The Preparation of Ultra Narrow Molecular Weight Distribution Poly(ethylene glycol)s by Fractional Crystallization from Solution

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ABSTRACT: The preparation of very narrow molecular weight distribution poly(ethylene glycol) (PEG) was investigated by fractional crystallization from solution. Fractionation experiments were conducted from the solutions of 1500, 2000, and 3000 molecular weight PEG in *n*-butanol/*n*-heptane mixtures. Size Exclusion Chromatography and Differential Scanning Calorimetric studies were performed for the characterization of fractions prepared at different crystallization temperatures and times. By suitable choice of these experimental parameters it was possible to obtain PEG fractions with $M_w/M_n \leq 1.05$. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1999–2005, 2001

Key words: poly(ethylene gylcol); fractional crystallization; size exclusion chromatography

INTRODUCTION

The techniques for preparing polymeric substances with low molecular weight distribution have been widely described in the literature.[1–3] Fractional crystallization, fractional precipitation, turbidimetric titration, chromatography, and ultrafiltration are some of these techniques. Among these methods, fractional crystallization and fractional precipitation techniques were frequently used for the fractionation of semicrystalline polymers such as polyethylene,[4,5] polypropylene,[6–8] and polystyrene.[9] Fractional crystallization can be applied directly from dilute solution of polymer and the melt phase. The same technique for polymer fractionation from the melt has not been analyzed, largely due to the experimental difficulties in separation of the fractionated material from the bulk crystalline phase,[10] although Mehda and Wunderlich proved that fractional crystallization from solution can be used very effectively when the crystallization conditions are well defined.[10]

The earliest studies for the fractionation of high molecular weight PEGs from methyl ethyl ketone, xylene, and benzene/isooctane solution mixture have been achieved by Booth and Price[11] and Beech and Booth.[12] However, only a few articles have been reported for fractionation from solution mixtures as a method for evaluation of very narrow molecular weight distribution, low molecular weight PEG fractions.[13–15] In the present work, optimum fractional crystallization conditions for the preparation of very narrow molecular weight distribution low molecular weight PEGs from *n*-butanol/*n*-heptane solution mixtures have been determined. The fractions were characterized with calorimetric and chromatographic techniques. The influence of crystallization temperature and time period on the weight distribution of fractions were examined.

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Table I Molecular Weights and Polydispersity of Samples Used

Polymer	M_w	M_n	M_w/M_n
PEG1500	1540	1080	1.43
PEG2000	2100	1750	1.20
PEG3000	3400	2800	1.21

EXPERIMENTAL

Poly(ethylene glycol)(PEG) [$HO(CH_2—CH_2—O)_n—H$] samples used in this study were obtained from Merck. The samples used are listed in Table I, together with the values of molecular weight and polydispersity. The solvents used in the crystallization experiments were obtained from BDH. Solvents were used as received without further purification.

Fractional Crystallization

To study fractional crystallization at moderate temperatures, all of the samples of PEG referred to above were crystallized from different *n*-butanol/*n*-heptane solvent mixtures,[16] which were selected in previous studies in solution crystallization of PEG. PEG1500 and PEG2000 were crystallized from a mixture of 23% vol. *n*-butanol and 77% vol. *n*-heptane, and PEG 3000 was crystallized from a mixture of 27% vol. *n*-butanol and 73% vol. *n*-heptane in a temperature range of 30.5–20°C. PEG solutions were prepared by dissolving 1 g PEG in 65 mL solvent mixture. To be sure of the dissolution of PEG, solutions were kept at 70°C for 15 min. The beaker was then quickly transferred to the crystallization bath previously thermostated (±0.01°C) at the crystallization temperature. After allowing crystallization to proceed for a given period of time, the solvent was removed by decantation. The crystalline phases were dried in a vacuum oven at 303 K and named "first fraction"(*Fr#1*). The process was repeated to obtain further fractions.

Size-Exclusion Chromatography (SEC)

The molecular weight distribution was determined by using a Waters 244 ALC/GPC chromatograph equipped with three Ultrastyragel columns with pore sizes 10^4–10^3 and 500 Å, THF being the eluting solvent. Number and weight average molecular weights were determined by using the primary calibration method. Details of molecular weight determination and primary calibration can be found elsewhere.[17]

Differential Scanning Calorimetry (DSC)

Du Pont 910 model Differential Scanning Calorimeter (DSC) was used in this study to identify the presence and extent of molecular fractionation of the fractions of PEG samples. Temperature and energy calibration were made using a standard In sample. The typical PEG sample size was approximately 5 mg, and the standard heating rate of 10°C/min was used in dynamic nitrogen atmosphere.

RESULTS AND DISCUSSSION

Fractional Crystallization

In this work, sample fractionation was intentionally chosen for crystallizing a polydisperse Poly(ethylene glycol)s isothermally from dilute solutions of *n*-butanol/*n*-heptane, where molecular fractionation results with the crystal phase precipitating. The rejected low molecular weight species remains in solution, and can be separated from the precipitated crystal by filtration at the crystallization temperature.

The volumetric compositions of *n*-butanol/*n*-heptane mixtures were arranged to give a calculated solubility parameter between the solubility parameter of the polymer, and solvent or solvent mixture is 2Hb higher than that of the polymer not dissolving in that solvent. The solubility parameters of PEGs determined by van Krevelen group contribution values[18] and solubility parameters of solvent mixtures with the difference between these parameters ($\Delta\delta$) are given in Table II.

As shown in the table, the $\Delta\delta$ value is higher than 2Hb; thus, it is expected that such solvent mixtures would provide the optimum polymer–solvent interaction to induce crystallization at

Table II Solubility Parameter of Polymers and Solvent Mixtures

Polymer	δ_{PEG}	$\delta_{sol.mix.}$	$(\Delta\delta)$
PEG1500	10.83	8.45	2.38
PEG2000	10.71	8.45	2.26
PEG3000	10.50	8.57	2.05

Table III The Fractionation Conditions of Polymers

Fr. No.	Fractionation Temperature (°C)	Fractionation Time (h)	*m* (g)
	PEG1500 *Method 1*		
1	30.5	4.5	0.1025
2	28.5	18.0	0.2827
3	20.0	18.0	0.2778
4	0.0	1.0	0.3358
	PEG1500 *Method 2*		
1	30.0	4.5	0.1637
2	28.5	4.0	0.1127
3	28.5	4.0	0.0801
4	28.5	4.0	0.0501
5	20.0	18.0	0.2979
6	0.0	1.0	0.0518
	PEG2000		
1	35.0	9.5	0.3422
2	33.0	48.0	0.0141
3	30.0	12.0	0.0033
4	20.0	18.0	0.0544
5	0.0	1.0	0.0449
	PEG3000		
1	35.0	4.5	0.3422
2	33.0	2.0	0.0141
3	30.0	12.0	0.0033
4	25.0	4.0	0.0544

moderate temperatures. The fractionation conditions and relative amount of fractions (m) obtained from 1 g of polymer are given for each polymer in Table III.

As shown in Table III, two methods were applied for the fractionation of PEGOH1500, and four fractions were obtained in method 1. To check the precision of separation with regard to crystallization time, two additional fractions were performed at 28.5°C in method 2. The effects of these two additional crystallizations on the molecular weight distribution of fraction are given in the latter section.

The effect of crystallization temperature on the relative amount of fraction was observed in the first fractions of PEGOH 1500 prepared by methods 1 and 2. Decreasing the crystallization temperature by 0.5°C increased the amount of fraction from 0.1025 to 0.1637 g, and the relative change is 25%. After removing the first crystals, the polymer solution was left again at the first crystallization temperature, but crystallization was not observed. This is due to the decrease in melting temperature and concentration of polymer solution after first crystallization.

The combined effect of concentration and temperature on crystallization from solution is given by the well-known Flory-Huggins equation.[19]

$$\frac{1}{T_m^\circ} - \frac{1}{T_s^\circ} = \frac{RV_u}{\Delta H_u V_1}[(1 - \phi_2) - \chi(1 - \phi_2)^2] \quad (1)$$

where the T_s° and T_m° are the equilibrium melting temperature of diluted and undiluted infinite molecular weight polymer. V_u and V_1 are molar volumes of polymer and solvent, respectively. ϕ_2 stands for the volume fraction of polymer and χ is the so-called polymer–solvent interaction parameter. ΔH_u is the heat of fusion of the repeating unit. For a given temperature the decrease of the concentration of a polymer in the crystallization medium decreases the melting temperature and

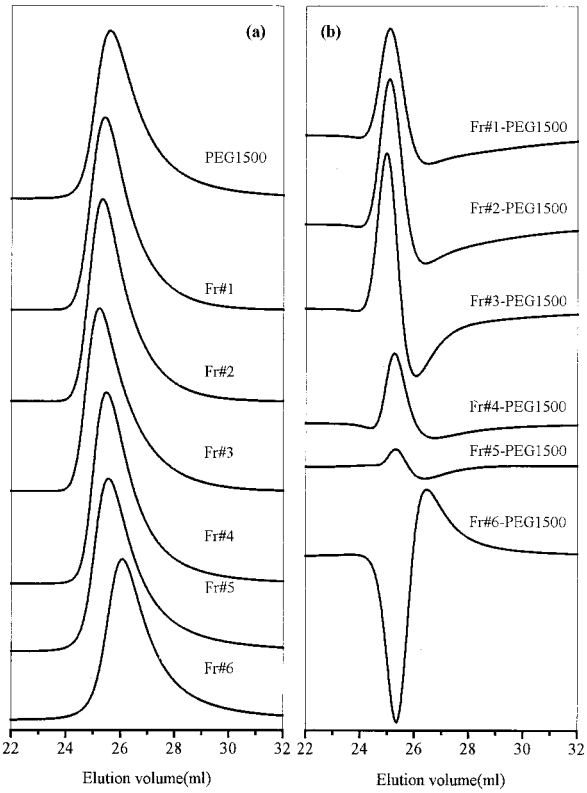

Figure 1 SEC chromatograms of PEG1500 fractions prepared with method 2: (a) normalized chromatograms, (b) difference chromatograms.

Table IV M_w, M_n, and Polypispersity of Fractions

Fr. No.	M_w	M_n	M_w/M_n
	PEG1500 *Method 1*		
1	1760	1520	1.16
2	1700	1620	1.05
3	1600	1420	1.13
4	1400	1140	1.19
	PEG1500 *Method 2*		
1	1750	1400	1.25
2	1800	1540	1.16
3	1570	1550	1.01
4	1600	1600	1.05
5	1450	1450	1.11
6	1220	1200	1.19
	PEG2000		
1	2050	1865	1.10
2	2010	1915	1.05
3	1900	1585	1.20
4	1820	1215	1.50
5	1500	835	1.79
	PEG3000		
1	4030	2815	1.43
2	3860	3140	1.23
3	3100	2790	1.11
4	3010	2595	1.16

T_s, and the extent of over cooling $\Delta T = T_s - T_c$ becomes smaller where T_c is the crystallization temperature of the polymer. The decrease in the ΔT value decreases the nucleation rate of polymer, so the second crystallization could not be achieved at the first crystallization temperature.

Size-Exclusion Chromatography Analysis

The molecular weight distribution (MWD) of the fractions were obtained by size-exclusion analyses. The representative size exclusion chromatograms of PEGOH 1500 fractions prepared with method 2 are given in Figure 1(a). The success of the fractionation procedure cannot be seen from the normalized chromatograms but from their respective difference chromatograms on the same figure [Fig. 1(b)].

The difference chromatograms showed that an increase in fraction number from 1 to 4 resulted in an increase in the number of high molecular weight chains and a decrease in the low molecular weight chains. This means that weight- and number-average molecular weights of the fractions were much higher than that of the unfractionated polymer. After the third fraction this behavior changed in the opposite direction. As shown from the difference chromatograms of fraction 6(*Fr#6*), the amount of high molecular weights is very small, whereas it is extremely high for low molecular weight chains. This change is clearly observed in the numerical values of the molecular weights. The weight and number average molecular weights of fractions and polydispersities are given in Table IV. As indicated above, the second fraction of PEG1500 in method 1 was subdivided into three fractions in method 2. This division decreased the molecular weight distribution of the fractions. The MWD of fraction 3 (1.05) in method 2 is lower than that of fraction 2 (1.10) in method 1.

M_w/M_n values reported in Table IV, given above especially for mid-fractions, show that by controlling concentration of solution, crystallization temperature, and time, it is possible to reduce the polydipersity from 1.37–1.43 to 1.01–1.10.

On the other hand, Differential Scanning Calorimeter studies are more susceptible to the presence of low molecular weight species, and they give direct information about the success of fractionation experiments.

Differential Scanning Calorimetry Analysis

Figures 2 and 3 show the melting endotherms of unfractionated PEG1500 and PEG2000, crystal-

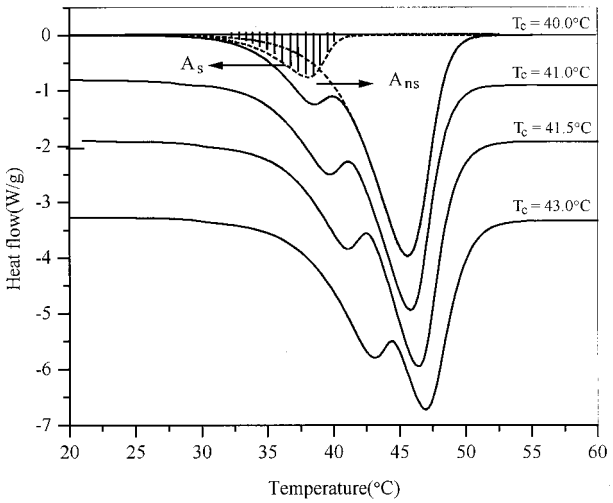

Figure 2 Melting endotherms of unfractionated PEG1500. Crystallization temperatures indicated in the curves.

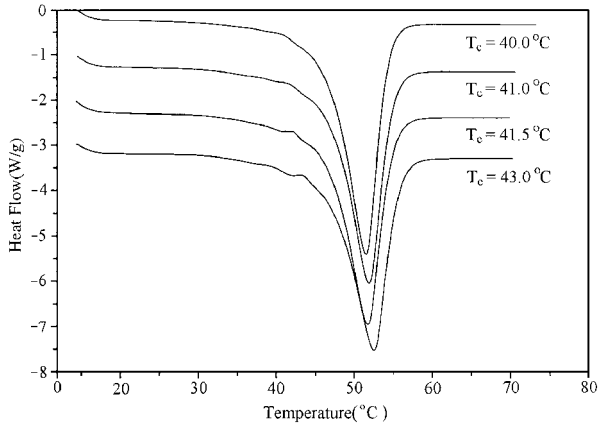

Figure 3 Melting endotherms of unfractionated PEG2000. Crystallization temperatures indicated in the curves.

lized at the temperatures indicated on the curves. The DSC curves of PEG1500 have one sharp peak, and those of PEG2000 have two small peaks before the high-temperature peak.

Investigating linear polyethylene from the melt isothermally crystallized at T_c, Mehta and Wunderlich[10] showed that the main high-temperature melting peak corresponds to the crystallized polymer; the smaller, low-temperature peak being due to the material fractionated during the crystallization process and crystallizing or segregating only during the quenching. The mass fractions of segregated (W_s) and nonsegregated component (W_{ns}) were evaluated by resolving DSC curves with a peak separation program. The upper melting curve in Figure 2 yields detailed information used in the analysis of the melting endotherms. The mass fraction of segregated component is defined as:

$$W_s = A_s/(A_s + A_{ns}) \tag{2}$$

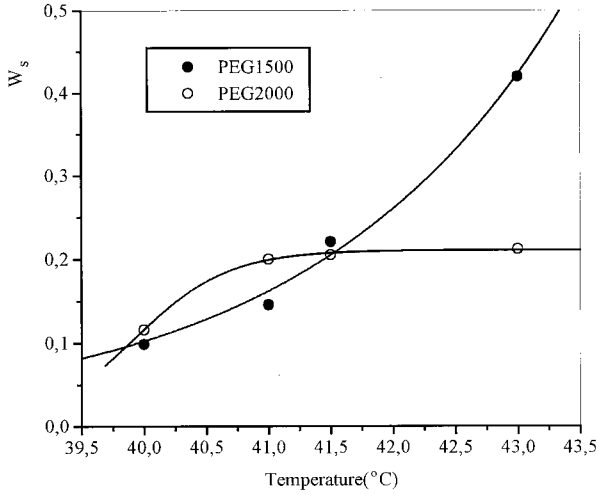

Figure 4 The changing of W_s values with crystallization temperature of PEG1500 and PEG2000.

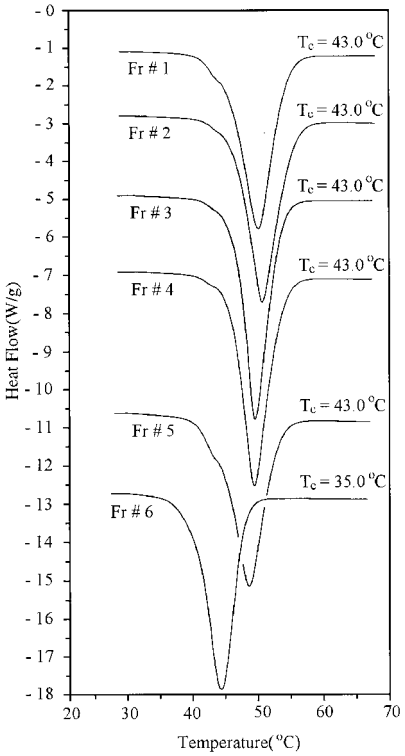

Figure 5 Melting PEG1500 prepared with method 2. Crystallization temperatures indicated on the figures.

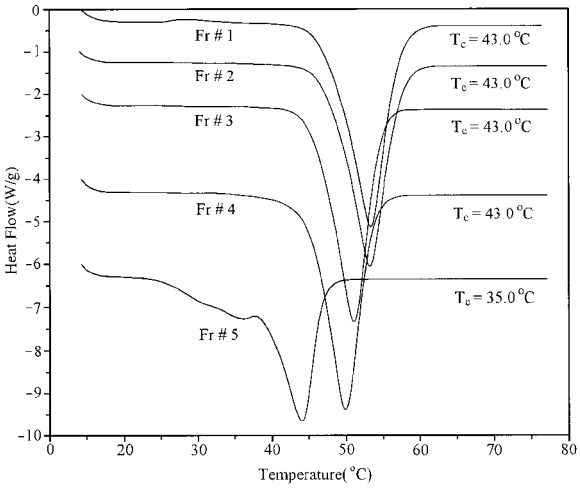

Figure 6 Melting PEG2000 prepared with method 2. Crystallization temperatures indicated on the figures.

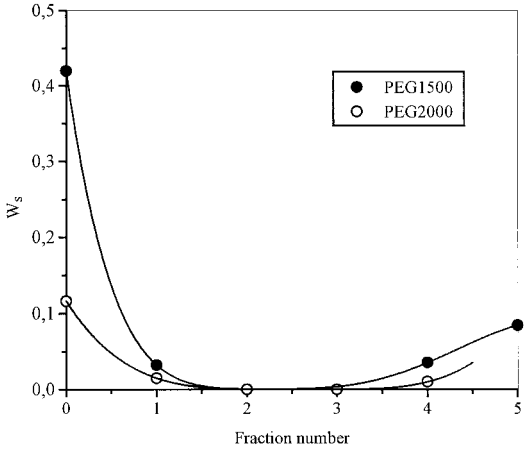

Figure 7 The changes of the relative mass fraction of segregated component with crystallization number of PEG1500 and PEG2000.

where A_s and A_{ns} are the areas of DSC curves corresponding to segregated and nonsegregated components, respectively. Owing to the difference in crystallinity between the two components and varying the shape of DSC curves with heating rate, the values estimated according to eq. (2) are not absolutely correct. However, the data may still be used to determine the selectivity of the fractional crystallization. The changes in W_s values with crystallization temperature for PEG1500 and PEG2000 are given in Figure 4. Due to high molecular weight distribution of PEG1500, the increase of W_s with temperature is much higher than in PEG2000.

The success of the fractionation was controlled by the change of the mass fraction of segregated component in the fractions of the polymer. For this purpose the fractions were crystallized again from melt at different temperatures, and melting thermograms were recorded. The melting curves of PEG1500 prepared with method 2 and PEG2000 are given in Figures 5 and 6, respectively. The crystallization temperatures are indicated on the figures. The changes of the relative mass fraction of segregated and nonsegregated components with crystallization number are given in Figure 7. It is seen that the mass fraction of the small temperature peak was close to zero at mid-fractions for PEG1500 and completely disappeared in the first two fractions of PEG2000. The last fractions of these polymers prove that the low molecular weight component was essentially removed from the samples by crystallization.

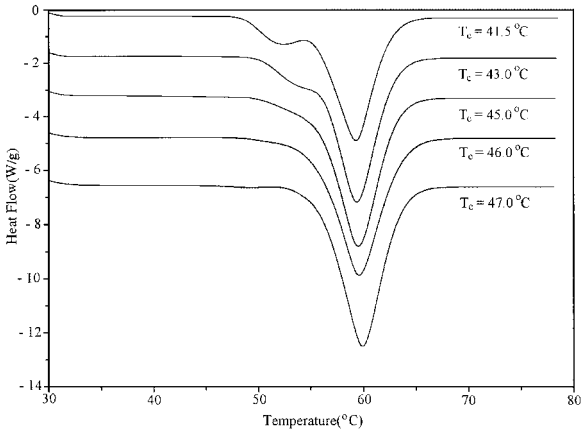

Figure 8 Melting curves of unfractionated PEG3000.

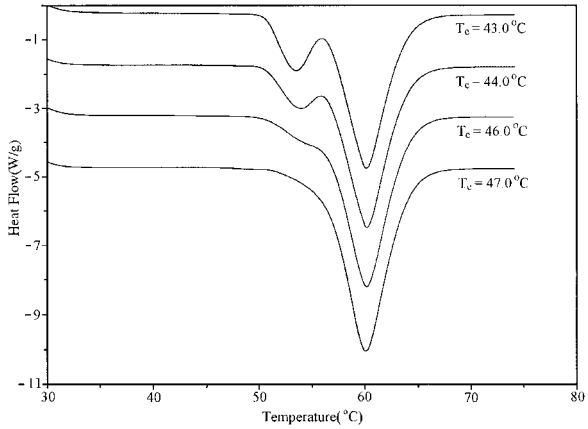

Figure 9 Melting curves of first fraction of PEG3000.

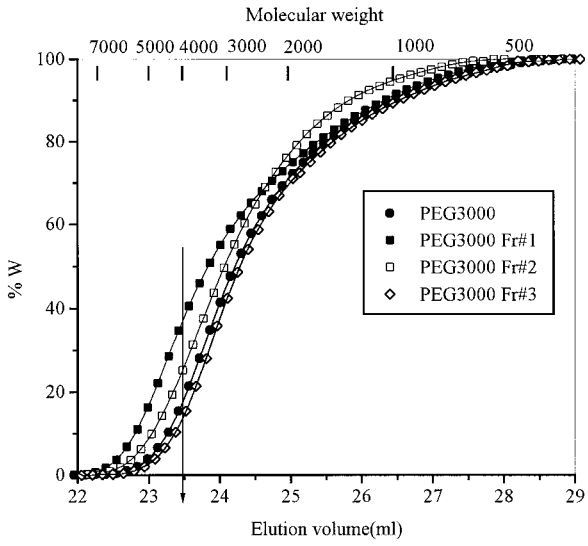

Figure 10 Differential molecular weight distribution curves of unfractionated PEG300 and its fractions.

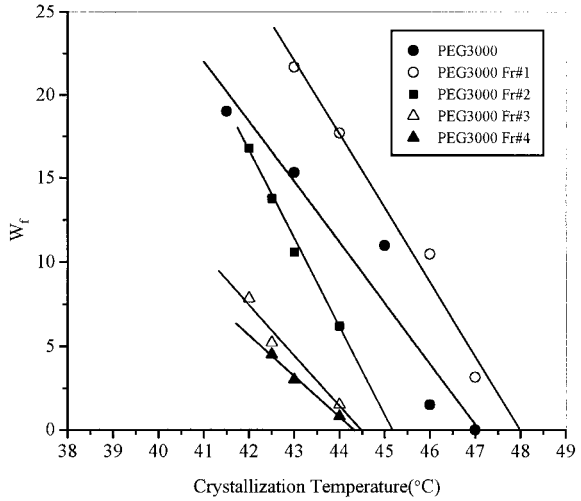

Figure 11 The mass of folded components (W_f) with crystallization temperature and fractionation number.

The efficiency of the fractionation was also checked by DSC for PEG3000. The melting curves of unfractionated and first fraction of PEG3000 crystallized at different temperatures are given in Figures 8 and 9. Similar curves were obtained for the other fractions of PEG3000. As shown in Figure 8, there is a low-temperature peak for PEG3000, but the relative amount of this peak decreased with increasing crystallization temperature, and completely disappeared at 47.0°C. These melting curves show typical behavior of extended and folded crystallized polymers. It has been very well established that PEGs with molecular weights higher than 4000 can be crystallized in extended chain configurations, depending on the crystallization temperature.[20,21] The differential MWD curves of PEG 3000 show that the ratio of the chains higher than 4000 is 20%, and the amount of this high molecular weight chain increases in the first fraction and decreases with increasing fractionation number (Fig. 10). The mass fraction folded components (W_f) with crystallization temperature and the fractionation number is given in Figure 11. The mass fraction of folded components (W_f) was evaluated by the same method used in the determination of W_s. Although the completely extended chains could be obtained at 47.0°C for PEG3000, this temperature shifted to 48.0°C in the first fraction, being rich with high molecular chains, and then decreased to 44.4°C for fraction 3, due to the lower amount of high molecular weight chains in the fraction.

CONCLUSION

The preparation of very narrow molecular weight distribution poly(ethylene gylcol)s by fractional crystallization from *n*-butanol/*n*-heptane mixture has been investigated. Chromatographic and calorimetric results indicated the possibility of obtaining PEG fractions with $M_w/M_n \leq 1.05$, independent of molecular weight and molecular weight distribution of the polymer, by a suitable choice of an *n*-butanol/*n*-heptane mixture and crystallization temperature.

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