

Molecular Weight Distribution of a Segmented Copolymer of PET–PCL

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SYNOPSIS

A recently developed method of combining both the results of static and dynamic laser light scattering (LLS) was applied to characterize the segmented copolymer of poly(ethylene terephthalate-*co*-caprolactone) (PET–PCL) with 48% PET content. Unlike the traditional three-solvent method proposed by Bushuk and Benoit for copolymers, this method requires only two solvents. For each solvent, the apparent weight average molecular weight ($M_{w,app}$) was measured by static LLS. Then $M_{w,app}$ was used as a constraint to convert the line-width distribution from dynamic LLS into the apparent molecular weight distribution. Finally, the two apparent molecular weight distributions were combined to give both the true molecular weight distribution and the estimated chain composition distribution of the copolymer. We found that the PET–PCL sample with 48% PET is nearly uniform in the chain composition. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The segmented copolymer of poly(ethylene terephthalate-*co*-caprolactone) (PET–PCL) is a thermal viscoelastic material. The hard segments (PET) can crystallize to form the physical crosslinking points and the soft segments (PCL) attribute to the elasticity of the materials. As the amount of hard segments increases, this segmented copolymer can gradually change from a low module elastomer to a high module tough plastic. Therefore, the characterization of this type of segmented copolymer, especially its absolute molecular weight and chain composition distribution, is crucially important to its various applications.

Traditionally, the weight average molecular weight (M_w) of a copolymer can be determined by using the Bushuk–Benoit light scattering theory.¹ According to this theory, at least three solvents in which the copolymer has different refractive index increments (ν) are required. However, the choice of three such solvents is usually very difficult because they have to simultaneously satisfy the following

conditions: first, the ν values of three solvents should be as different as possible; second, copolymer should be soluble in these solvents; third, the copolymer solution should have as little as possible absorption at the incident laser light wavelength; and last, but not least, the solution clarification, such as the removing of dust, should not be extremely difficult. Owing to the difficulty in selecting such three solvents, a modified laser light scattering (LLS) method of requiring only two solvents was proposed to determine the copolymer true molecular weight.² This work shows another application of this new method.

THEORY

Static Light Scattering

The angular dependence of the excess absolute time-averaged scattered intensity, known as the excess Rayleigh ratio, $R_{90}(\theta)$, of a dilute polymer solution at concentration C (g/mL) and scattering angle θ can be expressed as³

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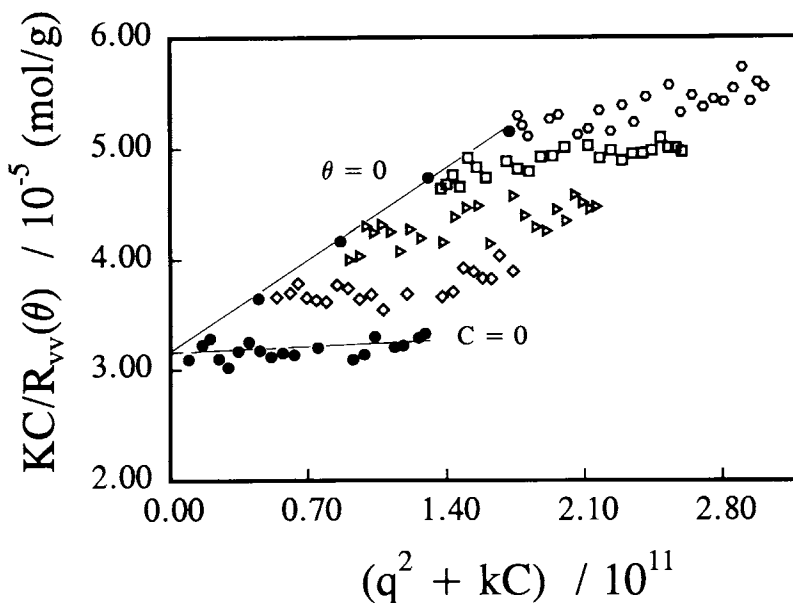


Figure 1 Typical static Zimm plot of the 48% PET/PET-PCL segmented copolymer in chloroform at 25°C. The concentration range is from 1.03×10^{-3} to 3.95×10^{-3} g/mL.

$$\frac{KC}{R_{vv}(\theta)} \approx \frac{1}{M_w P(\theta)} + 2A_2 C \quad (1)$$

$$M_{w,app} = \int_0^\infty f_w(M) \left(\frac{\nu(M)}{\nu} \right)^2 M dM \quad (2)$$

where $K = 4\pi^2 n^2 \nu^2 / (N_A \lambda_0^4)$ with N_A , n , λ_0 , and ν being Avogadro's number, the solvent refractive index, the wavelength of light *in vacuo*, and the refractive index increment (dn/dC), respectively. At $\langle R_g^2 \rangle_z q^2 < 1$, $1/P(\theta) \approx 1 + \frac{1}{3} \langle R_g^2 \rangle_z q^2$ where $\langle R_g^2 \rangle_z^{1/2}$ is root-mean-square z -average radius; and $q (= 4\pi n / \lambda_0 \sin(\theta/2))$ is the scattering vector. By measuring $R_{vv}(\theta)$ at a set of C and θ , we can determine M_w , $\langle R_g^2 \rangle_z^{1/2}$, and A_2 from a Zimm plot that incorporates θ and C extrapolations on a single grid.

For a polydisperse copolymer with both molecular weight and chain-composition distributions, M_w determined on the basis of eq. (1) will only be an apparent weight average molecular weight $M_{w,app}$, defined as¹

where $f_w(M)$ is the true molecular weight distribution and $\nu(M)$ is the refractive index increment for molecules with molecular weight M and weight distribution $f_w(M)$. $f_w(M)(\nu(M)/\nu)^2$ is defined as the apparent weight distribution $f_{w,app}(M)$ hereafter. On the basis of the additivity assumption of ν for a segmented copolymer composed of monomeric units A and B ¹ (in this study, A is ET and B is CL),

$$\nu(M) = W_A(M)\nu_A + W_B(M)\nu_B \quad (3)$$

and

$$\nu = W_A\nu_A + W_B\nu_B \quad (4)$$

Table I Summary of Static and Dynamic LLS Results of 48% PET/PET-PCL Segmented Copolymer in CHCl_3 and THF at 25°C

Solvent	$10\nu^a$ (mL/g)	$10^{-4} M_{w,app}$ (g/mol)	$10^3 A_2$ (mol mL/g ²)	$\langle R_g^2 \rangle_z^{1/2}$ (nm)	$10^7 \bar{D}$ (cm ² /s)	α_D	$10^4 k_D$	$10^{-4} M_w$ (g/mol)
Chloroform	1.00	3.22	2.5	< 10	5.85	0.61	3.64	3.3
Tetrahydrofuran	1.20	3.33	0.45	< 10	7.09	0.61	4.52	

^a The relative uncertainty of measured Δn is about $\pm 1\%$.

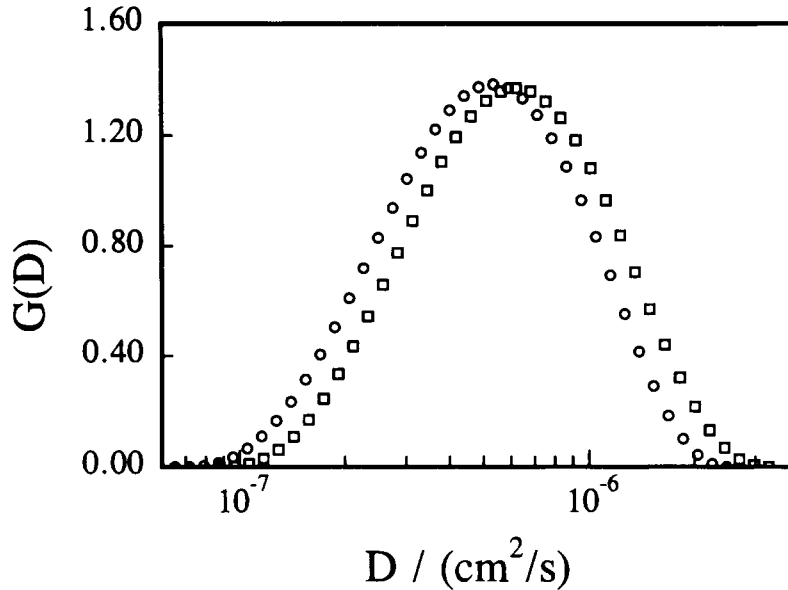


Figure 2 Translational diffusion coefficient distributions of the 48% PET-PCL segmented copolymer (○) in CHCl_3 and (□) in THF at 25°C .

where $W_A(M)$ and $W_B(M) [\equiv 1 - W_A(M)]$ are the weight fractions (chain composition) of A and B at a given M and $f_w(M)$, respectively, and W_A and W_B , the overall weight fractions (chain composition) of A and B, respectively. W_A and W_B are usually known parameters from polymerization. For a chosen solvent, ν_A , ν_B and ν are constants for a given copolymer at fixed experimental conditions. It is obvious that for a uniform chain composition, that is, $W_A(M) = W_A$, $W_B(M) = W_B$, and $\nu(M) = \nu$, we have $M_{w,app} = M_w$. It should be noted that eq. (3) is not unique because different chain compositions can give a polymer chain with the identical M and $f_w(M)$.

Dynamic Light Scattering

In dynamic LLS, a precise intensity-intensity time correlation function $G^{(2)}(t, \theta)$ in the self-beating mode can be measured that has the following form^{4,5}

$$G^{(2)}(t, \theta) = \langle I(t, \theta)I(0, \theta) \rangle = A[1 + \beta |g^{(1)}(t, \theta)|^2] \quad (5)$$

where A is a measured baseline, β is a parameter depending on the coherence of the detection, t is the delay time, and $g^{(1)}(t, \theta)$ is the normalized first-order electric field time correlation function. For a polydisperse sample, $g^{(1)}(t, \theta)$ is related to the line-width distribution $G(\Gamma)$ by

$$g^{(1)}(t, \theta) = \langle E(t, \theta)E^*(0, \theta) \rangle = \int_0^\infty G(\Gamma)e^{-\Gamma t} d\Gamma. \quad (6)$$

The mostly accepted Laplace inversion analysis program CONTIN⁶ was used in the present work to convert the measured $G^{(2)}(t, \theta)$ to $G(\Gamma)$. The line width Γ usually depends on both C and θ . This dependence can be expressed as

$$\frac{\Gamma}{q^2} = D(1 + k_d C)(1 + f \langle R_g^2 \rangle z q^2) \quad (7)$$

where D is the translational diffusion coefficient at $C = 0$ and $q = 0$, f is a dimensionless number, and k_d is the diffusion second virial coefficient. The value of f depends on the chain structure, polydispersity, and solvent power.

From eqs. (1), (2), and (6), at the conditions of $C \rightarrow 0$, $\theta \rightarrow 0$, and $t \rightarrow 0$, we have

$$R_{vv}(\theta) = KC \int_0^\infty f_w(M) M \left(\frac{\nu(M)}{\nu} \right)^2 dM \propto \langle I \rangle \quad (8)$$

and

$$\begin{aligned} g^{(1)}(0, \theta) &= \langle E(0, \theta)E^*(0, \theta) \rangle \\ &= \int_0^\infty G(\Gamma) d\Gamma \propto \langle I \rangle \end{aligned} \quad (9)$$

that leads to

$$\int_0^\infty G(D) dD = \gamma \cdot \int_0^\infty f_w(M) M \left(\frac{\nu(M)}{\nu} \right)^2 dM \quad (10)$$

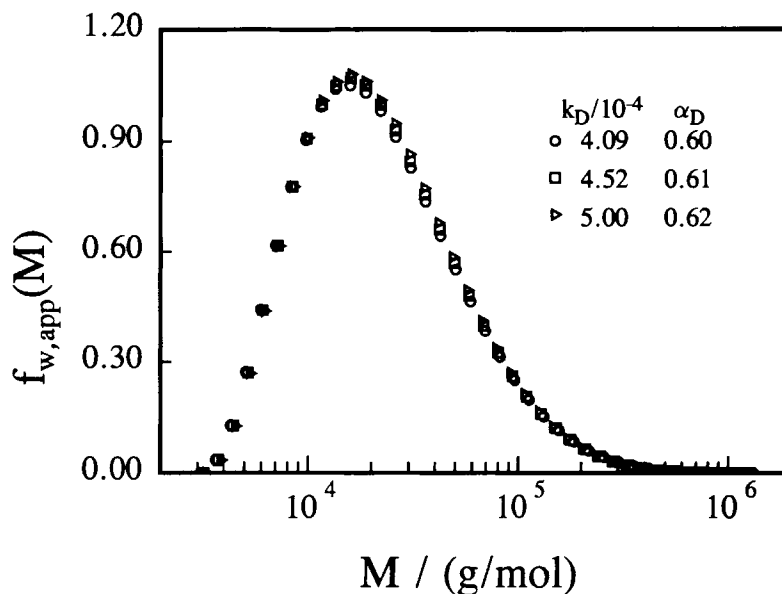


Figure 3 Comparison of three apparent molecular weight distributions of the 48% PET/PET-PCL segmented copolymer in THF, calculated using eqs. (11) and (13), with three different pairs of k_D and α_D .

where γ is a normalization constant. Normally, D can be related to M by using two scaling constants, k_D and α_D , that is

$$D = k_D M^{-\alpha_D} \quad (11)$$

where both k_D and α_D are independent on M for a given solvent and chain composition in given experimental conditions. Using eq. (11), we can re-written eq. (10) as

$$\int_0^\infty G(D) \frac{dD}{dM} dM = \gamma \cdot \int_0^\infty f_w(M) M \left(\frac{\nu(M)}{\nu} \right)^2 dM. \quad (12)$$

After comparing both sides of eq. (12), we have

$$f_{w,app}(M) = f_w(M) \left(\frac{\nu(M)}{\nu} \right)^2 \propto \frac{G(D)}{M} \cdot \frac{dD}{dM}, \quad (13)$$

where all proportional constants have been omitted because they are irrelevant to both distributions. For a given set of k_D and α_D , we are able to convert $G(D)$ into $f_{w,app}(M)$ by using eqs. (11) and (13).

As stated by Chu et al.,⁷ if the above procedure was repeated by using two solvents (s1 and s2) with different $\nu(M)$ and ν , we will have two different apparent weight distributions, $f_{w,app,s1}(M) = f_w(M)[\nu(M)/\nu]_{s1}^2$ and $f_{w,app,s2}(M) = f_w(M)[\nu(M)/\nu]_{s2}^2$

for a given copolymer sample. With the substitution of eq. (3), the ratio of two apparent weight distributions will be

$$\frac{f_{w,app,s1}(M)}{f_{w,app,s2}(M)} = \left\{ \frac{\nu_{s2}}{\nu_{s1}} \cdot \frac{W_A(M)\nu_{A,s1} + [1 - W_A(M)]\nu_{B,s1}}{W_A(M)\nu_{A,s2} + [1 - W_A(M)]\nu_{B,s2}} \right\}^2 \quad (14)$$

where ν_{s1} , ν_{s2} , $\nu_{A,s1}$, $\nu_{A,s2}$, $\nu_{B,s1}$, and $\nu_{B,s2}$ can be separately determined by a differential refractometer.⁸ Hence we can solve eq. (14) to get $W_A(M)$, the chain-composition distribution of polymer A, from two apparent weight distributions. After having $W_A(M)$, we are ready to calculate $\nu(M)$ [by eq. (3)], $f_w(M)$ (by definition of $f_{w,app}$), and M_w (by definition of M_w).

EXPERIMENTAL

Sample

The synthesis of the segmented copolymer of PET-PCL was performed in two separate steps:⁹ step I involves the esterification of terephthalic acid and ethylene glycol in the presence of a catalyst at 190°C; and step II is a polycondensation of ET with CL in the presence of a catalyst under vacuum at 250°C. The content of PET in the copolymer is 48% by weight.

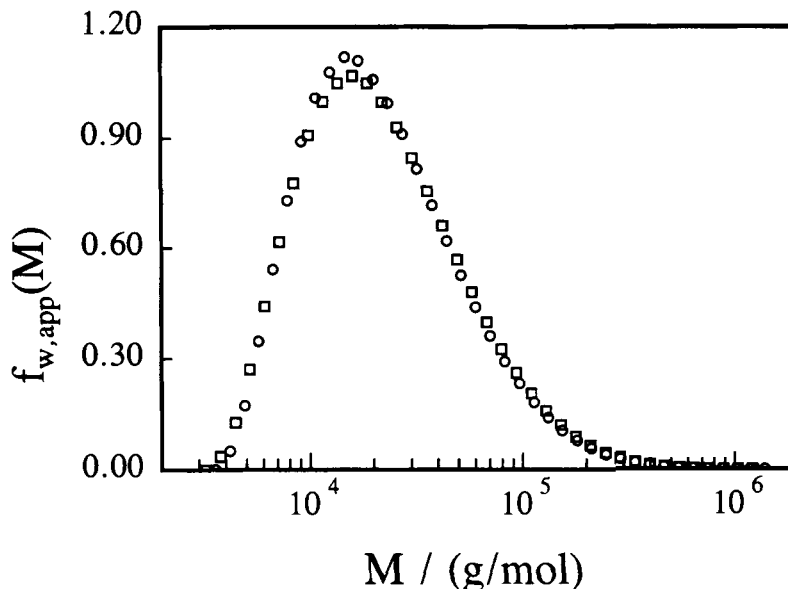


Figure 4 Apparent molecular weight distributions of the 48% PET-PCL segmented copolymer (○) in CHCl_3 and (□) in THF calculated from the distributions in Figure 2.

Solution Preparation

Two analytical grade solvents (Merck; chloroform, CHCl_3 , and tetrahydrofuran, THF) were used without further purification. The solution concentrations were in the range 1×10^{-3} to 6×10^{-3} g/mL. All polymer solutions were clarified at room temperature by using a 0.22- μm Millipore (Millex-GV₁₃) filter to remove dust.

LLS

A commercial LLS spectrometer (ALV DLS/SLS-5000, Langen, Hessen, Germany) was used with an argon ion laser (Coherent INNOVA 90, operated at wavelength 488 nm and 100 mW) as the light source. The primary beam is vertically polarized. All refractive index increments were determined by using a novel differential refractometer.¹⁰ The intensity-intensity time correlation functions was measured by an ALV 5000 multiple tau digital correlator. The detail of LLS instrumentation can be found elsewhere.⁵ All measurements were done at $25.0 \pm 0.2^\circ\text{C}$.

RESULTS AND DISCUSSION

Figure 1 shows a typical Zimm plot of 48% PET in chloroform. On the basis of eq. (1), we can calculate $M_{w,\text{app}}$, A_2 , and $\langle R_g^2 \rangle_Z^{1/2}$ from the extrapo-

lation of $[KC/R_{vv}(\theta)]_{\theta \rightarrow 0, C \rightarrow 0}$ and $[KC/R_{vv}(\theta)]_{\theta \rightarrow 0}$ vs. C and $[KC/R_{vv}(\theta)]_{C \rightarrow 0}$ vs. q^2 , respectively. The results are summarized in Table I. We should note that the molecular sizes of 48% PET are so small that the scattering intensities are virtually independent of the scattering angle. Therefore, it is impossible to determine the exact values of $\langle R_g^2 \rangle_Z^{1/2}$. The positive values of A_2 indicate that both CHCl_3 and THF are good solvents for the PET-PCL sample at 25°C .

Figure 2 shows two translational diffusion coefficient distributions of 48% PET in chloroform and tetrahydrofuran at 25°C . In the process of reducing $G(\Gamma)$ to $G(D)$, we have used \bar{f} and \bar{k}_d in Wu et al.² to get the $G(D)$ value at $\theta \rightarrow 0$ and $C \rightarrow 0$. On the basis of eq. (7), we can see that the correction of $(1 + \bar{k}_d C)(1 + \bar{f} \langle R_g^2 \rangle_Z q^2)$ are a few percent. The values of average \bar{D} in two solvents are listed in Table I. $G(D)$ in Figure 2 can be converted to $f_{w,\text{app}}(M)$ for a given pair of α_D and k_D . From the previous study,² we know that $\alpha_D = 0.61 \pm 0.01$ for a 58% PET sample in CHCl_3 and THF. Because α_D is only related to the polymer chain conformation in solution, we have assumed that for the 48% PET sample α_D remained unchanged.

Figure 3 shows that a slight mischoice of α_D has no significant effect on the final apparent molecular weight distribution. With this α_D we can determine k_D from $M_{w,\text{app}}$ and $G(D)$ by using the following equation¹¹⁻¹³

$$M_{w,\text{app}} = \frac{k_D^{1/\alpha_D} \int_0^\infty G(D) dD}{\int_0^\infty G(D) D^{1/\alpha_D} dD}. \quad (15)$$

The values of k_D and α_D for 48% PET sample in two solvents are listed in Table I. After having k_D and α_D , we are ready to transfer $G(D)$ in Figure 2 into $f_{w,\text{app}}(M)$ by eqs. (11) and (13).

Figure 4 shows two apparent molecular weight distributions based on two diffusion coefficient distributions in Figure 2. One interesting result in Figure 4 is that the two apparent weight distributions are almost identical if we consider the uncertainties in the experiment. This suggested that the chain composition [$W_{\text{PET}}(M)$ and $W_{\text{PCL}}(M)$] are nearly independent of M . Therefore, $f_{w,\text{app}}(M)$ s in Figure 4 represent an approximation of the true molecular weight distribution $f_w(M)$. The M_w/M_n calculated from $f_w(M)$ is ~ 2.1 that is slightly greater than 2.0 predicted by the polycondensation reaction kinetics. This might be due to the uncertainties introduced in both the experiment and the data analysis.

CONCLUSION

The molecular weight distribution of the PET-PCL segmented copolymer with 48% PET content was characterized by a combination of static and dynamic LLS where only two solvents were used. We found that the chain composition of this segmented copolymer is nearly independent of its molecular weight, so that the apparent molecular weight distributions in CHCl_3 and THF can be treated as the true molecular weight distribution. The successful application of this two-solvent LLS method to the 48% PET sample further shows that the following procedure can be used as a general method to characterize segmented copolymers. In this two-solvent

LLS method, one can first determine the apparent molecular weight M_w in two solvents from static LLS, then two apparent weight distributions $f_{w,\text{app}}(M)$ from dynamic LLS. Further, a ratio of these two $f_{w,\text{app}}(M)$ s at each M will lead to the chain composition $W_A(M)$. Finally, the true molecular weight distribution $f_w(M)$ can be calculated from $f_{w,\text{app}}(M)$ and $W_A(M)$.

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