The Characterization of a Poly(ethylene Terephthalate)–Poly(tetramethylene Ether) Multiblock Copolymer via Cross Fractionation and Size Exclusion Chromatography

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Synopsis

A poly(ethylene terephthalate)–poly(tetramethylene ether) multisegment block copolymer has been characterized by cross fractionation, where the individual fractions were then analyzed via size exclusion chromatography. The use of dual detectors (refractive index and ultraviolet) allowed both the compositional heterogeneities and molecular weight distributions to be evaluated. The SEC based molecular weights were supplemented by osmometric based molecular weights.

INTRODUCTION

Copolymeric materials usually exhibit distributions in both molecular weight and chemical composition. The chemical composition distribution is of importance in view of the control of physical properties such distribution can exert. The potential exists for an enhanced elucidation of composition by the use of the cross-fractionation approach.[1]

The principles of polymer fractionation have been reviewed[2,3] on the basis of the Flory–Huggins statistical thermodynamic treatment. The distribution of a copolymer (undergoing fractionation) between two phases in equilibria is given[4] as follows:

$$V'_{p,\alpha}/V''_{p,\alpha} = \exp[\, p(\sigma + K_\alpha)]$$ (1)

where p denotes the degree of polymerization, α is the chemical composition, $V'_{p,\alpha}$ and $V''_{p,\alpha}$ are the volume fractions of a component with a specific p and α in the precipitant and supernatant phases, respectively, and α is a fractionation parameter. K in turn is given by

$$K = (V'_3 - V_3)(\chi_A - \chi_B)$$ (2)

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for a single solvent system and by

$$K = (V_1 - V_1')(\chi_{1A} - \chi_{1B}) + (V_2 - V_2')(\chi_{2A} - \chi_{2B}) \qquad (3)$$

for a two-solvent system where V_1, V_2, and V_3 represent the respective volume fractions of solvent 1, solvent 2, and the copolymer. The prime corresponds to the precipitated phase while χ_{iA} and χ_{iB} are the interaction parameters of solvent i with the A and B chain units, respectively. When $K = 0$, (1) reduces to that given for homopolymers:

$$V_p'/V_p'' = \exp(p\sigma) \qquad (4)$$

Thus, the molecular weight distribution may be obtained by successive fractionations while the chemical composition distribution remains unresolved. For this reason fractionation based on composition should be treated as a function of σ and K as given in eq. (1).
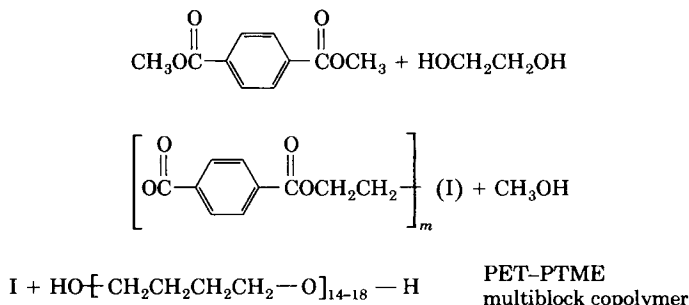
This approach led Litmanovich and Shtern[5] to propose the cross-fractionation technique as a means of evaluating the molecular weight and chemical composition distributions of a heterogeneous copolymer. The cross-fractionation technique is where two solvent–nonsolvent systems differing in sign with respect to the parameter K are used. The sample is first fractionated into intermediate fractions in one of the solvent–nonsolvent systems. This is followed by further fractionation of these intermediate fractions by the other solvent–nonsolvent systems.

Size exclusion chromatography (SEC) is an effective tool for the simultaneous measurements of compositional heterogeneity and molecular weight distributions; a procedure which has been described by Cantow and co-workers[6] where ultraviolet (UV) and differential refractive index (RI) detectors in series were used. Runyon and co-workers[7] applied this method to investigate the composition heterogeneity of a polystyrene–butadiene diblock while others[8,9] have used the cross-fractionation approach on regular diblock copolymers. In our work the multiblock poly(ethylene terphthalate–tetramethylene ether) (PET–PTME) copolymer was studied by a combination of the cross-fractionation technique and dual-detector SEC measurements. To the best of our knowledge, this is the first report of such work on a segmented block copolymer prepared via end-linking chemistry.

EXPERIMENTAL

The PET–PTME multiblock copolymer was prepared via a two-step polycondensation in the melt, i.e., ester exchange followed by the polycondensation event. Initially 28 g of dimethyl terephthalate (DMT) were reacted with 23 g of ethylene glycol in the presence of a binary catalyst (titanium potassium oxalate and zinc acetate) at 200°C under N_2. The resultant prepolymer was then reacted with 74 g of poly(tetramethylene glycol) (PTMG) having a number-average molecular weight of 2×10^3 g mol^{-1}. The reaction was carried out in the presence of ca. 0.2 wt % antioxidant 330 at 255°C and 0.1

torr for ca. 2 h. The overall reaction is given as follows:

$$CH_3OC-\langle\bigcirc\rangle-COCH_3 + HOCH_2CH_2OH$$

$$\left[OC-\langle\bigcirc\rangle-COCH_2CH_2\right]_m \text{ (I)} + CH_3OH$$

$$\text{I} + HO[CH_2CH_2CH_2CH_2-O]_{14-18}-H \quad \begin{array}{l}\text{PET–PTME}\\ \text{multiblock copolymer}\end{array}$$

The stoichiometric weight content of PET was 21% while [1]H-HMR analysis[10] (Varian XL-60) yielded a value of 20%. The number-average molecular weight from membrane osmometry was 5.2×10^4 g mol^{-1}. A Knauer osmometer with chloroform at 37°C was used for all number-average molecular weight measurements.

The tetrachloroethane–methanol (I) and trichlorethylene-n-heptane (II) systems were found to be appropriate for our fractionation work. About 15 g of the copolymer were first fractionated into six intermediate fractions with system (I). In turn each intermediate fraction was then refractionated into additional fractions with system (II). Thus, 18 fractions were obtained with each fractionation carried out at $20 \pm 0.2°C$. Equilibration times ranged from 1 to 2 days. Polymer concentration of each initial fractionation solution was 1.5 g/100 mL. Each fraction obtained was washed with methanol and then vacuum dried for about 24 h at 40°C. Total recovery was found to be 81.7 wt %.

Size exclusion chromatography was done using a Knauer high performance chromatograph equipped with UV (254 nm) and RI detectors and two TSK columns (3000H and 4000H) packed with a mixture of polystyrene gels of nominal porosity 10^3–10^6 Å. Freshly distilled chloroform was the mobile phase at 25°C with a flow rate of 1 mL min^{-1}. There was no lag time between the UV and IR measurements since the eluant solution was split prior to entering the two detectors. Thus, virtual simultaneous measurements were possible.

RESULTS AND DISCUSSION

It is imperative that the solvent–nonsolvent pairs chosen facilitate the desired selective fractionations according to molecular weight and composition. Teramachi[11] suggested that these pairs be chosen on the basis of the relative values of the interaction parameters χ for the A and B segments; i.e., where $\chi_A > \chi_B$ and $\chi_A < \chi_B$. Alternatively, the solubility parameters may be substituted for χ. This latter approach was followed in this work. However, difficulty was encountered in selecting the solvent–nonsolvent systems in view of the relatively imprecise nature of these values insofar as the interrelationship between the solvent–nonsolvent values and those (calculated) of the copolymer segments. This task was further complicated due to the relatively poor solubility of the PET component in solvents convenient for the experimental approach applied in this work.

TABLE I
PET–PTME Data from the Single Fractionation

Fraction	Weight fraction (W_i)	PET content $(X \%)$
P-1-0	0.021_9	31.6
P-2-0	0.189	23.6
P-3-0	0.286	22.5
P-4-0	0.064_0	20.2
P-5-0	0.200	19.4
P-6-0	0.240	17.0

In accordance with the solubility parameter approach, with PET [$\delta = 10.7$ $(\text{cal/cm}^3)^{0.5}$] and PTME [$\delta = 8.2$ $(\text{cal/cm}^3)^{0.5}$] used as guidelines, two solvent–nonsolvent systems were found through screening of numerous candidate pairs. The first system was tetrachloroethane–methanol. The solubility parameter of tetrachloroethane [$\delta = 9.7$ $(\text{cal/cm}^3)^{0.5}$] approaches that of PET, i.e.,

$$\delta_{\text{PET}} > \delta_{\text{C}_2\text{H}_2\text{Cl}_4} > \delta_{\text{PTME}}$$

$$\delta_{\text{PET}} - \delta_{\text{C}_2\text{H}_2\text{Cl}_4} = 1$$

$$\delta_{\text{C}_2\text{H}_2\text{Cl}_4} - \delta_{\text{PTME}} = 1.5$$

As a consequence of $\delta = 14.5$ for methanol, the initial fractionation would be anticipated to favor the separation of the PTME content. In contrast to this expectation the first fractionation tended to yield material relatively rich in PET, a result which is explainable on the basis of the poor solubility of that component. These results are summarized in Table I.

The second system used was trichloroethylene [$\delta = 9.2$ $(\text{cal/cm}^3)^{0.5}$] and n-heptane [$\delta = 7.4$ $(\text{cal/cm}^3)^{0.5}$], where

$$\delta_{\text{PET}} > \delta_{\text{C}_2\text{HCl}_3} > \delta_{\text{PTME}}$$

$$\delta_{\text{PET}} - \delta_{\text{C}_2\text{HCL}_3} = 1.5$$

$$\delta_{\text{C}_2\text{HCl}_3} - \delta_{\text{PTME}} = 1$$

This second system would be expected, based on the foregoing and the initial fractionation results, to exhibit the preferential fractionation of PET relative to PTME.

The cross-fractionation results are given in Table II and Figures 1 and 2. A comparison of the integral chemical composition distributions from cross fractionation and single fractionation (Fig. 3) show that fractions with the lowest PET content were obtained by the cross-fractionation approach although a broader distribution curve was obtained than that found from the single fractionation. Also, the chemical composition distribution curve derived from cross fractionation was closer to the actual distribution than that obtained by the single fractionation.

TABLE II
PTME Data from Cross Fractionation

Fraction	Weight fraction (W)	PET content[a] $(X\%)$	$\overline{M}_n$[b] $(\times 10^{-4})$	$\overline{M}_w/\overline{M}_n$[c]
P-1-0	0.025_0	31.6		
P-2-1	0.030_8	28.5	5.29	2.34
P-2-2	0.098_0	22.9	6.42	1.94
P-2-3	0.038_6	22.7	4.44	3.23
P-2-4	0.009_0	18.7		3.31
P-3-1	0.121_4	25.7	4.68	1.99
P-3-2	0.077_0	22.2	6.00	2.07
P-3-3	0.059	21.4	5.07	2.76
P-3-4	0.007_0	25.6		2.95
P-4-1	0.043_6	21.6	7.66	2.10
P-4-2	0.026_0	20.9	5.37	2.09
P-5-1	0.112_0	19.9	9.70	1.76
P-5-2	0.071_0	18.6	5.83	1.74
P-5-3	0.031_0	14.4	5.96	1.65
P-6-1	0.080_0	18.6	2.25	2.49
P-6-2	0.063_0	17.5	2.92	2.20
P-6-3	0.015_9	16.4		2.26
P-6-4	0.090_2	15.6	1.76	2.51

[a] Via ^{1}H-NMR measurements.
[b] Via osmometry measurements.
[c] Via SEC measurements.

Table II lists the characterization data of the PET–PTME copolymer. One can note that the $\overline{M}_w/\overline{M}_n$ ratio of the fractions are in the range of 1.6–3.3, a consequence of the fact that the two fractionation systems selected are relatively ineffective insofar as separation according to molecular weight is concerned. This feature is fortified by the observation (Fig. 1) that the molecular weight distribution obtained via cross fractionation is narrower than that obtained from the SEC measurements. We may thus conclude that the solubility of our copolymer is influenced by both the composition and molecular weight.
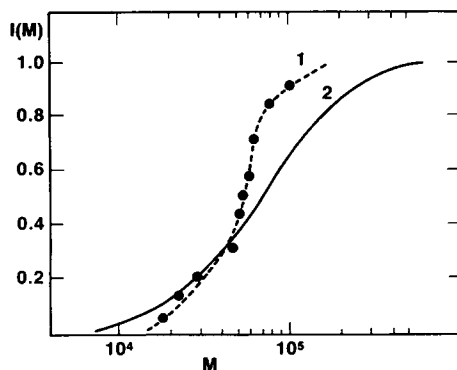

Fig. 1.   Integral molecular weight distribution curves obtained from cross fractionation (1) and SEC (2) for original PET–PTME sample (wt % PET).
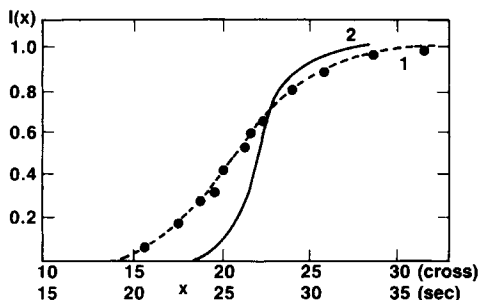
Fig. 2. Integral chemical composition distribution curves obtained from cross fractionation (1) and SEC (2) for original PET–PTME sample.

It has been shown from an intrinsic viscosity study in chloroform at 30°C that a useful Mark–Houwink–Sakurada equation was establishable.[12] This relation is as follows:

$$[\eta] = 4.60 \times 10^{-2}\overline{M}^{0.69} \tag{5}$$

for $[\eta]$ in mL g^{-1}. The PET composition range was 14–26% while the samples ranged in molecular weight from 10^4 to 10^5 g mol^{-1}. There was no detectable influence of the variation in composition on copolymer hydrodynamic volume over the investigated molecular weight range. This is further borne out by linear relation obtained for various fractions (Table III) where the number-average weight is plotted against the peak elution volume V_e (Fig. 4). This particular SEC calibration equation can be expressed as follows:

$$\log \overline{M}_n = 12.01 - 0.0664 V_e \tag{6}$$

Generally, proper SEC calibrations are obtained when the peak retention volume is equated with the weight-average molecular weight and the standards possess relatively narrow molecular weight distributions. Thus a method of using samples with broad distributions and number-average molecular weights was adapted in order to convert the primary SEC calibration (Fig. 4) into one from which meaningful insight into heterogeneity indices could be obtained. This process[13] is described as follows:
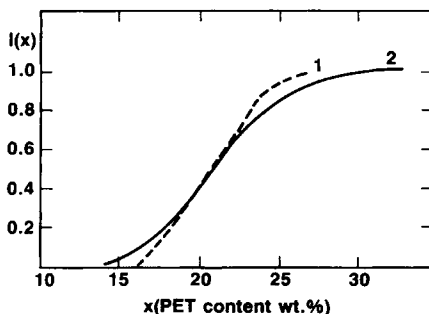

Fig. 3. Integral chemical composition distribution curves obtained from single fractionation (1) and cross fractionation (2) for original PET–PTME samples.

TABLE III
PET–PTME Data for SEC Calibration

Fraction	V_e	$\bar{M}_n{}^a$ ($\times 10^{-4}$) g mol^{-1}	$(\bar{M}_w/\bar{M}_n)_I$	$(\bar{M}_w)_I$ ($\times 10^{-5}$) g mol^{-1}	$(M_0)_I$ ($\times 10^{-4}$) g mol^{-1}	$(\bar{M}_w/\bar{M}_n)_{II}$	$(\bar{M}_n)_{II}$ ($\times 10^{-4}$) g mol^{-1}	$(\bar{M}_w)_{II}$ ($\times 10^{-5}$) g mol^{-1}
P-2-1	109.8	5.29	2.71	1.43	8.70	2.34	4.60	1.08
P-2-2	108.9	6.42	2.17	1.39	9.45	1.94	6.76	1.31
P-2-3	111.0					3.23	3.13	1.01
P-2-4	112.0					3.31	2.67	0.89
P-3-1	108.9					1.99	6.31	1.25
P-3-2	108.7	6.00	2.34	1.41	9.19	2.07	6.31	1.27
P-3-3	109.8	5.07	3.28	1.66	9.17	2.76	4.17	1.15
P-3-4	113.0					2.95	2.58	0.76
P-4-1	107.8	7.66	2.38	1.82	11.8	2.10	6.93	1.46
P-4-2	107.9					2.09	6.75	1.41
P-5-1	106.1	9.70	1.93	1.88	13.5	1.76	10.6	1.86
P-5-2	108.6					1.74	6.66	1.16
P-5-3	108.5					1.65	7.41	1.23
P-6-1	115.5	2.25	2.90	0.65	3.83	2.49	1.81	0.45
P-6-2	113.5	2.92	2.52	0.74	4.64	2.20	2.56	0.56
P-6-3	113.8					2.26	2.45	0.55
P-6-4	117.0	1.76	2.93	0.52	3.01	2.51	1.60	0.40

^{a} Via osmometry measurements.

The calculation of the $(\bar{M}_w/\bar{M}_n)_I$ ratio for each sample was done. $(M_w)_I$ was then obtained from this ratio and the known value of M_n. If the molecular weight distribution function can be described by Wesslau's distribution function, a first approximation of $(M_0)_I$ is given by

$$(M_0)_I = \left[(\bar{M}_w)_I \times (\bar{M}_n)\right]^{0.5} \tag{7}$$

where the osmometric values for $\bar{M}_n$ are used and the subscript I denotes the initial molecular weight value calculated from the primary SEC calibration whereas the subscript II denotes those values obtainable from the secondary
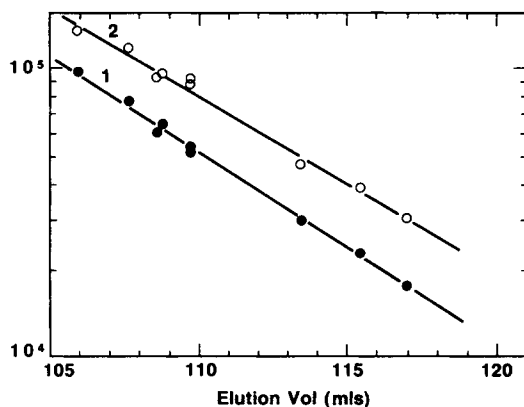

Fig. 4.   SEC calibration: (1) log M_n vs. V_e; (2) log$(M_0)_I$ vs. V_e.
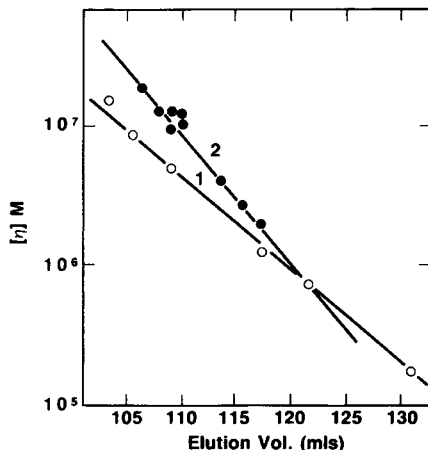
Fig. 5.   SEC universal calibration: (1) polystyrene; (2) PET–PTMG.

calibration.[13] This allows the construction of a secondary SEC calibration (Fig. 4) that is described as:

$$\log(M_0)_I = 11.64 - 0.0612V_e \tag{8}$$

The data calculated from this secondary calibration are given in Table III wherein it is seen that the value of the SEC based number-average molecular weights are in reasonable agreement with those determined via osmometry measurements. Thus, this secondary calibration was used to determine the polydispersity indices of the fractions and the integral molecular weight distribution of the original sample. The comparison with the cross-fractionation results shows that the SEC measurements yield a broader integral molecular weight distribution. As we have noted, the cross-fractionation procedure apparently favors composition rather than molecular weight for this copolymer and thus cannot be relied upon to lead to a reliable molecular weight distribution.

In order to investigate the applicability of the SEC universal calibration technique to characterization of the PET–PTME multiblock copolymer, the $\log[\eta]M$ product for some polystyrene standards and that of the PET–PTME fractions ($\log[\eta]M_0$) were plotted against V_e, respectively (Fig. 5). Obviously deviation of the two calibrations occurs. This implies that the universal calibrated method is not applicable for the evaluation, at least, some multiblock copolymers, where one of the two segments exhibits limited solubility (PET in our case) in the SEC mobile phase ($CHCl_3$).

The chemical composition distribution of the fractions was also examined by the SEC dual detector approach. Calibration of the detectors was done by injecting known concentrations of PTME and PET and then integrating the areas of each chromatogram. These findings are given in Figure 6. However, this method cannot be directly used to determine that RI response of PET since the refractive index increment of low molecular weight polymers is molecular-weight-dependent. To cope with this uncertainty, two fractions of PET–PTME copolymer of known PET contents were used to determine the
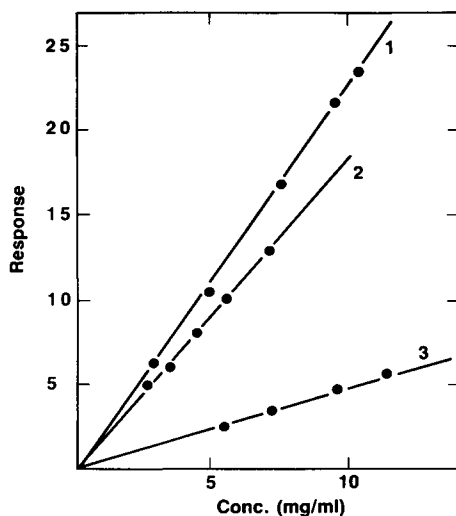
Fig. 6. Calibrations of SEC detectors: (1) UV response for PET homopolymer; (2) RI response for PTME homopolymer; (3) RI response for PET–PTME P-6-1 fraction.

refractometer response. This led to the equation

$$k_{RI(Co)} = x k_{RI(PET)} + (1 - X) k_{RI(PTME)} \qquad (9)$$

from which the corrected differential refractometer response of the PET obtained. In (9) k denotes the response parameter of the SEC detector and x the fraction of PET in the copolymer. We can then let K_1 denote the ratio of the respective refractometer responses of PET to PTME, where

$$K_1 = k_{RI(PET)}/k_{RI(PTME)} = 2.78 \qquad (10)$$

Likewise, K_2 represents the ratio of refractometer and UV spectrometer responses for PET:

$$K_2 = k_{RI(PET)}/k_{UV(PET)} = 0.414 \qquad (11)$$

Thus, the weight fraction of PET(X) at any given point of a chromatogram is given by

$$X = \frac{F_{UV} K_2}{(F_{RI} - F_{UV} K_2) K_1 + F_{UV} K_2} \qquad (12)$$

where F_{UV} is the UV chormatogram reading and F_{RI} is the corresponding RI chromatogram at the same elution volume.

Figure 2 shows the comparisons of the integral chemical composition distribution from SEC, based on eq. (12), and cross fractionation. Clearly, the apparent composition distribution as evaluated from the SEC measurements is narrower than that as determined from cross fractionation. Since separation in SEC is achieved according to the hydrodynamic size of the polymer, the

composition information obtained from such a measurement is strictly a function of apparent coil size and can reflect the composition distribution only insofar as that distribution influences chain dimensions in the measurement solvent of choice. The relative imprecision of the compositions obtained by the SEC measurements was underscored by the fact that these values were ca. 10% higher than those derived from ^{1}H-NMR. Thus cross fractionation is of value in evaluating the chemical composition distribution of multisegmented block copolymers whereas less benefit is obtained, relative to SEC measurements, for the molecular weight distributions. These findings were in part the product of the difficulty, in practice, of selecting solvent–nonsolvent systems which were equally effective in their respective functions of fractionation based on molecular weight and composition differences. This, coupled with the nonroutine nature of the cross-fractionation approach, demonstrates the value of SEC in the characterization of multisegmented materials.

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