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Improved thermal fractionation technique for chain structure analysis of ethylene/α-olefin copolymers

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Abstract

In this report, we describe an improved thermal fractionation technique used to characterize the polydispersity of crystalline ethylene sequence length (CESL) of ethylene/α-olefin copolymers. After stepwise isothermal crystallization, the crystalline ethylene sequences are sorted into groups by their lengths. The CESLs are estimated using melting points of known hydrocarbons. The content of each group is determined using the calibrated peak area. The statistical terms: the arithmetic mean $\bar{L}_n$, the weighted mean $\bar{L}_w$ and the broadness index $I = \bar{L}_w/\bar{L}_n$ are used to describe the distribution of CESL. Results show that improved thermal fractionation technique can quantitatively characterize the polydispersity of CESL with a high degree of accuracy. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thermal fractionation technique; Ethylene/α-olefin copolymer; Crystalline ethylene sequence length

1. Introduction

Recently, thermal fractionation technique has been widely used to investigate the molecular heterogeneities of LLDPE [1–12] and their blend [13–16]. Thermal fractionation is a temperature-dependent segregation process based on recrystallization and reorganization of ethylene sequence from the melt [4]. It is similar to temperature rising elution fractionation (TREF), but the segregation mode is different, the neighboring sequences can crystallize independently and subsequently melt at temperature corresponding to their crystal size or lamellar thickness. Large intramolecular sequence heterogeneity can also result in more levels of segregation. Keating et al. [4] first introduced the statistical terms to describe the polydispersity of crystalline ethylene sequence length (CESL) and their results show that it is an effective method to compare ethyl-based copolymers produced with different catalyst systems. Our work [17] suggests that this method can also be used to characterize and compare the polydispersity of lamellar thickness of ethylene copolymer. However, these works [4] assume that the heat of fusion (or area) of each melting peak is directly proportional to the weight percentage of each fraction with different CESL. As a matter of fact, the peak area cannot directly be converted because of the temperature-dependent of the specific heat capacity, which leads to an increase in the heat of fusion with increasing sequence length in the melting regime of copolymers. In this work, to quantitatively characterize the polydispersity of CESL, a correction factor is added to adjust for the variation of heat of fusion with sequence length level.

2. Experimental

The polymer materials examined in this study were narrow molecular weight distribution metallocene catalyzed ethylene/α-olefin copolymer fractions obtained by using solvent gradient fractionation (SGF) and cross-fractionation (CF) technique [18]. Detailed molecular characteristics of these fractions were listed in Table 1.

DSC thermal fractionation process was carried out at Perkin–Elmer differential scanning calorimeter, model 4, and the subsequent heating scan were conducted on a computerized Perkin–Elmer differential scanning calorimeter, Model DSC-7. The specimens were weighted in the range 3–5 mg. The temperature reading and calorific measurement were calibrated by using standard indium.

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Table 1
Molecular characterization of the samples used in this work

Sample	Comonomer (X)	Content (mol%)	M_n/K	M_w/K	M_w/M_n
CF5	1-Hexene	2.07	18.8	20.6	1.10
	1-Butene	0.08			
CF6	1-Hexene	2.11	36.9	41.4	1.12
	1-Butene	0.10			
CF7	1-Hexene	2.02	75	86.8	1.16
	1-Butene	0.11			
CF8	1-Hexene	1.75	122	156	1.28
	1-Butene	0.11			
SGF0	1-Hexene	3.37	39.4	46.2	1.17
SGF2	1-Octene	1.94	107	142	1.33
SGF3	1-Octene	3.90	107	139	1.30

The samples was melted at 160°C for 5 min and then quenched to 120°C. Isothermal crystallization was continued for 120 min at 120°C. The sample was then quenched to 116°C and another isothermal crystallization followed. This procedure was repeated in every 4°C step till 80°C and then quenched to 50°C. The heating scans were obtained by heating the thermal fractionated samples from 50 to 150°C at a heating rate 5°C/min.

3. Results and discussion

Fig. 1 shows the DSC heating curves after stepwise isothermal crystallization from the melt for all the copolymer samples used in this work. Multiple melting peaks can be seen which are formed during each step of isothermal crystallization. Each endotherm represents a population of crystals with almost the same thermodynamic stability and the melting temperature and difference among the endotherms is mainly caused by different crystal sizes [1]. The number and intensity of melting peak in heating curves qualitatively show the difference of the polydispersity of CESL among the samples.

To provide a quantitative structure analysis by thermal fractionation technique two calibration steps are required. First the melting temperature must be related to ethylene sequence length and then a correction factor should be applied for adjusting the variation of heat of fusion with sequence length level. Several authors [19,20] have reported the calibration curve of the relation between melting point and branching content. Here, we use the calibration curve proposed by Keating et al. to calculate the CESL for each fraction [4]. They recrystallized the commercially available hydrocarbons with the same program and measured the subsequent melting point. The plot of ln(CH_2 mole fraction) against $1/T$ shows a well linearship (Eq. (1)), and from this curve, the ESL of fractionated ethylene copolymers can be assigned from the melting temperatures of the fractions

$$-\ln(\mathrm{CH_2}\ \text{mole fraction}) = -0.331 + 135.5/T_{\mathrm{m}} \qquad (1)$$

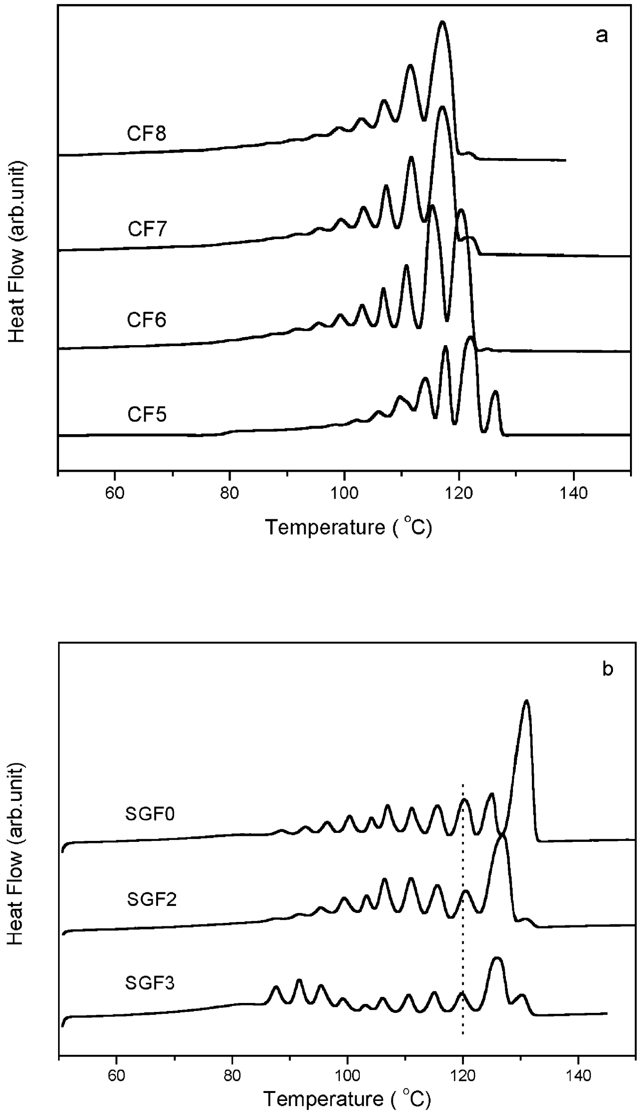

Fig. 1. DSC heating curves of ethylene/α-olefin copolymers after thermal fractionation: (a) CF samples and (b) SGF samples. The crystallization temperatures were 120, 116, 112, 108, 104, 100, 96, 92, 88, 84 and 80°C, and each temperature was maintained for 120 min.

As pointed by Gabriel et al. [21], one drawback of the DSC heating curve is that it cannot be directly converted into a weight percentage of the components of different length sequences. On the contrary, the TREF analysis can do it because the distribution curve directly reflects the concentration at a given elution temperature and the relative amount of differently branched fractions can be calculated from the peak area. The DSC heat flow depends on the amount of the material melted at a certain temperature as well as on the temperature-dependent of the specific heat capacity. The ethylene copolymers usually have a broad melting regime and it will lead to an increase in the heat of fusion by increasing the CESL (or decreasing branching content). Here we use the correction method proposed by Wild et al. [19] to adjust the amount of each fraction. They determined the heat of fusion for a series of preparative fractions of a 1-butene ethylene copolymer as a function

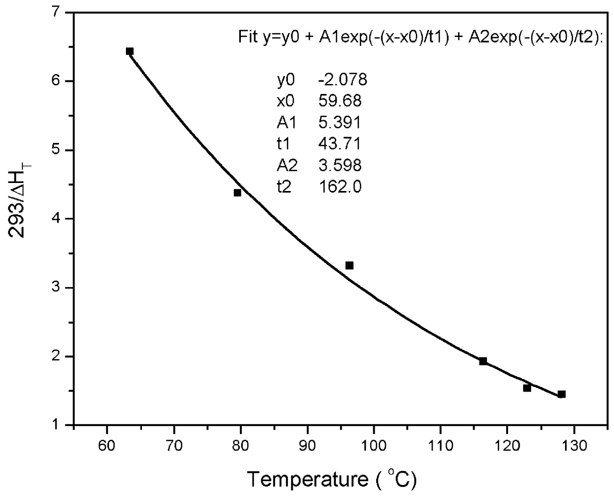

Fig. 2. Variation of heat of fusion with melting temperature.

of their melting temperature. Instead of taking the ratio of the heat of fusion at a temperature of 130°C for a linear fraction used in their work, we use the ratio of the heat of fusion of perfect crystal ($\Delta H_f = 293$ J/g) and the fusion of each fraction to convert the DSC peak area into weight percentage. The temperature-dependent function $293/\Delta H(T)$ is shown in Fig. 2 (the data used are obtained by Wild et al. [19]). Then, the content of each fraction can be obtained by multiplying the peak area with its corresponding ratio.

The statistical terms: arithmetic mean $\bar{L}_n$, weighted mean $\bar{L}_w$ and the broadness index I were first introduced by Keating et al. [4] to describe the polydispersity of CESL of ethyl-based copolymers

$$\bar{L}_n = \frac{n_1L_1 + n_2L_2 + \Lambda n_iL_i}{n_1 + n_2 + \Lambda + n_i} = \sum f_iL_i \tag{2}$$

$$\bar{L}_w = \frac{n_1L_1^2 + n_2L_2^2 + \Lambda + n_iL_i^2}{n_1L_1 + n_2L_2 + \Lambda + n_iL_i} = \frac{\sum f_iL_i^2}{\sum f_iL_i} \tag{3}$$

$$I = \bar{L}_w/\bar{L}_n \tag{4}$$

where n_i is calibrated and normalized peak area and L_i is the CESL or lamellar thickness for each fraction. By using these equations we determine the polydispersity parameters of all the samples used in this work. Table 2 lists the parameters after thermal fractionation by 4°C interval (Fig. 1).

From Table 2 we can see that the calibrated $\bar{L}_n$ and $\bar{L}_w$ are all smaller than that of uncalibrated, it further indicates that the temperature-dependence of heat of fusion really leads to the over estimation of the average CESL of ethylene/α-olefin copolymers. It has been demonstrated that the SGF samples, their comonomer distribution are both inter- and intra-molecularly heterogeneous and the CF samples can be considered as inter-molecularly homogeneous but intra-molecularly heterogeneous [1,18]. Thus the broadness indexes of CF samples are smaller than that of SGF samples and the broader distribution of CESL in SGF samples leads to the wider melting temperature regime (see Fig. 1(b)). Increasing the comonomer content can also widen the melting temperature regime. The wider the melting temperature regime, the more important is the temperature-dependent of heat capacity on the true content of each fraction as seen in Fig. 2.

Another factor that affects the values of $\bar{L}_n$ and $\bar{L}_w$ of CESL is molecular weight. For example, the comonomer content of SGF0 is 3.37 mol% similar to that of SGF3 (3.90 mol%), but the $\bar{L}_n$ of SGF0 is 24.8 nm larger than that of 15.6 nm. The molecular weight of SGF3 ($M_n = 107,000$) is much larger than that of SGF0 ($M_n = 39,400$). Thus, this tendency should be due to the enhanced entanglement with increasing molecular weight. When molecular weight is high enough, the effect of chain entanglement is so important that the effect of comonomer content seems not to be important. For example, the SGF2 and SGF3 have the same high molecular weight ($M_n = 107,000$) and different comonomer content (1.94 mol% for SGF2 and 3.90 mol% for SGF3), but they have almost the same $\bar{L}_n$ and $\bar{L}_w$ of CESL. It should be noted that the thermal fractionation technique only detect the ethylene sequences long enough to crystallize and the sequences too short to crystallize cannot belong to the crystalline ethylene sequence. This result indicates that the polydispersity of CESL in real system is quite complicated, and the improved thermal fractionation technique can reveal the crystallization ability of different copolymers in a novel aspect by getting the polydispersity parameters of CESL.

Table 2
Parameters of polydispersity for both CF and SGF fractions

Sample	Comonomer (mol%)	Uncalibrated			Calibrated		
		$\bar{L}_n$ (nm)	$\bar{L}_w$ (nm)	I	$\bar{L}_n$ (nm)	$\bar{L}_w$ (nm)	I
SGF0	3.37	24.8	35.5	1.433	21.8	30.7	1.410
SGF2	1.94	16.2	21.4	1.322	13.5	19.2	1.422
SGF3	3.90	15.6	22.7	1.450	12.3	19.1	1.553
CF5	2.15	15.0	17.0	1.133	13.9	15.9	1.144
CF6	2.21	12.2	13.6	1.119	10.1	11.0	1.097
CF7	2.13	11.2	12.3	1.105	10.4	11.6	1.115
CF8	1.86	11.0	12.0	1.091	10.3	11.4	1.107

4. Conclusion

Improved thermal fractionation technique gives a satisfied result for characterizing the polydispersity of CESL for ethylene/α-olefin copolymers quantitatively. For SGF samples having broad distribution of CESL, the melting temperature regime is wide and the effect of temperature-dependent of heat capacity is important, while for CF samples having relatively narrow distribution of CESL, the effect of temperature-dependent of heat capacity seems to be not very important. The distribution of CESL is more effective than comonomer content in the aspect of revealing the crystallization ability of copolymer.

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