

Comparison of Chain Structures between High-speed Extrusion Coating Polyethylene Resins by Preparative Temperature Rising Elution Fractionation and Cross-fractionation*

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Abstract Two polyethylene (PE) resins (samples A and B) are synthesized as high-speed extrusion coatings with similar minimum coating thickness and neck-in performance but different maximum coating speeds. Both samples are separated into seven fractions using preparative temperature rising elution fractionation. The microstructures of the original samples and their fractions are studied by high-temperature gel permeation chromatography, Fourier transform infrared spectroscopy, ^{13}C nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and successive self-nucleation/annealing thermal fractionation. Compared with sample B, sample A has a broader MWD, more LCB contents, and less SCB contents. Moreover, sample A contains slightly more 30 °C and 50 °C fractions with lower molecular weights, and more fractions at 75 °C and 85 °C with higher molecular weight. The chain structure and its distribution in the two PE resins are studied in detail, and the relationship between the chain structure and resin properties is also discussed.

Keywords: Polyethylene; High-speed extrusion coating; Chain structure; TREF; Cross-fractionation.

INTRODUCTION

Coating polyethylene (PE) resin has high strength, good toughness, strong adhesiveness, good film formation, and excellent heat-sealing performance, as well as water- and moisture-proof properties^[1–5]. With the development of the packaging industry, the range of applications and consumption of such coating resins has gradually increased, especially in the aseptic packaging of liquid food. With the application of specialized equipment, high-speed extrusion is required for PE resins. The evaluation of this type of chain structure PE is extremely important in the quality control in manufacturing industries. Analytical techniques such as gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), ^{13}C nuclear magnetic resonance spectroscopy (^{13}C -NMR), and rheological measurements have been used to study PE resins^[6–9]. However, the average properties measured by these techniques cannot sufficiently define the microstructure of novel resins. The fractionation of samples according to parameters such as molar mass, branching degree, or crystallization ability is necessary.

Temperature-rising elution fractionation (TREF) is a technique for the analysis of semi-crystalline polymers by separating the molecular species according to their crystallization abilities. Although TREF is a time-consuming process, fractions can be further analyzed to obtain information about the polymer chain

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microstructure. Wild, Soares, Monrabal, Pasch, and Xu *et al.* have separately reported many results in this field^[10–25]. TREF can also be combined with other fractionation techniques to study the chain structure of polyolefins^[26, 27]. 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 a combination of preparative TREF (P-TREF), FTIR, differential scanning calorimetry (DSC), and high-temperature two-dimensional liquid chromatography^[14]. Monrabal characterized polypropylene and PE blends with a combination of TREF and crystallization analysis fractionation^[26]. Yau applied GPC coupled with triple detectors and TREF to obtain valuable information on polyolefin microstructures^[28]. Wanke *et al.* investigated a commercial LDPE by TREF-DSC and TREF-GPC cross-fractionation and obtained detailed information on the molecular structures of the different types of LDPEs^[29]. Mahdavi characterized the chain structure of low density polyethylene (LDPE) by FTIR and TREF^[30]. Therefore, the effectiveness of cross-fractionation techniques could be enhanced further by combining TREF with other fractionation techniques to enable its widespread use in the analysis of polyolefins.

In this study, two PE resins are selected as high-speed extrusion coating resins with similar minimum coating thickness and neck-in performance but different maximum coating speeds. Both resins are fractionated by P-TREF according to their crystallizability. A comparison of the various chain microstructures and their distribution in the original samples as well as their respective fractions is investigated. In addition, the main reason which causes the different properties of the two resins is revealed on the basis of chain structure.

EXPERIMENTAL

Materials

One PE resin (sample A) was provided by American Dow Chemical Company. Another PE resin (sample B) was supplied by China Petrochemical Corporation. Two resins were both LDPE produced by high-pressure method. The properties of two samples are listed in Table 1. The two samples possess not only similar minimum coating thickness (~7.5 μm) but also similar neck-in performance (51 mm). However, Sample A exhibits much higher maximum coating speed than Sample B.

Table 1. The properties of Samples A and B ^a

Sample	Density (g/cm ³)	Melt index (g/10 min)	Maximum coating speed (m/min)	Minimum coating thickness (μm)	Neck-in (mm)
A	0.918	8.0	450	7.6	51
B	0.919	7.5	260	7.4	51

^a According to ASTM standards for testing

Preparative Temperature Rising Elution Fractionation (P-TREF)

The preparative temperature rising elution fractionation (P-TREF) procedure involves the crystallization of dilute polymer solutions and subsequent elution with solvents through a column. In the crystallization step, ~9 g of polymer sample was dissolved in 600 mL of 1,2,4-trimethylbenzene (TMB) at 130 °C. 2,6-Di-tert-butyl-4-methylphenol (BHT, 1×10^{-3} g/mL) was added to TMB as antioxidant. The polymer solution was then introduced into the column packed with 60–80 mesh glass beads at 130 °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 30, 50, 60, 65, 70, 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 a constant weight. Finally, powder fractions were obtained.

High-temperature Gel Permeation Chromatography (HT-GPC)

The molecular weight and molecular weight distribution (MWD) of samples and their 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 μm 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 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.

Gel Permeation Chromatography with Triple Detectors (GPC-RI-LS-VIS)

GPC-RI-LS-VIS analysis was performed using a PL-GPC220 coupled with triple detectors, namely, refractive index (RI), two angle laser light scattering (TALLS, 15° and 90°), and viscometer (VIS). The running conditions were the same as those in the GPC experiment. Data were collected and processed using the CirrusTM Multi Detector Software.

Fourier Transform Infrared Spectroscopy (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 150 °C, depending on the T_m of the samples.

¹³C-Nuclear Magnetic Resonance Spectroscopy (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.

Differential Scanning Calorimetry (DSC)

DSC scans were conducted using a DSC Q100 (TA Instruments Ltd.). Each sample (~6 mg) was first heated from 25 °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 flow 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 sample was 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^[31–34]. 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 °C 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 endotherm was obtained.

RESULTS AND DISCUSSION

Characterization of the Original Resins

The molecular weight distribution (MWD) profiles of samples A and B are presented in Fig. 1. Both samples have a bimodal distribution. The molecular weights of samples A and B are 1.43×10^5 and 1.47×10^5 g/mol,

respectively. Sample A has a broader MWD of 8.15 than sample B (MWD = 6.97). The original samples have similar weight-average molecular weights.

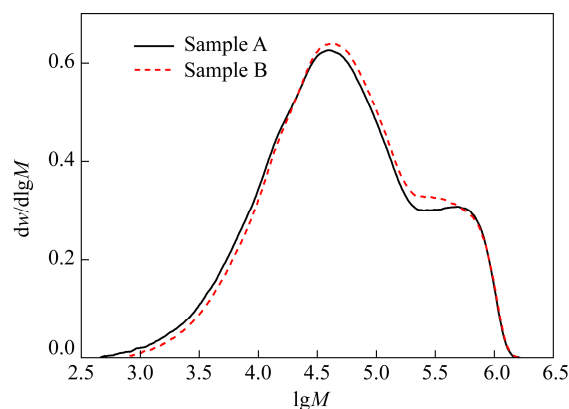


Fig. 1 Molecular weight distribution profiles of samples A and B

The ^{13}C -NMR spectra of samples A and B are shown in Fig. 2. Their ^{13}C -NMR assignments are based on previous studies^[7, 35]. After quantitative calculation, the total branching content of samples A and B is 4.34 mol% and 4.57 mol%, respectively. Sample A has 3.26 mol% SCB content, which is less than the 3.58 mol% of sample B. The former has 1.08 mol% LCB content, which is slightly higher than the 0.99 mol% of the latter.

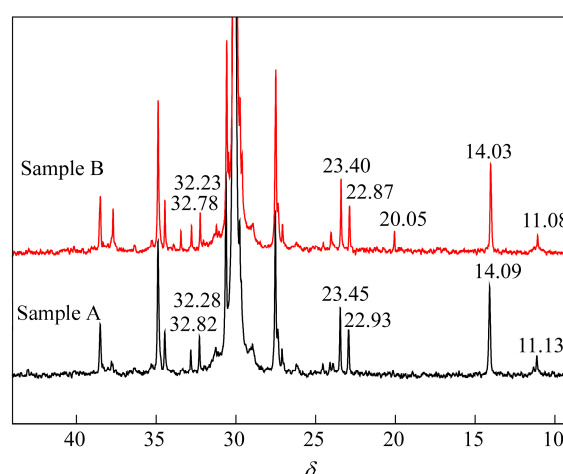


Fig. 2 ^{13}C -NMR spectra of samples A and B

Based on the DSC curve, the melting peak and degree of crystallinity of sample A are 105.8 °C and 31.4%, respectively, which are slightly higher than those of sample B (T_m of 104.3 °C and crystallinity of 30.9%). Generally, thermal behavior is mainly influenced by the SCB structure^[4, 9]. Sample A has a less SCB contents than sample B. Therefore, sample A may form thicker lamella and more perfect crystallization.

The abovementioned data present average values based on the microstructures of the original samples. Consequently, these data are insufficient for the complete elucidation of the relationship between the chain microstructure and the resin properties. The PE resins should be fractionated *via* P-TREF and the subsequent characterization of fractions should be performed by high-temperature GPC, FTIR, ^{13}C -NMR, DSC, and successive self-nucleation/annealing (SSA) thermal fractionation.

TREF Fractionation

Samples A and B are fractionated into seven fractions (Fractions 1 to 7), respectively, as described in the Experimental section. The total recovery of TREF fractionation is 99.2% and 99.0% for samples A and B, respectively. The P-TREF data of samples A and B are summarized in Table 2. The weight percentages of the fractions as a function of the elution temperatures are shown in Fig. 3. The two samples have different features in three temperature ranges. At low temperatures (30–50 °C), the fractions of sample A are slightly more than those of sample B. Both samples contain minor fractions eluted at 30 °C. At mid-range temperatures (60–70 °C), the fractions of sample A are less than those of sample B. The highest weight percentages of the fractions are eluted at 70 °C for both samples A and B, which were 38.71% and 45.67%, respectively. At high temperatures (75–85 °C), the fractions of sample A are more than those of sample B. The fraction of sample B only has 0.52 wt% content eluted at 85 °C, whereas sample A has 4.00 wt%. According to the TREF principle, the fractions eluted at high temperature have stronger crystallizability.

Table 2. TREF data of samples A and B

Fraction	Elution temperature (°C)	Sample A		Sample B	
		W_i (wt%)	$\sum W_i$ (wt%)	W_i (wt%)	$\sum W_i$ (wt%)
1	30	1.84	1.84	1.76	1.76
2	50	5.45	7.29	5.20	6.96
3	60	11.20	18.49	14.96	21.92
4	65	14.63	33.12	21.47	43.39
5	70	38.71	71.83	45.67	89.06
6	75	24.17	96	10.42	99.48
7	85	4.00	100	0.52	100

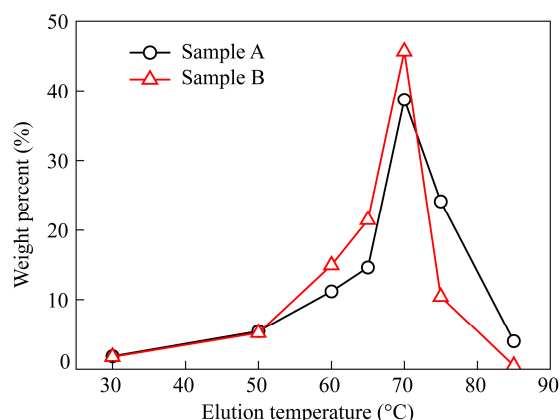


Fig. 3 Weight percentages of the fractions as a function of elution temperatures for samples

Molecular Weight and MWD of Fractions

The normalized MWD curves of the fractions of samples A and B are illustrated in Figs. 4(a) and 4(b), respectively; the detailed information is listed in Table 3. The summation of the molecular weights of the fractions are in good agreement with the molecular weights of original samples, which suggests that the fractionation method used in this work is efficient and no degradation occurred during fractionation. The molecular weights of fractions eluted at 30, 50, and 60 °C are relatively lower, and these fractions have a unimodal MWD. For samples A and B, the fractions eluted at 30 °C have the lowest molecular weights of 2.66×10^3 and 2.89×10^3 g/mol, respectively. By contrast, the fractions eluted at 70, 75, and 85 °C have relatively higher molecular weights, with a broad bimodal MWD. The fractions eluted at 70 °C have the highest molecular weights for samples A and B of 2.31×10^5 and 2.37×10^5 g/mol, respectively. The molecular weights of fractions don't follow a monotonous increase with the increase in elution temperature. Fractionation clearly depends on the crystallization abilities instead of the molar mass.

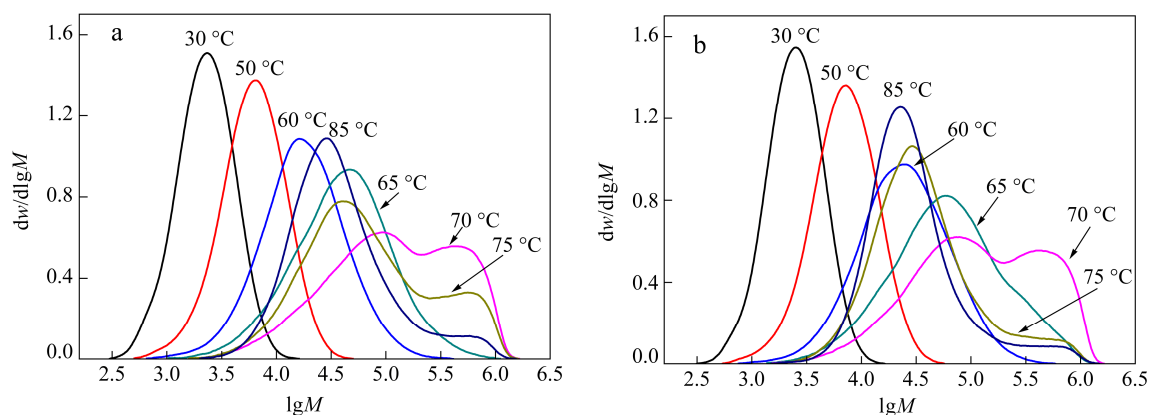


Fig. 4 MWD profiles for TREF fractions of samples A (a) and B (b)

Table 3. Molecular weight and MWD data for fractions of samples A and B

Fraction	Elution temperature(°C)	Sample A			Sample B		
		$M_w (10^3)$	$M_n (10^3)$	M_w/M_n	$M_w (10^3)$	$M_n (10^3)$	M_w/M_n
1	30	2.66	1.87	1.42	2.89	2.07	1.39
2	50	7.49	4.73	1.58	8.65	5.43	1.59
3	60	25.66	11.68	2.20	37.44	15.44	2.43
4	65	65.88	22.83	2.89	113.92	30.56	3.73
5	70	231.00	45.91	5.03	237.03	46.97	5.05
6	75	157.37	32.42	4.85	77.82	22.85	3.41
7	85	76.61	24.24	3.16	60.70	20.56	2.95
Sum		143.49	18.21	7.88	147.24	20.27	7.26
The original sample		143.43	17.61	8.14	147.70	21.17	6.98

Analysis of TREF-GPC Cross-fractionation Results

The three-dimensional (3D) surface and contour plots are available from the cross-fractionation results that were obtained by combining TREF and GPC data, as shown in Figs. 5 and 6, respectively. The $\lg M$ axis is obtained with the GPC curve in Fig. 5, whereas the temperature axis corresponds to the elution temperature of the different TREF fractions. Each region on the 3D surface provides the relative amount of each species with a given molecular weight and composition. The 3D surfaces show clear structural features of both samples and the slight difference in their microstructure distributions. The 3D plot presents four peaks formed by components with different crystallization abilities. Fewer fractions are eluted at temperatures below 50 °C. The main component is obtained at 70 °C, and sample B contains more components at 70 °C than sample A. The 3D surfaces of both samples clearly display a bimodal distribution at 70 °C.

The contour plots can further confirm the abovementioned results. The relative positions in the temperature- $\lg M$ plane are more evident in Fig. 6. Each point in the contour plot represents the relative amount of the corresponding species with a certain molecular weight and eluting temperature. Both samples contain minor weight percentages of fractions at the low temperature region below 50 °C. Sample A contains more components at 85 °C than sample B. Therefore, the 3D surface and contour plot can complement each other, and the results in Tables 2 and 3 are visually presented.

Branching Information from FTIR and ^{13}C -NMR Results

FTIR spectroscopy is a simple, fast, and low-cost technique that 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^[6, 36]. The original sample A has 52 $\text{CH}_3/1000\text{ C}$, which is less than the 57 $\text{CH}_3/1000\text{ C}$ of sample B. The calculated results of TREF fractions from the FTIR spectra are summarized in Table 4. As the elution temperature increases from 30 °C to 85 °C, the methyl numbers (per 1000 C) of the fractions gradually decrease

from 91 to 33 and from 84 to 38 for samples A and B, respectively. The FTIR results indicate that the fractions contain the SCB structure, as well as the SCB degree decreases with elution temperature.

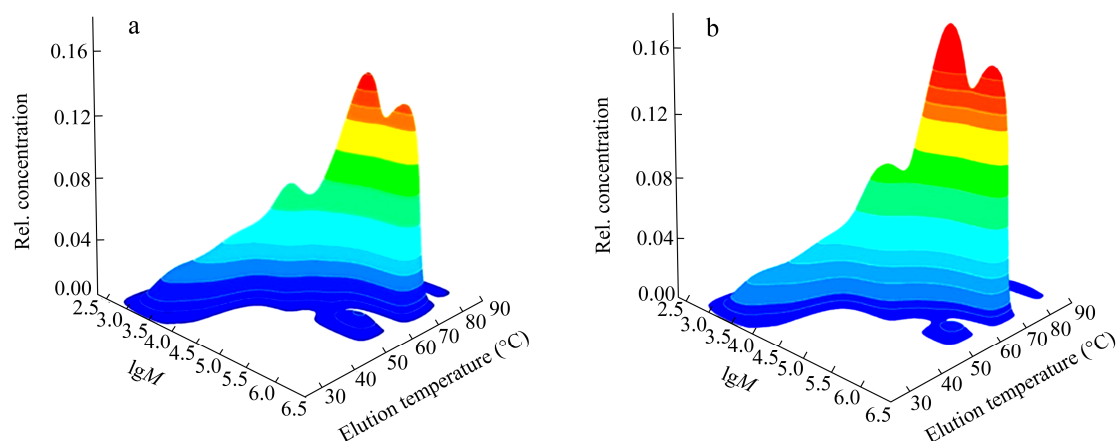


Fig. 5 3D-surface plots from TREF-GPC cross fractionation of samples A (a) and B (b)

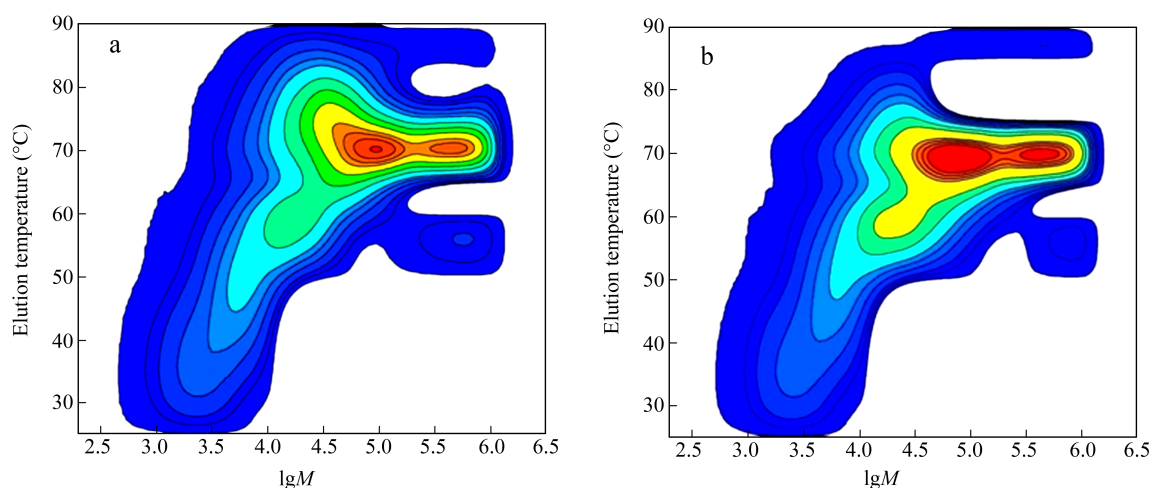


Fig. 6 Two-dimensional contour plots from TREF-GPC cross fractionation of samples A (a) and B (b)

Table 4. Methyl numbers per 1000 C of TREF fractions

Item	Sample	Elution temperature						
		30 °C	50 °C	60 °C	65 °C	70 °C	75 °C	85 °C
CH ₃ /1000 C	A	91	63	54	49	47	43	33
CH ₃ /1000 C	B	84	65	53	51	50	42	38

To confirm the microstructure of the fractions, several fractions are selected for ¹³C-NMR analysis. The branch contents of the fractions eluted at 30, 50, 60, 70, and 75 °C are listed in Table 5. The SCB and total branched content of the fractions from sample A are less than those of the fractions from sample B. The SCB branched contents gradually decrease from 6.55 mol% to 2.43 mol% and from 6.69 mol% to 2.96 mol% for samples A and B, respectively, whereas their total branched contents gradually decrease from 9.56 mol% to 3.43 mol% and from 10.03 mol% to 3.80 mol%. The LCB contents of the fractions similarly exhibit a definite decrease with the increasing elution temperature. The crystallization ability is mainly influenced by the SCB content. The FTIR and NMR results are consistent with the separation mechanism of TREF; that is, semi-crystalline polymers are fractionated according to their crystallization abilities. Moreover, TREF is an

effective method which separates not only short branching chains but also some long branching chains, but they cannot be completely separated.

Table 5. Branch contents of some selected TREF fractions

Elution temperature (°C)	Sample A			Sample B		
	SCB (mol%)	LCB (mol%)	Total (mol%)	SCB (mol%)	LCB (mol%)	Total (mol%)
30	6.55	3.01	9.56	6.69	3.34	10.03
50	4.74	2.25	6.99	5.44	2.05	7.49
60	3.70	1.26	4.96	4.06	1.23	5.29
70	3.01	0.82	3.83	3.55	1.07	4.62
75	2.43	1.00	3.43	2.96	0.84	3.80

Melting Behavior of Fractions Based on DSC Analysis

The morphology and consequent thermal behavior of each fraction are related to their thermal history and molecular heterogeneities, such as the types, amounts, and distribution of branches^[5, 37]. The fractions with different SCB contents form lamella with different thicknesses. A lower SCB content produces a thicker lamella, and the DSC melting curves reflect their differences. Thus, verifying the chain structures of different fractions through thermal analysis is necessary.

The DSC melting curves of each fraction are shown in Fig. 7, whereas Table 6 presents the detailed results. For samples A and B, the melting curves of the TREF fractions shift towards higher temperatures with sharper peaks as the elution temperature is increased. The fractions eluted at 30 °C have broader melting temperatures that range from 43 °C to 95 °C and from 47 °C to 96 °C for samples A and B, respectively. As the elution temperature increases, the melting peaks of the fractions gradually increase from 79.5 °C to 114.6 °C for sample A and from 81.5 °C to 114.5 °C for sample B. The SCB branch content of the fraction in the high elution temperature region is less than that in low elution temperature region; consequently, its melting peak is higher. The DSC results are in accordance with the ¹³C-NMR results. Nevertheless, the crystallinity of the fractions don't show a predictable increase with the fractionation temperature. We suspect that these results can be attributed to the restricted mobilities and imperfect crystallization in the high-molecular-weight fractions.

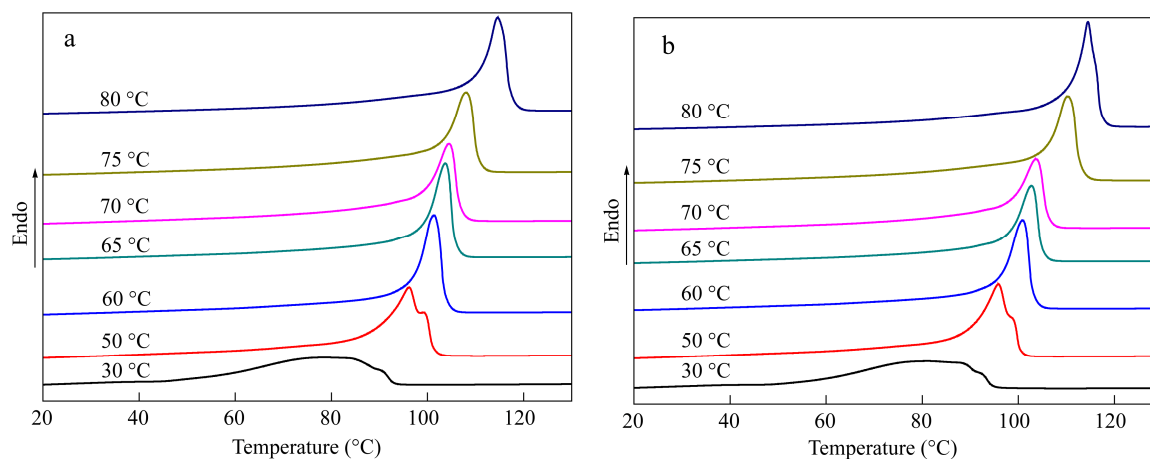


Fig. 7 DSC melting curves for TREF fractions of Samples A (a) and B (b)

MSL and Its Distribution Based on SSA Thermal Fractionation

SSA is a quick and effective thermal fractionation technique for the evaluation of chain heterogeneities in semicrystalline polymer materials^[32–34, 39–41]. SSA is particularly useful in studying the SCB distribution that resulted from the copolymerization of ethylene with α -olefins. In the present study, the TREF fractions were further segregated according to the methylene sequence length (MSL) by SSA thermal fractionation. 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 PE thermodynamic and crystallization behavior.

Table 6. DSC data of two samples and their fractions

Elution temperature (°C)	Sample A			Sample B		
	T_m (°C)	ΔH_m (J/g)	$W_{c,h}^a$ (%)	T_m (°C)	ΔH_m (J/g)	$W_{c,h}^a$ (%)
30	79.5	72.5	25.2	81.5	72.8	25.3
50	96.2	89.9	31.2	95.9	89.7	31.1
60	101.4	88.9	30.9	100.9	85.6	29.7
65	103.7	85.4	29.7	102.7	77.4	26.9
70	104.5	85.5	29.7	103.7	79.3	27.5
75	108.0	90.0	31.3	110.3	97.3	33.8
85	114.6	99.1	34.4	114.5	102.7	35.7

^a Observed heat of fusion divided by 288 J/g^[38]

The final DSC heating scans for the fractions after SSA fractionation are presented in Fig. 8. Each fraction has a broad endothermic curve with multiple melting peaks (more than eight peaks), and each melting 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 towards high temperatures with the elution temperature, thereby indicating that the intermolecular SCB distribution is heterogeneous. Intermolecular heterogeneity implies that the SCB distribution differs from one molecule to another. Given that SSA separates PE molecules according to their MSL, SSA can assess both intramolecular and intermolecular heterogeneities, unlike TREF, which can only evaluate the intermolecular heterogeneity.

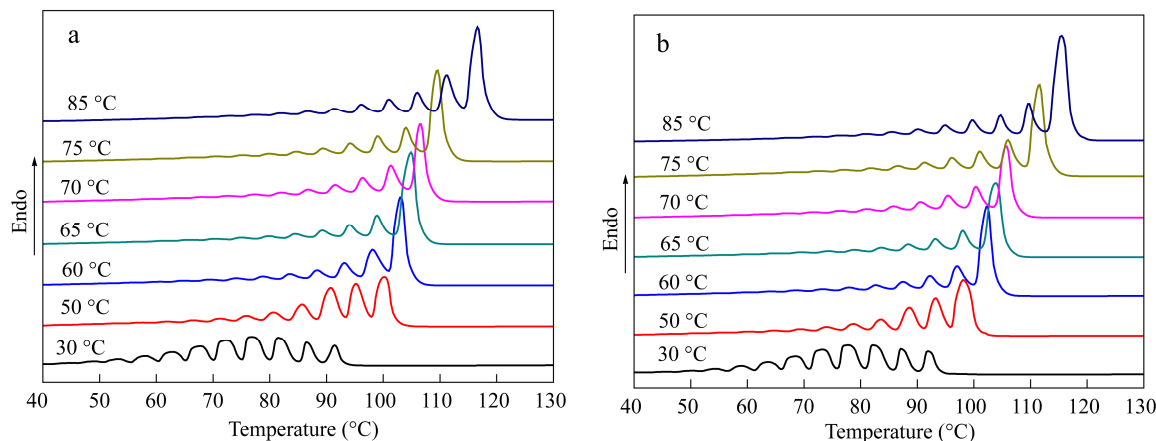


Fig. 8 DSC heating scans for TREF fractions of samples A (a) and B (b) after SSA thermal fractionation

The overlapped melting peak in Fig. 8 can be separated by the fitting software of multiple Gaussian functions. MSL can then be calculated from the peak temperatures of the SSA endotherms^[42]. The MSL distribution curves of all fractions can be drawn, as presented in Fig. 9. The MSL distribution of the fraction eluted at 30 °C displays the narrowest unimodal curve among the fractions. The MSL value of the fraction eluted at 30 °C varies from 17 to 44 for sample A and from 16 to 44 for sample B. For fractions eluted at 50, 60, 65, 70, 75, and 85 °C, their molar percentages monotonously increase with their increasing MSL. The MSL distribution of the fraction eluted at 85 °C is the broadest among the fractions, which varies from 26 to 100 and from 23 to 95, respectively. The arithmetic mean methylene sequence lengths (L_n) of fractions are further calculated

according to the statistic function, which are shown in Fig. 10. The L_n s of fractions gradually increase from 31 to 74 for sample A and from 32 to 72 for sample B with the elution temperature. The results are in accordance with the obtained results from ^{13}C -NMR, such that the SCB and total branch content gradually decrease with the increased elution temperature. For the TREF fractions of two samples, the L_n values of fractions eluted in the range of 30–50 °C are approximations. At temperatures between 60 °C and 75 °C, the fractions of sample A have slightly longer L_n than those of sample B. The 75 °C fraction of sample A has shorter L_n (58) than that of sample B (61). The 75 °C fraction of sample A probably has a much higher molecular weight than that of sample B, which causes the restricted mobility and imperfect crystallization in the high molecular weight fraction. These results indicate that all fractions have heterogeneous intramolecular and intermolecular SCB distribution.

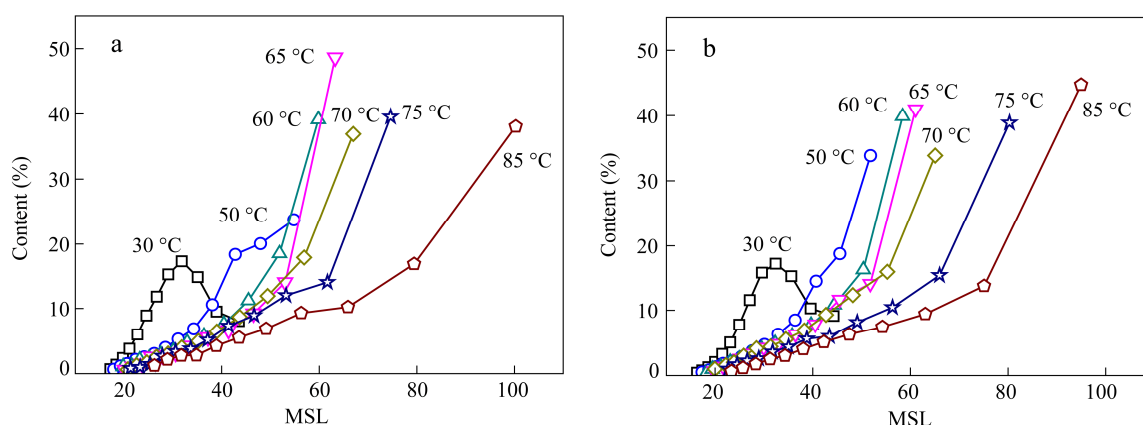


Fig. 9 MSL distributions for TREF fractions of samples A (a) and B (b)

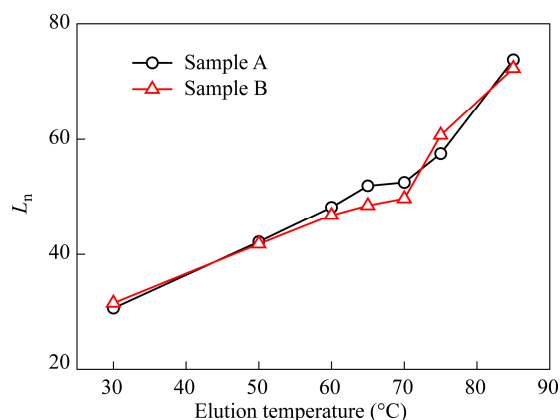


Fig. 10 The arithmetic mean sequence length for TREF fractions of samples A and B

Influence of Chain Microstructure on Properties

Based on the above results, the main differences between samples A and B are summarized in Table 7. Compared with sample B, sample A has a broader MWD, more LCB contents, and less SCB contents. The TREF-GPC cross-fractionation results indicate that sample A contains slightly more 30 °C and 50 °C fractions with lower molecular weights than sample B. And sample A contains more 75 °C and 85 °C fractions with higher molecular weights than sample B. The broader MWD is beneficial to enhance flowability during processing. In addition, the low-molecular-weight fractions can also improve processing property of the resin as the plasticizer. Therefore, sample A has better processing property than sample B. Long branching chains and high-molecular-weight components facilitate the intermolecular entanglement such that the resin film can be coated at high speeds without rupture. Therefore, sample A has a higher maximum coating speed than sample B.

Table 7. The main difference between sample A and sample B

	Item	Sample A	Sample B
The original resin	MWD	8.15	6.97
	T_m (°C)	105.8	104.3
	SCB (mol%)	3.26	3.58
	LCB (mol%)	1.08	0.99
TREF	Fractions at low temperatures (30 °C and 50 °C)	slightly more	slightly less
	Fractions at high temperatures (75 °C and 85 °C)	more	less
TREF-GPC	Molecular weight of fractions at low temperatures (30 °C and 50 °C)	lower	higher
	Molecular weight of fractions at high temperatures (75 °C and 85 °C)	higher	lower
Property	Melt index (g/10 min)	8.0	7.5
	Maximum coating speed (m/min)	450	260

CONCLUSIONS

Two high-speed extrusion coating PE resins with similar minimum coating thickness and neck-in performance but different maximum coating speeds are fractionated into seven fractions by P-TREF. The chain microstructure of the original samples and their fractions are studied by high-temperature GPC, FTIR, ^{13}C -NMR, DSC, and SSA thermal fractionation. The following conclusions are drawn:

- Both samples are complex branched PE resins.
- Compared with sample B, sample A has a broader MWD and slightly more low-temperature fractions (30 °C and 50 °C) with lower molecular weights, which enhances flowability during processing and improves processing property. Therefore, sample A has better processing property than sample B.
- Sample A contains more LCB and less SCB components. In addition, sample A also contains more high-temperature fractions (75 °C and 85 °C) with higher molecular weights, which facilitate intermolecular entanglement. Therefore, sample A has a higher maximum coating speed than sample B.

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