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Microstructure of Ethylene/Propylene Random Copolymers Prepared by a Fluorinated Bis(phenoxy-imine)Ti Catalyst

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Summary

Living copolymerization of ethylene and propylene was catalyzed by a fluorine-containing bis(phenoxy-imine) titanium catalyst. A series of ethylene-propylene copolymers with different propylene contents were prepared and the copolymers were characterized by ^{13}C-NMR, GPC and DSC. The copolymers were found to have the following characteristics: (1) Molecular weight distribution of the copolymer is rather narrow; (2) There exist only isolated propylene units distributed along the polymer chains even at propylene content as high as 14.9 mol%; (3) The distribution of ethylene sequence are not homogeneous. Insertion of propylene changes from 2,1-insertion in homopolymerization into 1,2-insertion when the preceding unit is ethylene.

Keywords

ethylene/propylene copolymer; structure; composition distribution

Introduction

Ethylene copolymers have wide applications and study on structure-properties of ethylene copolymers is of great importance. For ethylene copolymer, comonomer is the most important factor that influences properties of copolymers [1]. However, the distribution of comonomer units in the copolymer is usually not homogeneous, even in the ethylene copolymers synthesized by so-called “single-site” metallocene catalysts [2-4]. There exist both inter-molecular composition distribution (referring to distribution of comonomer units among different polymer chains) and intra-molecular composition distribution (referring to distribution of comonomer units along a single polymer chain) [5-7]. These two types of composition distributions affect polymer properties together with molecular weight distribution [8-14], and make it difficult to correlate structure of ethylene copolymers with their properties. In order to establish a clear structure-properties relationship, common polymers were fractionated by cross fractionation to obtained fractions with narrow molecular weight distribution and homogeneous intermolecular composition distribution [15]. Nevertheless, cross fractionation is a hard work and time consuming. Some authors also managed to synthesize ethylene copolymers with regular structure. For example, Smith et al. prepared ethylene/propylene and ethylene/butene copolymers with precisely spaced branches [16,17]. Peculiar crystallization behavior has been observed in some of this special type of copolymer [18]. However, the molecular weigh distribution of this type ethylene copolymer is not monodispersed. By using bis(phenoxy-imine) titanium complexes as catalyst, living polymerization of propylene has been conducted and the obtained copolymers have a narrow molecular weight distribution [19-27]. Polyethylene-*b*-poly(ethylene-*co*-propylene) block copolymers with narrow molecular weight distribution have been prepared as well [19,24,28]. The monodispersed samples are of great advantage to structure-properties study, since the effect of molecular weight distribution can be ignored. Although ethylene-propylene copolymerization has been conducted using bis(phenoxy-imine) titanium catalysts [19,24], chain structure of this type of ethylene copolymer was only scarcely reported in literature [26]. The properties of the prepared ethylene copolymers have not been studied either.

In this paper, living copolymerization of ethylene and propylene was catalyzed by a fluorine-containing bis(phenoxy-imine) titanium catalyst employing methyl aluminoxane (MAO) as cocatalyst. The microstructure of ethylene/propylene copolymers was characterized by ^{13}C-NMR. It is found that not only the prepared copolymers have a narrow molecular distribution, but also only isolated propylene units distribute along the polymer chains even at high propylene content ([propylene] mol% = 15.0 %). This type of ethylene/propylene copolymer is extremely suitable for study on the effect of intra-molecular composition distribution on polymer properties. It can also be used to distinguish the effect of isolated and blocky comonomer units on crystallization behavior of ethylene copolymers.

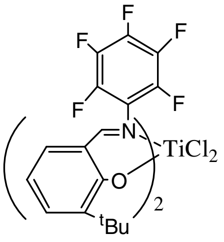
Experimental

Materials

Toluene was first purified with concentrated sulfuric acid and then refluxed over sodium/benzophenone. Cocatalyst methylaluminoxane (MAO, 10 wt % solution in toluene) was purchased from Albemarle. The residual trimethylaluminum was removed by evacuation prior to use. Polymerization-grade ethylene and propylene gases were purified by passing through a Ni catalyst and 3-Å molecular sieves to remove oxygen and water, respectively. The argon used was purified by passing through columns of Ni catalyst and K-Na alloy. All operations were carried out under a dry Ar atmosphere with Schlenk technique. The structure of fluorinated bis(phenoxy-imine) Ti catalyst (**1**) was shown in Scheme 1. The catalyst was synthesized according to reference [21] and the structure was verified by ^{1}H-NMR.

Copolymerization

Copolymerization of ethylene and propylene was carried out at 25°C under atmospheric pressure in a 100-mL glass reactor equipped with a propeller-like stirrer and thermostat water bath. Toluene (50 mL) was introduced into the nitrogen-purged reactor and stirred (600 rpm), then the ethylene/propylene mixed gas were rapidly bubbled through the reactor. The flow rates of ethylene and propylene were regulated to levels that are much larger than the monomer consumption rate during the polymerization, so the monomer concentrations in the solution can be kept at



Scheme 1. Structure of catalyst (**1**).

a constant level. After 10 min, polymerization was initiated by adding a toluene solution of MAO (1.0 M, 4.0 mL) and then a toluene solution of catalyst (10 mM, 1.0 mL) into the reactor with stirring (600 rpm). Polymerization was terminated by addition of *sec*-butyl alcohol (10 mL), followed by introduction of ethanol (250 mL) and concentrated HCl (2 mL). The polymer was collected by filtration, washed with ethanol (200 mL), and dried in vacuum at 80°C overnight. Copolymers with different propylene content were prepared by changing the flow rates of ethylene and propylene.

Characterization

Molecular weight and molecular weight distribution of the ethylene-propylene copolymers were measured by GPC in a PL 220 GPC instrument (Polymer Laboratories Ltd.) at 150°C in 1,2,4-trichlorobenzene. Three PL mixed-B columns (500–10^7) were used. Universal calibration against narrow polystyrene standards was adopted. Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer Pyris-1 DSC calorimeter. The polymer (about 6 mg) was sealed in aluminum pan, which was put into a glass tube at argon atmosphere. The glass tube was immersed in an oil bath and heated to 180°C, kept at that temperature for 30 min, and then annealed at 140°C, 130°C, 120°C, 110°C, 100°C, 90°C, 80°C, 70°C, 60°C, 50°C and 40°C respectively, each for 12 h. The treated samples were then scanned in DSC from 50 to 200°C at a heating rate of 10°C/min. For DSC studies of non-isothermal crystallization, the sample was sealed in an aluminum pan, heated to 160°C and held at that temperature for 5 min and then cooled to 50°C at a rate of 10°C/min in the DSC instrument. Heat flow during the cooling process was recorded. Quantitative ^{13}C NMR spectra were recorded on a Varian Mercury 300-plus spectrometer at 120°C in 10% (w/v) solution of o-$C_6D_4Cl_2$. $Cr(acac)_3$ was used to reduced the relaxation time of carbon atoms and the delay time was set as 3 s [29]. The pulse angle was 90°, and 8000 scans were collected.

Results and Discussion

Table 1 shows the results of copolymerization of ethylene with propylene catalyzed by catalyst (**1**). It is found that both polymer yield and molecular weight decreases with increasing flow rate of propylene gas fed, showing that catalyst (**1**) exhibits higher activity toward ethylene polymerization than propylene. All these samples have narrow molecular weight distributions. However, the polydispersity of polymer decreases with increasing flow rate of propylene as well. The slightly broadened

Table 1. Results of ethylene-propylene copolymerization[a].

Run No	E/P feed[b] (mL/min)	Yield (g)	M_w ($\times 10^{-3}$)	M_w/M_n	[P] (mol %)
1	300/60	0.960	17.11	1.27	5.1
2	300/150	0.935	16.55	1.25	8.1
3	300/300	0.785	13.25	1.19	11.4
4	300/600	0.785	11.57	1.16	14.9

[a] Polymerization conditions: [Ti] = 10.0 μmol, Al/Ti = 400, 1 atm, 50 ml toluene, 25°C, polymerization time $t_p = 5$ min.

[b] Flow rate of ethylene and propylene feeds.

molecular weight distribution at lower flow rate of propylene may be resulted by higher polymerization activity of ethylene than propylene, because the duration of injecting catalyst solution into the reactor is the main source of broadening the polymer molecular weight distribution. The propylene content in the copolymers increases with the flow rate of propylene, ranging from 5 mol% to 15 mol%.

Figure 1a shows the ^{13}C-NMR spectrum of the copolymer with propylene content of 11.4 mol%. The assignments of the observed resonances are indicated in the figure. The nomenclature of the carbon atoms in the polymer chain follows that proposed by Carman [30]. It is found that five peaks from $S_{\alpha\delta+}$, $S_{\beta\delta+}$, $S_{\gamma\delta+}$, $T_{\delta+\delta+}$, $P_{\delta+\delta+}$ appear besides the long ethylene sequences ($S_{\delta+\delta+}$). This shows that only isolated propylene units distribute along the long polyethylene chains in this copolymer, and the methine carbons in two adjacent propylene units are spaced by at least four methylene carbons. Absence of resonances in the region from 45 ppm to 48 ppm, which is produced by PP dyads, also supports this conclusion. The ^{13}C-NMR spectrum of another copolymer with propylene content of 14.9 mol% is illustrated in Figure 1b. We noticed that apart from the peaks assigned to $S_{\alpha\delta+}$, $S_{\beta\delta+}$, $S_{\gamma\delta+}$, $T_{\delta+\delta+}$, $P_{\delta+\delta+}$ and $S_{\delta+\delta+}$, some new peaks of low intensity, such as $S_{\alpha\gamma}$, $S_{\alpha\beta}$, $S_{\beta\gamma}$, $S_{\beta\beta}$, and $T_{\gamma\delta+}$, appear as well. These weak peaks correspond to three different structures, as shown in Figure 2. The peaks $T_{\gamma\delta+}$ and $S_{\alpha\beta}$ are produced by the structure of two methine carbons spaced by two methylene carbons (structure (a)). $S_{\alpha\gamma}$ and $S_{\beta\beta}$ are formed by the structure of two methine carbons spaced by three methylene carbons (structure (b)), and $S_{\beta\gamma}$ is from the structure of two methine carbons spaced by four methylene carbons (structure (c)). Observation of these structures shows that with increase of the propylene units incorporated, the distance between two adjacent propylene units decreases.

There are two possible routes for the formation of each structure shown in Figure 2, which are depicted in Figure 3. Structure (a) may be formed by a 1,2-insertion followed by a 2,1-insertion (Figure 3a) or by a 2,1-insertion of propylene sequentially followed by an insertion of ethylene and a 1,2-insertion of propylene (Figure 3b). Structure (b) is produced by a 1,2-insertion of propylene followed by an insertion of ethylene and then another 1,2-insertion of propylene (Figure 3c) or by a 2,1-insertion of propylene followed by an insertion of ethylene and then another 2,1-insertion of propylene (Figure 3d). The structure (c) is formed by a 1,2-insertion followed by an insertion of ethylene and then a 2,1-insertion of propylene (Figure 3e) or by a 2,1-insertion followed by two insertions of ethylene and then a 1,2-insertion of propylene (Figure 3f). Coates and co-workers have revealed that the insertion of propylene units in the homopolymerization of propylene catalyzed by bis(phenoxyimine) Ti catalyst proceeds in an unusual 2,1-insertion mode [26]. As a result, we tend to draw the

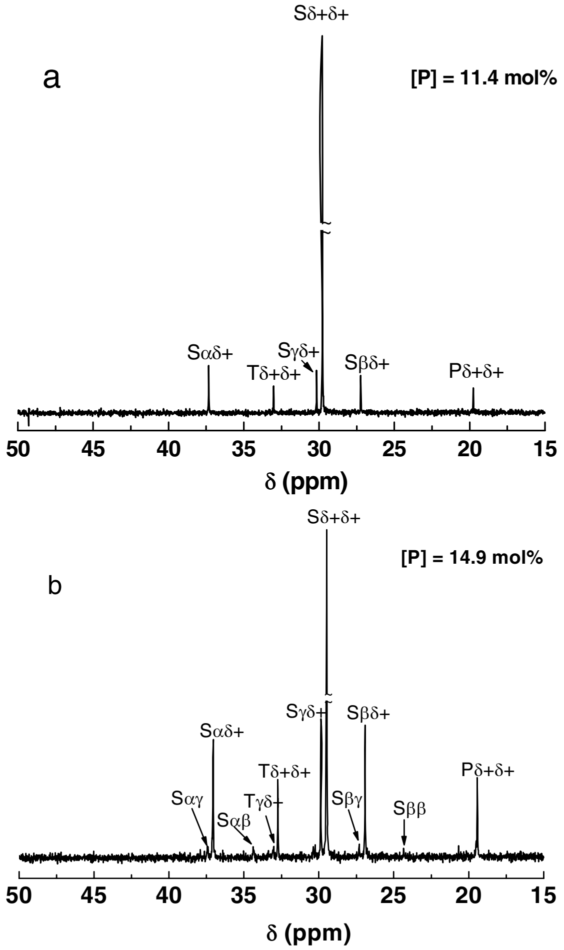


Figure 1. ^{13}C-NMR spectra of ethylene/propylene copolymers prepared by catalyst (**1**). (a) [P] = 11.40 mol% and (b) [P] = 14.93 mol%.

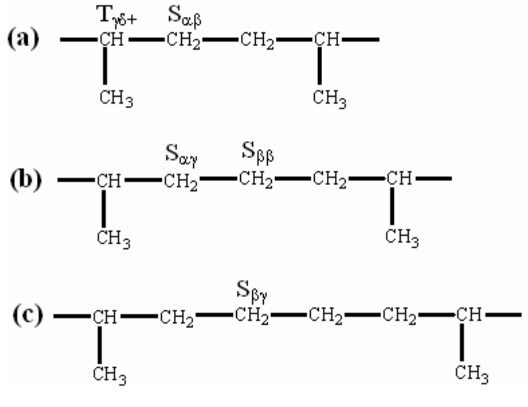


Figure 2. Three types of structure corresponding to the resonances (a) $S_{\alpha\beta}$ and $T_{\gamma\delta+}$; (b) $S_{\alpha\gamma}$ and $S_{\beta\beta}$; (c) $S_{\beta\gamma}$ in Figure 1(b).

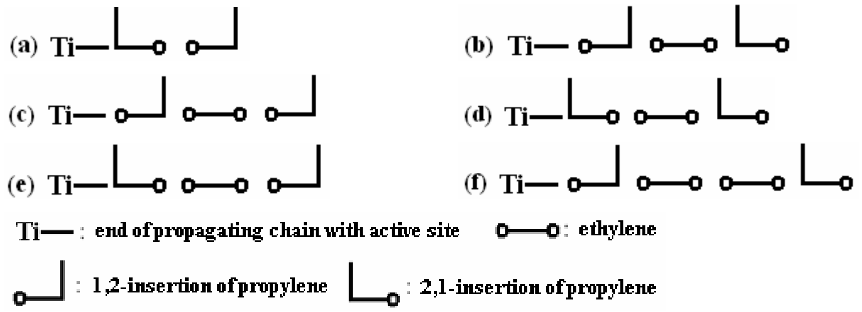


Figure 3. Possible routes for formation of the structures in figure 2.

conclusion that structures (a)-(c) in Figure 2 are formed according to the routes (b), (d) and (f) in Figure 3, respectively. The presence of structures (a) and (c) shows that addition mode of propylene becomes 1,2-insertion instead of original 2,1-insertion when the preceding unit is ethylene, as reported in literature [26].

Above analysis indicates that even in the ethylene-propylene copolymer with propylene content as high as 14.9 mol%, there are no successive propylene units (PP dyad). This is the most striking feature of the ethylene/propylene copolymer prepared by catalyst (**1**), because usually when propylene content in the copolymer reaches 8-10 mol%, PP dyads will be detectable by ^{13}C-NMR [31,32]. Therefore, average length of ethylene sequences can be readily regulated by controlling the amount of propylene units incorporated. Due to the absence of successive propylene units, such copolymers can be used to distinguish the effects of isolated and blocky comonomer units on crystallization of ethylene copolymers. This is especially important for ethylene-propylene copolymers, in which propylene units can be included into crystal lattice of polyethylene [33-36]. We believe that, as structural defects, the degree of inclusion of isolated and successive propylene units into PE crystals will be different. On the other hand, since the ethylene-propylene copolymers prepared by catalyst (**1**) have narrow molecular weight distribution, which means that different polymer chains are similar in chemical composition, the effects of molecular weight distribution and inter-molecular composition distribution on crystallization can be ignored. As a result, if the distribution of propylene units along the polymer chain is not homogeneous, the effect of intra-molecular composition distribution on crystallization can be evaluated in a simple way without consideration of the effects of molecular distribution and inter-molecular composition distribution.

Figure 4 shows the DSC traces of non-isothermal crystallization of the copolymer samples, in which the ethylene/propylene copolymers of different propylene contents were cooled down from 160°C at a rate of 10°C/min. It is found that crystallization temperature decreases with the propylene content, and the copolymer with propylene content of 14.9 mol% is non-crystallizable at such a cooling rate. We also notice that there appear two crystallization peaks for the samples with propylene contents of 5.1 mol% and 8.1 mol%, respectively. Since crystallization temperature strongly depends on comonomer content, double crystallization peaks may be an implication that the distribution of propylene units along the polymer chains is not homogeneous. To further evaluate the intra-molecular composition distribution of ethylene/propylene copolymers prepared by catalyst (**1**), stepwise crystallization experiment was carried out for these four samples. Stepwise crystallization is usually used to measure the

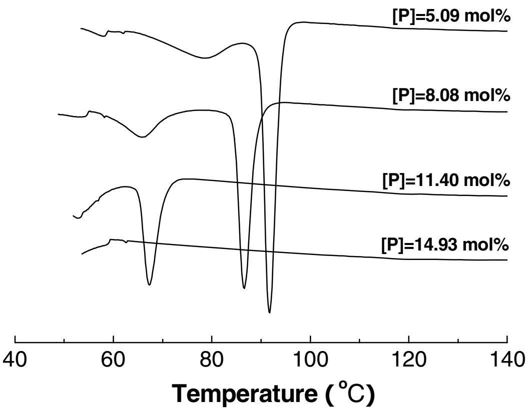


Figure 4. Non-isothermal crystallization DSC traces of ethylene/propylene copolymers cooled from melt at a rate of 10°C/min.

length distribution of ethylene sequences in ethylene/α-olefin copolymers [2-5,37], in which the comonomer units are excluded from the crystal lattice. For ethylene/propylene copolymer, the propylene unit may be included into the crystal lattice of polyethylene due to its smaller volume compared to other α-olefins [33-36]. However, since the presence of propylene units will inevitably affect crystallization of ethylene sequences, we believe that stepwise crystallization can still be used to characterize the length distribution of ethylene sequences (i.e. composition distribution) of ethylene/propylene copolymers in an approximate way.

Figure 5 shows the melting DSC curves of copolymer after stepwise crystallization from 140°C to room temperature at an interval of 10°C for 12 hr at each temperature. First, one can see that there are multiple melting peaks in all these four copolymer samples. This clearly shows that polyethylene crystals with different lamellar thickness are formed, indicating that the length distribution of ethylene sequences is not homogeneous. It is found that the positions of melting peaks are similar for all samples, if there appear melting peaks at these positions. This is because all the

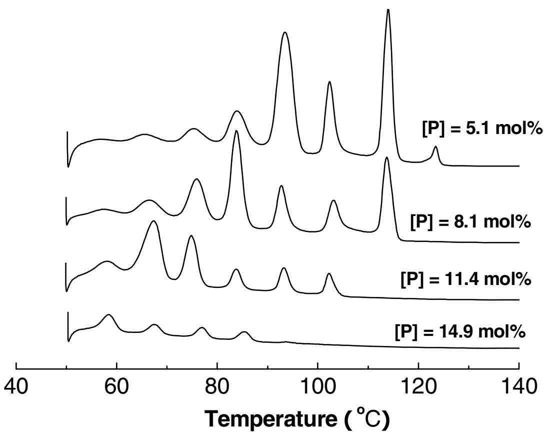


Figure 5. Melting DSC traces of ethylene/propylene copolymers after stepwise crystallization.

samples undergo the same crystallization procedure. With increase in propylene content, the number of melting peak decreases and the melting peaks at high temperature disappear gradually. This shows that the length of ethylene sequences decreases as propylene content increases. We also notice that for the copolymers with propylene content of 5.1 mol% and 8.1 mol%, apart from a strong melting peak at medium temperature (83~93°C), an equally strong melting peak at high temperature (about 114°C) also appeared. There seems to be a bimodal distribution of lamella thickness in these samples. If the melting temperature really reflects the length of crystallizable ethylene sequences and the fusion enthalpy reflects the weight percentage of the ethylene sequences, this phenomenon shows that the length distribution of ethylene sequences does not agree with a simple statistical distribution. Nevertheless, since only one type of active site is present in the catalytic system, and the concentrations of two monomers are kept constant during polymerization, the length distribution of ethylene sequences should agree with a simple statistical distribution. Therefore, we thus speculate that the strong melting peak at high temperature is due to easier inclusion of propylene units into the polyethylene crystal lattice when the propylene units are spaced by longer ethylene sequences. This inclusion of propylene units in polyethylene crystal lattice lead to thicker crystalline lamella that show high melting temperature. In other words, propylene units isolated in long polyethylene segments can not interfere much the crystallization of the later, but the crystallization will be strongly influenced when the propylene units are too close to each other. In contrast, in the other two ethylene/propylene copolymers with higher propylene content, there is no melting peak with abnormal intensity at high temperature. This means that inclusion of propylene units spaced by shorter polyethylene sequences into the PE crystal lattice may be more difficult. Further study on crystallization of this type of ethylene/propylene copolymer is underway.

Conclusions

In summary, ethylene/propylene random copolymers prepared with fluorinated bis(phenoxy-imine) titanium catalyst have following characteristics: (1) Molecular weight distribution of the copolymer is narrow; (2) There exist only isolated propylene units distributed along the polymer chains even at propylene content as high as 14.9 mol%; (3) Insertion of propylene changes from 2,1-insertion in homopolymerization into 1,2-insertion when the preceding unit is ethylene; (4) The distribution of ethylene sequence are not homogeneous.

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