

Microstructure Characterization of a Complex Branched Low-density Polyethylene*

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Abstract A low-density polyethylene (LDPE) resin with excellent processing and film-forming properties is fractionated through temperature rising elution fractionation (TREF) technique. The chain structures of both the original resin and its fractions are further analyzed using high-temperature gel permeation chromatography (GPC) coupled with triple detectors (refractive index (RI)-light scattering (LS)-viscometer (VIS)), ¹³C-nuclear magnetic resonance spectroscopy (¹³C-NMR), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and successive self-nucleation/annealing (SSA) thermal fractionation. The ¹³C-NMR results show that the original resin has both short chain branch (SCB) (2.82 mol%) and long chain branch (LCB) (0.52 mol%) structures. The FTIR results indicate that the methyl numbers (per 1000 C) of the fractions gradually decrease from 81 to 46 with increasing elution temperature from 25 °C to 75 °C. The TREF-GPC cross-fractionation results show that the main component is collected at around 68 °C. The molecular weight of the components in the high elution temperatures of 60 °C to 75 °C is from 2.0×10^3 g/mol to 2.0×10^6 g/mol, and the relative amount is more than 80%. In the low elution temperature region below 50 °C, the molecular weights of the components range from 1.0×10^3 g/mol to 1.6×10^4 g/mol, and the relative amount is less than 10%. In the DSC results, the melting peaks of the fractions gradually increase from 80.1 °C to 108.8 °C with elution temperature. In the SSA thermal fractionation, each resin fraction shows a broad range of endotherm with multiple melting peaks (more than eight peaks). The melting peaks shift toward high temperatures with the elution temperature. The characteristic chain microstructure for the resin is also discussed in detail.

Keywords: Polyethylene; Cross-fractionation; Microstructure; Characterization; TREF.

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INTRODUCTION

Given that polyethylene is produced in large volumes and is becoming a growing petrochemical commodity in the world, considerable number of studies has focused on the structure-property relationship of ethylene-based polymers. LDPE is a valuable product used in various film applications because of its superior clarity with stiffness and light mass. LDPE has a very complex molecular structure and consists of SCB and LCB^[1–3]. SCBs influence the polymer morphology and solid-state properties^[4–7], whereas LCBs have remarkable effects on solution viscosity and melt rheology^[8–11]. Polymer microstructure and property have direct relationship; thus, evaluating the chain structure of such polymers is very important.

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Various analytical techniques, such as GPC-RI-LS-VIS^[12, 13], FTIR^[14, 15], ¹³C-NMR^[16, 17], and rheological measurements^[18, 19], have been used to study the different branching types in polymers. Among these methods, the branching types are qualitatively and quantitatively analyzed through FTIR and ¹³C-NMR, respectively. Temperature rising elution fractionation (TREF) has been recently considered as a technique for analyzing semi-crystalline polymers by separating the molecular species according to their crystallizabilities. In particular, several researchers have conducted numerous studies in this field^[20–25]. TREF is a time-consuming experimental process, but can generate detailed information about the polymer microstructure. TREF can also be combined with other fractionation techniques. Wanke *et al.* investigated a commercial LDPE through TREF-DSC and TREF-GPC cross-fractionation, and obtained detailed information about the molecular structures of the different types of LDPEs^[26]. Yau used the recently developed triple detectors (RI, VIS, and LS detectors) for GPC coupled with TREF to obtain valuable information on the polymer microstructure at each crystallization temperature (T_c)^[27]. Mahdavi characterized the microstructure of LDPE by FTIR and TREF^[28]. Pasch *et al.* studied the correlation between the polymer chain microstructure and the thermal behavior of various components in a complex impact polypropylene copolymer through the combination of preparative TREF, high-performance liquid chromatography, FTIR, and high-performance DSC^[29]. Thermal fractionation techniques are less time-consuming compared with the TREF method. Müller *et al.* first presented the SSA thermal fractionation method when they fractionated ethylene/ α -olefin copolymers^[30]. Wanke conducted a quantitative determination of SCB content and distribution in commercial PEs. In addition, the relationship between melting temperature (T_m) and SCB content has been determined^[31]. However, a single characterization method or technique can barely meet the requirements as the polyolefin technology improves. The progress requires better polymer characterization techniques to analyze the polymer microstructure. Therefore, it is very necessary to further enhance the efficacy of cross-fractionation techniques by combining TREF with other fractionation techniques and pave the way for its wider use in analyzing polyolefins.

In this study, an LDPE resin exhibits excellent processing and film-forming properties. However, only analyzing the whole resin cannot provide a complete understanding of its microstructure and distribution. To establish the relationship between structure and property, the molecular chain heterogeneity of the resin is systematically studied by multiple methods. The combination of TREF with other techniques can probe information on chain microstructure in greater detail than any single characterization technique and is very helpful for understanding the complex chain microstructures. The original resin is fractionated through preparative TREF (P-TREF). The corresponding fractions are studied using high-temperature GPC, DSC, SSA, ¹³C-NMR and FTIR. The three-dimensional (3D) surface plot obtained from the TREF-GPC cross-fractionation results provides the stereoscopic and intuitionistic microstructure distribution features of the resin. Moreover, TREF-SSA cross fractionation allows a direct observation of the methylene sequence length (MSL) and SCB distributions. The compositional heterogeneity and complex branched structure of the resin are studied in detail.

EXPERIMENTAL

Materials

The LDPE resin (Sample A) was graciously provided by China Petrochemical Corporation, and exhibited excellent processing and film-forming properties. Table 1 presents the physical parameters of the resin: density of 0.916 g/cm³, melt index of 7.0 g/10 min, tensile strength at break of 11.8 MPa, and elongation at break of 510%. The original resin is granular. The standard reference material (SRM 1475) issued by the American National Bureau of Standards was selected as the standard linear PE for comparison.

Table 1. Physical parameters of Sample A^a

Sample	Density (g/cm ³)	Melt index (g/10 min)	Tensile yield strength (MPa)	Tensile break strength (MPa)	Elongation at break (%)
Sample A	0.916	7.0	8.6	11.8	510

^a According to ASTM standards for testing

P-TREF

The P-TREF fractionation procedure involves the crystallization of dilute polymer solutions and subsequent elution with solvents through a column. In the crystallization step, ~12 g of polymer sample was dissolved in 600 mL of 1,2,4-trimethylbenzene (TMB) at 140 °C. 2,6-Di-tert-butyl-4-methylphenol (1×10^{-3} g/mL) was added to TMB as antioxidant. The polymer solution was then introduced into the column packed with 60 mesh to 80 mesh glass beads at 140 °C, and the column was slowly cooled to room temperature at a rate of 2 K/h to allow the polymer to completely crystallize onto the glass beads. A series of elution temperatures were set at 25, 40, 50, 55, 60, 68, 75, and 85 °C. At each step, the column content was allowed to equilibrate overnight to the set temperature before the solution was eluted with 1200 mL of TMB. The eluted solution was cooled, precipitated using acetone with twice its volume, and then filtered. The obtained fractions were dried in a vacuum oven at 40 °C until constant weight. Powder fractions were obtained.

GPC

The molecular weight and molecular weight distribution (MWD) of Sample A and its fractions were determined using a PL-GPC 220 high-temperature GPC (Polymer Laboratories Ltd.) at 150 °C. The columns used were three PL gel 10 μ m mixed-B LS columns (300 mm $\times$ 7.5 mm). The eluent consisted of 1,2,4-trichlorobenzene stabilized with BHT (1×10^{-3} g/mL) and was filtered through a 0.20 μ m pore size membrane before use. All sample solutions were prepared at 150 °C using a PL-SP 260 high-temperature sample preparation system (Polymer Laboratories Ltd.). The sample concentration in the eluent was ~0.2% (W/V). The solutions were maintained at 150 °C for 2 h to 4 h, and then filtered before the experiment. The injection volume was 200 μ L, and the flow rate was 1.0 mL/min. Polystyrene standards (Polymer Laboratories Ltd.) with narrow MWDs were used for calibration.

GPC-RI-LS-VIS

GPC-RI-LS-VIS analysis was performed using a PL-GPC220 coupled with triple detectors, namely, RI, LS and VIS. The running conditions were the same as those in the GPC experiment. Data were collected and processed using the CirrusTM Multi Detector Software.

FTIR

FTIR spectra were obtained using a Bruker Vertex 70 spectrometer with a resolution of 2 cm^{-1} . The samples were prepared by hot pressing ~100 mg of polymer between polyimide films at temperatures ranging from 110 °C to 160 °C, depending on the T_m of the samples.

¹³C-NMR

The polymer solution was prepared by dissolving ~80 mg of sample in 0.5 mL of *o*-dichlorobenzene- d_4 at 125 °C. ¹³C-NMR spectra were obtained at 125 °C using a Bruker AV400 NMR spectrometer at 100.58 MHz. The *o*-dichlorobenzene- d_4 solvent was used to provide the internal lock signal with its highest peak at $\delta = 133.22$ as the standard reference. In all measurements, inverse gated decoupling was used to remove nuclear overhauser enhancement and ¹³C-¹H couplings, and the pulse angle was 90°. The number of scans was 5000, and the delay time was 8 s.

DSC

DSC scans were conducted using a DSC Q100 (TA Instruments Ltd.). Each sample (~6 mg) was first heated from 40 °C to 200 °C at a rate of 10 K/min, and the temperature was then maintained at 200 °C for 5 min to erase its thermal history. The samples were subsequently cooled to 20 °C at a rate of 10 K/min, maintained at 20 °C for 5 min, and then reheated to 200 °C at a rate of 10 K/min under nitrogen atmosphere. Temperature calibration was performed using indium. The crystallization temperature (T_c) and T_m were measured throughout the cooling and reheating experiments, respectively.

SSA Thermal Fractionation

The thermal fractionation of the sample was performed using the DSC Q100 instrument. The instrument furnace was purged with nitrogen during the sample (~6 mg) measurements. The complete thermal treatment was performed through the following steps: First, the previous thermal history was erased. The sample was initially heated from 20 °C to 200 °C at a rate of 10 K/min, which was maintained at 200 °C for 3 min to remove its thermal history. Second, the samples were cooled to 0 °C at a rate of 10 K/min and held for 5 min. Third, the sample was heated from 0 °C to a selected self-seeding temperature (T_s) at a rate of 10 K/min^[32, 33]. The sample was maintained at T_s for 5 min. Fourth, the DSC cooling scan was set at 10 K/min from T_s to 0 °C, in which the thermal treatment effects would be reflected on the crystallization of the samples. Fifth, the sample was heated to a new T_s , which was 5 K lower than the previous T_s , and held for 5 min. Sixth, the third to fifth steps were repeated with a lower T_s . Finally, the sample was heated from 0 °C to 200 °C at a rate of 10 K/min, and the multiple melting endotherms were obtained.

RESULTS AND DISCUSSION

Characterization of the Original Resin

Figure 1 shows the broad MWD profile of Sample A, which is a bimodal curve shape. Table S1 summarizes the molecular weight and MWD of Sample A (Supporting Information). The weight-average molecular weight of Sample A is 2.14×10^5 g/mol and the MWD is 11.1, which is extremely broad.

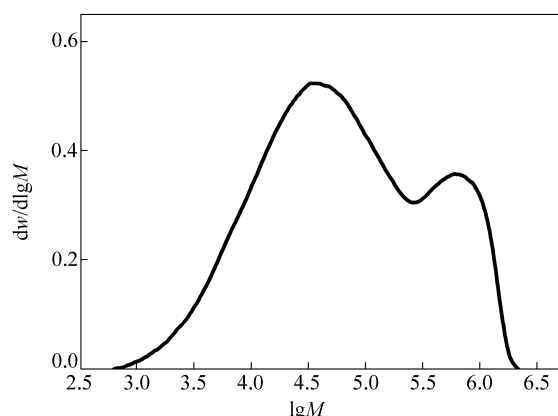


Fig. 1 Molecular weight distribution profile of Sample A

Figure 2 shows the ^{13}C -NMR spectrum of Sample A. The ^{13}C -NMR assignments are based on the literature^[16, 17, 34, 35]. Branches are named as $x\text{B}_n$ where n is the length of the branch and x is the carbon number starting from the methyl group as “1”. Given that the isolated peaks 1B_1 at $\delta = 19.99$ and 2B_3 at $\delta = 20.30$ cannot be observed, we deduce that the resin does not contain any methyl or propyl branches. Resonance peaks of specific carbons at $\delta = 11.25$ (1B_2), 23.61 (2B_4), and 32.94 (3B_5) are observed, indicating that the resin has ethyl, butyl, and amyl branches. In addition, the resonance peak at $\delta = 32.42$ (3B_n) indicates the presence of LCB ($n \geq 6$). After quantitative calculation, the total amount of branching is 3.34 mol%, and the SCB and LCB ($n \geq 6$) contents are 2.82 mol% and 0.52 mol%, respectively.

Table 2 lists the DSC data of Sample A, with melting peak at 103.3 °C, crystallization peak at 90.9 °C, and degree of crystallinity of 25.1%, which are evidently lower than those of SRM1475 (T_m : 133.2 °C, T_c : 114.7 °C, and crystallinity of 65.7%, respectively). The results indicate that Sample A has some SCBs. Figure 3 shows the final DSC heating scan for Sample A after SSA fractionation. Multiple melting peaks (more than ten peaks) at 104.9, 100.1, 95.1, 90.3, 85.4, 80.6, 75.7, 71.2, 66.0, 61.5, and 56.9 °C can be observed, which are caused by the crystalline methylene sequences with different lengths and are a typical characteristic of SCB polyethylene. The

MSL for each fraction is calculated using the calibration curve proposed by Wanke *et al.*^[31]. Figure 4 shows the MSL distribution plot, and the percent content monotonously increased with the corresponding MSL. The distribution curve is broad, with MSL ranging from 22 to 64, and the main content is centralized at 64. The above results indicate that the SCB distribution of Sample A is heterogeneous.

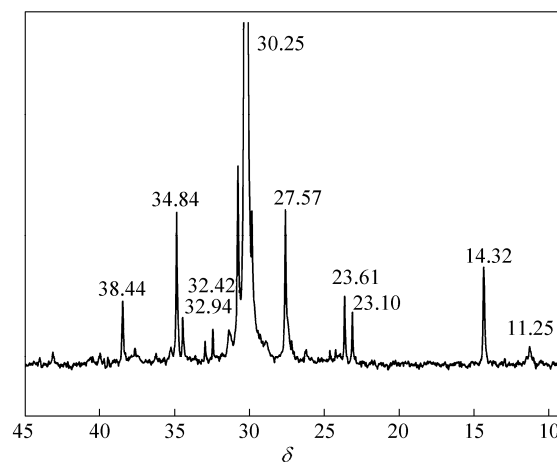


Fig. 2 ^{13}C -NMR spectrum of Sample A

Table 2. DSC data of Sample A and SRM1475

Sample	ΔH_m (J/g)	T_m (°C)	ΔH_c (J/g)	T_c (°C)	$W_{c,h}^a$ (%)
Sample A	72.3	103.3	60.5	90.9	25.1
SRM 1475	189.2	133.2	192.1	114.7	65.7

^a Observed heat of fusion divided by 288 J/g^[36]

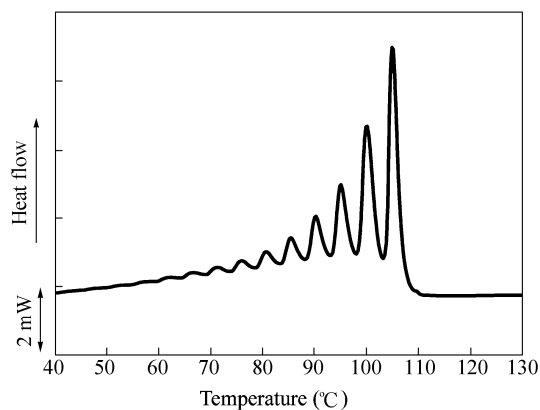


Fig. 3 DSC heating scan of Sample A after SSA fractionation

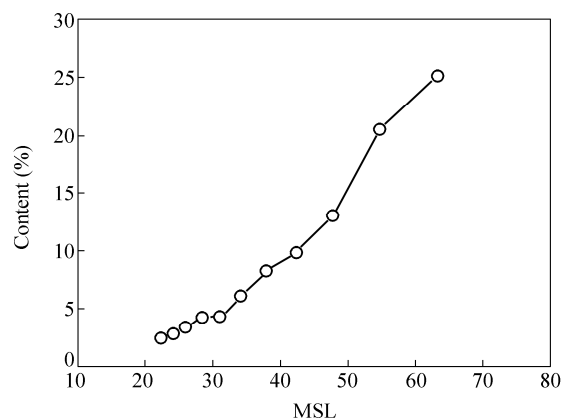


Fig. 4 MSL distribution curve of Sample A

The data above exhibit average values based on the microstructures of the original samples; hence, the data are insufficient for completely elucidating the relationship between the chain microstructure and the property of the resin. The resin should be fractionated using P-TREF; the microstructure of its fractions should be subsequently characterized using high-temperature GPC, GPC-RI-LS-VIS, DSC, SSA, ^{13}C -NMR and FTIR techniques.

TREF Fractionation

To study the chain microstructure in detail, TREF fractionation must be applied and a few fractions are obtained for further characterization. Based on the previous literatures^[37–41], the elution temperature of Sample A is set as follows: 25, 40, 50, 55, 60, 68, 75, and 85 °C. Sample A is actually fractionated into seven fractions following

the procedure given in the experimental part. The total recovery ratio of TREF fractionations is 99.3 wt%. Table 2S summarizes the fractionation data (Supporting Information). Figure 5 shows the weight percent as a function of the elution temperature. The weight percent of the fractions eluted at 25, 40, 50, and 55 °C are 1.75 wt%, 2.81 wt%, 5.34 wt%, and 5.85 wt%, respectively. In addition, the weight percent of the fractions eluted at 60, 68 and 75 °C is 13.37 wt%, 60.18 wt%, and 10.70 wt%, respectively. These eluted fractions are the main compositions of Sample A, and the fraction eluted at 68 °C has the largest weight percent for the whole sample. No fraction is collected at 85 °C, indicating that all fractions are eluted prior to 85 °C.

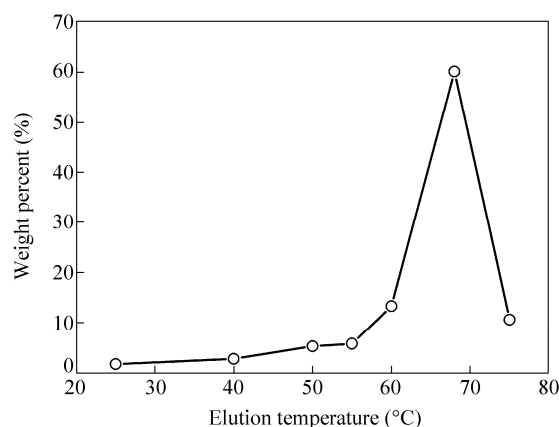


Fig. 5 Weight percent of fractions as a function of elution temperature

Molecular Weight and MWD of Fractions

Figure 6 presents the MWD curves of Sample A and its TREF fractions. Table S3 lists the molecular weight and MWD data (Supporting Information). The molecular weights of the fractions increase with elution temperature, except for the fraction eluted at 75 °C. The MWD curves of the fractions elute at 25, 40, 50, 55 and 60 °C are unimodal, but the fractions eluted at 68 and 75 °C display bimodal curves, particularly the fraction at 68 °C, which exhibits high content in the high molecular weight region. The molecular weights of the fractions eluted at 25, 40, and 50 °C are 3.07×10^3 , 5.91×10^3 , and 1.28×10^4 g/mol, respectively, which are low, and their MWDs are 1.35, 1.49, and 1.75, respectively. By contrast, the fractions eluted at 60, 68, and 75 °C have higher molecular weights of 7.01×10^4 , 2.99×10^5 , and 1.04×10^5 g/mol, and broader MWDs of 3.40, 6.85, and 5.27, respectively. The fraction eluted at 68 °C evidently has the highest molecular weight and broadest MWD.

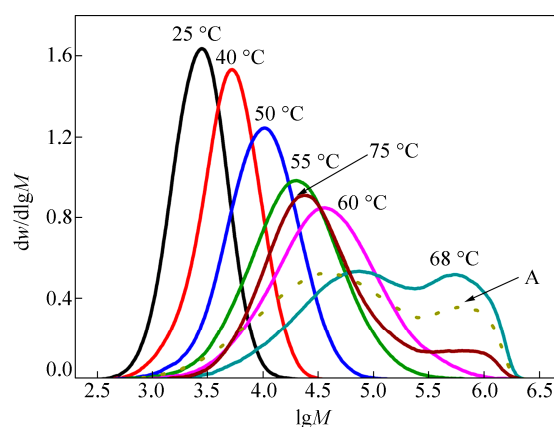


Fig. 6 MWD profiles of Sample A and its TREF fractions

Analysis of TREF-GPC Cross-fractionation Result

The 3D surface and contour plots are obtained from the cross-fractionation results by combining the TREF and GPC data, and are shown in Fig. 7.

Figure 7(a) shows that the $\lg M$ axis can be obtained using the GPC calibration curve, and the temperature axis corresponds to the elution temperature of the different TREF fractions. The 3D figure is not unimodal and presents three peaks formed by components with different crystallization abilities. The main component is obtained at 68 °C, and its 3D surface displays bimodal. Each region on the 3D surface provides relative amount of each species with a given molecular weight and composition. The 3D plot stereoscopically and intuitively shows the structural feature of Sample A and its microstructure distribution.

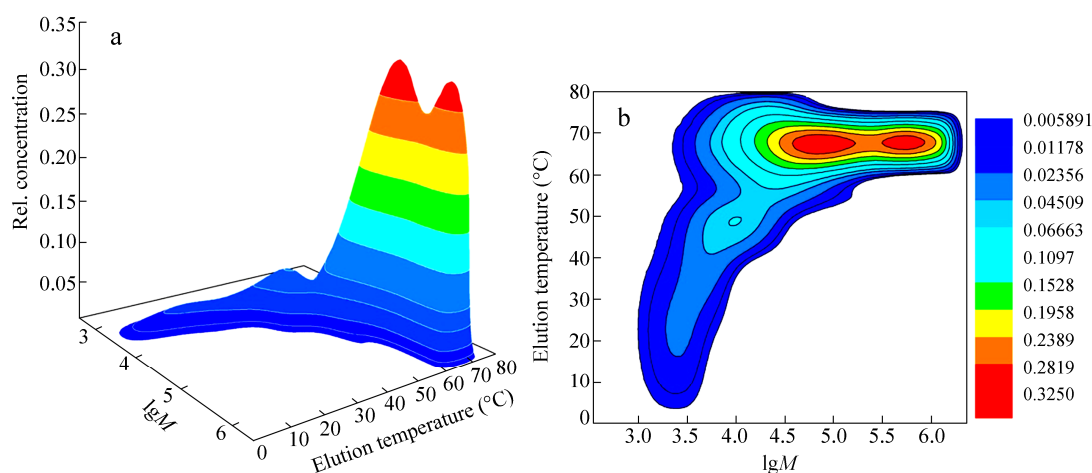


Fig. 7 (a) 3D-surface plot and (b) two-dimensional contour plot of Sample A

The contour plot can further confirm the results. Figure 7(b) shows the relative positions in the temperature- $\lg M$ plane. Every point in the contour plot represents the relative amount of a corresponding species with a certain molecular weight and eluting temperature. The main component is obtained at 68 °C, and the $\lg M$ values within the high elution temperatures of 60 °C to 75 °C are 3.3 to 6.3, indicating that the MWDs of high-temperature fractions are broad. The relative amount occupies more than 80% in the high elution temperature region. The $\lg M$ values in the low elution temperature region below 50 °C range from 3.0 to 4.2, and the relative amount is less than 10%. Therefore, the 3D surface and contour plot can complement each other, and the results are more visually presented in Tables S2 and S3.

Branching Information from GPC-RI-LS-VIS, FTIR and ^{13}C -NMR Results

GPC with triple detectors is used to study the branching structure of each fraction. To gain further insight into the microstructure of each fraction, the radius of gyration (R_g) is determined as a function of the molecular weight (measured using the LS). The results are compared with the values of the linear PE SRM1475. The molecular chain conformation of the polymers in solution is generally described by the scaling law in Eq. (1), which relates R_g and molecular weight M_w :

$$R_g = KM^\alpha \quad (1)$$

where K and α are constants. Figure 8 shows the scaling relationship between R_g and M_w for each fraction. In Fig. 8(a), the R_g values of the two fractions eluted at 25 °C and 40 °C gradually increase with the increase in molecular weight. The plots of the two fractions eluted at 25 °C and 40 °C show linear relationship, but they have lower intercept values and move toward parallel to and below the linear SRM1475 reference because of the SCB effect^[8]. Therefore, the two fractions have SCB components. For the fractions eluted at 50, 55, 60, 68 and 75 °C, they all have critical molecular weights which divide them into two parts. Two different cases at different

molecular weight regions are observed, as shown in Fig. 8(b). For case I in the low molecular weight region, the $\lg R_g$ - $\lg M$ plots have linear relationship and slightly move down parallel to the linear plot for SRM 1475 because of the SCB structure in these fractions. For case II in the high molecular weight region, their plots deviate from the linear relationship and move toward smaller values, indicating a contraction of the coils in the solution. This contraction is a typical feature of long-chain branched molecules^[11]. Therefore, the fractions obtained at 50, 55, 60, 68 and 75 °C possess LCB structures along with SCB structures.

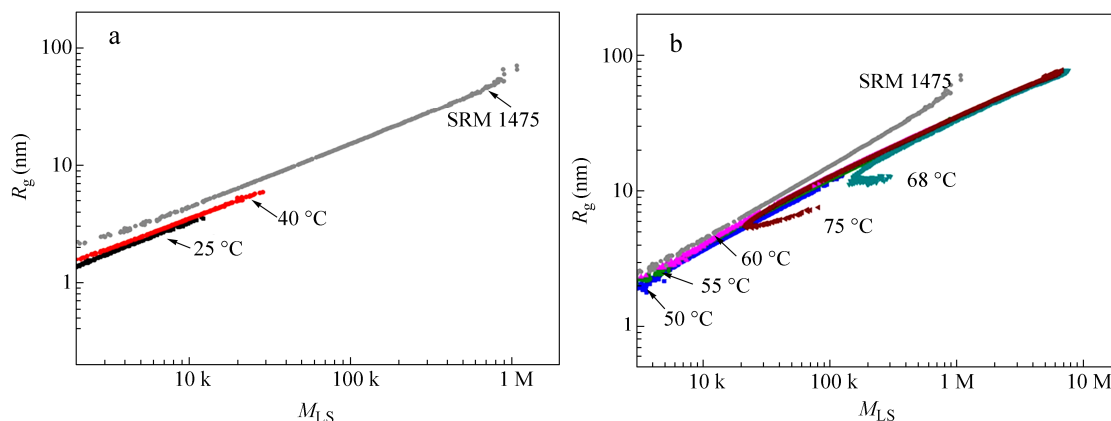


Fig. 8 Variation of the radius of gyration with molecular weight for fractions eluted at (a) 25 and 40 °C, (b) 50, 55, 60, 68 and 75 °C

The intrinsic viscosity of polymers in solution is influenced by the branching structure. The Mark-Houwink (M-H) equation reflects the scaling relationship between $[\eta]$ and M_w , as described in Eq. (2).

$$[\eta] = KM^\alpha \quad (2)$$

Typical M-H plots obtained from the GPC data can show the difference in the branching structures of the different fractions. Figure 9 shows the relationship between $[\eta]$ and M_w for each fraction. The linear plot for SRM 1475 is used as reference to determine the sample LCB. In Fig. 9(a), the $[\eta]$ values of the two fractions eluted at 25 °C and 40 °C gradually increase with the increase in molecular weight. The plots of the two fractions eluted at 25 °C and 40 °C have linear relationship, but have lower intercept value and move below and relatively parallel to linear plot of SRM because of the SCB effect^[42], similar to Fig. 8(a). In Fig. 9(b), the fractions eluted at 50, 55, 60, 68 and 75 °C all have critical molecular weights which divide them into two parts. Two different cases at different molecular weight regions are observed for them, similar in Fig. 8(b). For case I in the low molecular weight region, the $\lg[\eta]$ - $\lg M$ plots show linear relationship and move down in parallel relative to the linear plot of SRM 1475 because of the SCB structure in these fractions. For case II in the high molecular weight region, the plots deviate from the linear relationship and bend because of the LCB structure in these fractions. Low curves indicate high LCB extents^[27]. Therefore, the fractions eluted at 50, 55, 60, 68 and 75 °C contain both SCB and LCB structures. We infer that the original resin has a complex branched structure, with both LCB and SCB.

The branching factors g and g' are important parameters that characterize the chain branching degree obtained from the mean square radius of gyration (R_g^2) and $[\eta]$, respectively. The equations are as follows:

$$g = \frac{\langle R_g^2 \rangle_B}{\langle R_g^2 \rangle_L} \quad (3)$$

$$g' = \frac{[\eta]_B}{[\eta]_L} \quad (4)$$

where the values for the branched (B) and linear (L) species are obtained at the same molecular weight. Figures 10 and 11 show molecular weight dependence of g and g' , respectively. The g and g' of fractions eluted at 25 °C and 40 °C are all close to 1, indicating that they have no larger LCB. However, the g and g' of fractions eluted at 50, 55, 60, 68 and 75 °C gradually decrease when the molecular weight reaches the critical molecular weight. A higher branching degree results in a lower branching factor. The branching factors g and g' in the same fraction also get smaller and smaller when the molecular weight gradually increases. The two curves span different ranges, consistent with the considerations on the sensitivity limits of the two detectors. In addition, both endpoints are not accurate because of the sensitivity limits. Especially, the fraction eluted at 68 °C in the low molecular weight region cannot precisely obtain g and g' .

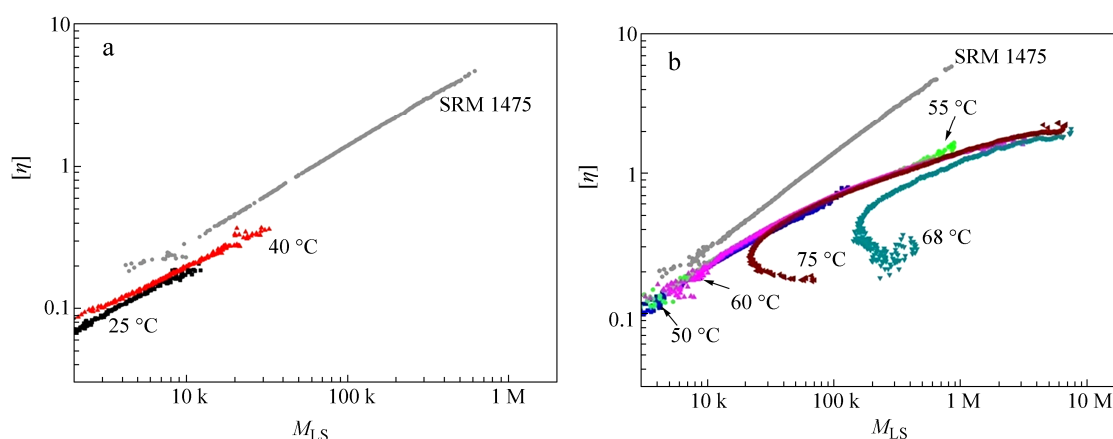


Fig. 9 Relationship of intrinsic viscosity and molecular weight for fractions eluted at (a) 25 and 40 °C, (b) 50, 55, 60, 68 and 75 °C

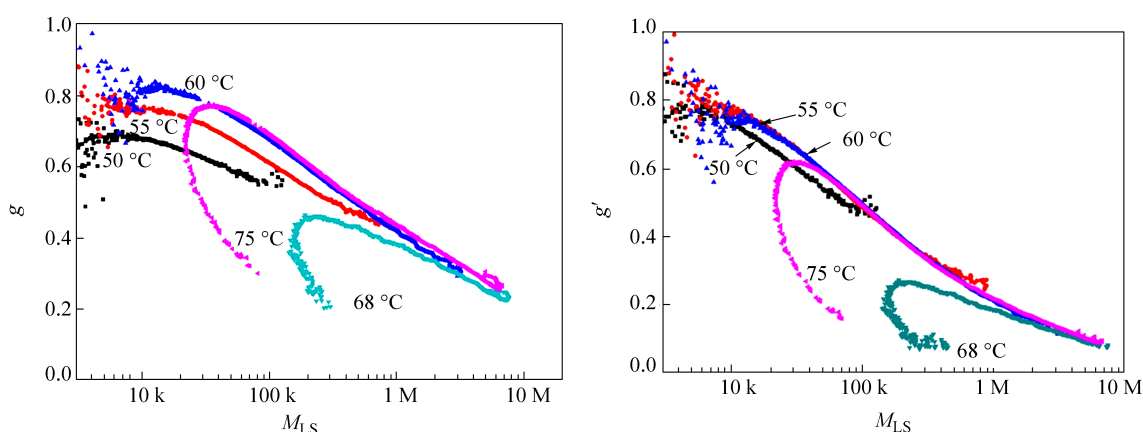


Fig. 10 Relationship between branching factor g and molecular weight for the fractions eluted at 50, 55, 60, 68 and 75 °C

Fig. 11 Relationship between branching factor g' and molecular weight for the fractions eluted at 50, 55, 60, 68 and 75 °C

The relationship between the g' and g of $[\eta]$ and R_g is generally described as follows:

$$g' = g^\varepsilon \quad (5)$$

The branching index ε is a sensitive parameter for the segment (or chain) density distribution in the molecular domain. The value is directly related to the branching structure and number of LCBs. Theoretically predicted values for ε are between 0.5 and 1.5. Table 6 shows that ε of Sample A is 1.26, and those of the fractions eluted

from 50 °C to 75 °C are within 1.06 to 1.40.

The relationship between g and the number of branch points n_w for a randomly branched polydisperse polymer with trifunctional branch points is expressed as follows:

$$g = \frac{6}{n_w} \left[\left(\frac{2 + n_w}{4n_w} \right)^{\frac{1}{2}} \ln \frac{(2 + n_w)^{\frac{1}{2}} + n_w^{\frac{1}{2}}}{(2 + n_w)^{\frac{1}{2}} - n_w^{\frac{1}{2}}} - 1 \right] \quad (6)$$

The n_w per unit molecular weight is calculated as follows:

$$\bar{\lambda} = \frac{\bar{n}_w}{\bar{M}_w} \quad (7)$$

The critical molecular weight at which LCB appears is given by

$$M^* = \frac{I}{\lambda} \quad (8)$$

Table 3 lists the branching parameters of Sample A and its fractions eluted at 50, 55, 60, 68 and 75 °C. The R_g gradually increases from 4.7 nm to 14.6 nm for fractions eluted at temperatures from 50 °C to 75 °C. The average g and g' gradually decrease from 0.64 to 0.23 and from 0.63 to 0.21 for fractions eluted at temperature from 50 °C to 75 °C, respectively. The n_w and critical molecular weight gradually increase from 3.32 to 29.02 and from 0.50×10^4 g/mol to 1.18×10^4 g/mol, respectively. The fraction eluted at 68 °C is special because it has the highest molecular weight, the lowest average g and g' (0.22 and 0.12, respectively), the highest number of branch points (31.18) and the highest critical molecular weight (4.51×10^4 g/mol). The information of the original resin includes $R_g = 23.7$ nm, $g = 0.23$, $g' = 0.16$, $\varepsilon = 1.26$, $n_w = 29.01$, and $M^* = 2.93 \times 10^4$.

Table 3. Branching parameters of Sample A and its selected fractions

Sample	R_g (nm)	g	g'	ε	n_w	$\lambda (10^{-5})$	$M^* (10^4)$
50 °C fraction	4.7	0.64	0.63	1.06	3.32	19.88	0.50
55 °C fraction	7.6	0.51	0.49	1.07	6.30	12.63	0.79
60 °C fraction	12.0	0.41	0.34	1.22	10.22	7.25	1.38
68 °C fraction	30.6	0.22	0.12	1.40	31.18	2.22	4.51
75 °C fraction	14.6	0.23	0.21	1.09	29.02	8.46	1.18
Sample A	23.7	0.23	0.16	1.26	29.01	3.41	2.93

FTIR spectroscopy, as a simple, fast and low-cost technique, is widely applied to characterize the SCB degree of resins. As reported in the literature, the absorbance at 1378 cm^{-1} can determine the methyl number per 1000 C^[14, 15]. Table 4 lists the calculated result from the FTIR spectra. Sample A has 58 CH₃/1000 C, whereas the fraction eluted at 25 °C has 81 CH₃/1000 C, which is the highest among all fractions. The fraction eluted at 75 °C has 46 CH₃/1000 C, which is the lowest among all fractions. The methyl numbers (per 1000 C) of fractions gradually decrease from 81 to 46 with the elution temperature from 25 °C to 75 °C. This result is consistent with the TREF separation mechanism, which fractionates the semi-crystalline polymers according to their crystallization abilities. The FTIR results indicate that the fractions contain SCB structure, in which the SCB degree decreases with elution temperature. As mentioned previously, the scaling curves also indicate some SCB in the original resin and all fractions.

Table 4. Methyl number per 1000 C of TREF fractions ^a

Fraction	25 °C	40 °C	50 °C	55 °C	60 °C	68 °C	75 °C
CH ₃ /1000 C	81	72	59	58	56	54	46

^a Calculated from FTIR spectra

To further confirm the microstructure of the fractions, all fractions are characterized by ^{13}C -NMR. Table 5 shows the branch contents of TREF fractions. All fractions have ethyl, butyl, amyl and long branches ($n \geq 6$). Because the branches which contain more than six carbon atoms are very difficult to distinguish in ^{13}C -NMR spectra, they are usually defined as long branches. They all have no methyl and propyl branches. The total branch and SCB contents gradually decrease from 8.18 mol% to 3.19 mol% and from 6.76 mol% to 2.48 mol% with the elution temperature from 25 °C to 75 °C, respectively. The ethyl and butyl branch contents gradually decrease with the increase of elution temperature as a whole. The amyl and long branches ($n \geq 6$) contents have no obvious change rules. Based on the ^{13}C -NMR results, the fractions conclusively contain both SCB and LCB structures.

Table 5. Branch contents of TREF fractions ^a

Fraction	Methyl (mol%)	Ethyl (mol%)	Propyl (mol%)	Butyl (mol%)	Amyl (mol%)	SCB (mol%)	Long branches (mol%)	Total (mol%)
25 °C	0	2.15	0	3.86	0.75	6.76	1.42	8.18
40 °C	0	1.82	0	3.06	0.61	5.49	1.65	7.14
50 °C	0	1.09	0	2.76	1.04	4.89	1.74	6.63
55 °C	0	1.30	0	2.41	0.83	3.24	0.97	4.21
60 °C	0	0.61	0	1.76	0.83	3.20	0.86	4.06
68 °C	0	0.47	0	1.64	1.07	3.18	0.29	3.47
75 °C	0	0.18	0	1.43	0.87	2.48	0.71	3.19

^a Calculated from ^{13}C -NMR spectra

Melting Behavior of Fractions Based on DSC Analysis

The morphology and, consequently, the thermal behavior, such as the types, amounts and distributions of branches, of each fraction are related to the thermal history and molecular heterogeneity. Thus, verifying the chain structures of different fractions through a thermal analysis is necessary. The fractions with different SCB contents form lamellae with different thicknesses^[43], therefore, the DSC melting curves reflect their presence.

Figure 12 shows the DSC melting curves of each fraction, and Table 6 presents their detailed results. The melting peaks of the fractions gradually increase from 80.1 °C to 108.8 °C with the elution temperature. The SCB branch contents obtained in ^{13}C -NMR results gradually decrease with the increase of elution temperature. And the thermal behavior is mainly influenced by SCB structure. The fractions with different SCB contents form lamellae with different thicknesses. A lower SCB contents results in a thicker lamella. The SCB branch content of the fraction in high elution temperature region is less than that in low elution temperature region, so its melting peak is higher. The DSC results are in accordance with ^{13}C -NMR results. The fractions eluted at 25 °C and 40 °C have broader melting ranges from 50 °C to 95 °C and from 70 °C to 100 °C, respectively. The fraction eluted at 75 °C has the highest T_m at 108.8 °C. Meanwhile, the melting enthalpy and crystallinity of the fractions gradually increase with the elution temperature, except for the fraction at 68 °C. The crystallinity of the fraction at 25 °C is 22%, which is the lowest. The fraction at 75 °C has the highest crystallinity at 29%. These above results are consistent with that obtained in TREF, which separates macromolecules according to their crystallizable sequence^[20, 24]. In addition, the fraction collected at 68 °C has a crystallinity of 23.5%, which is

Table 6. DSC data of the resin and its fractions

Elution temperature (°C)	ΔH_m (J/g)	T_m (°C)	$W_{c,h}^a$ (%)
25	63.5	79.9	22.0
40	69.8	92.9	24.2
50	71.9	96.3	25.0
55	73.3	99.5	25.5
60	74.4	101.5	25.8
68	67.7	102.5	23.5
75	83.5	108.8	29.0

^a Observed heat of fusion divided by 288 J/g^[36]

very low, but its molecular weight is the highest among all fractions. The decrease in the crystallinity for the high molecular weight fraction can be attributed to the imperfect crystallization caused by the restricted mobility of the extremely long chains in the fractions. These results confirm that the fractions have SCB structures, which further proves that the original resin has a complex branching structure.

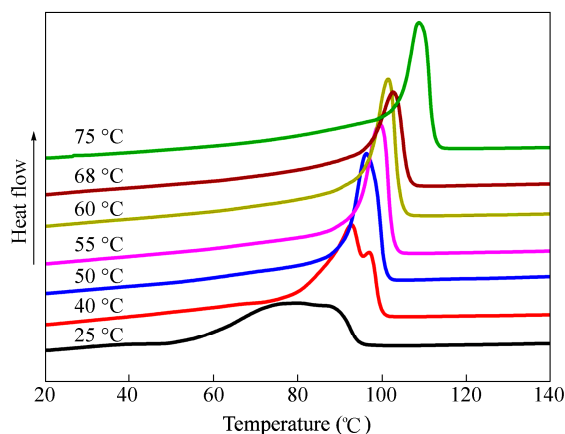


Fig. 12 DSC melting curves of fractions

MSL and Its Distribution Based on SSA Thermal Fractionation

SSA is a quick and effective thermal fractionation technique for evaluating the chain heterogeneities in semicrystalline polymer materials^[44–48]. SSA is particularly useful in studying the SCB distribution that resulted from the copolymerization of ethylene with α -olefins. In this study, the TREF fractions are further segregated according to the MSL through SSA thermal fractionation. The TREF-SSA cross-fractionation can provide more detailed information about SCB distribution, particularly the SCB intermolecular and intramolecular distribution, which is essential in determining the LDPE thermodynamic and crystallization behavior.

Figure 13 shows the final DSC heating scans for the fractions after SSA fractionation. Each fraction has a broad range endotherm with multiple melting peaks (more than eight peaks), and each SSA endotherm peak represents a group of methylene sequences with equal or similar lengths. The multiple peaks in each fraction reflect the intramolecular heterogeneous SCB distribution. Intramolecular heterogeneity means that the SCB distribution of individual macromolecules in the system is not uniform along the chain backbone. The melting peaks shift toward high temperature with the elution temperature, indicating that the intermolecular SCB distribution is heterogeneous. Intermolecular heterogeneity means that the SCB distribution differs from one molecule to another. As mentioned previously, the SSA separates LDPE molecules according to their MSL. Therefore, unlike TREF, which can only evaluate the intermolecular heterogeneity, SSA can assess both intramolecular and intermolecular heterogeneities.

The overlapped melting peak in Fig. 13 can be separated using the fitting software of multiple Gaussian functions. MSL can then be calculated from the peak temperatures of the SSA endotherms^[31]. The MSL distribution curves of all fractions can be drawn. Figure 14 presents the MSL distributions of the fractions. The MSL distribution of the fraction eluted at 25 °C is the narrowest among all fractions and is unimodal, with peak at 33 and MSL from 16 to 44. The MSL distribution of the fraction eluted at 40 °C is also narrow, and its MSL varies from 18 to 51. For the fractions eluted at 50, 55, 60, 68 and 75 °C, the percent contents monotonously increase with their MSL. The longest MSL of the fraction eluted at 50 °C is 53, and its corresponding percentage is 35.6%. The longest MSL of the fraction eluted at 55 °C is 56 and its corresponding percentage is 43.4%. The longest MSL of fraction eluted at 60 °C is 60 and its corresponding percentage is 43.9%. The longest MSL of fraction eluted at 68 °C is 63 and its corresponding percentage is 34.3%. The MSL distribution of fraction eluted at 75 °C is the broadest among all fractions, and its MSL varies from 25 to 78. The arithmetic mean methylene

sequence lengths of fractions are further calculated according to statistic function. The arithmetic mean methylene sequence lengths of fractions eluted at 25, 40, 50, 55, 60, 68 and 75 °C are 32, 40, 44, 47, 50, 50 and 61, respectively. The arithmetic mean methylene sequence length of fractions gradually increases from 32 to 61 with the increase of elution temperature (Fig. S1). The SCB and total branch contents obtained in ^{13}C -NMR results gradually decrease with the increase of elution temperature, which are in accordance with the above results. All fractions have heterogeneous intramolecular and intermolecular SCB distribution. These results further prove that the original sample has a complex branching structure.

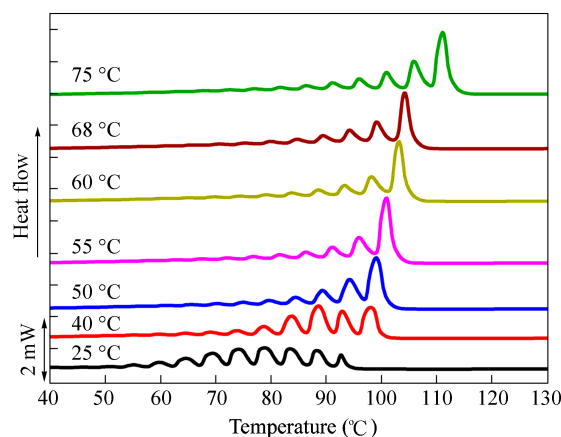


Fig. 13 DSC heating scans for fractions after SSA fractionation

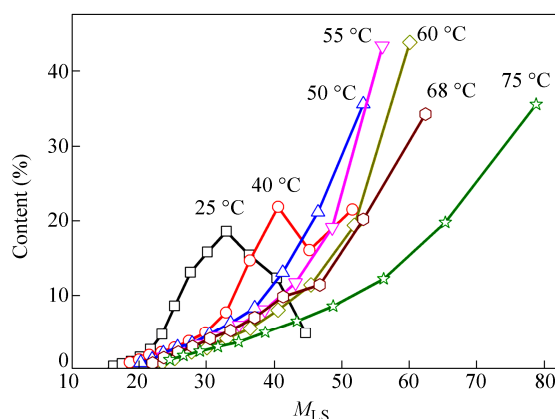


Fig. 14 MSL distributions of fractions

CONCLUSIONS

A LDPE resin with excellent processing and film-forming properties is fractionated through TREF, and the chain structure of each fraction is further analyzed using GPC coupled with triple detectors (RI-LS-VIS), FTIR, NMR, DSC and SSA. The conclusions are summarized as follows.

- i. In the TREF experiment, the main component is collected at high elution temperatures from 60 °C to 75 °C, and the relative amount occupies more than 80%. In addition, the relative amount eluted below 50 °C is less than 10%.
- ii. In the FTIR results, the methyl numbers (per 1000 C) of the fractions gradually decrease from 81 to 46 with elution temperature ranging from 25 °C to 75 °C.
- iii. In the SSA thermal fractionation, each fraction shows a broad endotherm range with multiple melting peaks (more than eight peaks), and the melting peaks shift toward the high temperature region with the

elution temperature. These results indicate that both intramolecular and intermolecular SCB distributions are heterogeneous. The FTIR, DSC and SSA results verify that all the fractions contain SCB structures.

- iv. The results of the analysis using combined GPC-triple detectors and ^{13}C -NMR data suggest that the original resin and its fractions (50, 55, 60, 68, and 75 °C) have both SCB and LCB structures. In other words, the original resin is a mixture of high molecular weight (dominant content) and low molecular weight components (less than 10%). The high molecular weight component has a complex branched structure, having both LCB and SCB. The low molecular weight component only has SCB. Such microstructure distribution of the resin confers the polymer with excellent processing and film-forming properties.
- v. The TREF-GPC and TREF-SSA cross-fractionation techniques are effective for evaluating the microstructure distribution of the complex branched PE and establishing the relationship between chain structure and properties.

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