Synthesis and Characterization of Branched Polyethylene by Ethylene Homopolymerization with Monotitanocene and Modified Methylaluminoxane Catalysts

Fangming Zhu,* Yutang Fang, Hanbin Chen, and Shangan Lin

Institute of Polymer Science, Zhongshan University, Guangzhou 510275, China

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ABSTRACT: Branched polyethylene was synthesized in the presence of a monotitanocene complex of η^5-pentamethylcyclopentadienyltribenzyloxytitanium [Cp*Ti(OBz)$_3$] activated by five kinds of modified methylaluminoxanes (mMAO) which contained different amounts of residual trimethylaluminum (TMA). The oxidation states of titanium active species in Cp*Ti(OBz)$_3$/mMAO catalytic systems were determined by the redox titration method. The results showed that Ti(IV) active species were more beneficial for ethylene polymerization. Influences of polymerization temperature and Al/Ti molar ratio on catalytic activity, degree of branching, and molecular weight of polyethylene were investigated. The resultant products obtained were confirmed by GPC, ^{13}C NMR, and IR characterization to be high molecular weight polyethylene with isolated long branched chain (longer than six carbons in length) and methyl pendant groups. The branched chain polyethylene is formed mainly by in-situ copolymerization of ethylene growing chain with macromonomers of α-olefin produced through β-hydride elimination reaction. The presence of methyl pendant in the main chain of polyethylene implied in-situ 2,1-insertion of the macromonomers to [Ti^{IV}]−H active species following by β-hydride elimination. The polyethylene resulted with density in the range 0.898−0.947 g/cm^3, and the melting temperature of 116.5−139.8 °C is in accord with the degree of branching from 25.0 to 6.9 branch numbers of 1000 carbon atoms in the polymer main chain.

Introduction

Recent research into ethylene-based polymers has centered around the advances made with metallocene catalysts.[1−3] The metallocene catalysts, sometimes referred to as single active species catalysts, have been regarded as a trend of polyolefin technology. Polyethylene and ethylene/α-olefin copolymers[4−7] synthesized by the single active species metallocene catalysts are decidedly different in structure and properties when compared with that synthesized by conventional Ziegler−Natta catalysts, such as high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and ultralow-density polyethylene (ULDPE). Typical molecular structures of metallocene-catalyzed polyethylene are narrow molecular weight distribution ($M_w/M_n \sim 2$) and homogeneous branch distribution. Branched polyethylene has been prepared by binary η^5-cyclopentadienyl (Cp) metallocene catalysts through copolymerization of ethylene with α-olefin,[8−10] but the branches were always shorter than six carbons in length owing to the effect of steric hindrance of active species with two bulky Cp ligands to high α-olefins or macromonomers of α-olefin. The geometric structure of monometallocene catalysts will allow the active species open to coordination polymerization of high α-olefin or macromonomers. Dow Chemical's monometallocene catalyst of constrained-geometry catalyst (CGC) has offered the possibility of yielding long chain branched polyethylene from only ethylene feed polymerization.[11] The results have been discussed in terms of a mechanism which proposed that ethylene is copolymerized with macromonomers of α-olefin which can be obtained via β-hydride elimination and/or chain transfer to ethylene monomers.[12−15]

Monotitanocene/methylaluminoxane (MAO) catalysts have been found to be favorable for syndiospecific polymerization of styrene[16−19] as well as for the polymerization of ethylene,[20−22] propylene,[23,24] and diene.[25,26] Recently, we have reported that the catalytic activity for polymerization of styrene,[27,28] propylene,[28] and butylene-1[29] depended on the different titanium oxidation states of active species. Ti(III) complexes is the best active species with high activity for the syndiospecific polymerization of styrene, while the Ti(IV) complexes contribute the active species for producing atactic polypropylene and stereoblock polybutylene-1. The coexisted trimethylaluminum (TMA) in MAO has a pronounced influence on the distribution of titanium oxidation states in the monotitanocene/MAO system.[27−30] The higher the content of TMA in mMAO is, the more Ti(IV) monotitanocene complexes are reduced to Ti(III). However, very little work on preparation of polyethylene with monocyclopentadienyltitanium/MAO catalysts has been reported in the open literature.

Herein, we describe the synthesis of branched polyethylene using catalysts composed of a monotitanocene complex of η^5-pentamethylcyclopentadienyltribenzyloxytitanium [Cp*Ti(OBz)$_3$] and five kinds of modified methylaluminoxanes (mMAO) containing different amounts of residual trimethylaluminum (TMA). The influences of the content of residual trimethylaluminum (TMA) in mMAO on the formation of active species for ethylene polymerization are reported. The microstructure and property of the resultant polyethylene are characterized by GPC, ^{13}C NMR, IR, DSC, and melt flow indexes. The branch length is mainly controlled by polymerization temperature, and its distribution is mainly controlled by catalyst structure, molecular weight of macromonomer, and polymerization temperature.

Experimental Section

Materials. Polymerization-grade ethylene and extra-pure-grade nitrogen were further purified before feeding into the reactor by passing them through a DC-IB gas purification instrument. Toluene was refluxed over metallic sodium for 24 h and distilled under nitrogen atmosphere before use.

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Table 1. Ethylene Polymerization Using Cp*Ti(OBz)$_3$ Activated by Different mMAO as Cocatlysts[a]

run no.	mMAO sample	TMA in mMAO (wt %)	Ti oxidation state (mol %)			activity × 10^{-4} (g of PE/(mol of Ti h))	$M_w \times 10^{-5}$	degree of branching[b]	T_m (°C)
			Ti(II)	Ti(III)	Ti(IV)				
1	mMAO1	15.4	0.1	11.4	88.5	15.3	5.1	16.4	123.7
2	mMAO2	16.2	0.7	17.2	82.1	12.5	5.0	21.6	120.5
3	mMAO3	20.0	1.8	21.3	76.9	7.8	4.5	22.5	118.2
4	mMAO4	22.5	5.1	64.6	30.3	3.2	3.9	25.0	116.5
5	mMAO5	26.1	12.1	71.8	16.1	1.6	3.2	26.1	116.2

[a] Polymerization conditions: [Ti] = 4.0 × 10^{-4} mol/L, Al/Ti = 400 mol/mol, $P(C_2H_4) = 0.13$ MPa, $T_p = 40$ °C, $t_p = 1$ h, toluene used as solvent. [b] Degree of branching (branching numbers of 1000 carbon atoms in polyethylene main chain) determined by infrared spectra.

η^5-Pentamethylcyclopentadienyltribenzyloxytitanium [Cp*Ti(OBz)$_3$] was prepared by the reaction of η^5-pentamethylcyclopentadienyltrichloride titanium (Cp*TiCl$_3$) with benzyl alcohol in the presence of the absorbent of HCl [such as N(Et)$_3$]. A yellow liquid product (yield 93%) was obtained and identified. ^{1}H NMR (CDCl$_3$): δ 1.86 (s, 15H, Cp*), δ 4.53 (s, 6H, (OCH$_2$)$_3$), δ 7.22 (s, 15H, Ph$_3$). ^{13}C NMR (CDCl$_3$): δ 11.3 ($-$CH$_3-$), δ 64.6 ($-$OCH$_2-$), δ 77.5$-$78.4 (Cp* C), δ 126.6 (Ph C-4), δ 127.1 (Ph C-3,5), δ 128.1 (Ph C-2,6). δ 140.9 (Ph C-1). Anal. Calcd for $C_{31}H_{36}O_3Ti$: C, 73.81; H, 7.14. Found: C, 73.26; H, 7.02.

Modified methylaluminoxane (mMAO) was prepared by first the controlled reaction of trimethylaluminum (TMA) with H_2O from $Al_2(SO_4)_3{\cdot}18H_2O$ dispersed in toluene for several hours, then filtration, and finally evaporation under vacuum. The contents of TMA retained in mMAO were determined by ^{1}H NMR.[31] Five kinds of mMAO solid, i.e., mMAO1, mMAO2, mMAO3, mMAO4, and mMAO5, containing 26.1, 22.5, 20.0, 16.2, and 15.4 mol % of TMA, respectively, were obtained by regulating the molar ratio of H_2O and TMA.

Polymerization of Ethylene. The polymerization runs were carried out under an extra-pure-grade nitrogen atmosphere in 150 mL glass flasks equipped with a magnetic stirrer. The mMAO, toluene, and Cp*Ti(OBz)$_3$ were introduced into the reactor, and then the oxidation states of titanium were determined by the potassium dichromate redox titration method under nitrogen atmosphere.[30] The solution was saturated by ethylene monomer, and the pressure was maintained at 0.13 MPa during full runs. The polymerizations were terminated by the addition of 10 wt % HCl in ethanol. The polymers were washed with ethanol and dried in a vacuum at 60 °C to constant weight.

Characterization. Gel-permeation chromatography (GPC) of polymers was performed on a Water 150C at 100 °C using standard polystyrene as reference and *o*-dichlorobenzene used as solvent. The viscosity-average molecular weights (M_v) of the polymers were also calculated by $[\eta] = 6.67 \times 10^{-4} M_v^{0.67}$, and $[\eta]$ was measured in decahydronaphthalene at 135 °C. ^{13}C NMR spectra of polyethylene samples were recorded at 100 °C in a 10 mm tubes using an INOVA 500 MHz spectrometer. The samples were dissolved in *o*-dichlorbenzene/benzene-d_6 to form a 15 wt % solution. The chemical shift value (30.00 ppm) of main backbone methylene was used as an internal standard. The degree of branching of polyethylene was mainly determined by infrared spectra analysis with a Nicolet 205 Fourier transform infrared spectrometer, and the absorbance of the methyl group of the branch at about 1380 cm^{-1} was adopted for the determination. Differential scanning calorimetry (DSC) analysis was conducted with a Perkin-Elmer DCS-7 system at 10 °C/min. Melt flow indexes, I_2 and I_{10}, were measured at 190 °C in a μPXRZ-400C melt indexer. The testing loads for I_2 and I_{10} were 2.16 and 10 kg, and all polyethylene samples were mixed with 0.5 wt % Irganox 1010.

Results and Discussion

Relationship of Trimethylaluminum Content in Modified Methylaluminoxane with Productivity, Degree of Branching, and Molecular Weight of Polyethylene. Despite that methylaluminoxane (MAO) is one of the best cocatalyst used commonly in metallocene catalysts promoting olefin polymerization, effects of its structure and composition on formation of active species of metallocene catalyst still remain unclear. During preparation, the solid MAO product always contains some amount of unreacted trimethylaluminum (TMA) which cannot easily be removed by vacuum evaporation. The so-called modified MAO (mMAO) containing various amounts of residual TMA has been known to have significant influences on productivity, molecular weight, and even the structure of polyethylene.[31] The results of ethylene polymerization with Cp*Ti(OBz)$_3$ activated by five different mMAO are given in Table 1. From run 1 to run 5, the lower the content of TMA in mMAO is, the more Ti(IV) active species are created. The catalytic activity is decreased with the decrease in the content of Ti(IV) active species. In run 1, the Ti(IV) active species approach 88.5 mol %, and the catalytic activity is up to 15.3 × 10^5 g of PE/(mol of Ti h). TMA is not only a stronger reducing agent but also a good chain transferring agent.[31,32] Therefore, as in run 5, the excess TMA in mMAO leads to creation of most of the Ti(III) active species of less positive affinity and results in a decrease of catalytic activity and molecular weight of polyethylene.

It is fairly interesting that all ethylene homopolymerization products present branching chains as confirmed by ^{13}C NMR and IR characterizations. We suggest that the active species of propagating polyethylene chain would cause transfers of β-hydride elimination to give macromonomers of α-olefin. The branched polyethylene is produced by in-situ insertion of these macromonomers into active species of polyethylene propagating chain as displayed in the following scheme.

$$[\text{Ti}]{-}\text{CH}_2{-}\text{CH}_2{-}\text{CH}_2{-}\,-\,-\,-\text{CH}_3 \xrightarrow{\beta\text{-hydride elimination}} [\text{Ti}]{-}\text{H} + \text{CH}_2{=}\text{CH}{-}\text{CH}_2{-}\,-\,-\,-\text{CH}_3 \quad (\text{macromonomer})$$

$$[\text{Ti}]{-}\text{CH}_2{-}\text{CH}_2{-}\text{CH}_2{-}\,-\,-\,-\text{CH}_3 + \text{CH}_2{=}\text{CH}{-}\text{CH}_2{-}\,-\,-\,-\text{CH}_3 \xrightarrow{\text{long chain branching}} \text{long branching polyethylene}$$

As shown in Table 1, the degree of branching of polyethylene was increased with increase of the content of TMA in mMAO. We have reported[27] that the reaction of Cp*Ti(OBz)$_3$ with mMAO gave mainly two kinds of CpTi^{IV}Me(OBz)$_2$ and CpTi^{III}Me(OBz) active species. β-Hydride elimination is easier to occur in CpTi^{III}R(OBz) growing chain active species than in CpTi^{IV}R(OBz)$_2$ growing chain active species, owing to larger steric hindrance of the latter which possesses two OBz ancillary ligands.

The influence of temperature on ethylene polymerization with Cp*Ti(OBz)$_3$/mMAO2 catalyst is shown in Table 2. The catalyst exhibits a maximum activity at 40 °C. Higher temperature depressed the dissolved concentration of ethylene monomer and caused a de-

Table 2. Influences of Polymerization Conditions on Preparing Branched Polyethylene with Cp*Ti(OBz)$_3$/mMAO2 Catalyst[a]

run no.	polymerization temp (°C)	Al/Ti (mol/mol)	activity × 10^{-4} (g of PE/(mol of Ti h))	M_w × 10^{-5}	degree of branching	T_m (°C)
6	0	400	6.2	7.9	6.9	139.8
7	20	400	9.3	6.3	12.8	126.2
2	40	400	12.5	5.0	21.6	120.5
8	60	400	7.7	4.2	22.3	121.9
9	80	400	2.8	3.6	25.2	119.8
10	40	100	1.1	5.7	20.7	122.6
11	40	200	8.7	5.6	15.7	125.5
12	40	300	11.6	5.2	18.2	123.2
13	40	500	10.3	4.7	22.5	119.3
14	40	600	7.9	4.5	22.8	118.8

[a] Polymerization conditions: [Ti] = 4.0 × 10^{-3} mol/L, $P(C_2H_4)$ = 0.13 MPa, t_p = 1 h, toluene used as solvent.

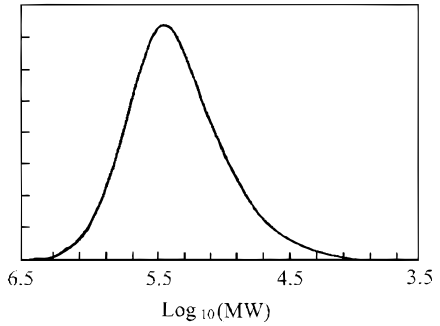


Figure 1. GPC curve of polyethylene sample obtained from run 2 in Table 1.

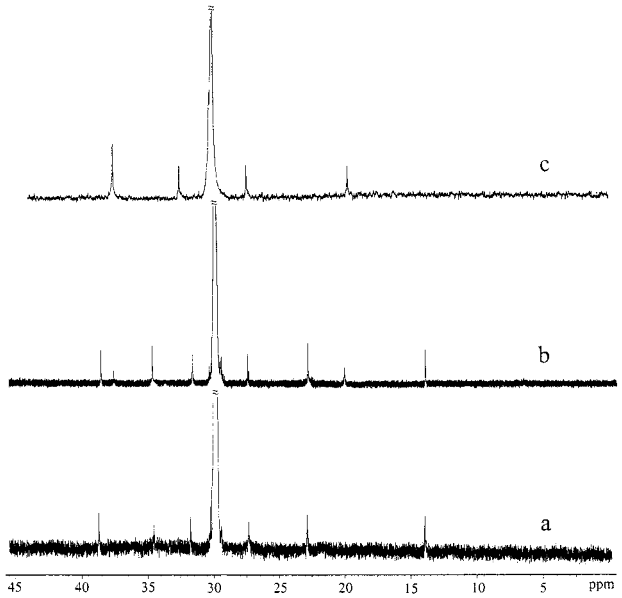


Figure 2. ^{13}C NMR spectra of branched polyethylene: (a) run 7, (b) run 2, (c) run 8.

Table 3. ^{13}C NMR Chemical Shift Calculated and Observed and Their Assignments

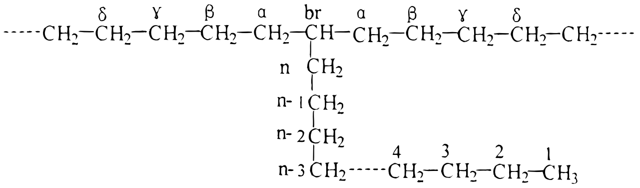
chemical shifts (ppm) observed in Figure 2			chemical shifts (ppm) calcd	assignments
run 7	run 2	run 8		
14.02	14.06		14.06	1(n≥6)
	20.02	19.82	19.63	1(n=1)
23.06	22.58		22.81	2(n≥6)
26.95	27.46	27.45	27.42	β(n=1)
			27.38	β(n≥6)
30.00	30.00	30.00	29.96	δ(n=1), δ(n≥6)
30.46	30.48	30.36	30.21	γ(n=1)
			30.46	γ(n≥6)
31.56	31.50		32.40	3(n≥6)
	33.43	33.16	33.08	br(n=1)
34.47	34.49		34.61	α(n≥6)
	37.42	37.51	37.47	α(n=1)
38.01	38.34		38.25	br(n≥6)

crease of the molecular weight as a result of acceleration of chain transferring reaction. It should be noted that the degree of branching of polyethylene increased with the elevation of polymerization temperature. The results suggest strongly that more macromonomers of α-olefin would be yielded due to the favoring of β-hydride elimination at higher polymerization temperature. At the same time, higher temperature would lead to more Ti(IV) complexes to be reduced to Ti(III) active species which are favorable to the increase of α-olefin macromonomers and generate branched polyethylene chain as discussed above.

As shown in Table 2, under the adopted polymerization conditions, tests performed with mMAO2 as cocatalyst to promote Cp*Ti(OBz)$_3$ for ethylene polymerization are also dependent on the molar ratio of Al and Ti (Al/Ti). The catalytic activity (at 40 °C) increases with increase of Al/Ti and reaches a maximum value of 12.5 × 10^5 gof PE/(mol of Ti h) at Al/Ti = 400 mol/mol. A minimum value of Al/Ti (about 100 mol/mol) is required because the mMAO is necessary for reaction of mMAO with Cp*Ti(OBz)$_3$ to produce active species for ethylene polymerization and used to scavenge impurities. MAO has been well-known to act as a chain transfer agent,[33] so the higher Al/Ti ratio makes the molecular weight of polyethylene obtained decrease. It can be understood that a higher content of Ti(III) active species exists in Cp*Ti(OBz)$_3$/mMAO catalyst at higher Al/Ti, and the degree of branching of polyethylene also increased with the increase of Al/Ti ratio.

Characterization of Structure and Property of Resultant Polymers. The molecular weight and molecular weight distribution of the representative polyethylene sample obtained from run 2 in Table 1 was determined by GPC (Figure 1). The polymer shows rather narrow molecular weight distributions of 2.13. This result shows the characteristic of branched polyethylene polymerized by single active species.

^{13}C NMR spectra of polyethylene prepared with Cp*Ti(OBz)$_3$/mMAO catalyst are shown in Figure 2. As compared with "linear" polyethylene (such as high-density polyethylene), the presence of many new resonance peaks in ^{13}C NMR spectra of the polymers obtained from run 7 (Figure 2a), run 2 (Figure 2b), and run 8 (Figure 2c) in Table 2 implies that all polyethylenes are branched. According to the assignments of each resonance peaks based on chemical shift calculations by Linderman and Adamsand method[34] (listed in Table 3), all branches are isolated. Symbolization of Usami and Takayama[35] is used for polymer with isolated branches as in the following scheme:



The carbon in the branch is denoted by "n", starting with

Table 4. Properties of Branched Polyethylene Prepared by Cp*Ti(OBz)$_3$/mMAO Catalyst

sample	$M_w \times 10^{-5}$	M_w/M_n	deg of branching	I_2 (g/10 min)	I_{10}/I_2	T_m (°C)	density (g/cm^3)
run 6	7.9	2.20	6.9	0.92	16.4	139.8	0.947
run 7	6.3	2.16	12.8	0.85	19.9	126.2	0.926
run 2	5.0	2.13	21.6	0.81	23.2	120.5	0.898
run 8	4.2	2.12	22.3	4.6	8.5	121.9	0.912

the methyl end group of branch as “1”. The Greek letters are used to mark the carbon of methylene from the branch point “br” in the main chain. The most attractive result in this investigation is the presence of a lot of isolated long branches (longer than six carbons in length) in polyethylene samples from runs 2 and 7. These long branches are confirmed by the presence of the br, α, β, γ, δ, 1, 2, and 3 ($n \geq 6$) carbon resonances at 38.34, 34.49, 27.46, 30.48, 30.00, 14.06, 22.58, and 31.50 ppm in Figure 2b of run 2 and at 38.01, 34.47, 26.95, 30.46, 30.00, 14.02, 23.06, and 31.56 ppm in Figure 2a of run 7.

It is very interesting to note that the resonance peaks of isolated methyl pendant and corresponding br, α, β, γ, δ, and 1 carbon resonances are observed at 33.43, 37.42, 27.46, 30.48, 30.00, and 20.02 ppm in Figure 2b of run 2 and at 33.16, 37.51, 27.45, 30.36, 30.00, and 19.82 in Figure 2c of run 8. The results are discussed in terms of a mechanism that in-situ 2,1-insertion of macromonomers to [Ti^{IV}]−H active species follows β-hydride elimination as in the following scheme.

$$[\mathrm{Ti}]\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!-\!-\!-\!CH_3 \xrightarrow{\beta\text{-hydride elimination}} [\mathrm{Ti}]\!-\!H + CH_2\!=\!CH\!-\!CH_2\!-\!-\!-\!-\!CH_3 \quad \text{(macromonomer)}$$

$$[\mathrm{Ti}]\!-\!H + CH_2\!=\!CH\!-\!CH_2\!-\!-\!-\!-\!CH_3 \xrightarrow{2,1\text{-insertion}} [\mathrm{Ti}]\!-\!C(CH_3)H\!-\!CH_2\!-\!CH_2\!-\!-\!-\!-\!CH_3$$

The chance of 2,1-insertion increases with the increase of polymerization temperature, so isolated methyl pendants were only found in polyethylene of run 8 obtained at 60 °C and without long branches (Figure 2c). The reasons for this behavior seem likely that steric hindrance effect result in a sufficiently high energy of activation for 2,1-insertion.

The properties of melt flow index, density, and melting temperature of resultant branched polyethylene are summarized in Table 4. It is well-known that the melt flow index data I_2 are also characteristic of the molecular weight: the higher the molecular weight, the lower the I_2 is for polymer with the same degree of branching of short branches (short than six carbons in length). As shown in Table 4, sample of run 8 reveals higher I_2 values contributed by lower molecular weight and higher degree of branching of methyl pendants. However, the polyethylene with long branches synthesized by ethylene homopolymerization using Cp*Ti(OBz)$_3$/mMAO catalyst gave very low I_2 values (sample of runs 6, 7, and 2). Although the molecular weight of the polymers is in the order of sample of run 6 > run 7 > run 2, the I_2 is in the same order of run 6 > run 7 > run 2 due to the more important effect of long branches. The ratio of I_{10} and I_2 is a rheological measurement of branched polyethylene. A narrowly distributed molecular weight of linear polyethylene normally gives a I_{10}/I_2 value in the range of 6−8. Sample of runs 6, 7, and 2 with MWD of 2.20−2.13 have I_{10}/I_2 values increasing from 16.4 to 19.9 to 23.2, also indicating the presence of the effect of long chain branching.

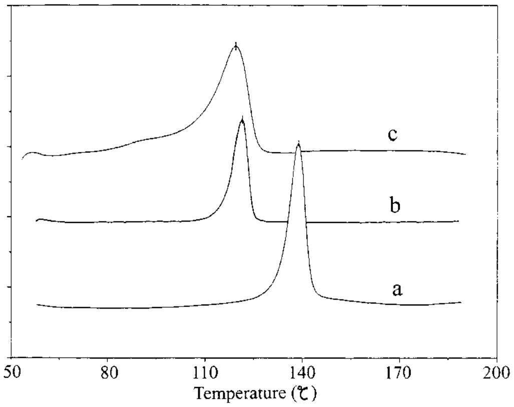


Figure 3. DSC curves of branched polyethylene: (a) run 6, (b) run 8, and (c) run 2 in Table 4.

Another unique property of these branched polyethylenes as shown in Table 4 is that their density and melting temperature rely not only on the degree of branching but also on the length and distributing uniformity of branches in polyethylene main chain. Depending on degree of branching of these resultant polymers, it is possible to obtain from a high-density polyethylene to a highly branched linear low-density polyethylene. But run 8 with the higher degree of branching than run 2 possesses higher density and melting temperature due to the effect of isolated methyl pendants. Figure 3 displays DSC curves of run 6 (Figure 3a) with fewer long branches, run 2 (Figure 3c) with mainly long branches and fewer methyl pendants, and run 8 (Figure 3b) with only methyl pendants. Run 6 exhibits the highest melting temperature and crystal degree since it has the highest molecular weight and the lowest degree of branching, while both melting temperature and crystal degree of runs 2 and 8 become low. However, run 8 has a narrower melting peak and higher crystal degree than run 2.

Conclusions

The homopolymerization of ethylene with η^5-pentamethylcyclopentadienyltribenzyloxytitanium [Cp*Ti(OBz)$_3$] complex and various modified methylaluminoxanes (mMAO) catalysts was carried out to synthesize branched polyethylene. The catalytic activity, molecular weight, degree of branching, and branch length of resultant polymers depend on the oxidation states of active species of titanium and polymerization conditions including temperature and molar ratio of Al and Ti. The residual TMA in mMAO could strongly reduce Ti(IV) complexes to Ti(III) and Ti(II) ones, and Ti(IV) active species was suggested to be more favorable for ethylene polymerization. The open structure of monotitancoene catalyst permitted macromonomers of α-olefin to copolymerize with ethylene to form long branched polyethylene. The macromonomers of α-olefin are produced by β-hydride elimination. The possible presence of isolated long branch and methyl pendant in the main chain of polyethylene conformed by ^{13}C NMR indicated that branching chain propagation reaction included both in-situ 1, 2-insertion of macromonomers to Ti(IV) active species with a polyethylene propagating chain and 2,1-insertion of macromonomers to [Ti^{IV}]−H active species following β-hydride elimination. There is a remarkable increase in 2,1-insertions with the increase of polymerization temperature. The presence of isolated long branches makes this polyethylene very interesting in density, crystallinity, and rheological properties. As compared with short branched polyethylene with the same molecular weight and molecular weight distribution, the long branched polyethylene reveals lower density, melting temperature, and melt flow index I_2 and a more higher I_{10}/I_2 value.

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