the cross-linking reaction of PP chain proceed in conjunction with the silane grafting of functional groups. The high temperature melt-mixing tends to advance the β-scission of the PP chains quite rapidly, which makes silane grafting and crosslinking difficult. The decomposition has significant negative impact on the physical properties, which prevents the effective enhancement

of these properties during the formation of a crosslinking structure.

Functional groups can be introduced through copolymerization. But it is difficult to introduce a comonomer like alkoxysilane into PP backbone because of the deactivation of catalytic active sites by the comonomer. Consequently, there are very few reports written on propylene copolymerization with vinylalkoxysilane as a comonomer.

This research investigated the introduction of a small amount of alkoxysilane as a reactive functional comonomer in the PP chains with the objective of enhancing the physical properties of the PP-based copolymer. Introduction of a small amount of functional group can improve the PP properties without deteriorating the base properties of PP. Recently, Taniike *et al.* studied the effects of a small amount of aromatic group incorporated into PP chain on crystallization behavior [17]. Melting temperature and crystallinity were almost not affected by the small amount of aromatic functional group (under 0.10 mol%). The nucleation effect on crystallization was clearly observed by the introduction of the functional groups even though only a small amount was incorporated. It may be possible to greatly increase the PP properties if optimal functional groups are incorporated. The copolymerization of propylene and a small amount of comonomer having alkoxysilyl group was performed in this study using a Ziegler-Natta (ZN) catalyst in order to obtain a high-performance PP-based copolymer.

2. MATERIALS AND METHODS

2.1. Materials

Research grade propylene donated by Japan Polypropylene Co., Ltd. was used without further purification. *n*-Heptane (purchased from Kanto Chemical Co., Inc.) was dried by passing through a column of molecular sieve 4A followed by N_2 bubbling for 2 h. A $MgCl_2$-supported Ziegler-Natta catalyst containing a diether as an internal donor was prepared based on a patent [18]. Triethylaluminum (TEA) (donated from Tosoh Finechem Co.) and trimethoxy(7-octen-1-yl)silane (OTMS) (purchased from Aldrich Chemical Inc.) were used without further purification. Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate

(AO-50, donated by ADEKA Co.) was used for stabilizing the obtained polymers.

2.2. Polymerization

Polymerization was performed using the $TiCl_4$/diether/$MgCl_2$ catalyst in a 1 L stainless steel reactor. 200 mL of heptane was introduced into the reactor after sufficient N_2 replacement. Propylene was saturated with 0.5 MPa in the solvent at 50 °C for 15 min. 0-5.0 mmol of trimethoxy(7-octen-1-yl) silane as a comonomer was added prior to the addition of 2.0-7.0 mmol of TEA as a co-catalyst, 30 mg of catalyst and 8.0 mmol of hydrogen. Polymerization was conducted for 30 min at 50 °C under a total pressure of 0.5 MPa. Repetitive washing of the obtained polymer powder was carried out with acidic ethanol and water. Thereafter, the polymer was purified by dissolving in hot xylene and re-precipitating in cold acetone followed by drying *in vacuo*.

2.3. Post-polymerization

A twin screw extruder (Xplore Instruments, Micro Compounder IM5) was used to mix 3.5 g of polymer at 185 °C under nitrogen at a mixing rate of 100 rpm. The polymer was previously impregnated in 1.0 wt% AO-50 in acetone, and the mixing force during mixing was monitored.

2.4. Sample film preparation

A film with a thickness of 200 μm was prepared by hot press at 230 °C under 20 MPa for 5 min. A stepwise quenching at 100 °C for 5 min and at 0 °C for 1 min was conducted after the hot press.

2.5. Polymer characterization

The gel content was measured to estimate the degree of crosslinking in the samples. After melt-mixing, the samples were finely cut, wrapped in a stainless steel net with a 150 μm mesh, and their initial weight was measured. The above samples were soaked in 200 mL of xylene, which was boiled for 6.5 h. The samples wrapped in the net were washed with acetone and dried *in vacuo* at 60 °C for 1.5 h, and their weight after drying was measured. The gel content (wt%) was calculated based on their weight after the test relative to the initial weight.

NMR (Bruker 400 MHz) was conducted at 120 °C to analyze the polymer structure. The comonomer

content was determined by ^{1}H NMR, which was operated at the scan number of 1000, and using 1,2,4-trichlorobenzene (TCB) as a diluent, 1,1,2,2-tetrachloroethane-d2 as an internal lock and reference, and dibutylhydroxytoluene (BHT) as a stabilizer. The stereostructure of the polymer was analyzed by ^{13}C NMR. The scan number was 5000 and the used solvents were same as ^{1}H NMR measurement.

Gel-permeation chromatography (GPC, Waters ALC/GPC 150C) was conducted to measure the molecular weight and molecular weight distribution of the polymers at 140 °C. A o-dichlorobenzene was used as an eluent at a flow rate of 1 mL/min. Polystyrene standards were used for calibration.

Differential scanning calorimetry (DSC, Mettler Toledo DSC 822) was carried out under N_2 to evaluate the crystallization behavior. The melting temperature (T_m) and the crystallinity (X_c) were obtained from the melting endotherm during the first heating to 230 °C at the heating rate of 20 °C/min in an aluminum pan. In order to erase the thermal history, a film sample was kept heated at 230 °C for 10 min. Isothermal crystallization rates ($t_{1/2}^{-1}$) were defined as the inverse of the half time of the exothermic peak of crystallization during cooling down to 144 °C at the cooling rate of 50 °C/min. The crystallization temperature (T_c) was also determined from the exothermic peak observed by non-isothermal crystallization measurement, where the sample was heated at 230 °C for 10 min to erase the thermal history before cooling down at a cooling rate of 20 °C/min.

Spherulite growth at 144 °C was observed using a polarized optical microscope (POM) (Leica DMLP) with an automated hot-stage (Mettler Toledo FP82HT). A polymer film sample with a thickness of 50 μm was heated at 230 °C for 10 min before cooling down to 144 ºC at a cooling rate of 20 ºC for observing isothermal crystallization.

Tensile test at a crosshead speed of 1 mm/min was conducted at room temperature using a tensile tester (Abecks Inc., Dat-100). Dumbbell-shaped specimens of thickness 200 μm prepared from the film sample were used for the measurement of tensile properties. The values of Young's modulus and tensile strength were determined from the average of the values obtained from five or more measurements.

3. RESULTS AND DISCUSSION

Trimethoxy(7-octen-1-yl)silane (OTMS), which has a long spacer between the double bond and the functional group, was used as a comonomer to perform copolymerization with propylene (Scheme 1).

Table 1 summarizes the polymerization results. Catalytic activity was observed to decrease as the comonomer content increased (Fig. 1). However, there was almost no effect on catalytic activity at extremely low comonomer concentrations. This clearly indicates that low level functionalization is effective in terms of synthesizing PP-based copolymer, that is functionalized PP. ^{1}H NMR measurements were conducted to analyze the polymer structure (Fig. 2). Even for the PP-OTMS5 copolymer, which is expected to have the highest introduced comonomer content, the spectrum showed


(7-Octen-1-yl)trimethoxysilane (OTMS)

Poly(propylene-co- trimethoxy(7-octen-1-yl)silane)
(PP-OTMS)
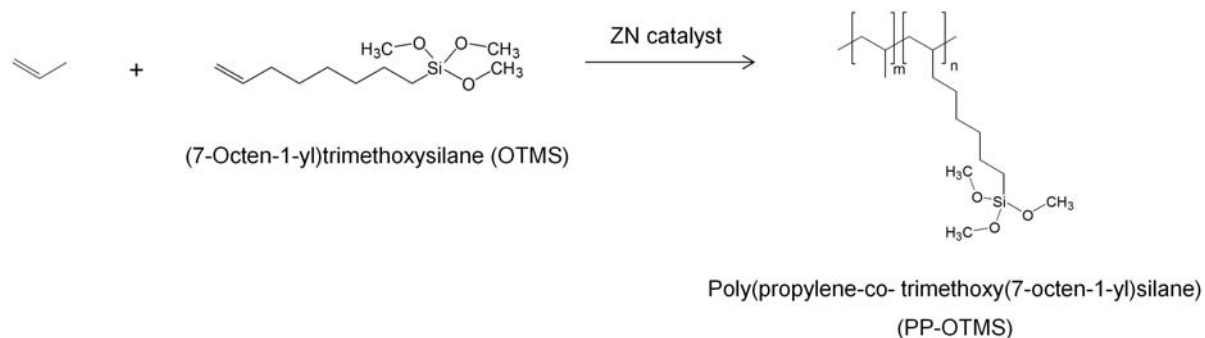
Scheme 1

Table 1. Summary of reaction conditions and results of copolymerization.

Sample	Amount of comonomer addition (mmol)	Activity (kg-polymer/ mol-Ti · h)	Comonomer content[a] (mol%)	M_n (g/mol)	M_w/M_n	Number of functional groups per polymer chain	mmmm[b] (mol%)
homo-PP	0	3450	-	4.84×10^4	4.26	0	92
PP-OTMS1	1	3500	1.3×10^{-3}	5.18×10^4	4.44	0.02	93
PP-OTMS2	2	2950	2.2×10^{-3}	5.65×10^4	4.11	0.03	95
PP-OTMS3	3	2650	2.9×10^{-3}	6.40×10^4	4.05	0.04	96
PP-OTMS5	5	1350	4.4×10^{-3}	-	-	-	96

[a]Analyzed by ^{1}H NMR; [b]Analyzed by ^{13}C NMR.
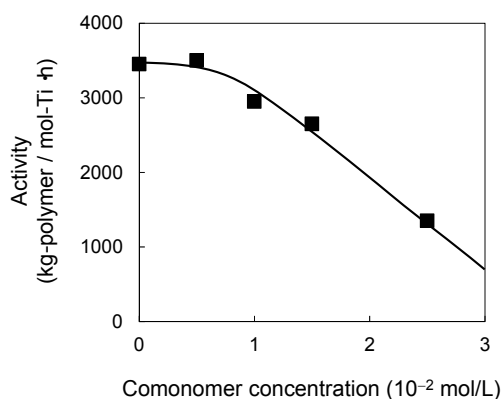
Fig. 1. Effect of comonomer concentration on the catalytic activity.

the main chain structure of PP in almost all respects. A peak assigned to the methoxy group was observed around $\delta = 3.7$ ppm in the expanded spectrum for the region from $\delta = 3.5$ ppm to 6.0 ppm. Since no H^4 or H^5 peak assigned to the protons of the vinyl end group originating from the comonomer was observed in the ^{1}H NMR spectrum for the OTMS copolymer, it is clear that all the unreacted comonomer residues in the samples were completely removed by the washing process. The comonomer content introduced in the copolymer chains was evaluated by ^{1}H NMR using the equation (1), based on the methine protons found in the PP main chain at $\delta = 1.72$ ppm and on the strength of the peak assigned to the protons of the methoxy group found at the chemical shift of $\delta = 3.7$ ppm.

$$\text{Comonomer content (mol\%)} = \frac{\underline{H^8 / 9}}{\underline{H^3}} \times 100 \qquad (1)$$

The results from ^{1}H NMR showed that the addition of the OTMS comonomer in the polymerization from 1 to 5 mmol led to the increase in the comonomer content in the resultant PP in the range of 1.3×10^{-3} to 4.4×10^{-3} mol% (Table 1). As the comonomer concentration in the polymerization system rose, the comonomer content increased (Fig. 3). Moreover, the increase in comonomer concentration also led to the increase in molecular weight of the resultant polymer (Table 1). The isotactic sites which can synthesize high molecular weight PP having high isotacticity may be difficult to be poisoned by alkoxysilane because of their steric-hindrance. The degree of polymerization calculated from the number average molecular weight M_n and the comonomer content evaluated by ^{1}H NMR were used to deduce the average number of functional groups per polymer chain (Table 1). Since this value was much lower than 1 for all polymers, it is likely that the polymers obtained contain a mix of polymer chains with and without functional groups. The mmmm value calculated using ^{13}C NMR exhibited a tendency to increase as comonomers were added (Table 1), indicating the polar comonomers selectively poisoned the atactic sites.

Melt-mixing of the PP-OTMS copolymer was applied as a post-polymerization process leading to the reaction among the reactive methoxysilyl groups in the PP chains. The observed mixing
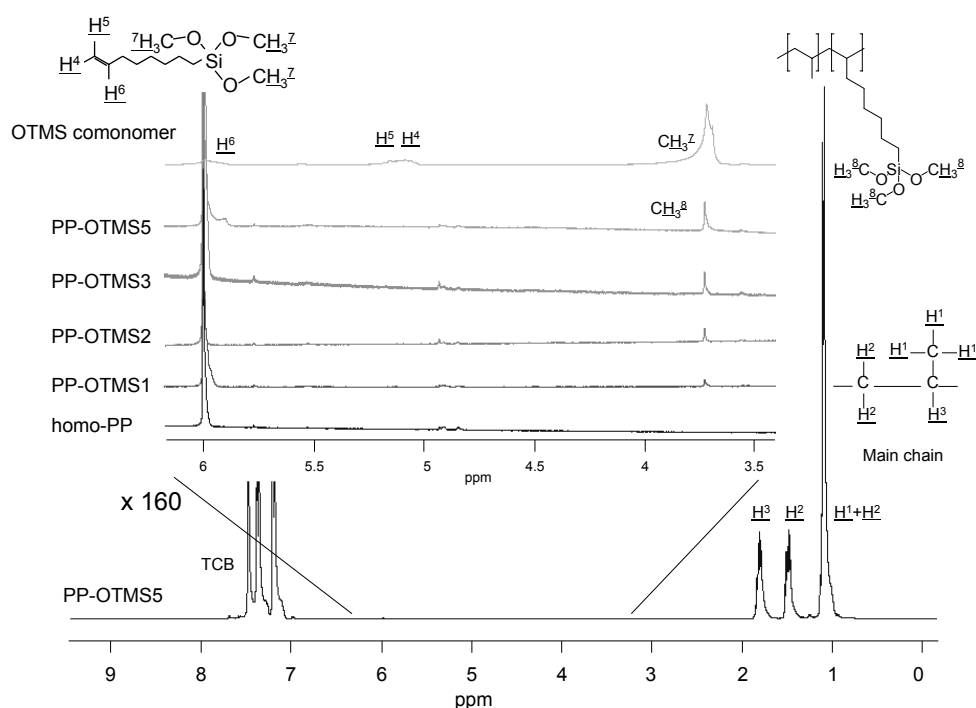
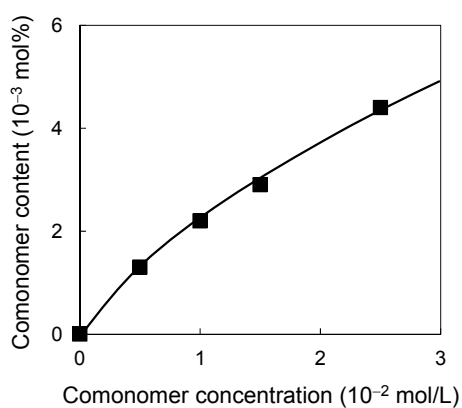**Fig. 2.** ^{1}H NMR spectra of homo-PP and PP-OTMS.

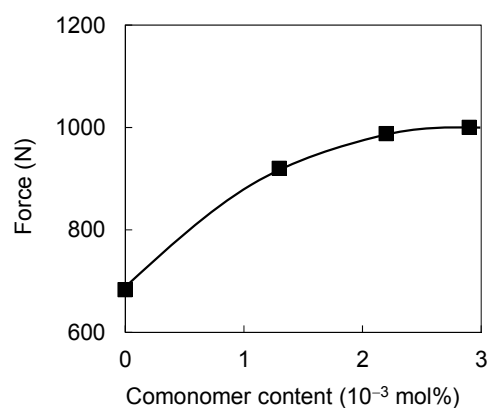**Fig. 3.** Relationship between comonomer concentration and comonomer content.

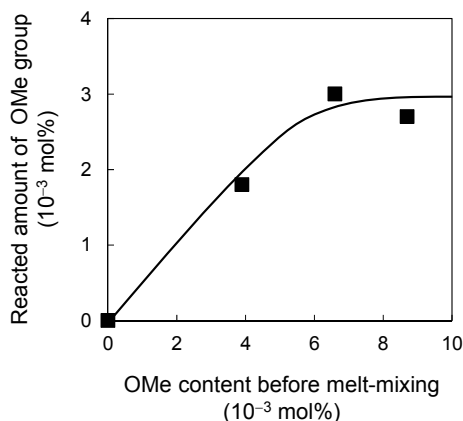**Fig. 4.** Relationship between comonomer content and mixing force.

force showed that it tended to increase in proportion with a higher comonomer content in the polymer chains (Fig. 4). GPC measurements were conducted and the results showed almost no changes due to melt-mixing (Table 2).

In order to investigate the progress of the reaction of functional groups during post-polymerization, ^{1}H NMR measurements were used to analyze the

structure of the PP-OTMS copolymer. The OMe content in the copolymer calculated from the ^{1}H NMR spectrum after melt-mixing became lower (Fig. 5). This decrease in OMe content suggests the possibility that melt-mixing induced PP chain crosslinking *via* dehydrative condensation after the hydrolysis of the OMe groups. Fig. 6 shows the relationship between the OMe content before

Table 2. Results of GPC measurements of polymer after melt-mixing.

Sample	M_n (g/mol)	M_w/M_n
homo-PP	4.58×10^4	4.15
PP-OTMS1	5.39×10^4	4.12
PP-OTMS2	5.68×10^4	4.00
PP-OTMS3	5.49×10^4	4.44
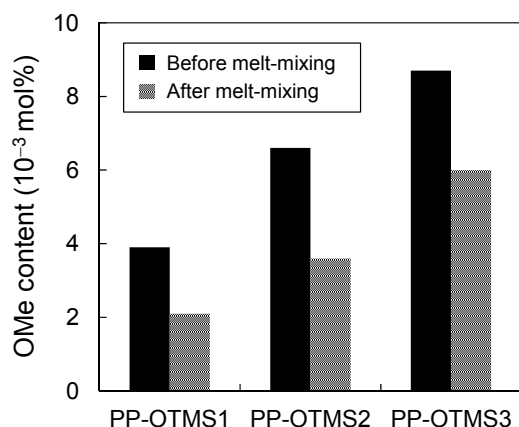
Fig. 5. OMe content of PP-OTMS before and after melt-mixing.

Fig. 6. Relationship between OMe content and reacted amount of OMe group.

melting and the reacted amount of the OMe groups during melt-mixing. While the amount of reacted functional groups rose as their contents in the polymer increased, the amounts of reacted

OMe groups were approximately constant for PP-OTMS2 and PP-OTMS3.

DSC measurement was conducted to investigate the crystallization behavior of PP-OTMS after the post-polymerization process (Table 3). The melting temperature and crystallinity almost maintain their values of homo-PP, regardless of the difference of the number of functional groups. In contrast, the crystallization temperature of PP-OTMS copolymer measured for the non-isothermal crystallization rose by about 10 °C above that for homo-PP. The crystallization rate was calculated from the isothermal crystallization measurements at 144 °C. At this temperature, homo-PP shows no clear exothermic peak for crystallization even after extending the crystallization to 40 min (Fig. 7). In the PP-OTMS copolymers, crystallization was much faster and almost completed within a retention time of approximately 10 min. Fig. 8 shows the relationship between OMe content before melt-mixing and the crystallization rate after that process. The crystallization rate improved as the OMe content increased, and eventually reached saturation at a point that matches the saturation of the reacted amount of OMe group shown in fig. 6. The reacted OMe groups must be responsible for the enhancement in the crystallization rate.

The spherulites in the isothermal crystallization process at 144 °C were observed using POM (Fig. 9). In the PP-OTMS copolymers, crystallization was almost completed by 15 min after the start of the isothermal process, and many spherulites were observed. Only a few spherulites were observed in the homo-PP even after 80 min, and crystallization was not completed. Compared to homo-PP, a clear increase in the number of nuclei was observed in the PP-OTMS copolymers, which indicates the

**Table 3.** Results of DSC measurements.

Sample	T_m^a (°C)	X_c^a (%)	T_c^b (°C)	$t_{1/2}^{-1\ c}$ (s^{-1})
homo-PP	163	43	113	n. d.^{d}
PP-OTMS1	165	41	124	3.2×10^{-3}
PP-OTMS2	164	43	126	3.9×10^{-3}
PP-OTMS3	164	43	125	3.8×10^{-3}

^{a}Obtained from the melting endotherm in the first heating, where the sample was heated to 230 °C at a heating rate of 20 °C/min.
^{b}Crystallization temperature was determined from a non-isothermal crystallization measurement, where the sample was heated at 230 °C for 10 min before cooling down at a cooling rate of 20 °C/min.
^{c}Isothermal crystallization rate at 144 °C.
^{d}n. d.; not detected.
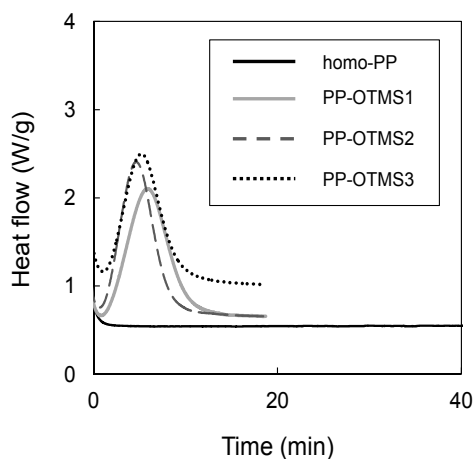
Fig. 7. Exotherms of isothermal crystallization at 144 °C.
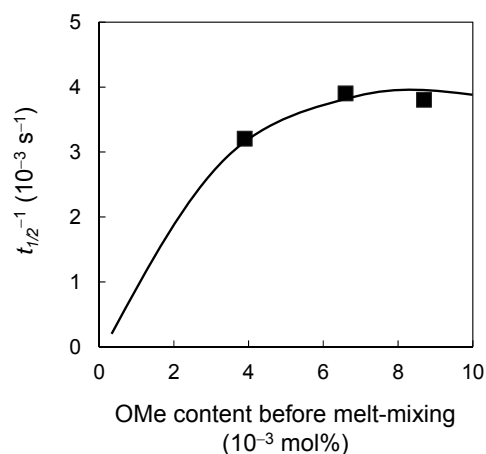
Fig. 8. Effect of OMe content on crystallization rate.

improvement of crystallization rate owing to the nucleation effect.

The gel formation was observed and its content is shown in fig. 10. The crosslinkage must be formed through a dehydrative condensation reaction between the methoxysilyl groups in the PP chains as described in scheme 2. Since 99% of each copolymer dissolved in xylene, it was deduced that three-dimensional crosslinking hardly progressed in the copolymers. But, the presence of xylene-insoluble moiety in PP-OTMS2 and PP-OTMS3 suggests the formation of three-dimensional crosslinking structures. Despite almost the identical amounts of OMe group reacted during melt-mixing,

PP-OTMS3 exhibited a higher gel content than PP-OTMS2. The higher gel content in PP-OTMS3 is attributed to the intermolecular reactions arising from the higher number of functional groups in the polymer chain compared to PP-OTMS2. Though the gel was not observed for PP-OTMS1, it does not negate the possibility of two-dimensional reactions between the functional groups.

The film samples of homo-PP and PP-OTMS after post-polymerization were treated at 130 °C and 140 °C for isothermal crystallization and their POM observation is shown in fig. 11. The spherulite size became smaller as more functional groups were introduced in the PP chains.
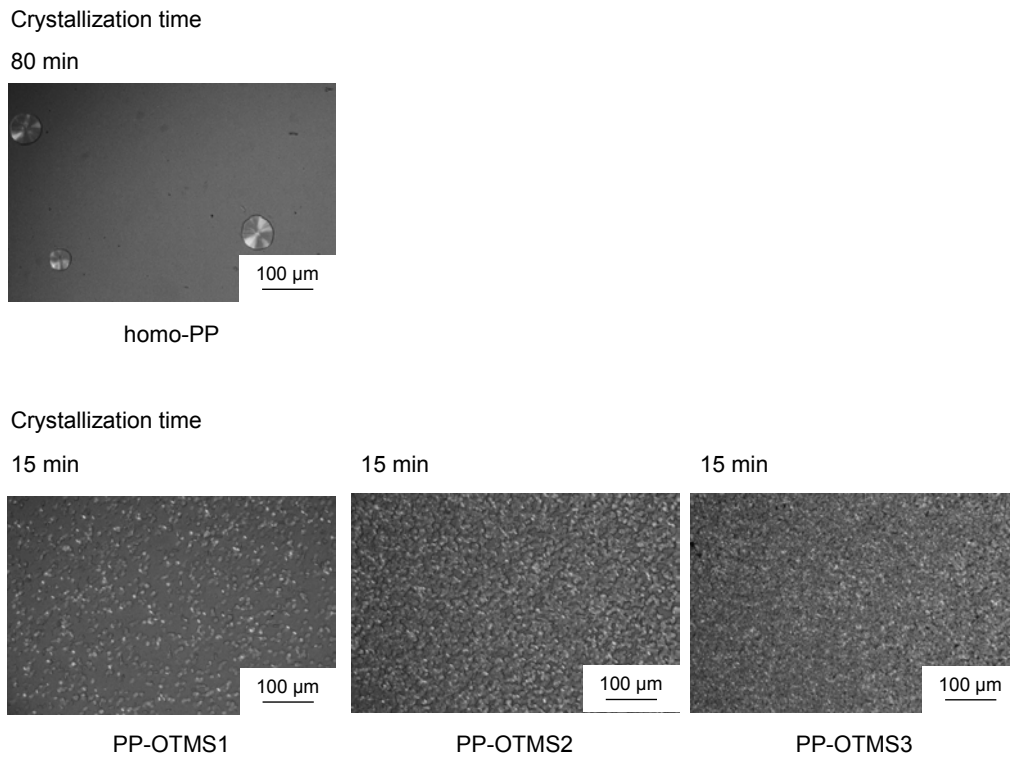
Crystallization time

80 min

homo-PP

Crystallization time

15 min   15 min   15 min

PP-OTMS1   PP-OTMS2   PP-OTMS3

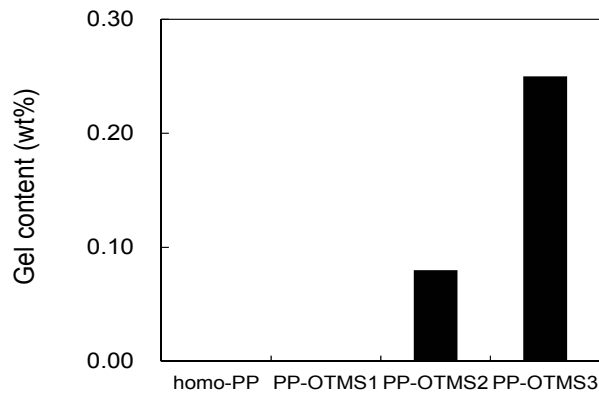**Fig. 9.** POM images during isothermal crystallization at 144 °C.


Fig. 10. Gel content of PP-OTMS copolymer.

Given that the number of functional groups introduced in the PP chains was exceedingly small and that the gel content was extremely small, it is possible that even in PP-OTMS3 the majority of the structure was similar to that of long-chain branching PP (LCB-PP) rather than a three-dimensional crosslinking structure. It is widely accepted that LCB-PP acts as a nucleating agent

and enhances crystallization rate [19-22]. Wang *et al.* found that the number of crystal nuclei increased and crystallization temperature rose as a result of blending LCB-PP with PP [19]. Su *et al.* found that LCB-PP crystallizes from the melt as a mixture of α crystals and γ crystals [20]. Based on those findings it is conceivable that, in this research as well, a nucleation effect manifested
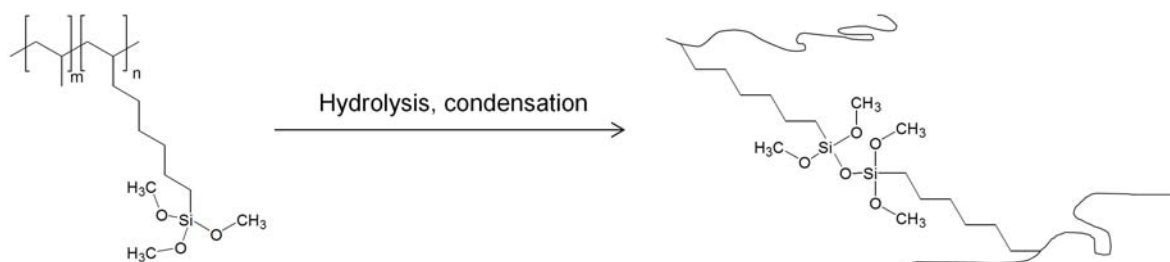
Scheme 2

Isothermal crystallization at 130°C

homo-PP   PP-OTMS1   PP-OTMS2
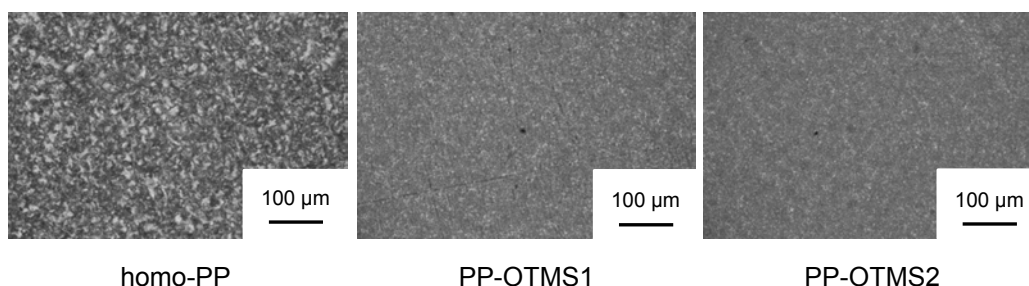
Isothermal crystallization at 140°C

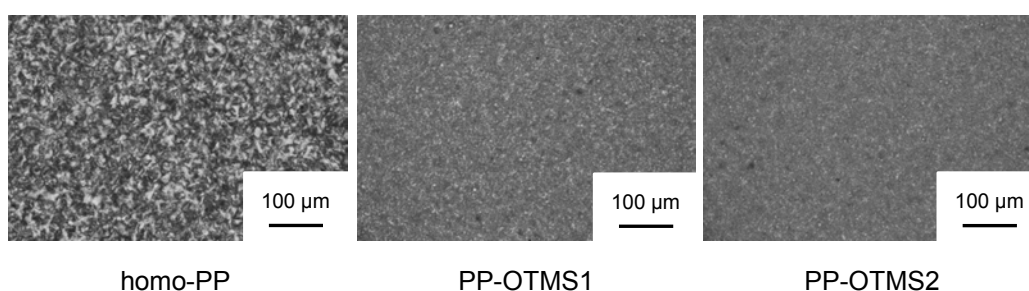homo-PP   PP-OTMS1   PP-OTMS2

Fig. 11. POM images of the isothermal crystallization samples at 130 °C and 140 °C.

itself through the introduction of reactive functional groups in the PP chains causing the formation of a long-chain branching structure after the dehydrative condensation reaction during melt-mixing. Alternatively, it is also possible that the intermolecular bond formed between the PP chains through the reactive functional groups led to restricting the movement of the polymer chains and resulted in the nucleation effect.

Tensile tests were conducted to evaluate the mechanical properties of the polymers. Both Young's modulus (Fig. 12a) and tensile strength (Fig. 12b) rose as the number of functional groups

in the polymer increased. They saturated in tandem with the saturation of the reacted amount of the functional groups. The improvement in tensile strength is attributed to the increased intermolecular interaction resulting from the reactions of functional groups. The spherulite size also has a significant effect on mechanical properties [23]. The interfaces between larger spherulites are weaker because voids are prone to form at the spherulite interfaces [24]. The reduction in spherulite size by nucleation effect arising from the branch-like structure could play an important role in the improvement in mechanical properties.
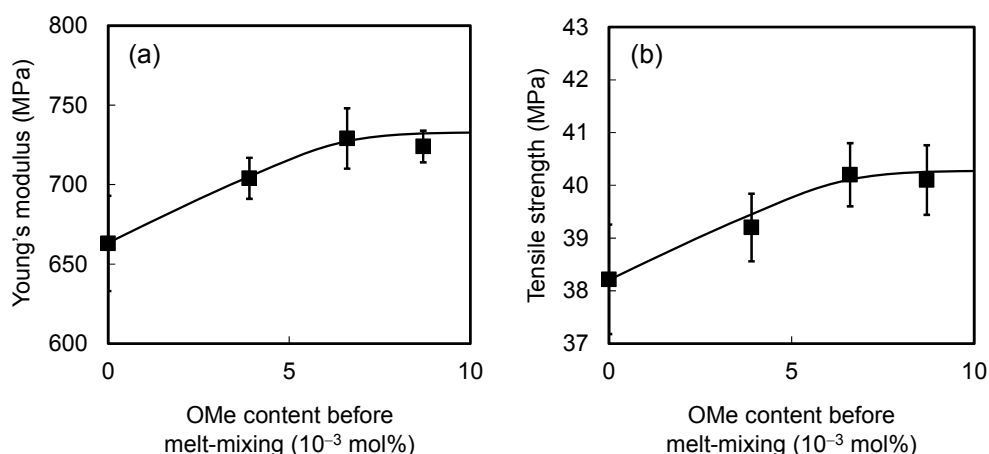
Fig. 12. Effects of OMe content on mechanical properties: (a) Young's modulus and (b) tensile strength.

As described above, the copolymerization of propylene and OTMS using a ZN catalyst was performed to introduce a small amount of functional group in the PP chain. The obtained copolymers exhibited an improved crystallization behavior and mechanical properties, which might be attributed to the crosslinking structure obtained through the condensation reaction of the functional groups introduced in the PP chains.

4. CONCLUSION

This research investigated the development of a high-performance PP-based copolymer containing a small amount of reactive functional group. Copolymers with an extremely low trimethoxysilyl group content ranging from 1.3×10^{-3} to 4.4×10^{-3} mol% were synthesized using ZN catalyst with minimum reduction in catalytic activity. The ^{1}H NMR analysis after melt-mixing of the copolymer identified a reduction in the strength of the peaks originating from the methoxysilyl groups. The presence of gel was observed, which is suggestive of a possible reaction between the OMe groups in the PP chains. Moreover, a drastic enhancement in crystallization was indicated through the isothermal crystallization measurements of the functionalized PP after melt-mixing. The POM observation clearly showed a significant improvement in the nucleation ability of the copolymer. Considerable improvements were observed for mechanical properties. The crosslinking of the polymer chains formed by the

reactions had considerable effects on the crystallization behavior and the mechanical properties.

This research achieved the enhanced crystallization with improved physical properties of PP-based copolymer through the reaction of functional groups in the PP chains using a ZN catalyst, which opens a new route for the development of various high-performance polyolefins.

CONFLICT OF INTEREST STATEMENT

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

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