

## Calibration Curve Establishment and Fractionation Temperature Selection of Polyethylene for Preparative Temperature Rising Elution Fractionation\*

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**Abstract** A series of copolymers of ethylene with 1-hexene synthesized using a metallocene catalyst are selected and mixed. The blend is fractionated *via* preparative temperature rising elution fractionation (P-TREF). All fractions are characterized *via* high-temperature gel permeation chromatography (GPC), <sup>13</sup>C nuclear magnetic resonance spectroscopy (<sup>13</sup>C-NMR), and differential scanning calorimetry (DSC). The changes in the DSC melting peak temperatures of the fractions from P-TREF as a function of elution temperature are almost linear, thereby providing a reference through which the elution temperature of TREF experiments could be selected. Moreover, the standard calibration curve (ethylene/1-hexene) of P-TREF is established, which relates to the degree of short-chain branching of the fractions. The standard calibration curve of P-TREF is beneficial to study on the complicated branching structure of polyethylene. A convenient method for selecting the fractionation temperature for TREF experiments is elaborated. The polyethylene sample is fractionated *via* successive self-nucleation and annealing (SSA) thermal fractionation. A multiple-melting endotherm is obtained through the final DSC heating scan for the sample after SSA thermal fractionation. A series of fractionation temperatures are then selected through the relationship between the DSC melting peak temperature and TREF elution temperature.

**Keywords:** TREF; Calibration curve; Fractionation temperature; SSA; Polyethylene.

### INTRODUCTION

The term "Temperature Rising Elution Fractionation" (TREF) was first applied by Shirayama *et al.* to describe the method used to fractionate low-density polyethylene (LDPE) based on the degree of short-chain branching (SCB)<sup>[1]</sup>. The actual technique used was described earlier by Desreux and Spiegels who first recognized the potential use of elution at differing temperatures to achieve crystallization separation<sup>[2]</sup>. The technique was developed by Wild *et al.*, who also developed the TREF apparatus<sup>[3–5]</sup>. Since then, TREF has become a technique for analyzing semi-crystalline polymers by separating the molecular species based on their crystallizabilities<sup>[6–13]</sup>. This technique is finally established in polymer analysis laboratories as a routine procedure, especially the introduction of an automated TREF system by Polymer Char in Spain.

TREF can be applied in analytical or preparative modes (called A-TREF or P-TREF, respectively)<sup>[3, 4]</sup>. In A-TREF, the eluted solution concentration is continuously monitored by detector at gradually increased elution temperature. Information on macromolecular structure is obtained on-line through a calibration curve. The technique requires smaller columns, smaller sample amounts and shorter time than P-TREF but generates less information about the polymer microstructure. In P-TREF, a series of fractions are collected at predetermined

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temperature intervals and larger columns and sample amounts are generally used. In this technique, information on macromolecular structure is obtained off-line through further analysis *via* other techniques. The technique is time-consuming but can generate detailed information on the polymer microstructure. TREF can also be combined with other fractionation techniques, such as GPC or SSA. These cross-fractionation techniques can provide valuable information on the chain microstructure<sup>[14–22]</sup>. TREF is a very powerful technique for studying the compositional heterogeneity of polyolefins and has earned remarkable success in determining the microstructure of polyethylene because this type of fractionation is based on crystallizability, which has been shown to be mainly influenced by the degree of branching or co-monomer content. The SCB distribution in linear low-density polyethylenes (LLDPEs) is a fundamental structural parameter, together with the molecular weight distribution, that nearly defines the ultimate performance of resins. Numerous studies have focused on studying the SCB distribution in polyethylene<sup>[23–30]</sup>. Galland *et al.* studied the influence of the reaction parameters on the composition of metallocene-catalyzed ethylene copolymers *via* TREF and <sup>13</sup>C-NMR<sup>[31]</sup>. Aust *et al.* investigated the effects of the initial temperature of crystallization, cooling rate, heating rate and elution speed on the separation quality of A-TREF by using a heterophasic ethylene/propylene copolymer<sup>[32]</sup>. The recent development of a triple-detector system (refractive index, differential-pressure viscometer and light scattering detectors) for GPC coupled with TREF, the so-called 3D-GPC-TREF, could provide valuable information about the polymer microstructure at each crystallization temperature. Yau presented a process using 3D-GPC-TREF to solve polyolefin characterization problems<sup>[17]</sup>. 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/ $\alpha$ -olefin copolymers<sup>[33, 34]</sup>. 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<sup>[35]</sup>.

In the present study, the selected samples are mixed and then fractionated *via* P-TREF. It is demonstrated how to establish the P-TREF standard calibration curve of ethylene/1-hexene copolymers. In addition, we try to demonstrate a method for selecting the fractionation temperature for TREF experiments with the help of the SSA results and the fitting curve equation.

## EXPERIMENTAL

### Materials

The sample was polymerized in a 150 mL vacuum-dried glass reactor. Toluene, 1-hexene, and metallocene catalyst Et[Ind]<sub>2</sub>ZrCl<sub>2</sub>/MAO solution (Al/Zr = 2000) were first loaded into the reactor, and the total volume of the feeding liquid was 100 mL. The polymerization was initiated by introducing ethylene gas. The glass reactor was stirred and maintained at 60 °C for 60 min. The polymerization was terminated by venting the ethylene gas and adding acidified ethanol solution. The product was filtered, washed with a large amount of ethanol and acetone, and then dried in a vacuum at 60 °C for 24 h. The samples used in this study were synthesized by adding different amounts of 1-hexene and coded as samples M1, M2, M3, M4, M6, M7, M8, and M9. M1, M2, and M3 were ethylene homopolymers, whereas M4, M6, M7, M8, and M9 were copolymers obtained *via* the copolymerization of ethylene with 1-hexene. An industrial LDPE resin (Resin A) was graciously provided by China Petrochemical Corporation.

### Preparative Temperature Rising Elution Fractionation (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, ~10 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,  $1 \times 10^{-3}$  g/mL) was added to TMB as an antioxidant. The polymer solution was then introduced into the column packed with 60 mesh to 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 predetermined, respectively. 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 with twice its volume of acetone, and then filtered. The obtained fractions were dried in a vacuum oven at 40 °C until a constant weight. Powder fractions were available.

#### **High-temperature Gel Permeation Chromatography (GPC)**

The molecular weights and molecular weight distributions (MWD) of the 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 PLgel 10 µm mixed-B LS columns (300 mm × 7.5 mm). The eluent consisted of 1,2,4-trichlorobenzene stabilized with BHT ( $1 \times 10^{-3}$  g/mL) and was filtered through a 0.2 µm 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 experiments. The injection volume was 200 µL, and the flow rate was 1.0 mL/min. Polystyrene standards (Polymer Laboratories Ltd) with narrow MWDs were used for calibration.

#### **Differential Scanning Calorimetry (DSC)**

DSC scans were recorded using a TA instrument model DSC Q100. 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. Samples were subsequently cooled to 20 °C at a rate of 10 K/min, maintained at 20 °C for 5 min, and then again heated to 200 °C at a rate of 10 K/min. Temperature calibration was performed using indium. The crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) were measured throughout the cooling and reheating experiments, respectively. Measurements were conducted in a nitrogen atmosphere at a purge gas flow rate of 50 mL/min.

#### **$^{13}\text{C}$ Nuclear Magnetic Resonance Spectroscopy ( $^{13}\text{C}$ -NMR)**

The polymer solutions were prepared by dissolving ~80 mg of the sample in 0.5 mL of *o*-dichlorobenzene- $d_4$  at 125 °C.  $^{13}\text{C}$ -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 NOE and  $^{13}\text{C}$ - $^1\text{H}$  couplings, and the pulse angle was 90°. The number of scans was 5000, and the delay time was 8 s.

#### **Successive Self-nucleation and Annealing (SSA)**

The SSA thermal-fractionation process was performed using the DSC Q100 (TA instrument). The instrument furnace was purged with nitrogen during the sample (~6 mg) measurements. The temperature calibration of the instrument was performed using standard indium. The complete thermal treatment comprised the following steps. (a) The previous thermal history was erased. The sample was initially heated from 20 °C to 200 °C at a rate of 10 K/min, and then held at 200 °C for 5 min to remove its thermal history. (b) The sample was cooled at a rate of 10 K/min to 0 °C and held for 5 min. (c) The sample was heated at a rate of 10 K/min from 0 °C to a selected self-seeding temperature ( $T_s$ ) according to a region defined by Fillon *et al.*<sup>[33, 36]</sup>. The sample was kept at  $T_s$  for 5 min. (d) DSC cooling was performed at a rate of 10 K/min from  $T_s$  to 0 °C, in which the effects of the thermal treatment reflected on the crystallization of the sample. (e) The sample was heated to a new  $T_s$  that was 5 K lower than the previous  $T_s$  and held for 5 min. (f) Steps “c” to “e” were repeated at  $T_s$ . (g) Finally, the sample was heated at a rate of 10 K/min from 0 °C to 200 °C, and a multiple-melting endotherm was obtained.

## **RESULTS AND DISCUSSION**

### **Calibration Curve Establishment of Polyethylene for P-TREF**

#### **Sample selection for P-TREF**

The samples used in this study are synthesized using a metallocene catalyst and coded as M1, M2, M3, M4, M6, M7, M8, and M9. M1, M2, and M3 are ethylene homopolymers, whereas M4, M6, M7, M8 and M9 are copolymers obtained *via* the copolymerization of ethylene with 1-hexene. In order to contain broad molecular

weight distribution and branching distribution, we design a blend sample for TREF experiments, *i.e.* a mixture of M1, M2, M3, M4, M6, M7, M8 and M9. Thus, the TREF fractions collected at different elution temperature with enough amounts can be applied in various analysis and characterization in the following section. Table 1 shows the main parameters and the weights taken for the blend sample. M7 has 8.73 mol% 1-hexene, which is much lower than those of M8 and M9. However,  $T_m$  of M7 is only at 82.8 °C, which is obviously lower than that of M8 and M9. This unusual phenomenon is discussed in another published paper<sup>[25]</sup>. The reason is that the average methylene sequence length (MSL) and distribution of M7 significantly influence its melting behavior rather than the total comonomer content.

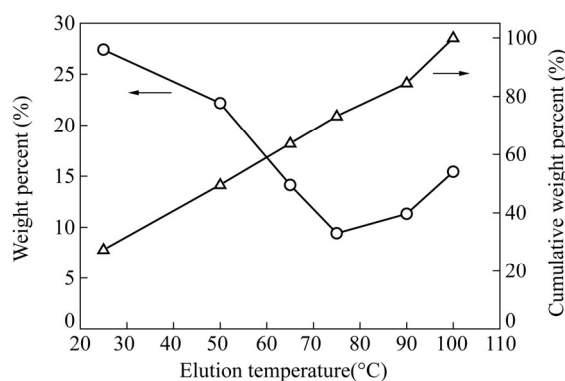
**Table 1.** Parameters of the samples used in this study

Sample	$M_w$ ( $10^4$ )	$M_w/M_n$	1-hexene (mol%)	$W_i$ (wt%)	$T_m$ (°C)	$\Delta H_m$ (J/g)	$W_{c,h}^a$ (%)
M1	4.8	2.4	0	2	131.0	170.8	59.3
M2	16	3.9	0	2	131.6	150.5	52.3
M3	23	3.4	0	2	132.2	143.5	49.8
M4	10	2.6	2.04	26	120.4	92.8	32.2
M6	9.2	3.3	4.86	26	103.2	44.0	15.3
M7	4.4	3.3	8.73	15	82.8	26.4	9.2
M8	5.0	3.0	14.18	10	98.1	9.4	3.3
M9	4.9	2.8	15.05	17	89.0	4.8	1.7

<sup>a</sup> Observed heat of fusion divided by 288 J/g<sup>[37]</sup>

#### Fractionation results

The blend sample composed of M1, M2, M3, M4, M6, M7, M8, and M9 are fractionated *via* P-TREF. The pre-determined elution temperatures are 25, 50, 65, 75, 90, 100, 110, 120, and 130 °C. The actual TREF fractions are eluted at 25, 50, 65, 75, 90 and 100 °C. No fraction is collected above 100 °C. The weight percent of the fractions eluted at 25, 50, 65, 75, 90 and 100 °C are 27.42 wt%, 22.19 wt%, 14.15 wt%, 9.45 wt%, 11.35 wt% and 15.44 wt%, respectively. The total recovery of fractionation is 98.9 wt%. Figure 1 shows the weight fraction and cumulative weight percent as a function of elution temperature for the blend sample.



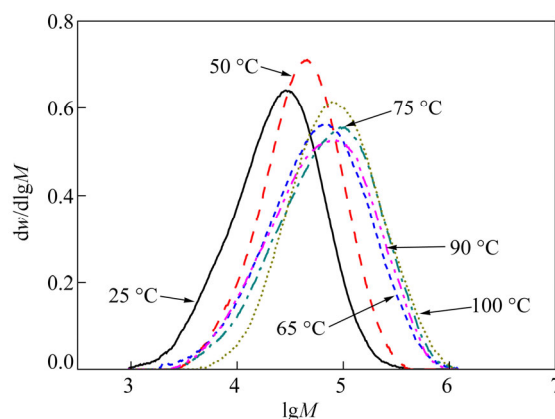
**Fig. 1** Weight percent and cumulative weight percent of the fractions as a function of elution temperatures for the blend sample

#### GPC analysis of TREF fractions

Table 2 shows the molecular weight and molecular weight distribution (MWD) data of the fractions. The molecular weights of the fractions are between  $3.55 \times 10^4$  and  $1.27 \times 10^5$ . The fractions' MWDs are relatively narrow approximately between 2 and 3. Figure 2 presents the MWD curves of the fractions. Although Fig. 2 shows that the MWD peaks also shift to the higher molecular weight region with increasing elution temperature as a whole, these fractions are not separated according to molar mass, only depending on their crystallization ability.

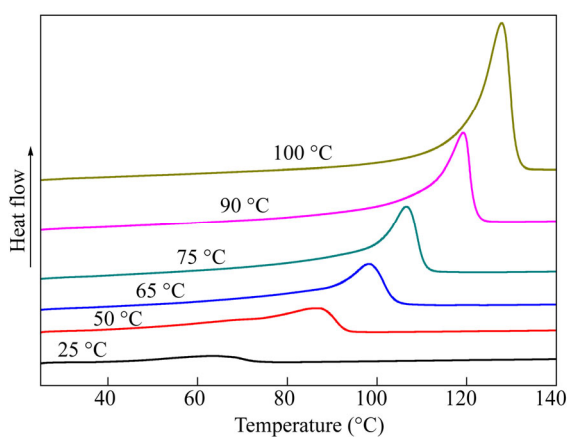
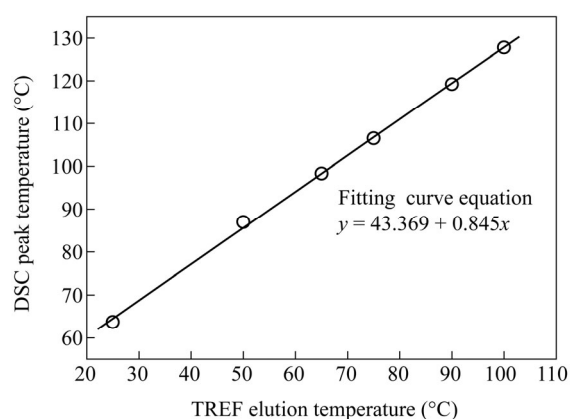
**Table 2.** Molecular weight and MWD data of the fractions

Elution temperature (°C)	$M_w (10^4)$	$M_n (10^4)$	$M_w/M_n$
25	3.55	1.44	2.47
50	5.63	2.74	2.06
65	9.64	3.14	3.07
75	11.6	3.91	2.97
90	10.3	3.38	3.04
100	12.7	5.31	2.40

**Fig. 2** Molecular weight distribution profiles of the fractions

#### DSC analysis of TREF fractions

Figure 3 and Table 3 present the thermal analysis results of the fractions. Figure 3 shows that the melting temperatures of the fractions gradually increase with increasing elution temperature. In addition, Fig. 4 presents the DSC melting peak temperature of the fractions separated *via* P-TREF as a function of elution temperature, which shows a nearly linear relationship. Most of all, it established the temperature relationship between solid state and dissolved state for the same sample. Table 3 shows that the crystallization temperatures and crystallinities of the fractions gradually increase with increasing elution temperature. The above results are in agreement with the separation mechanism of the TREF technique.

**Fig. 3** DSC scans of the fractions**Fig. 4** DSC melting peak temperatures of the fractions produced by P-TREF as a function of elution temperatures

**Table 3.** DSC data of the fractions

Elution temperature (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$W_{c,h}^a$ (%)
25	63.7	9.4	36.9	12.6	3.2
50	87.0	39.0	66.7	33.6	13.3
65	98.3	49.1	82.4	42.9	16.8
75	106.5	60.0	91.9	53.1	20.5
90	119.2	76.7	104.4	71.3	26.2
100	127.8	116.0	113.9	107.7	39.6

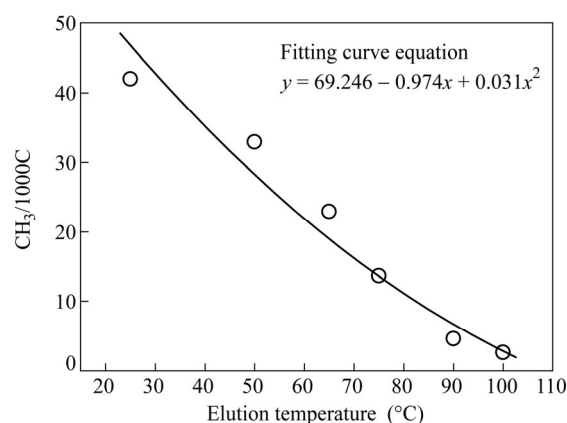
<sup>a</sup> Observed heat of fusion divided by 288 J/g<sup>[37]</sup>

#### Calibration curve establishment of P-TREF

In the study, the SCB content is equal to the comonomer (1-hexene) content. The branches which contain lower than six carbon atoms are usually defined as short chain branches in <sup>13</sup>C-NMR spectra. The comonomer contents of fractions are calculated from <sup>13</sup>C-NMR spectra<sup>[38]</sup>. Table 4 lists the SCB data of all fractions. The comonomer content gradually reduced from 10.10 mol% to 0.54 mol% with increasing elution temperature. Then the 1-hexene contents are converted into methyl numbers per 1000 carbons (CH<sub>3</sub>/1000C) in order to compare with the results obtained from Fourier transform infrared spectroscopy in other literatures. Figure 5 shows the relationship between elution temperature and methyl numbers (per 1000C) of the fractions, which is also called the standard calibration curve (ethylene/1-hexene) of P-TREF. The SCB calibration curve (ethylene/1-octene), as a function of elution temperature, has been obtained for A-TREF in a previous study<sup>[39]</sup>. The SCB degree and elution temperature are inversely related because the crystallinity of the polyethylene decreases with increasing branching degree.

**Table 4.** The SCB data of all fractions

Elution temperature (°C)	25	50	65	75	90	100
1-hexene (mol%)	10.10	7.59	5.07	2.90	0.94	0.54
CH <sub>3</sub> /1000C	42.0	33.0	23.0	13.7	4.6	2.6



**Fig. 5** Relationship between elution temperature and methyl content of ethylene/1-hexene copolymers for P-TREF fractions

#### Fractionation Temperature Selection of Polyethylene for P-TREF

Generally, the fractionation temperatures in the TREF experiment are chosen on the basis of experience or previous literatures. As a result, the selected temperatures may not be very suitable for an unknown sample. Therefore, it is necessary to establish a semi-quantitative selection method.

A method for choosing the TREF fractionation temperature using the SSA approach is described as follows. First, an unknown sample is fractionated by SSA thermal fractionation. And a DSC heating scan after SSA fractionation is obtained. In the scan curve, multiple melting peaks are usually observed. Each SSA endotherm peak represents a group of methylene sequences with equal or similar lengths. Second, each peak valley

temperature can be obtained by the above curve. Third, a series of temperature points may be estimated by the peak valley temperatures and the fitting curve equation in Fig. 4. In other words, the TREF fractionation temperature could be fixed based on the SSA results and the fitting curve equation in Fig. 4.

To illustrate this method, an industrial polyethylene Resin A is used for P-TREF fractionation. First, Resin A is fractionated *via* the SSA thermal fractionation method, and Fig. 6 shows the final DSC heating curve of Resin A after SSA thermal fractionation. The peak valley temperatures can be obtained through Fig. 6. The fractionation temperatures are then estimated based on the peak valley temperatures shown in Fig. 6 and the fitting curve equation in Fig. 4. The data of peak valley and estimated fractionation temperatures are listed in Table 5. Last, the actual elution temperatures are chosen as follows: 25, 40, 50, 55, 60, 68, 75 and 85 °C. It should be noted that the highest elution temperature at 85 °C is applied to ensure all components are completely eluted.

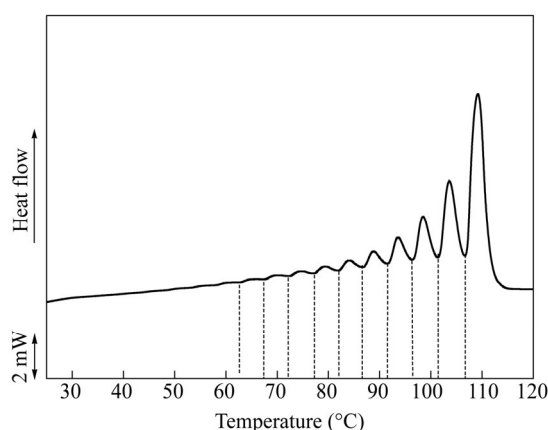


Fig. 6 DSC heating scan for Resin A after SSA thermal fractionation

Table 5. Selection of fractionation temperatures for Resin A

Number	Peak valley temperature (°C)	Fractionation temperature estimation (°C)	Actual fractionation temperature (°C)
1	106.6	75	75
2	101.2	67	68
3	96.3	61	60
4	91.6	55	55
5	86.7	50	
6	81.9	45	50
7	77.2	40	
8	72.4	33	40
9	67.6	29	
10	63.1	24	25

Sample A is actually fractionated into seven fractions. The total recovery ratio of TREF fractionations is 99.3 wt%. Figure 7 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. The high temperature 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. The fractionation results indicate the selection fractionation temperature method using the SSA approach is effective.

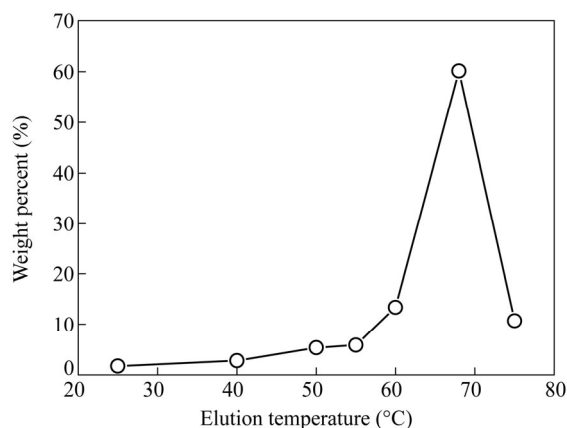


Fig. 7 Weight percent of fractions as a function of elution temperature

## CONCLUSIONS

Several polyethylene homopolymers and ethylene/1-hexene copolymers are mixed and then fractionated *via* the P-TREF method. All fractions are characterized *via* high-temperature GPC,  $^{13}\text{C}$ -NMR, and DSC. The conclusion is summarized as follows:

- (i) A linear relationship between the DSC melting peak temperatures of the fractions from P-TREF and elution temperatures is found and it is used as a reference for choosing the elution temperature of TREF.
- (ii) The P-TREF standard calibration curve (ethylene/1-hexene) is established and is based on the SCB degree of the fractions, as determined *via*  $^{13}\text{C}$ -NMR analysis.
- (iii) The fractionation temperature of polyethylene for TREF could be selected by combining the SSA results and through the linear relationship of the DSC melting peak and elution temperatures.
- (iv) Finally, this study presents a convenient and effective method for selecting the fractionation temperature using the SSA approach.

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