

SEMI-QUANTITATIVE CHARACTERIZATION OF SEGMENT DISTRIBUTION IN LLDPE BASED ON THERMAL SEGREGATION*

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Abstract Based on successive multiple-step isothermal crystallization and self-nucleation annealing methods, a novel semi-quantitative method for the characterization of segment distribution in linear low density polyethylene (LLDPE) was established by treating the thermal analysis data using the Gibbs-Thomson equation. The method was used to describe the segment distribution of Ziegler-Natta catalyzed LLDPE (Z-N LLDPE), metallocene catalyzed LLDPE (*m*-LLDPE) and two commercial LLDPEs with wide molecular weight distribution. The differences of the results obtained from the two thermally treated samples were compared. The results of segment distribution of the polymers were discussed according to their microstructure data and were compared with their characteristics. It can be deduced from the results that this characterization method is effective to characterize the sequence structure of the branched ethylene copolymers.

Keywords Characterization, Segment distribution, Linear low density polyethylene, Thermal segregation

INTRODUCTION

Ethylene has long been polymerized with different α -olefins to control the crystallinity and applicability of the copolymers obtained in various ways. The segment structure of ethylene copolymers, especially the segment distribution, plays an important role in establishing their physical and mechanical properties, including melting point, crystallinity, elasticity, temper, strength and rheological behavior, which determine their processing conditions and application fields^[1].

Linear low density polyethylene (LLDPE) is a typical representative of branched ethylene copolymers. In its early stage of development, LLDPE was synthesized by a conventional Ziegler-Natta catalyst system (*i.e.* Z-N LLDPE). Due to the different activity sites and the heterogeneity of the catalyst system, the macromolecules obtained show a great disparity in both molecular weight (MW) and the amount of short chain branches (SCB). Wild *et al.* first characterized the heterogeneity of LLDPE using a unique method of temperature-rising elution fractionation (TREF) based on the different crystallizability of the macromolecular fractions. The results showed that the LLDPE exhibits a very broad molecular weight distribution (MWD) with M_w/M_n around 5 or more and their SCB has a bimodal feature^[2]. Usami *et al.* examined LLDPE in detail by TREF, size exclusion chromatography (SEC), ¹³C-NMR, DSC and FT-IR, and pointed out that the bimodal feature of the polymers was caused by two kinds of activity sites in the catalyst system^[3]. Hosoda *et al.* also elucidated the multiple distribution with a contour map by TREF and solvent-gradient elution fractionation (SGEF)^[4].

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Comparatively, metallocene based LLDPE (*m*-LLDPE) has a uniform chain structure because of the unique features of metallocene catalyst systems, such as high catalyst activity, long catalytic life and homogeneity. *m*-LLDPE shows narrower MWD (M_w/M_n around 2) than that of Z-N LLDPE, and more uniform comonomer content, *i.e.* narrower SCB distribution^[5]. Fu *et al.* recently found that certain *m*-LLDPE exhibited at least intermolecular heterogeneity in SCB; direct experimental proofs was obtained using a cross-fractionation (CF) technique, which combined a solvent gradient fractionation (SGF) with a subsequent temperature gradient fractionation (TGF)^[6, 7]. The SGF results indicated that the SCB content of *m*-LLDPE does not vary significantly with MW; that is in good agreement with the characteristics of metallocene catalyzed polymers. But the results of TGF revealed that there was a tendency for the SCB content to increase slightly with MW.

It is well known that there are some methods available to characterize the segment structure or branching content of copolymers. GPC was used in combination with viscosity measurement to determine the variation of average degree of long chain branches with the molecular weight of macromolecules^[8, 9]. But as far as ethylene copolymers are concerned, they should be run at a higher temperature (about 120 °C) and were not suitable for the short chain branched copolymers. ¹³C-NMR was used to characterize the type and quantity of branched functional groups in a polymer chain at a higher operating temperature (about 130 °C), but it could not provide the chain information for more than the segment length of six carbons in branched ethylene copolymers^[10, 11]. Though, general DSC measurement could provide some information on the thermal effect of ethylene segments^[12], yet the measurement could not afford the real segment structure because of the kinetic factors. Comparatively, the thermal segregation DSC is more meaningful in that it qualitatively gives some indirect information on segment distribution in branched ethylene copolymer chains^[13]. However, all the methods mentioned above can only supply average information about branching degree. TREF is quite effective for characterizing the segment distribution of ethylene copolymers, but the complicated and time-consuming experimental procedures are the drawbacks for its general application. Moreover, it can not reflect the intramolecular segment distribution.

For developing a convenient characterization method of the segment distribution in ethylene copolymers, thermal segregation DSC and related mathematical calculation have been reported^[13, 14, 15]. The pretreatment processes used previously were coarse and the results were either qualitative or only indirectly reflected the segment distribution in the polymer chains because of the nonlinear relationship between the melting temperature and the segment length. In this work, a simple and semi-quantitative method based on thermal segregation was carried out to characterize more precisely the real segment distribution in branched ethylene copolymers.

EXPERIMENTAL

The samples used in this work were all commercial products. Z-N catalyzed LLDPE, LLDPE-1 and metallocene catalyzed LLDPE, LLDPE-2 were supplied by Panjin Petroleum Co. and Exxon Co., respectively. Two other LLDPE with wide MWD, LLDPE-3 and LLDPE-4, were obtained from British Petroleum Company. The structure parameters of the samples are listed in Table 1. The MW and MWD of PE samples were measured by a PL GPC210 instrument operated at 160 °C with dichlorobenzene as the eluant at a flow rate of 10 mL/min and calibrated with polystyrene standards. The branching degree was calculated from the ¹³C-NMR spectra recorded by a Bruker DMX-300 NMR spectrometer in 10% solution of 1,2,4-trichlorobenzene (TCB) at 125 °C, and the calculation was performed by following the literature^[16]. DSC was performed on a Perkin-Elmer DSC4 and a Mettler-Toledo DSC822 instrument, using a heating rate of 10 K/min in N₂. Calculation of crystallinity was based on the heat of fusion of 273 J/g for the perfect polyethylene crystals.

Table 1. The fundamental characterization results of the PE samples

Samples	$M_w (\times 10^3)$	M_w/M_n	T_m (°C)	X_c (%)	SCB/1000C
LLDPE-1	537	4.6	123.7	34.5	18.3
LLDPE-2	295	2.0	119.3	35.0	13.2
LLDPE-3	112	23	123.0	31.8	14.9
LLDPE-4	143	35	122.7	23.0	20.9

The samples were treated by the following two different thermal segregation methods.

Successive multi-step isothermal crystallization (SIC)^[13]: About 5 mg of the sample was maintained at 150°C for 10 min, then annealed for 360 min from a pre-selected temperature which was close to its maximum melting temperature (120–130°C) to 60°C through a stepwise lowering of temperature at descending 3°C each step in DSC instrument. The annealed sample was then scanned from room temperature to 150°C at a heating rate of 10 K/min.

Successive self-nucleation annealing (SSA)^[14]: The sample was melted at 150°C for 10 min, and then cooled to room temperature at a rate of 10 K/min. Subsequently, the temperature was raised at a rate of 5 K/min to a pre-selected self-nucleation and annealing temperature (T_{s1}), where the sample was isothermally maintained for 360 min before quenching to room temperature. Then the sample was heated again at a rate of 5 K/min to T_{s2} , 3°C below T_{s1} and maintained for the same period of time as the previous step, then quenched to room temperature. This procedure was repeated until the T_s reached 60°C. The treated sample was then scanned from room temperature to 150°C at a rate of 10 K/min. The detailed procedures for performing SIC and SSA are expressed in Fig. 1.

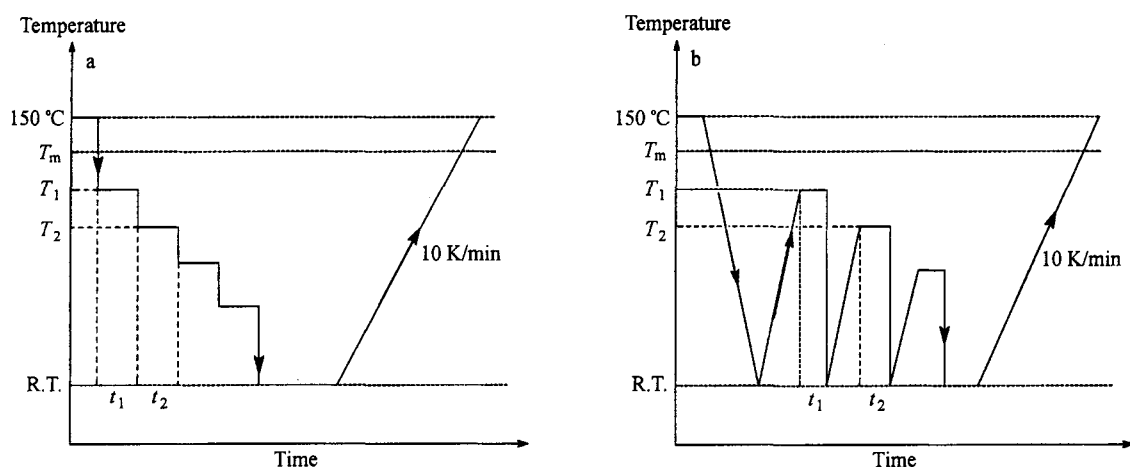


Fig. 1 Schematic pathways of SIC (a) and SSA (b)

RESULTS AND DISCUSSION

The segments with a certain length in ethylene copolymer chains crystallized at a corresponding temperature according to Gibbs-Thomson relation^[17]. If the crystallization time is long enough, it is assumed that all the possible ethylene segments with a fixed length crystallized together. After multiple step isothermal crystallization, the segments with various lengths can thus be crystallized separately to form lamellae with different thickness and short chain branches are rejected to the interface between the crystal and the amorphous zone^[18]. During a subsequent DSC heating measurement, the lamellae with different thickness melt at different temperature with the thinner lamellae melting at a lower temperature. Therefore, a DSC curve with multiple melting peaks was obtained.

Figure 2 shows two DSC heating curves of LLDPE-2 having different thermal history of thermal segregation (curve 1) and slowly cooling at 10 K/min (curve b) respectively. It can be found that the melting range and the distribution of melting peaks on the DSC heating curves are quite different due to the different thermal history of the crystallites. It is speculated that curve 1 properly represents the ethylene segments distribution in the polymer chains.

The DSC heating curves of LLDPE-1 treated by SSA (curve a) and SIC (curve b) are showed in Fig. 3. The segregation effect of SSA method seems to be better than that of the SIC method in detail. In fact, the larger interval between two temperatures of the cooling process, the faster the real cooling rate is for the influence of circumstance. In principle, the SIC method is a process of cooling in a narrow temperature range, while the SSA

method is a process of cooling to a much low temperature then melting and recrystallization at a constant higher temperature. The annealing temperatures of the SSA method are steady and this makes the polymer segments crystallize in a real isothermal condition. Also, the experimental time can be reduced by the self-nucleation effect for the SSA method. Therefore SSA is taken as the thermal segregation method in the later experiments.

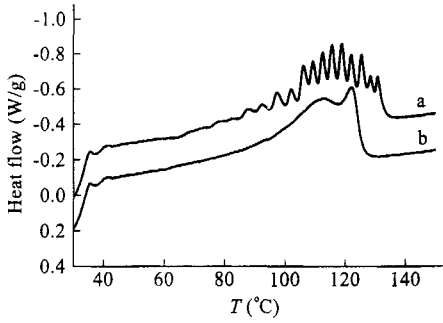


Fig. 2 DSC heating curves of thermally segregated (curve a) and slowly cooled (curve b) LLDPE-2

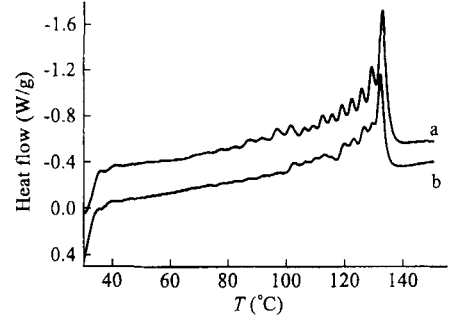


Fig. 3 DSC heating curves of LLDPE-1 treated by SSA (curve a) and SIC (curve b)

Based on the theory of thermodynamics and crystal nucleation, the crystal thickness determines the metastability of the lamellar crystals and their melting temperatures based on the Gibbs-Thomson equation (Eq. 1), while the heat of fusion for each of the melting endotherms is the population of each crystallizable ethylene segments. Note that the scale of segment length is larger than that of the lamellar thickness due to the methylene units at the folding surface, therefore this concept is called the semi-quantitative characterization. The relations are described by the following equations:

$$\frac{T_{m,i}}{T_m^0} = 1 - \frac{2\sigma_e}{l_i \cdot \Delta H_u} \quad (1)$$

$$l_i = \frac{2\sigma_e T_m^0}{\Delta H_u (T_m^0 - T_{m,i})} \quad (2)$$

$$Q_i = \frac{\Delta H_i}{14.03\Delta H_u} \cdot \frac{0.2534}{2l_i} = \frac{0.2534(T_m^0 - T_{m,i})\Delta H_i}{56.12\sigma_e T_m^0} \quad (3)$$

where T_m^0 is the equilibrium melting temperature (146°C for polyethylene and calibrated by the branching content according to Flory's equation^[19]), $T_{m,i}$ is the melting temperature of each melting peak, σ_e is the basal surface energy (90 mJ/m²) of ethylene polymer crystals, l_i is the segment length between the adjacent branch points (Eq. 2). ΔH_u and ΔH_i are the heat of fusion for a repeating unit (7.71 kJ/mol for C₂H₄) and for each melting peak, respectively. Q_i is the semi-quantitative amount of segments with a certain length l_i in the unit mass of sample (Eq. 3). In fact, during each step of thermal segregation, the segments with the lengths relevant to the temperature range of the step crystallized together at an isothermal temperature, therefore the values of Q_i have physical meaning on average. Then, the heat enthalpies obtained in DSC are normalized according to the area below the heat flow curves and then calculated with Eq. (3) to obtain continuous distribution of segment amount.

The segment distribution results of LLDPE-1 and LLDPE-2 are shown in Figs. 4 and 5. It indicates that the segment lengths of LLDPE-1 are distributed mainly between 3–30 nm (about 12–118 ethylene units; the segments shorter than 12 units melt at room temperature). On the whole the segments of LLDPE-1 distribute in a somewhat wide range, which agrees with the features of Z-N LLDPE as reported in the literatures^[2, 3, 4]. In Fig. 5 the segments of LLDPE-2 are distributed in a relatively narrower confine and center at about 8.8 nm on average (about 35 ethylene units, which is relevant to the melting temperature of about 110°C), similar to the theoretical segment distribution pattern reported for ideal random ethylene copolymers^[20]. Along with the molecular

structure parameters listed in Table 1, it can be proved that not only the molecular weight distribution but also the segment distribution of macromolecular chains are narrower in metallocene catalyzed ethylene copolymers. As a result, the branched chains disperse more homogeneously in LLDPE-2 than that in LLDPE-1. That is to say, the efficiency of branched chains of LLDPE-2 is higher than that of LLDPE-1. The same amount of branched chains in metallocene catalyzed copolymers can reduce the crystallinity more obviously, or the same crystallinity needs fewer of branched chains (cf. the results in Table 1).

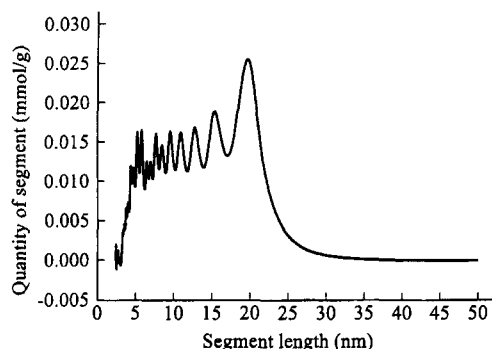


Fig. 4 Segment distribution of Z-N LLDPE-1

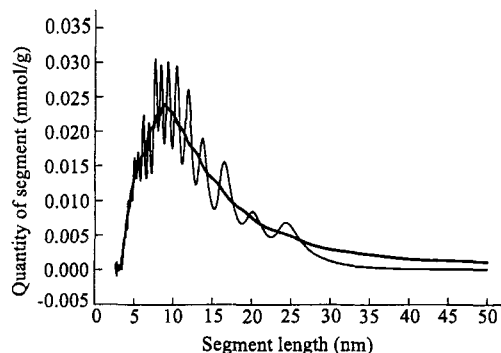


Fig. 5 Segment distribution of m-LLDPE-2

It can be seen that the peak value of average segment distribution of LLDPE-2 is neither relevant to the peak melting point in normal DSC nor the main peak melting point in thermal segregation DSC. The conclusion can be drawn from above that the results of both normal DSC and thermal segregated DSC could not directly represent the segment distribution in polymer chains. Equation 3 indicates that the segment amounts depend not only on the heat of fusion but also on the melting temperature, *i.e.* the segment length. The higher the melting temperature, the longer will be the segment length, as illustrated in Fig. 4. Calculating from the branching content data in Table 1, the average segment length of LLDPE-2 is about 9.6 nm (about 38 ethylene units), which is close to the peak value of average segment distribution of 8.8 nm in Fig. 5 (about 35 ethylene units). Their difference is caused by the choice of different parameter values in the equations, the distinction between the concept of segment length and the real crystal thickness, and the ideal degree of random distribution of branches in polymer chains. It also proves that the characterization method is relatively accurate and effective.

The polymer chains of *m*-LLDPE are similar to each other in both MW (for the narrow MWD) and intermolecular branching content. The narrow distribution of *m*-LLDPE segments infers that only the intermolecular, but not the intramolecular distribution of the branched chains is homogeneous. Comparatively, the branch distribution in a polymer chain of *m*-LLDPE is regarded as homogeneous from the statistical point of view. Therefore, the multiple peaks appearing in thermal segregated DSC could not lead to the conclusion that the sample used is heterogeneous, which was formerly quoted extensively in the literature. However, it is not enough since there are at least four possible homogeneity patterns in a copolymer^[6]. As long as Z-N LLDPE is concerned, the polymer chains are different from each other in both MW (for the wide MWD) and intermolecular branching content (the shorter polymer chains contain more branches than the longer ones). One can not distinguish between inter- and intramolecular heterogeneity from the results of LLDPE-1 since its MWD is wide. A proposed way is to examine the fractions of the parent polymers by this method.

Figure 6 shows the segment distribution results of LLDPE-3 and LLDPE-4 with wide molecular weight distribution. Though their MWD are very different from that of LLDPE-1 and LLDPE-2, their segment lengths are distributed almost in the same range of 3–30 nm. The amounts of branched chains of LLDPE-3 and LLDPE-4 are nearly equal to those of LLDPE-1 and LLDPE-2, while their segment distribution results are quite different from those of the latter. The segment length of LLDPE-3 primarily distributed in a somewhat wider range (as seen in Fig. 6a) and centered at about 12 nm. For LLDPE-4, the segment length has a bimodal character, mainly at about 6 and 16 nm respectively. The amount of the longer segments is slightly less than that of the shorter

ones. As above, one can not distinguish between intermolecular and intramolecular heterogeneity since the MWD of the samples is too large.

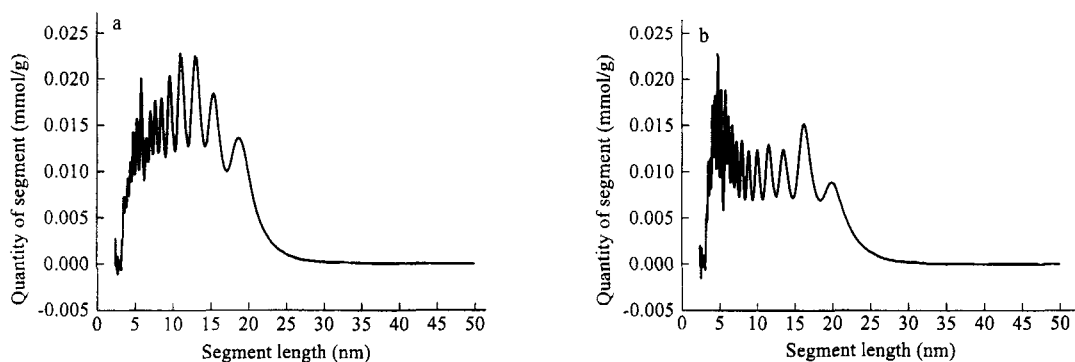


Fig. 6 Segment distribution of LLDPE-3 (a) and LLDPE-4 (b)

From the above results, it is manifest that the characterization method of segment distribution based on SSA is of value in reflecting the individual features of the samples polymerized in different ways and can act as an effective characterization means. The method should also be effective for other ethylene copolymers, since the branching type mainly affects the crystallization kinetics because of the intermolecular interaction, but it could not alter the lamellar structure significantly^[18].

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