Chemical Modification of Isotactic Polypropylene by Melt Blending

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Abstract: The branched polypropylene (*b*-PP) was prepared by melt blending process with initiator, antioxidant, and functional monomers to improve the melt strength through the melt grafting. The melt flow index (MFI) of the *b*-PP was increased with increasing the initiator content. On the introduction of the alkylamine as the branching agents the MFI of the *b*-PP was increased, while that of the *b*-PP with the pentaerythritol triacrylate (PT) was decreased. It may be caused by the chain scission of the *i*-PP backbone due to the reduced thermal stability of the *i*-PP on the melt blending. The MFI of the *b*-PP without the antioxidant was increased due to the chain scission occurred during the melt processing, while on the introduction of the antioxidant, the MFI of the *b*-PP was decreased. The crystallization temperature of the *b*-PP was higher than that of PP, which was attributed to the branched chain structure. It was found that the PT was the most effective functional monomers for enhancing the melt properties of the *b*-PP.

Keywords: Branching, Gel content, Isotactic polypropylene, Melt strength

Introduction

At present, polyolefin-based polymers have been the most widely utilized in various industrial fields since the Zigler-Natta discovery in 1955 [1-3]. Among them, the isotactic polypropylene (*i*-PP) is a semicrystalline polymer with desirable properties such as high mechanical properties, good chemical resistance and abrasion resistance, low dielectric constant, and excellent elasticity, and is one of the most widely used thermoplastic polymers because of its various applications and low cost. However, the *i*-PP has several drawbacks such as low melt strength and impact strength, poor interfacial adhesion and thermal stability, non-polarity, inherent poor compatibility, and linear chain structure, which have been limited in its application requiring high melt strength such as blow molding and thermoforming [4-6]. The branching can enhance the melt properties of a polymer, and various methods to produce the branched PP (*b*-PP) have been reported [7-10]. Therefore, the drawbacks of the *i*-PP may be overcome by the chemical modification through the grafting technique with functional monomers [11-15]. Recently, the modification of the *i*-PP through the reactive extrusion process has been widely used due to its efficiency and cost effectiveness, and the grafted or branched PP was produced by adding an organic peroxide [16-18].

In this research, the *b*-PP was prepared by melt blending process with adding the initiator, antioxidant, and functional monomers to improve the melt properties through the chemical modification. The effects of the branching agent and antioxidant on the properties of the *b*-PP were investigated.

Experimental

Materials and Preparation

The *i*-PP used for in this research was supplied by Sam Sung General Chemicals Co., and it has a melt flow index (MFI) of 7 g/10 min. The initiator masterbatch (I-MB) of commercial grade Perkadox 14S which contains 10 wt% of bis(t-butyl-peroxy-i-propylbenzene) was used as the initiator. Dodecylamine (DA), hexadecylamine (HA), octadecylamine (OA), trimethylolpropane triacylate (TT), pentaerythritol triacrylate (PT), and thiourea (TU) used as the branching agents in this research were purchased from Aldrich Co. Tetrakis[methylene(3,5-di-tert-butyl-4-hydroxy)hydrocinnamate] methane (TM) and tris(2,4-di-tert-butyl-phenyl)phosphate (TP) used as the antioxidants, were supplied by Sam Sung General Chemicals Co. The *i*-PP was dried by 60 °C for 2 hr before being used, and the branching agents and antioxidants were used as received without further purification. The *i*-PP was melt blended with I-MB and the branching agents in a Haake Rheomix 600 internal mixer at 200 °C with the fixed rotor speed of 60 rpm. The melt blending time and the I-MB

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content were 5 min and 0.1 %, respectively, which was determined to be the effective condition from our preliminary experiment.

Characterization

The MFI measurement was carried out in a Dynisco melt indexer at 190 °C using a load of 2.16 kg according to the ASTM-D1238 standard. The gel content was determined by extracting the soluble portion with *p*-xylene in a Soxhlet at 140 °C for 2 hr in accordance with the ASTM-D2675 standard. The insoluble gel traction of the samples was dried *in vacuo* at 100 °C for 24 hr and weighted to calculate the gel content. The gel content was calculated from the following equation:

$$\text{Gel content (\%)} = 100 - [(W_0 - W)/W] \times 100 \qquad (1)$$

where W_0 and W are the weight of the samples before and after the extraction, respectively. Thermal properties of the samples were investigated by DSC (TA instrument 2010) under the nitrogen in the temperature range from the room temperature to 250 °C with the scanning rate of 10 °C/min. The variation of the mixing torque with the content of the branching agents was measured using a Haake rheometer. The *b*-PP was purified by using the precipitation method to remove the residual monomers, and the samples were compression molded into the films with the thickness of 0.3 mm. The Fourier transform infrared (FT-IR) spectra of the samples were obtained using a Magna-IR 706 spectrometer (Nicolet Co.).

Results and Discussion

The *i*-PP was melt blended with different I-MB contents to investigate the effect of the chemical reaction by the *i*-PP and organic peroxide on the apparent and thermal characteristics of the melt blends. As the reaction time was increased from 5 min to 15 min, the amount of bubble was increased, which was caused by the oxidation reaction by organic peroxide. When the reaction time was over 10 min, the melt viscosity was decreased significantly, while the thermal properties of the melt blends remained unchanged. It resulted from the fact that the fast oxidation reaction by organic peroxide may caused the reduction in the molecular weight by the chain scission of the *i*-PP backbone. When the I-MB content was over 0.5 wt%, the amount of bubble was increased and the color of the melt blends was changed, which was considered that the crosslinking did not occur by the addition of organic peroxide [19]. The effect of the branching agent (TT and TU) on the characteristics of the melt blends was investigated, and their compositions were shown in Table 1. In order to improve the melt properties, the *b*-PP were prepared by melt grafting reaction, which could explained by melt free radical grafting and recombination. It is well known that hydrogen

Table 1. Characteristics of the *b*-PP with the contents of I-MB and branching agent

I-MB (wt%)	TT (wt%)	Characteristics
0.5	0.0025	Small amount of bubble
	0.005	Small amount of bubble
	0.01	Small amount of bubble
1.0	0.005	Little increasing of bubble
	0.01	Little increasing of bubble
	0.02	Little increasing of bubble, little changes of color
1.5	0.0075	Large amount of bubble
	0.015	Large amount of bubble
	0.03	Large amount of bubble, little changes of color

I-MB (wt%)	TU (wt%)	Characteristics
0.5	0.0025	Small amount of bubble
	0.005	Small amount of bubble
	0.01	Small amount of bubble
1.0	0.005	Little increasing of bubble
	0.01	Little increasing of bubble
	0.02	Little increasing of bubble, little changes of color
1.5	0.0075	Large amount of bubble
	0.015	Large amount of bubble
	0.03	Large amount of bubble, little changes of color

atom on the tertiary carbon atom in the *i*-PP is very reactive and the site for the reaction to form hydroperoxide upon decomposition, resulting in the generation of the radicals required for grafting [20,21]. As organic peroxide was incorporated into the *i*-PP with the branching agent during melt blending, the radicals were generated by thermal decomposition of that, and they could abstract the tertiary hydrogen atoms from the *i*-PP backbone, resulting in the formation of the *i*-PP macroradicals [22,23]. The resulting macroradicals could then undergo chain scission, where new PP chains of lower molecular weights are generated, and leads to termination of the *i*-PP macroradicals by recombination reaction, depending on the molecular structure of the monomers, the reaction temperature, the concentration of the initiators, and the additives [20,21].

The amount of bubble for the melt blends with both the initiator and branching agent after the extraction was decreased compared with the melt blends with the initiator. However, the melt blends with both the initiator and branching agent exhibited the increase in the viscosity and the decrease in the MFI, and those values were higher than those of the *i*-PP. From the above results, it may be concluded that the amount of organic peroxide and the type of the branching agent can significantly influence the branching of the *i*-PP, and that the excessive addition of the I-MB may cause the chain scission of the *i*-PP backbone, resulting in both the decrement of the
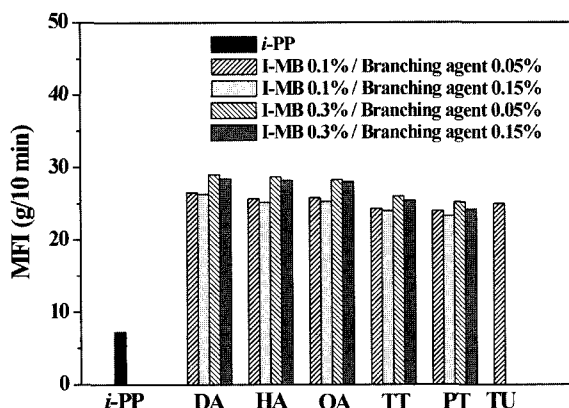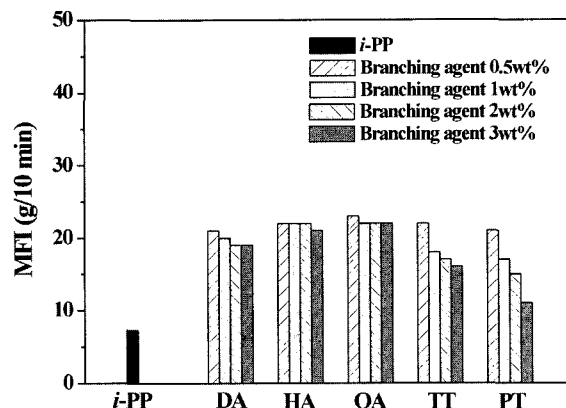
Figure 1. The variation of the MFI for the *b*-PP with the contents of I-MB and various branching agents.

Table 2. Compositions and sample codes of the branching agents with the I-MB concentration of 0.1 %

| Content	Sample codes				
(wt%)	DA	HA	OA	TT	PT
0.5	DA05	HA05	OA05	TT05	PT05
1	DA1	HA1	OA1	TT1	PT1
2	DA2	HA2	OA2	TT2	PT2
3	DA3	HA3	OA3	TT3	PT3

molecular weight and the increment of the amount of bubble. It was expected that the value of the MFI for the *b*-PP was lower than that of the *i*-PP because of the high viscosity in the molten state and the network structure formed on the introduction of the branching or crosslinking in the main chain. The changes of the MFI of the *b*-PP with various branching agents are shown in Figure 1, and the compositions with the content and type of the branching agent are presented in Table 2. It was reported that the value of the MFI was increased irrespective of the content of the branching agent when the I-MB content was over 0.2 wt%, while at lower content of the I-MB the MFI was decreased with increasing the content of the branching agent [24]. Thus, the I-MB content of 0.1 wt% was determined to be the optimum content in this research, and the *b*-PP were prepared by adding various types and contents of the branching agent. Usually, as the branching or crosslinking was occurred in the *i*-PP backbone, it was expected that the value of the MFI was lower than that of the MFI of the *i*-PP due to the higher melt viscosity and network structure. However, the value of the MFI of the *b*-PP with the branching agents such as DA, HA, and OA was increased significantly as shown in Figure 2. The MFI of the *b*-PP with PT was decreased down to 10.8 g/10 min with increasing PT content and was higher than that of the *i*-PP (7.9 g/10 min), which was attributed to the chain scission by the oxidation of the *i*-PP backbone. Therefore, the TP and TM as the antioxidant in this research were added to the *b*-PP for preventing the

Figure 2. The variation of the MFI for the *b*-PP with the content of the branching agents (the I-MB concentration: 0.1 %).
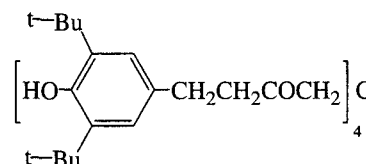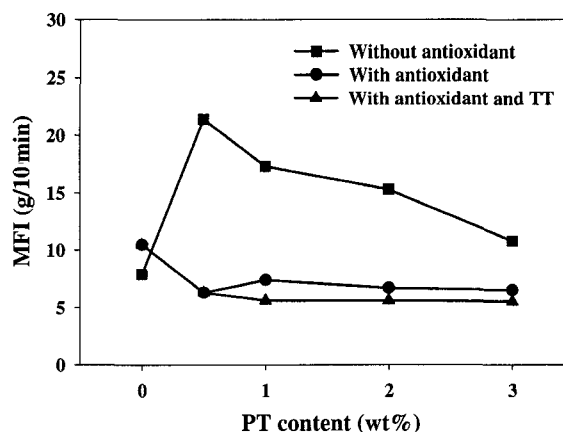

Tetrakis[methylene(3,5-di-tert-butyl-4-hydroxy)hydrocinnamate]methane (TM)
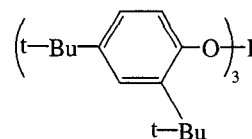
Tris(2,4-di-tert-butyl-phenyl)phosphate (TP)

Figure 3. Chemical structures of the antioxidants used.

Figure 4. The variation of the MFI of the *b*-PP with the PT content.

chain scission by the oxidation reaction of the *i*-PP main chain, and their chemical structures were shown in Figure 3.

Also, the 1 wt% TP and 1 wt% TM were simultaneously added to the *b*-PP because the introduction of both the phenol-based TM and phosphorous-based TP could improve the thermal stability [25]. The variations of the MFI of the *b*-PP with PT content are shown in Figure 4. For the *b*-PP with DA, HA, and OA, the introduction of the antioxidant has no significant effect on the value of the MFI. However, on the addition of the antioxidant, the MFI of the *b*-PP with PT was decreased, and that of the MFI for the *b*-PP with PT, TT, and antioxidant was significantly decreased down to 5.5 g/10 min. It suggested that the chain scission was inhibited by the antioxidant, resulting in the decrement of the MFI [26-28].

The gel contents of the *b*-PP with branching agent are presented in Table 3. It could be seen that there was no evidence of any gel formation on the introduction of the DA, OA, and HA regardless of the content of the branching agent, which indicated that on the introduction of the branching agents having the aliphatic alkyl chains the gel was not formed irrespective of the chain length. For the *b*-PP with PT, no formation of the gel was occurred below the content of 0.5 wt%, while the small amount of the gel was formed above the content of 1 wt%. The antioxidant and branching agents have no significant effect on the gel content of the *b*-PP as shown in Table 4. However, the gel content of the b-PP was increased slightly up to 4 % on the introduction of the PT and TT simultaneously.

The FT-IR spectra of the *b*-PP with PT are shown in Figure 5. The characteristic peak (I_{PT}) from the stretching vibration mode of the carbonyl group in PT was observed at 1740 cm^{-1}, and the intensity of that was increased with increasing PT content. The absorption peak ($I_{i\text{-}PP}$) observed at 840 cm^{-1} was attributed to the C-CH$_3$ vibration in the *i*-PP backbone. The ratio of the relative absorbance between the I_{PT} and $I_{i\text{-}PP}$ ($I_{PT}/I_{i\text{-}PP}$) for the *b*-PP was shown in Figure 6.

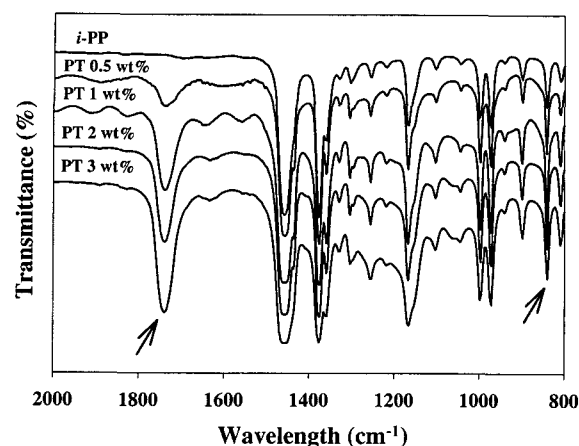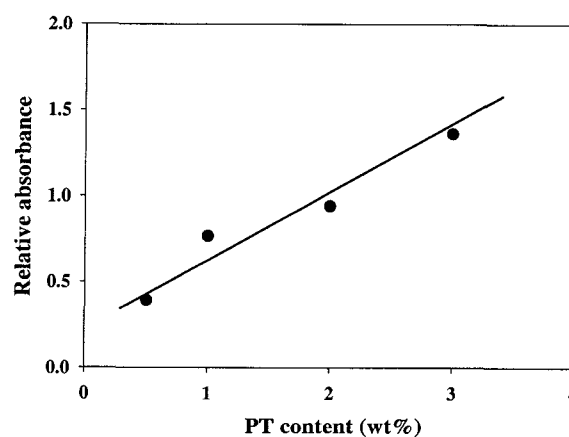**Figure 5.** FT-IR spectra of the *b*-PP with the PT content.

Figure 6. The ratios of the relative absorbance between the I_{PT} and $I_{i\text{-}PP}$ ($I_{PT}/I_{i\text{-}PP}$) of the *b*-PP with PT content.

Table 3. Gel content of the *b*-PP without the antioxidant

Content (wt%)	Gel content (%)				
	DA	HA	OA	TT	PT
0.5	0	0	0	0	0
1	0	0	0	0	0.8
2	0	0	0	0.3	0.8
3	0	0	0	0.5	1.2

Table 4. Gel content of the *b*-PP with the antioxidant

Sample codes	Gel content (%)	Sample codes	Gel content (%)	Sample codes	Gel content (%)
A-DA3	0	A-PT05	0	A-TT3-PT05	2.2
A-HA3	0	A-PT1	0.9	A-TT3-PT1	2.5
A-OA3	0	A-PT2	1.0	A-TT3-PT2	3.8
		A-PT3	1.3	A-TT3-PT3	4.0

The PT incorporated by recombination reaction such as branching or crosslinking would influence significantly the relative intensity of that. The ratio of the relative absorbance peaks ($I_{PT}/I_{i\text{-}PP}$) was increased with PT content, which suggested that more PT content might enhance the recombination reaction between the *i*-PP and PT [24].
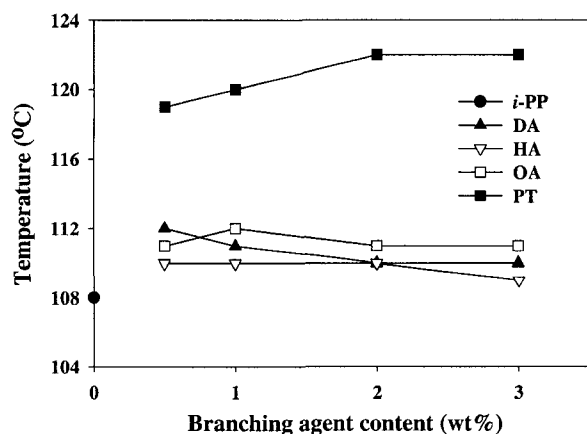
Thermal properties of the *b*-PP are presented in Tables 5 and 6. The melting temperature (T_m), crystallization temperature (T_c), and the enthalpy of the crystallization (H_c) for the *i*-PP were 163 °C, 108 °C, and 93 J/g, respectively. The variations of the Tc for the *b*-PP with the branching agents are shown in Figure 7. The introduction of the alkylamine (DA, OA, and HA) have no significant effect on the thermal properties of the *i*-PP, and the T_c of the *b*-PP was slightly higher that that of the *i*-PP on the addition of the branching agents having aliphatic alkyl chains. However, on the introduction of the PT, the T_c was significantly increased up to 122 °C with increasing the content. Phillips *et al.* reported that the introduction of a small number of crosslinks resulted in the

Table 5. Thermal properties of the *b*-PP with the content of the branching agents (without the antioxidant)
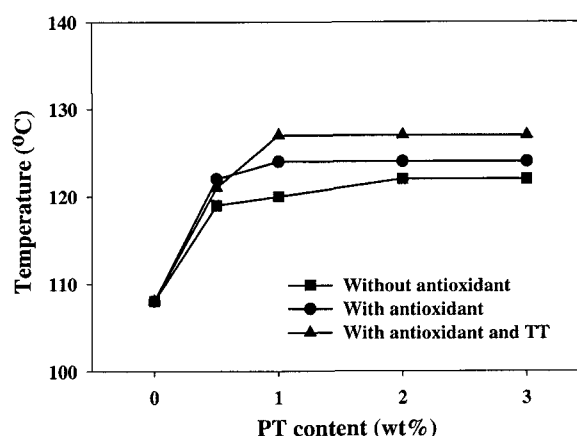
Content (wt%)	DA			OA			HA			TT			PT		
	T_m (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	T_c (°C)	ΔH_c (J/g)
0.5	164	112	101.6	164	111	102.9	166	110	96.5	165	112	96.5	164	119	95.8
1	164	111	100.7	163	112	101.3	165	110	91.6	164	112	95.6	164	120	96.4
2	164	110	99.1	164	111	98.2	165	110	95.8	165	113	96.2	164	122	95.7
3	164	110	108.9	163	111	98.7	164	109	94.8	164	115	97.0	165	122	87.0

Table 6. Thermal properties of the *b*-PP with the branching agents (with the antioxidant)

Sample codes	T_m (°C)	T_c (°C)	ΔH_c (J/g)
A-DA3	163	112	101.6
A-OA3	164	110	100.7
A-HA3	164	112	100.3
A-PT05	163	122	97.9
A-PT1	162	124	81.2
A-PT2	163	124	57.2
A-PT3	164	124	101.1
A-TT3-PT05	164	121	83.8
A-TT3-PT1	163	127	113.3
A-TT3-PT2	163	127	106.4
A-TT3-PT3	163	127	125.5

Figure 8. The variation of the T_c for the *b*-PP with PT content.

Figure 7. The variation of the T_c for the *b*-PP with the branching agent.

increased nucleation density of the crosslinked low-density branched PE [29,30]. It was also reported by DeNicola *et al.* that the T_c of the *b*-PP was higher than that of the linear PP at the same TREF elution temperature and the nucleation density of the *b*-PP was much higher than that of the linear precursor [31], and they suggested that the increase in the T_c may result from the increased nucleation density by the

branching or crosslinking of the linear PP. The variations of the T_c with the content and the type of the branching agents are shown in Figures 8. The T_c of the *b*-PP was higher than that of the *i*-PP and was increased with PT content. It could be seen that the PT having the tertiary structure had significant effect on the T_c of the *i*-PP compared with the alkylamines (DA, OA, and HA) having the linear structure. This result was attributed to the nucleating effect of the PT incorporated in the *b*-PP, resulting in the increment of the Tc. The T_m, ΔH_m, and ΔH_c of the *b*-PP were 164 °C, 90 J/g, and 95 J/g, respectively, and were similar to those of the *i*-PP. DSC measurements demonstrated that the branching by the PT was more effective than the alkylamine with different chain lengths, which corresponded with the results of the MFI and gel content measurements. Thermal properties of the *b*-PP with the antioxidant are shown in Table 6, and the T_c of the *b*-PP with the antioxidant was also increased. It was found that the value of the MFI was affected by the chain scission, while thermal properties were not affected. When two branching agents (TT and PT) were added to the *b*-PP simultaneously, the T_c of the *b*-PP that exhibited the gel content of 4 % was increased up to 127 °C with increasing PT content. The increase in the T_c can be attributed to the PT acting as a nucleating agent in the *b*-PP, and Rybnikar *et al.* also reported the nucleation due to incorporation of carbonyl groups into the *i*-PP [32]. Therefore, this result was attributed to

Table 7. The values of the torque of the *b*-PP with the PT content

Sample codes	Torque[a] (Nm)	Total torque[b] (NmM)
i-PP (without antioxidant)	4.5	28.5
i-PP (with antioxidant)	5.5	32.0
PT05	5.6	32.7
PT1	5.6	37.0
PT2	6.8	44.0
PT3	7.3	49.2

[a]The value of final torque at the blending time of 5 min.
[b]The value of total torque for 5 min during the melt blending.

the nucleation effect induced by many junction points and the difficulty in the movement of the chains when the branching and crosslinking was occurred at the same time [26-28].

Changes of the values of the torque for the *b*-PP with the PT content on the melt blending are presented in Table 7. The final torque and total torque were increased with increasing the PT content, and the values were higher than those of the *i*-PP. The value of the torque for the *b*-PP with both the PT and antioxidant was higher than that of the *b*-PP with the antioxidant, which suggested the occurrence of the branching and the enhancement of the melt properties [33-36].

Conclusions

The branched PP (*b*-PP) was prepared by melt blending process with adding the initiator, antioxidant, and functional monomers to improve the melt properties through the melt grafting. The MFI of the *b*-PP was higher than that of pure *i*-PP, which was attributed to the chain scission occurred competitively. For the *b*-PP with the alkylamine, the addition of the antioxidant had little effect on the MFI. The MFI of the *b*-PP with PT, TT, and antioxidant was significantly decreased, which was caused by the restriction of the chain scission by the antioxidant. The T_c of the *b*-PP was increased by nucleating effect of the PT incorporated in the *b*-PP. The PT was the most effective functional monomers for enhancing the melt properiies of the *i*-PP. When PT and TT were added to the *i*-PP simultaneously, the MFI was decreased down to 5.5 g/10 min and gel content was increased up to 4 %. It was expected that the addition of the PT or two branching agents simultaneously might enhance the melt properties of the *b*-PP.

Acknowledgement

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