Characterization of Ethylene-butene Polyethylene Copolymers by DSC and SSA

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Abstract. Two copolymers of M1 and M2 were studied by DSC and SSA. The SSA test was applied to characterized the distribution of methylene sequence length (MSL) in the M1 and M2 copolymers. The butene comonomer contents of M1 and M2 were 4.66 mol% and 4.83 mol%, respectively. The content of butene comonomer of M1 and M2 is low, and the distribution of MSL increases monotonously with that of MSL. The longest MSL of M1 is 195.4, and the mole fraction is 0.96%, which is higher than M2. The influence of MSL and distribution on the crystallinity and T_m is greater than that of the total monomer content, which are different with traditional opinions.

Keywords. copolymers, methylene sequence length (MSL), DSC, SSA.

1. Introduction
Polyethylene (PE) is one of the most widely used commercial polymers in the world. The control of its multi-functional chain can be realized by copolymerizing ethylene with different α-olefins monomer [1]. The distribution of different comonomer along the copolymer main chain can present a greatly isomeric intramolecular or intermolecular comonomer distribution. Short chain branched (SCB) PE has attracted much more interest in industry and academia due to its influence on the properties including density, crystallinity, melting temperature and so on [2]. The general methods of characterizing SCB are Fourier transform infrared spectrum [3] and 13C NMR spectrum [4].

More time-saving methods, for example thermal fractionation, have recently been developed [5]. These methods are based on the difference of crystallizability of chain with inhomogeneous structure. The two main methods are step crystallization (SC) and SSA.

Mandelkren calculated the layer thickness distribution of ethylene copolymer in constant temperature by SC [6]. The thermal analysis after SC showed that Z-N catalyzed LLDPE has a wide bimodal SCB, and the lamellar thickness and single point catalyzed VLDPE have a narrow lamellar distribution, while the VLDPE has a narrow lamellar distribution, while the VLDPE has a more lamellar distribution [7].

SSA is a self nucleation and annealing step based on continuous application. Muller and his colleagues separate ethylene /different α-olefin copolymers by SSA firstly [8]. Using Gibbs Thomson equation, Muller and his colleagues got the same result as SAXS [9]. Vanke determined the content and distribution of SCB in polyethylene. SSA has much shorter time and higher resolution than SC or temperature rise elution fractionation (tref) [10].

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In this study, the distribution heterogeneity of ethylene/1-butene copolymer comonomers was characterized by DSC and SSA. The distribution of MSL was determined by SSA. The effect of MSL and their distribution on the crystallization and melting behavior of the two copolymers was discussed.

2. Experimental

2.1. Materials
The sample M1 containing with 4.66 mol % butene and sample M2 containing with 4.83 mol % butene was supplied by Petrochemical Research Institute.

2.2. \(^{13}\text{C}\)-NMR Spectroscopy
The polymer solution was prepared in 0.5ml o-dichlorobenzene-d4 with ~80mg sample at 125 ℃. The \(^{13}\text{C}\)-NMR spectrum was recorded at 125 ℃ with frequency of 100.58 MHz by Bruker av400. The internal phase-locked signal is provided by o-dichlorobenzene-d4 solvent, and the highest peak value is 133.22 as the standard reference. The number of scans is 5000 and the delay time is 8 seconds.

2.3. Differential Scanning Calorimetry (DSC)
The temperature of DSC Q100 was calibrated with indium. The sample (6 mg) is heated from 20 ℃ to 200 ℃ at 10 ℃/min, and its heat history is deleted at 200 ℃ for 5 minutes, cooled from 200 ℃ to 20 ℃ for 5 minutes at speed of 1, 5, 10, 20, 30, 40, 50 ℃/min respectively, and then heated to 200 ℃ at a rate of 10 ℃/min. \(T_m\) and melting heat (\(\Delta H_m\)) are measured in heating experiment.

2.4. SSA Method
The weight of the sample is about 6mg. The temperature of the DSC Q100 was calibrated with standard indium. The process includes steps as below: (a) The sample was heated from 20 ℃ to 200 ℃ at a rate of 10 ℃/min, and then stored at 200 ℃ for 5 min to erase the thermal history; (b) the sample is cooled to 0 ℃ at 10 ℃/min and held for 5 minutes; (c) the sample is heated from 0 ℃ at 10 ℃/min to the self seeding temperature (\(T_s\)). Place the sample at \(T_s\) for 5 min; (d) the sample was cooled from \(T_s\) to 0 ℃ at 10 ℃/min; (e) the sample is heated to a new \(T_s\) that is 5 ℃ lower than the previous \(T_s\) for 5 minutes. Step “e” of “c” (f) is repeated at \(T_s\); (g) the sample was heated from 0 ℃ to 200 ℃ at 10 ℃/min, the multiple melting curve was obtained.

3. Results and Discussion

3.1. \(^{13}\text{C}\)-NMR Spectroscopy Test
The SCB content which is the comonomer content of the two sample is calculated from \(^{13}\text{C}\)-NMR spectrum [11]. The comonomer content of the sample M1 and M2 is 4.66 mol% and 4.83 mol%.

3.2. DSC Test
As shown in figure 1, at the cooling rate of 10 ℃/min, M1 has a melting peak at about 117.4 ℃ with a crystallinity of 37.6%, M2 has a melting peak at about 117.8 ℃ with a crystallinity of 38.3%, and M1 has a crystallinity and \(T_m\) lower than M2. For M1 and M2, with the increase of cooling rate, the melting peak generally moves towards low temperature. As shown in figure 2, with the increase of cooling rate, the crystallinity of copolymer M1 gradually decreased from 39.5% to 35.6%. With the increase of the cooling rate, the crystallinity of the copolymer M2 decreased from 41.0% to 33.6%. In general, with the increase of 1-butene content, the 1-butene insertion into crystallizable methylene sequence increases, the lamellar thickness becomes thinner and melting point \(T_m\) decreases[12].

At the same time, M1 and M2 show special cases. The content of 1-butene in M1 was 4.66 mol%, lower than that in M2. However, the crystallinity of M1 and \(T_m\) are lower than M2. This special phenomenon is discussed in the next section.
Figure 1. DSC curves of the sample M1 (left) and M2 (right) measured after non-isothermal crystallization at different cooling rates.

Figure 2. Variation of the degree of crystallinity with cooling rate for the two samples of M1 and M2.

3.3. SSA Test

The SSA test is based on the continuous application of self nucleation and annealing steps on polymer samples. After the heat treatment, the final DSC heating operation revealed the melting point distribution caused by SSA treatment due to the heterogeneity of the analyzed polymer chain structure. Compared with DSC results, the SSA curves show the difference of SCB distribution in copolymers. Figure 3 shows the DSC temperature curve of the sample after the SSA. For M1 and M2, SCB breaks the ethylene crystal sequence and forms different length of crystalline methylene sequence. The number and strength of melting peaks qualitatively reflect the difference of MSL distribution for different samples [13]. In general, the several melting peaks of different samples move towards low temperature with the increase of comonomer content, which is the result of intermolecular heterogeneity. Especially, the several melting peak of M1 is lower than that of M2.

The ln(CH₂ mole fraction) is linear with 1/T (equation (1)). According to this curve, the relative molecular mass fraction of ethylene copolymer can be determined by the TM of the fraction. The distribution curve of MSL in the two copolymers was obtained.

\[
\ln(\text{CH}_2 \text{ mole fraction}) = 0.3451 \times 142.2/T_m \tag{1}
\]

The CH₂ mole fraction can be calculated to MSL using equation (2).

\[
MSL = \frac{2X}{1-X}, X = \text{CH}_2 \text{ mole fraction} \tag{2}
\]
Using equations (1), (2) to calculate the MSL. the MSL distribution of M1 and M2 are shown in figure 4. The molar percentile of MSL increased monotonously with the increase of MSL. The sample of M1 and M2 contain with 1-butene 4.66 mol% and 4.83 mol%. The monomer content discrepancy is only about 0.17 mol%, their MSL distribution is very wide, ranging from 20 to 200. The longest MSL of M2 is 195.4, and the percentage is 0.96%. Meanwhile, the longest MSL of M1 was 194.2, accounting for 0.60%. This result explains why M2 contains more 1-butene and higher T_m than M1.

Figure 3. DSC heating scans after SSA.

Figure 4. MSL distributions of M1 and M2.

Figure 5 shows the MSL distribution of M1 and M2, which shows a very wide distribution. The peak value of M1 is mainly between 78 and 131, and MSL is between 20 and 194.2. The peak value of M2 is mainly between 80 and 138, and its MSL is between 20 and 195.4. Therefore, the content of 1-butene in these samples (M1 and M2) increased gradually, but the longest MSL decreased. The peak value of M1 is 33, the MSL distribution is narrow and T_m is lower than M2.

Figure 5. MSL content of M1 and M2.

4. Conclusions
Thermal analysis of DSC and SSA provide a fast and simple method to characterize the structural heterogeneity of ethylene/α-olefin copolymer. The influence of MSL and its distribution on the
crystallinity and $T_m$ is greater than that of the total monomer content, and the influence of monomer distribution on the crystallinity and $T_m$ is greater than that of monomer content.

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