Copolymerization of 4-methyl-1-pentene with α,ω -alkenols

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Abstract. Copolymerization of 4-methyl-1-pentene (4M1P) with 9-decen-1-ol (9D1O) or 4-penten-1-ol (4P1O) was conducted by using metallocene catalysts. The activity could be improved under the higher polymerization temperature. The dyad distribution of poly(4M1P-co-4P1O) was presented. The results showed that 4P1O was uniformly distributed in the copolymer chain. The melting temperature (T_m) of the copolymer was lower than that of poly(4M1P), and was decreased with the increase of the incorporation of comonomer. T_m of poly(4M1P-co-4P1O) was determined as 185 °C, even the incorporation of 4P1O was high as 15.0 mol%. WAXD (wide-angle X-ray diffraction) results showed that the poly(4M1P) was observed as crystalline form II, and turned to form I when the incorporation of α,ω -alkenols were high. Some new peaks, which were never observed in the previous researches, appeared in the X-ray diffraction profiles for poly(4M1P-co-4P1O). It is inferred that the similar chain length of 4P1O and 4M1P may be the key factor.

Keywords: polymer synthesis, molecular engineering, 4-methyl-1-pentene, α,ω -alkenols, copolymerization

1. Introduction

The synthesis of polyolefin with functional groups was considered as an important and pioneering area, due to the unique and excellent properties of the modified polymer superior to the traditional material [1]. The incorporation of polar groups into the polyolefin chain is believed to provide a polymer with improved surface properties [2]. Such material is desired because it combines the polarity and non-polarity into an integral whole. It could be utilized extensively as the modifier of a polymer to improve the property; furthermore, it could be hopefully used in the areas of energy, information and environmental protection [3]. Direct copolymerization of olefin monomer with vinyl comonomer with a polar group(s) by using Ziegler-Natta polymerization is straightforward and efficient to obtain these functional polyolefin materials. Polyethylene and polypropylene are the polyolefin resins with the largest

commercial scale. It follows then that most researches on the synthesis of the functional polyolefin concern ethylene [4–13] and propylene [14–18] copolymerization. The investigation on the copolymerization of higher α -olefin with functional monomer was rather rare.

Studies on the polymerization of higher α -olefin have drawn considerable attention for long years. Polymerization of either linear or branched α -olefin has been fully explored by using various catalyst systems, including the traditional Ziegler-Natta catalyst [19, 20], metallocene catalyst [21–24], non-metallocene single-site catalyst [25] and later transition metal catalyst [26, 27]. Properties of poly(α -olefin) could be improved by incorporating the second monomer with a functional group, but the successful examples were limited so far [28, 29].

Previously, we reported the synthesis of the copolymer of ethylene with the hydroxyl-ended vinyl mono-

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mers by using half titanocene catalysts [12, 13]. In those works, we gave the detailed ^{13}C -NMR (nuclear magnetic resonance) analysis and the sequence distribution of the copolymer of ethylene with α,ω -alkenols for the first time. Furthermore, we found the influence of the functional group of the comonomer on the structure of the resulted copolymer could be reduced by the methylene spacers between the vinyl bond and the functional group. Because of the lack of research on the copolymerization of higher α -olefin and the functional comonomer, we have the interest to set foot in this subject. In the present work, we would introduce the copolymerization of 4-methyl-1-pentene (4M1P) with 4-penten-1-ol (4P1O) and 9-decen-1-ol (9D1O).

2. Experimental section

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques, unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Toluene was distilled in the presence of sodium and benzophenone under a nitrogen atmosphere, and was stored in a Schlenk tube in the drybox over molecular sieves. Metallocene catalysts, *rac*- $\text{Me}_2\text{Si}(\text{2-Me-Ind})_2\text{ZrCl}_2$ (99%) was purchased from Boulder Scientific Company (CO, USA), and *rac*- $\text{Me}_2\text{Si}(\text{2-Me-4-Ph-Ind})_2\text{ZrCl}_2$ (99%) from APAC Pharmaceutical (MD, USA). MAO (Methylaluminoxane) solution in toluene (10 wt%) was purchased from Albemarle (LA, USA), 4-methyl-1-pentene (4M1P, 98+%), 9-decen-1-ol (9D1O, 99%) and 4-penten-1-ol (4P1O, 99%) from TCI (Japan), and were used as received.

Polymerization was conducted in toluene in a 100 mL glass reactor with an oil bath. The glass reactor was purged with nitrogen and charged with a nitrogen atmosphere. For example run 1 in Table 1, keeping the oil bath at 25 °C, toluene (5 mL), 4M1P (3.0 mL, 23.7 mmol) were introduced. And then MAO solution (6 mL, 10 mmol) and *rac*- $\text{Me}_2\text{Si}(\text{2-Me-Ind})_2\text{ZrCl}_2$ solution in toluene (1 mL, 10 μmol) were injected to start the polymerization. The mixture was stirred magnetically for 20 hours. Subsequently, the mixture was poured into ethanol containing concentrated hydrochloric acid and stirred for 6 hours. The resultant polymer was gathered on a filter paper by

filtration, and washed thoroughly with EtOH, and was then dried in vacuo under 60 °C for 24 hours. 1.56 g of polymer was obtained.

The molecular weight was determined by using gel permeation chromatography (GPC, polystyrene calibration) on a Waters Alliance GPCV2000 at 150 °C with 1, 2, 4-trichlorobenzene as the eluent, and the infrared (IR) as the detector.

The melting temperature of the polymer was determined on TAQ 100. Approximately 2 mg of polymer sample was heated from room temperature to 240 °C with a heating rate of 10 °C per minute, under a nitrogen atmosphere. After keeping the temperature for 1 minute, the sample was cooled down to room temperature, and kept the temperature for 1 minute again. Then sample was heated to 240 °C with a heating rate of 10 °C per minute and the data was recorded.

Solution ^{13}C -NMR experiments were performed on a Bruker AVANCEIII-400 MHz spectrometer with a 10 mm PASEX ^{13}C - $^1\text{H}/\text{D}$ Z-GRD probe. Sample solutions were prepared with approximately 250 mg of the polymer material dissolved in 2.5 mL of d_4 -*o*-dichlorobenzene (ODCB- d_4) in a 10 mm tube at 130 °C. All ^{13}C -NMR experiments were carried out at 125 °C, 20 Hz spinning rate, 90° pulse angle, continuous Waltz-16 decoupling, 120 ppm spectral width, 5 s acquisition time, and 10 s relaxation delay.

Wide Angle X-ray Diffraction (WAXD) experiment was carried out on a Bruker D8 DISCOVER 2D X-ray diffractometer. The X-ray was generated using IS micro Focus X-ray source incorporating a 50 W sealed-tube X-ray generator with Cu target. The wavelength was 0.1542 nm. The power of the generator used for measurement was 45 kV and 0.9 mA. The X-ray intensities were recorded on a VANTEC-500 2D detector system with a pixel size of $68 \times 68 \mu\text{m}^2$. The distance from the sample to detector was 198 mm. The spot size of the beam was 0.5 mm. The exposure time was 2 min. Polymer powder was used as generated without other treatment.

3. Results and discussion

Copolymerization of 4M1P with 9D1O or 4P1O were conducted by using *rac*- $\text{Me}_2\text{Si}(\text{2-Me-Ind})_2\text{ZrCl}_2/\text{MAO}$ as the catalyst system, and the results were summarized in Table 1.

For both the homopolymerization and copolymerization, the higher was the polymerization tempera-

Table 1. Copolymerization of 4M1P with 4P1O or 9D1O^a

Run	Cat [μmol]	Al/Zr	Comono. [mmol]	T [°C]	t	Act. ^b	M _w ^c [k]	pdi ^c	T _m ^d [°C]	Incorp. ^e [mol%]
1	10	1000	–	25	20 hrs	7.8	17.1	2.2	222	–
2	10	1000	–	50	3 hrs	36.0	10.0	2.0	211	–
3	50	400	9D1O, 2.80	25	2 hrs	8.3	8.4	1.8	n.d. ^f	– ^g
4	50	400	9D1O, 2.80	50	20 min	51.0	5.7	1.7	n.d. ^f	8.8
5	20	1000	9D1O, 0.56	50	20 min	96.0	8.2	1.8	183	3.9
6	20	1000	9D1O, 1.68	50	20 min	79.5	8.0	1.7	171	7.9
7	20	1000	9D1O, 2.80	50	20 min	57.0	7.3	1.6	n.d. ^f	– ^g
8	20	750	4P1O, 1.94	25	20 hrs	1.8	18.5	2.1	223	1.2

^aPolymerization conditions: catalyst *rac*-Me₂Si(2-Me-Ind)₂ZrCl₂, MAO cocatalyst, 4M1P 23.7 mmol, in toluene, total volume 15 mL; ^bActivity in kg-polymer/mol-Zr/hr; ^cGPC data; ^dMelting temperature, determined by DSC; ^eComonomer incorporation, estimated by ¹³C-NMR; ^fNo melting point; ^gNot determined.

ture, the higher was the activity. Introduction of 9D1O into the polymerization system increased the activity. Analogous result was often observed in the olefin copolymerization [30]. The activity decreased while the 9D1O feeding amount increased (run 5–7). The so-called ‘comonomer effect’ has been observed in several manners for the ethylene copolymerization with α -olefin [30, 31]. The incorporation of 9D1O into the polymer chain improved the solubility of the resulting polymer in the reaction mixture; therefore the resistance of the mass and heat transfer would be reduced, leading to the increased activity. On the other hand, because the lone pair electrons on the oxygen atom would coordinate to the catalytic centre and kill the active species, the higher concentration of 9D1O would depress the activity, although the effect of long chain monomer could be reduced by the methylene spacers [13]. 4P1O possesses less methylene spacers, with the consequence that the activity was much lower than the homopolymerization of 4M1P and the copolymerization of 4M1P and 9D1O.

All polymer samples were obtained with narrow molecular weight distribution. The molecular weight was not high. It was lower at higher polymerization temperature, because the chain transfer reaction would be more drastic at high temperature. When the comonomer feeding concentration increased, the molecular weight of the resulted polymer also became lower. The high concentration of comonomer probably resulted in a larger probability of the terminal reaction due to the coordination of the oxygen atom to the active species, which followed by the lowered molecular weight of the polymer.

Figure 1. ¹³C-NMR spectra of sample 1 and sample 4

The ¹³C-NMR spectrum of sample 1 was shown in Figure 1. Five main peaks were observed in $\delta = 46.2, 42.7, 31.5, 26.0, 23.7$ ppm, corresponding to the five carbon atoms of 4M1P [24]. ¹³C-NMR spectrum of sample 4 was also shown in Figure 1. Besides the similar peaks to that of sample 1, other some resonances appeared in the spectrum. The peak at 63.0 ppm is the typical resonance of the carbon atom adjacent to the hydroxyl group of 9D1O [9, 13]. Other resonances, $\delta = 42.1, 35.5, 33.4, 30.7, 30.0, 29.8, 26.9, 26.3$ ppm, are assigned to the other carbon atoms of 9D1O. Calculation according to the integrated intensity showed that 8.8 mol% of 9D1O was incorporated into the copolymer. The incorporation of 9D1O in samples 5 and 6 was calculated as 3.9 and 7.9 mol%, respectively. By using the similar calculation method, the incorporation of 4P1O of sample 8 was found as 1.2 mol%.

The melting point (T_m) of the homopolymer of 4M1P produced at 25 °C was determined as 222 °C, and higher polymerization temperature gave a poly-

mer with the lower T_m . The results tallied with the previously reported values [24].

T_m s of the copolymer of 4M1P with 9D1O were lower than that of the homopolymer of 4M1P, and when the feeding amount of 9D1O increased, T_m decreased (see Figure 2). Furthermore, whereas sample 1 displayed a single melting endotherm, samples 2, 5, and 6 exhibited a shoulder peak or multiple melting endotherms in the DSC curves. This phenomenon was observed in the stereoregular polymer produced by the less stereospecific catalyst systems [32]. The broadened melting range of sample 2 indicated that the isospecificity of the catalyst was weakened under the higher polymerization temperature. On the other hand, incorporation of comonomers would interrupt the successive insertion of the crystallizable monomer unit, resulting in the decreased melting point and the inhomogeneity of the crystallizable segment. The multiple melting endotherm in the DSC curve could be attributed to the process of melting, recrystallization and remelting: metastable crystallites are recrystallized into a more perfect form following the initial melting [24, 32].

While the T_m s of the copolymers of 4M1P and 9D1O were lower than that of the homopolymer of 4M1P, and decreased with the increase of the 9D1O incor-

poration, it was surprisingly found that the T_m of the copolymer of 4M1P with 4P1O was almost equal to or a little bit higher than that of the homopolymer of 4M1P.

To some extent, the comonomer 4P1O is different from the other one 9D1O. The chain length of 4P1O is much shorter than 9D1O; more importantly, the chain length is closer to that of 4M1P. It is attractive enough to inspire us to explore more details of this copolymerization.

Another metallocene, *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂, was used as the catalyst for copolymerization of 4M1P and 4P1O, and the results were summarized in Table 2. The experiments were designed for producing the copolymer with the high incorporation of 4P1O. Although the catalyst, *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂, exhibited high activity and offered the polymer with the high molecular weight in propylene polymerization [33], the activity for the copolymerization of 4M1P was pretty low, and the molecular weight of the resulted polymer was also low.

The ¹³C-NMR spectrum of the copolymer of 4M1P with 4P1O (sample 9) was given in Figure 3, in comparison to that of sample 1. The carbon atoms of 4M1P unit gave the nearly identical resonances with the homopolymer. In addition, peaks at $\delta = 63.53$ and 30.45 ppm were corresponding to the two carbon atoms adjacent to the hydroxyl group of 4P1O. The resonance of the branched carbon atom appeared at 33.05 ppm. The signals at the range of 41.3–42.7 ppm would be assigned to the $[\alpha\alpha]$ structure. The resonance of the carbon atom closed to the branch should be overlapped by the backbone carbon of 4M1P. All assignments were depicted in Figure 3, as well as summarized in Table 3. ‘P’ and ‘O’ are used to represent 4M1P and 4P1O monomer unit respectively. The dyad sequence distributions for all copolymer of 4M1P and 4P1O were presented in Table 4. The products of the reactive ratios, $r_P r_O$, were calculated as 1.22 and 1.38 for samples 9 and 10, respectively. It

Figure 2. DSC curves of the copolymers of 4M1P with 9D1O

Table 2. Copolymerization of 4M1P with 4P1O^a

Run	4M1P [mmol]	4P1O [mmol]	Act. ^b	M_w^c [k]	pdI^c	T_m^d [°C]	Incorp. ^e [mol%]
9	6.32	1.94	0.77	4.9	1.7	199	9.7
10	4.74	3.87	0.48	4.0	1.5	185	15.0

^aPolymerization conditions: catalyst *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂, 20 μ mol, MAO cocatalyst 10 mmol, Al/Zr = 500, in toluene, total volume 15 mL, 25 °C, 24 hrs; ^bActivity in kg-polymer/mol-Zr/hr; ^cGPC data; ^dMelting temperature, determined by DSC; ^eComonomer incorporation, estimated by ¹³C-NMR.

Figure 3. ^{13}C -NMR spectra of sample 1 and sample 9

means that the structure of the copolymer is still random. Another parameter RMD (Relative Monomer Dispersity) [34], developed on the base of Hsieh and Randall's work [35], was also calculated. All RMD for the three copolymer samples were obtained as 100% or thereabouts, indicating that the comonomer, 4P1O, is uniformly distributed in the polymer chain. This coincides that we concluded from the analysis of the products of reactive ratios.

It is worth noting that even in the copolymer (sample 10) containing a high 4P1O unit fraction of 15.0 mol%, the T_m of the polymer was still high as 185 °C. The results echoed the high T_m of the sample with the low 4P1O incorporation (sample 8). The performance is distinct from the observation of the copolymer of 4M1P with 9D1O. To search to the bot-

tom, the reason probably lies in the chain length of the functional monomer.

As we can summarize the data in references, for olefin copolymer, for example propylene copolymer with higher α -olefin, the melting temperature is always lower than that of homopolypropylene. It is natural because the incorporation of a comonomer would interrupt the crystallization of the successive propylene unit, therefore reduce the lamellar crystal. However, if the chain length of the comonomer is closer to the main monomer, the impact would become weak. The change of the melting temperature of the propylene copolymer with 1-butene [36], 1-hexene [37, 38], 1-octene [37] and 1-decene [37] showed that, the incorporation of the shorter comonomer would be less efficient to decrease the melting temperature of the copolymer. Previous research revealed that 1-butene was more inclined to be incorporated into the crystalline phase than ethylene, 1-hexene and 1-octene for propylene copolymers [39]. It could be probably concluded that, if the length of the comonomer was extremely close to the main monomer, the melting temperature of the copolymer would not decrease, without consideration of the polarity of the monomers.

It is difficult to find or design such a comonomer for ethylene or propylene copolymerization, but is possible for the copolymerization of higher α -olefin. The unusual melting temperature of the copolymer of 4M1P with 4P1O, especially the example with the high incorporation, gave evidence for the above-mentioned deduction. Because of the parallel chain lengths, the major monomer (4M1P) unit tolerates the incorporation of the minor comonomer (4P1O) into the lamella, although the loss of the lamellar thickness is unavoidable. Apart from this, the additional adhesion provided by the hydrogen bond of the hydroxyl group of 4P1O increases the thermal consumption in the melting process; therefore increases the melting temperature.

X-ray powder diffraction was used to characterize the crystal structure of the polymer samples (see Figure 4). The homopolymer of 4M1P, sample 2, was affirmed as crystalline form II, according to the literature [40]. Polymer sample with low 9D1O incorporation (sample 5, 9D1O 3.7 mol%) gave a similar profile, implying that few changes occurred in the

Table 3. ^{13}C -NMR assignments of copolymer of 4M1P with 4P1O

Carbon	Sequence	Main Peak
B(–CH ₂ –OH)	[O]	63.53
3B(P)	[P]	46.16
$\alpha_P\alpha_P$	[PP]	42.67
$\alpha_P\alpha_O$	[PO]	41.98
$\alpha_O\alpha_O$	[OO]	41.31
CH(O)	[O]	33.05
CH(P)+3B(O)	[P]+[O]	31.49
2B(O)	[O]	30.45
2B(P)	[P]	25.94
1B(P)	2[P]	23.60

Table 4. Sequence distributions of Poly(4M1P-co-4P1O)

Run	[P]	[O]	[PO]	[PP]	[OO]	$r_P r_O$	RMD [%]
8	98.8	1.2	2.4	97.6	0	0	101.2
9	90.3	9.7	17.2	81.7	1.1	1.22	98.4
10	85.0	15.0	24.3	72.9	2.8	1.38	95.4

Figure 4. X-ray powder diffraction profiles of polymer samples

crystal structure. High 9D1O incorporation brought significant change to the crystal structure. When the incorporation of 9D1O was 7.9 mol%, the X-ray profile indicated that the crystalline was detected as form I of poly(4M1P) [40]. Polymer sample 8, with the low 4P1O incorporation, gave the small but important changes in the X-ray profile. The peaks between 12~14° had the tendency of splitting. The most important is that a new peak appeared at $2\theta = 7.9^\circ$, which was never observed in all the five crystalline forms of poly(4-methyl-1-pentene) found. [40, 41] While the incorporation of 4P1O was high as 15.0 mol%, the new appeared peak at $2\theta = 7.9^\circ$ was distinctly observed, and the peak between 12~14° evidently split at $2\theta = 12.2$ and 13.4° . Comparing the patterns of samples 6 and 10, it could be found that the pattern of the latter is similar to the former, besides the peaks at $2\theta = 7.9$ and 12.2° . It is supposed that there are the mixed crystal forms in sample 10, including the form I of poly(4-methyl-1-pentene) and an unidentified one. It may be concluded that the high incorporation of α,ω -alkenol, either 9D1O or 4P1O, turns the crystalline from form II to form I. Because all samples for WAXD were directly generated from the polymerization without any treatment, it may be reasonably inferred that the high incorporation of α,ω -alkenol changed the crystallization process of the copolymer. The reason for the new peaks could be ascribed to the incorporation of 4P1O, no matter how much it was incorporated. Because such result could not be observed in the case

of copolymerization of 9D1O, the difference of the chain length of the α,ω -alkenol may play the important role.

4. Conclusions

We have described the copolymerization of 4M1P with α,ω -alkenol, namely 9D1O and 4P1O, by using the metallocene catalysts. T_m of polymer decreased with the increase of the incorporation of comonomers. While T_m of the copolymer of 9D1O sharply decreased with the incorporation of 9D1O, T_m of 4P1O maintained the high level, even the incorporation was high as 15.0 mol%. Results of WAXD indicate the high incorporation of α,ω -alkenol would result in the transformation of the crystalline of the polymer from the form II to form I. Furthermore, the incorporation of 4P1O led to the appearance of new peaks in the X-ray diffraction patterns. The unique observation may be ascribed to the comparable length of 4M1P and 4P1O.

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