

# Study of Segmented Ethylene Terephthalate–Caprolactone Copolymer by Differential Refractometry and Light Scattering

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## SYNOPSIS

A segmented ethylene terephthalate (ET)–caprolactone (CL) copolymer was characterized by light scattering in chloroform tetrahydrofuran and butanone. The flexibility of the copolymer chain is comparable with that of typical flexible chains, such as polystyrene. In the process of applying the Bushuk–Benoit light scattering theory to the segmented PET–PCL copolymer, we encountered not only the problem of finding three solvents with different refractive index but also the problem of determining the specific refractive index increments for the PET and PCL segments in the copolymer, i.e.,  $\nu_{\text{PET}}$  and  $\nu_{\text{PCL}}$ . In principle, the approximate values of  $\nu_{\text{PET}}$  and  $\nu_{\text{PCL}}$  can be obtained from the PET and PCL homopolymers, respectively. In reality, it involves many practical problems, e.g., to find three solvents not only for copolymer but also for the PET and PCL homopolymers. In this study, a different method was used to find both  $\nu_{\text{PET}}$  and  $\nu_{\text{PCL}}$ , wherein the  $\nu$  values of at least two segmented PET–PCL copolymers with different PET compositions were used. With  $\nu_{\text{PET}}$ ,  $\nu_{\text{PCL}}$ , and  $\nu$ , we characterized the absolute molecular weight. Further, we show that the composition of an unknown segmented PET–PCL copolymer can be estimated from  $\nu_{\text{PET}}$ ,  $\nu_{\text{PCL}}$ , and  $\nu$ .

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## INTRODUCTION

The segmented ethylene terephthalate (ET)–caprolactone (CL) copolymer (PET–PCL) is a thermal viscoelastic material. The hard segments (PET) can crystallize to form the physical crosslinking points. Usually, the soft segments (PCL) are not expected to form crystalline, so that they contribute to the elasticity of the materials. As the amount of PET increases, this polymer can gradually change from a low module elastomer to a high module tough plastic. Therefore, its characterization, especially its absolute molecular weight and chain composition, is crucially important to its various applications.

For the determination of the absolute weight-average molecular weight of copolymers, a theoretical treatment of copolymer in solution was first developed by Stockmayer et al.<sup>1</sup> and then refined into a

more practical form by Bushuk and Benoit<sup>2</sup> a long time ago, which shows that the apparent weight-average molecular weight ( $M_{w,\text{app}}$ ) obtained from a light-scattering experiment is related to the absolute weight-average molecular weight ( $M_w$ ) by

$$M_{w,\text{app}} = M_w + 2P\left(\frac{\nu_A - \nu_B}{\nu}\right) + Q\left(\frac{\nu_A - \nu_B}{\nu}\right)^2 \quad (1)$$

with  $P = \sum W_i M_i (x_i - \langle x \rangle)$  and  $Q = \sum W_i M_i (x_i - \langle x \rangle)^2$ , where  $\nu_A$ ,  $\nu_B$ , and  $\nu$  are the specific refractive index increments of segment A, segment B, and copolymer, respectively;  $x_i$  is the composition of A component in a copolymer molecule with a molecular weight  $M_i$ , and  $\langle x \rangle$  is the average composition. For each chosen solvent, we can obtain one set of  $M_{w,\text{app}}$ ,  $\nu_A$ ,  $\nu_B$ , and  $\nu$ . In order to solve Eq. (1), we will have to use at least three solvents with as large as possible difference in the refractive index ( $n$ ). Thus, the application of Eq. (1) requires at least three times the amount of work in comparison with that for a ho-

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mopolymer.<sup>3-7</sup> Besides this time-consuming nature, on the one hand, there is no guarantee that we are able to find three solvents with different  $\nu_A$ ,  $\nu_B$ , and  $\nu$  in practice for a given type of copolymer, and on the other hand, even if there exist three solvents, we may still have problems obtaining the true values of  $\nu_A$  and  $\nu_B$  of the segments in copolymer since  $\nu$  is a function of molecular weight when the segment length is short, i.e.,  $\nu_A$  and  $\nu_B$  obtained from a high-molecular-weight homopolymer might be quite different from that of the corresponding small segments in copolymer.

For a given copolymer, we are often interested in its average composition  $\bar{x}$  and composition distribution  $x_i$ . Sometimes, even finding  $\bar{x}$  is very difficult, e.g., if monomers A and B are unevenly consumed in an incomplete A-B copolymerization, we may not be able to use the initial ratio of A to B as  $\bar{x}$ .

In this work, we present a study of the segmented PET-PCL copolymer. A simple, but different, method was used to get the precise refractive index increments of both the PET and PCL segments in the copolymer, i.e.,  $\nu_{\text{PCL}}$  and  $\nu_{\text{PET}}$ , wherein the  $\nu$  values of several PET-PCL copolymers with different compositions were used. On the base of Eq. (1), we calculated  $M_w$  from three values of  $M_{w,\text{app}}$  obtained in each of three solvents by laser light scattering.

## BASIC PRINCIPLES

For a dilute solution at concentration  $C$ , the measured Rayleigh ratio  $R_{\nu\nu}(\theta)$  in static light scattering at angle  $\theta$  can be approximately expressed as<sup>2,7,8</sup>

$$\frac{HC}{R_{\nu\nu}(\theta)} \cong \frac{1}{M_{w,\text{app}}} \left( 1 + \frac{1}{3} \langle R_g^2 \rangle_z^{1/2} q^2 \right) + 2A_2C \quad (2)$$

where  $H = 4\pi^2 n^2 \nu^2 / (N_A \lambda_0^4)$  and  $q = (4\pi n / \lambda_0) \sin(\theta/2)$  with  $N_A$ ,  $n$ , and  $\lambda_0$  being Avogadro's number, the solvent refractive index, and the wavelength of light *in vacuo*, respectively.  $A_2$  is the second-order virial coefficient.  $M_{w,\text{app}}$  defined as the apparent weight-average molecular weight is related to  $\nu$  by

$$M_{w,\text{app}} = \int_0^\infty f_w(M) \left[ \frac{\nu(M)}{\nu} \right]^2 M dM \quad (3)$$

where  $f_w(M)$  is the weight distribution;  $\nu(M)$  the refractive index increment for copolymer molecules with molecular weight  $M$  and weight distribution  $f_w(M)$ . It can be seen that  $f_w(M) [\nu(M)/\nu]^2$  can be defined as an apparent weight distribution,

$f_{w,\text{app}}(M)$ . Based on the additivity principle of  $\nu$  for a segmented A/B copolymer,<sup>1</sup>

$$\nu(M) = w_A(M)\nu_A + w_B(M)\nu_B \quad (4)$$

and

$$\nu = w_A\nu_A + w_B\nu_B \quad (5)$$

where  $w_A(M) [ = 1 - w_B(M) ]$  is the weight fraction of segment A (i.e., composition) in the particular copolymer chain whose molecular weight and weight distribution are  $M$  and  $f_w(M)$ , respectively.  $w_A (= 1 - w_B)$  is the average weight fraction of segment A in the copolymer. It is obvious from Eqs. (3), (4), and (5) that for a uniform copolymer chain composition, i.e.,  $w_A(M) = w_A$ ,  $w_B(M) = w_B$  and  $\nu(M) = \nu$ ,  $M_{w,\text{app}}$  will be reduced to the true weight-average molecular weight,  $M_w$ . For each solvent, by measuring  $R_{\nu\nu}(\theta)$  at a set of  $C$  and  $\theta$ , we can determine  $M_{w,\text{app}}$ ,  $\langle R_g^2 \rangle_z^{1/2}$ , and  $A_2$  from a so-called Zimm plot.

For each chosen solvent, in principle, we could obtain the approximations of  $\nu_A$  and  $\nu_B$  by measuring  $\nu$  of the corresponding homopolymers with a similar molecular weight as the segments in the copolymer, where we have to assume that both  $\nu_A$  and  $\nu_B$  are independent on molecular weight. But, this procedure is usually limited by several practical reasons: (i) homopolymers are not available; (ii) the segments in the copolymer are quite different from homopolymers in  $M$ ; and (iii) three common solvents not only for the copolymer, but also for both homopolymers, are not available. Considering these difficulties, we solved this problem in a different way. Equation (5) can be rewritten as

$$\nu = \nu_B + (\nu_A - \nu_B)w_A \quad (6)$$

It shows that  $\nu_B$  and  $(\nu_A - \nu_B)$  can be solved if we have at least two values of  $\nu$  from two copolymer samples that have the same types of segments A and B, but different compositions. With this simple method, the above-mentioned problems are simultaneously solved. In reverse, with the precise values of  $\nu_A$ ,  $\nu_B$ , and  $\nu$ , we are able to estimate the composition of an unknown copolymer sample, such as the samples obtained from fractionation, which might have different compositions in comparison with the original copolymer.

## EXPERIMENTAL

### Samples

The detail synthesis of the segmented PET-PCL copolymer has been reported previously.<sup>9</sup> The syn-

thesis was performed in two separate steps: the first is an esterification of terephthalic acid and ethylene glycol at 190°C; and the second a polycondensation of ethylene terephthalic acid with poly-(caprolactone) diol ( $M_n = 2000$ ) under vacuum at 250°C. The content of ET in the copolymer can be controlled by the initial ratio of ET to CL. Four samples with different ET contents (13, 48, 58, and 72%) were prepared.

### Solution Preparation

Three analytical-grade solvents (chloroform, butanone, and tetrahydrofuran) were used without further purification. The copolymer concentrations were in the range of  $1 \times 10^{-3}$  to  $5 \times 10^{-3}$  g/mL. Before the light-scattering and differential refractive index measurements, all solutions were clarified at room temperature by using a 0.1- $\mu\text{m}$  Millipore filter in order to remove dust.

### Laser Light Scattering

A commercial laser light-scattering spectrometer (ALV DLS/SLS-5000, Langen in Hessen, Germany) was used with an argon ion laser (Coherent INNOVA 90, operated at wavelength 488 nm and 400 mW) as the light source. The primary beam is vertically polarized. By placing a polarizer in front of the detector, we measured only the vertically polarized scattered light. Laser light-scattering instrumentation and its operation can be found elsewhere.<sup>8</sup> All laser light-scattering experiments were done at  $25.0 \pm 0.1^\circ\text{C}$ .

### Refractive Index Increment

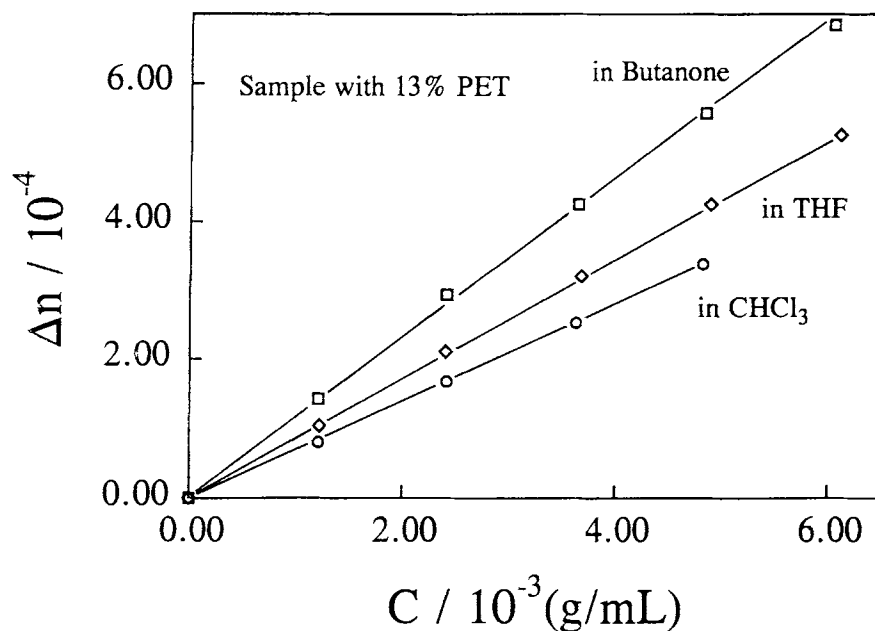
All refractive index increments were determined by using our recently developed differential refractometer.<sup>10</sup> In this novel refractometer, a small pinhole with a diameter of 400  $\mu\text{m}$  is illuminated with a laser light. The illuminated pinhole is imaged to a position-sensitive detector (Hamamatsu S 3932) by a lens located in equal distance between the pinhole and the detector. The distance between the detector and the pinhole is four times the focal length ( $f = 10$  cm) of the lens, i.e., we have used a ( $2f - 2f$ ) optical design instead of a conventional ( $1f$ ) design where a parallel incident light beam is used, and the distance between the detector and the lens is only one focal length. This ( $2f - 2f$ ) design is *optically* equivalent to placing the detector directly behind the pinhole, so that the laser beam drift is eliminated. A refractometer cuvette (Hellma 590.049-QS)

is placed just in front of the lens. The pinhole, the cuvette, the lens, and the detector are rigidly mounted on a small optical rail. The refractometer has dimensions of only 40 cm in length, 15 cm in width, and 10 cm in height. The output voltage of the detector is proportional to the displacement of the light spot from the center of the detector. The detector resolution is 0.2  $\mu\text{m}$ , which corresponds a resolution of  $10^{-6}$  in the refractive index measurement. This refractometer has been incorporated into our existing laser light-scattering spectrometer, wherein the same laser has been used as the light sources in both the laser light-scattering spectrometer and differential refractometer. Thus, the problem of wavelength correction is eliminated. In comparison with a conventional differential refractometer where a micrometer is normally used to read the beam displacement, the use of the position-sensitive detector together with the data acquisition system not only increases the accuracy of measured  $\nu$  but also makes a large amount of measurements possible and easier.

## RESULTS AND DISCUSSION

Figure 1 shows a typical concentration dependence of the refractive index difference ( $\Delta n$ ) between the polymer solution and solvent for the segmented ET-CL sample with 13% ET, where the lines are the results of the least-square fitting. The copolymer samples with high content of ET (> 58% in weight) are not soluble in butanone and tetrahydrofuran. Later, we found experimentally that both tetrahydrofuran and butanone are poor solvents for poly(ethylene terephthalate) (PET). Therefore, we could not directly measure the specific refractive index increments of homopolymer PET in both butanone and tetrahydrofuran. Due to the quite different nature of the PET segments and PCL segments, it is nearly impossible in practice to find three solvents, which not only have enough contrast in refractive index but also dissolve poly(caprolactone) and poly(ethylene terephthalate) and the segmented copolymer.

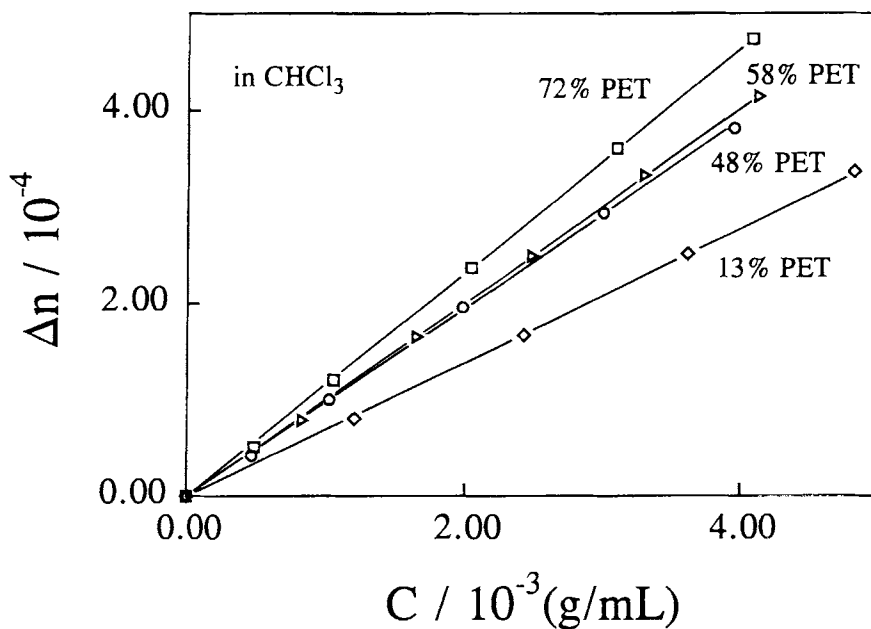
Figure 2 shows the concentration dependence of the refractive index difference ( $\Delta n$ ) for four segmented PET-PCL copolymers with different ET contents (up to 72%) in chloroform, where the lines represent the least-square fitting. The specific refractive index increment  $\nu$  of each sample in each chosen solvent can be calculated from the slope of the corresponding line of  $\Delta n$  vs.  $C$ . It can be seen from Figure 2 that the slope increases as the ET



**Figure 1** Typical concentration dependence of the refractive index difference ( $\Delta n$ ) between the polymer solution and solvent for the segment ethylene terephthalate/caprolactone copolymer with 13% ethylene terephthalate, where the lines are the least-square fitting results.

content, which means that  $\nu_{\text{PET}}$  is higher than  $\nu_{\text{PCL}}$ . The calculated  $\nu$  values of four segmented copolymers with different ET contents in three chosen solvents are summarized in Table I.

On the one hand, due to the solubility problem stated before, the  $\nu$  values of PET and the copolymers with higher ET content are not obtainable for tetrahydrofuran and butanone. On the other hand,



**Figure 2** Concentration dependence of the refractive index difference ( $\Delta n$ ) for four segmented ethylene terephthalate/caprolactone copolymers with different ethylene terephthalate contents in chloroform, where the lines represent the least-square fitting.

**Table I** Specific Refractive Index Increments ( $\nu$ ) of Segmented ET-CL Copolymers with Different Amounts of ET<sup>a</sup>

Sample (% ET)	$\nu$ (mL/g) in Solvents at 25°C		
	Chloroform	Tetrahydrofuran	Butanone
13	$7.09 \times 10^{-2}$	$8.99 \times 10^{-2}$	$1.20 \times 10^{-1}$
48	$1.00 \times 10^{-1}$	$1.20 \times 10^{-1}$	$1.49 \times 10^{-1}$
58	$1.05 \times 10^{-1}$	$1.29 \times 10^{-1}$	—
72	$1.20 \times 10^{-1}$	—	—

<sup>a</sup> Relative uncertainty of all measured  $\Delta n$  is about  $\pm 1\%$ .

according to Eq. (1), we have to have  $\nu_{\text{PET}}$  and  $\nu_{\text{PCL}}$  in each chosen solvents so that we are able to calculate the absolute weight-average molecular weight.

Figure 3 shows a plot of specific refractive index increment ( $\nu$ ) versus the ET content ( $W_{\text{ET}}$ ) in chloroform, butanone, and tetrahydrofuran. Based on Eq. (6) where A and B can be read as PET and PCL, respectively, we know that the plot of  $\nu$  versus  $W_{\text{ET}}$  should be a straight line, and the intercepts at the ends of  $W_{\text{ET}} = 1$  and  $W_{\text{ET}} = 0$  are  $\nu_{\text{PET}}$  and  $\nu_{\text{PCL}}$ , respectively. The lines in Figure 3 are the least-square fitting results. The values of  $\nu_{\text{PET}}$  and  $\nu_{\text{PCL}}$  from the extrapolation, i.e., the least-square fitting, are listed in Table II. In reverse, we were able to use these  $\nu$  values in practice to estimate the composition

**Table II** Specific Refractive Index Increments of PET and PCL in Chloroform, Tetrahydrofuran, and Butanone at 25°C<sup>a</sup>

Solvent	$\nu_{\text{PET}}^b$	$\nu_{\text{PCL}}^b$	$\nu_{\text{PCL}}^c$
Chloroform	$1.43 \times 10^{-1}$	$6.03 \times 10^{-2}$	$4.71 \times 10^{-2}$
Tetrahydrofuran	$1.65 \times 10^{-1}$	$7.88 \times 10^{-2}$	$7.39 \times 10^{-2}$
Butanone	$1.94 \times 10^{-1}$	$1.08 \times 10^{-1}$	$1.18 \times 10^{-1}$

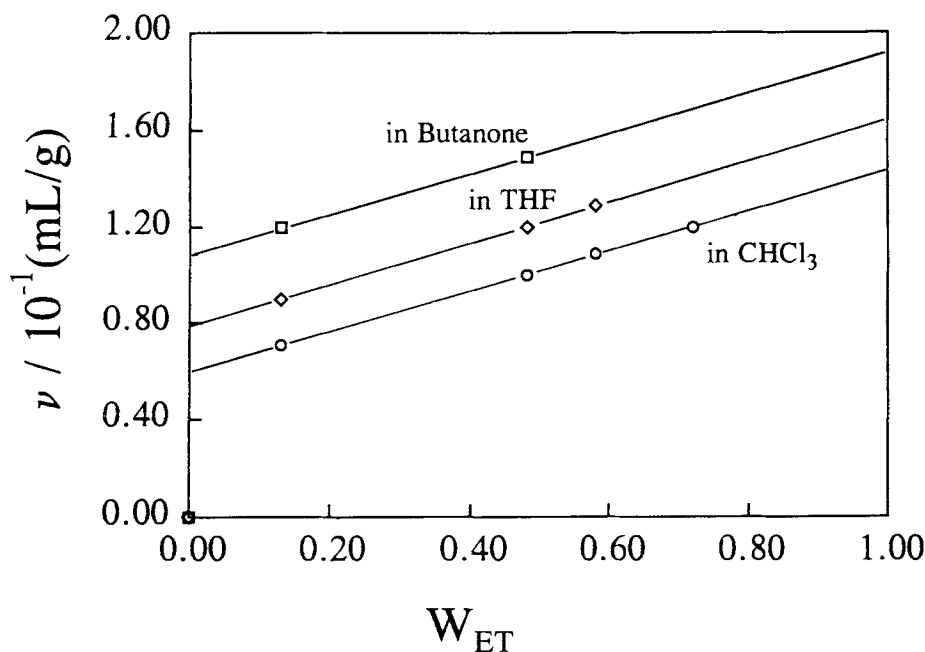
<sup>a</sup> Relative uncertainty of all measured  $\Delta n$  is about  $\pm 2\%$ .

<sup>b</sup> Calculated from  $\nu$  and  $W_{\text{PET}}$  according to Eq. (6).

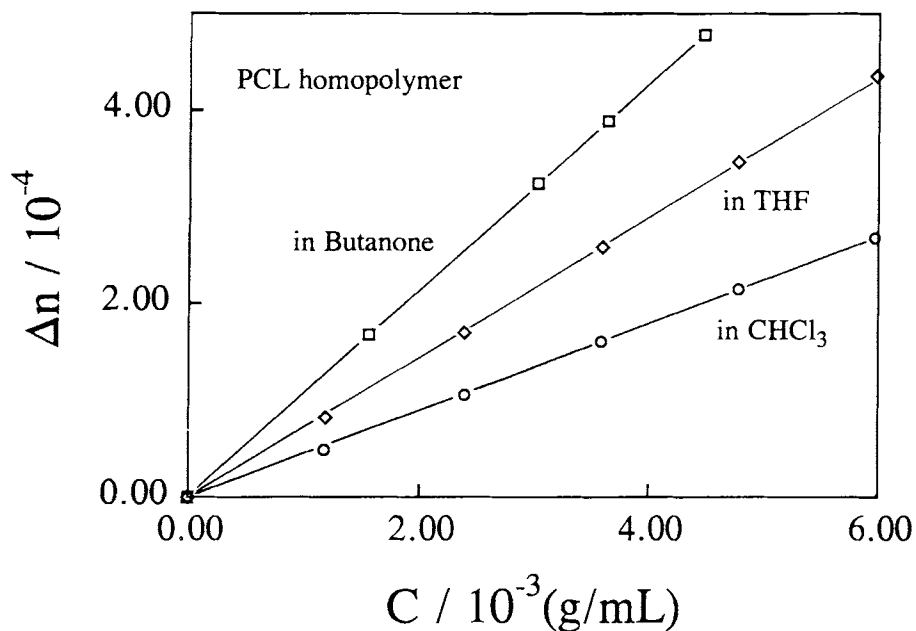
<sup>c</sup> Measured directly from the PCL homopolymer ( $M_n = 2000$ ).

of an unknown PET-PCL copolymer sample, such as the copolymer samples obtained from the fractionation of a given PET-PCL copolymer. The validity of this application of  $\nu_{\text{PET}}$  and  $\nu_{\text{PCL}}$  has been confirmed by using a PET-PCL copolymer with a known composition of 72% ET. The relative error of the calculated composition from  $\nu$ ,  $\nu_{\text{PET}}$ , and  $\nu_{\text{PCL}}$  to the initial ratio of ET-CL is only  $\pm 2\%$ .

Naturally, we like to find any existing difference between the values of  $\nu_{\text{PET}}$  and  $\nu_{\text{PCL}}$  obtained from Figure 3 and from the direct measurements of the PCL and PET homopolymers. However, for the reason (solubility) mentioned before, we are not able to measure the values of  $\nu_{\text{PET}}$  in tetrahydrofuran and butanone. Actually, it is not necessary for us to compare both the values of  $\nu_{\text{PET}}$  and  $\nu_{\text{PCL}}$ , since they are interconnected through Eqs. (5) and (6).



**Figure 3** Plot of specific refractive index increment ( $\nu$ ) vs. the ethylene-terephthalate (ET) content ( $W_{\text{ET}}$ ) in chloroform, butanone, and tetrahydrofuran. The lines are the least-square fitting results.

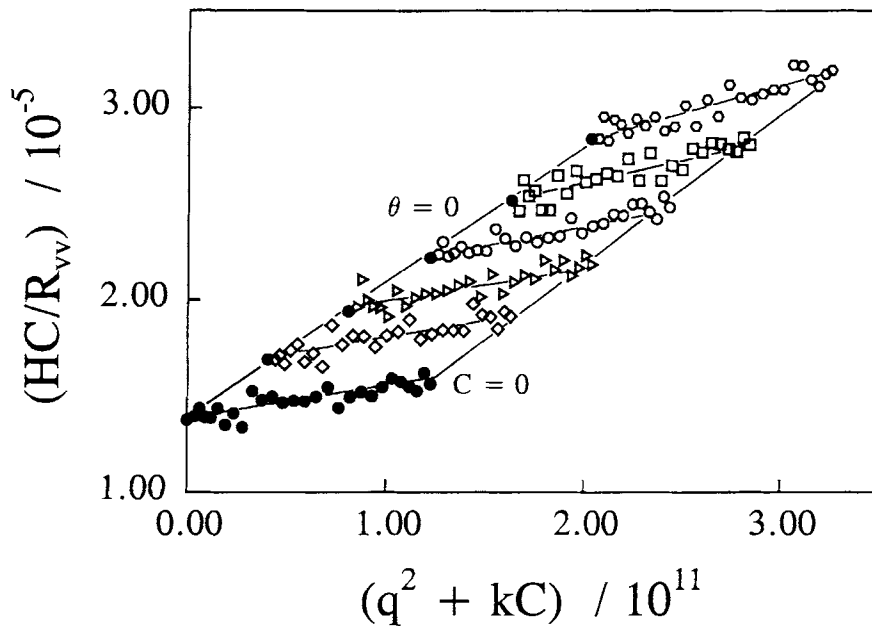


**Figure 4** Concentration dependence of the refractive index difference ( $\Delta n$ ) between the polymer solution and solvent for poly(caprolactone) diol (a homopolymer,  $M_n = 2000$ ) in chloroform, tetrahydrofuran, and butanone, where the lines represent the least-square fitting.

Therefore, we only did the specific refractive index measurements on poly(caprolactone) diol (a PCL homopolymer,  $M_n = 2000$ ) in three chosen solvents.

Figure 4 shows the concentration dependence of

the refractive index difference ( $\Delta n$ ) for the sample of poly(caprolactone) diol ( $M_n = 2000$ ) in chloroform, butanone, and tetrahydrofuran, where the lines represent the least-square fitting. The specific



**Figure 5** Typical Zimm-plot for the segmented ethylene terephthalate/caprolactone copolymer with 13% ethylene terephthalate in tetrahydrofuran at 25°C.

**Table III Laser Light-Scattering Results of a Segmented ET-CL Copolymer with 13% ET at 25°C**

	$10^{-4}M_{w,app}$	$\langle R_g^2 \rangle_z^{1/2}$ (nm)	$10^3 A_{2,app}$ (mol · mL/g <sup>2</sup> )	$10^{-4}M_w$ (g/mol)	$10^{-4}P$ (g/mol)	$10^{-4}Q$ (g/mol)
Chloroform	7.84	28	2.4	6.58	-0.19	1.24
Tetrahydrofuran	7.35	22	1.2			
Butanone	6.94	21	0.6			

refractive index increments calculated from the slopes of the lines are also listed in Table II (the third column). As we expected, they are different from the corresponding  $\nu_{PCL}$  values calculated from  $\nu$  and  $W_{PET}$ . In comparison with the PCL segments in the PET-PCL copolymer, the hydrogen atoms at both ends of poly(caprolactone) diol are replaced by the PET segments that have a different refractive index. The difference in  $\nu_{PCL}$  show that in the application of Eq. (1) we cannot simply replace the  $\nu$  values of the segments in a given copolymer with that of the corresponding homopolymers, even when the average length of the segments is similar to that of the corresponding homopolymers.

Figure 5 shows one typical Zimm plot for the segmented PET-PCL copolymer with 13% ET in tetrahydrofuran at 25°C. Based on Eq. (2), we were able to calculate  $A_2$ ,  $\langle R_g^2 \rangle_z^{1/2}$  and  $M_{w,app}$  from the data of  $(HC/R_{vv})_{\theta \rightarrow 0}$ ,  $(HC/R_{vv})_{C \rightarrow 0}$ , and  $(HC/R_{vv})_{\theta \rightarrow 0, C \rightarrow 0}$ , respectively. The laser light-scattering results in three chosen solvents are summarized in Table III. The  $M_{w,app}$  are different from each other in the three solvents. In chloroform, the value of  $\langle R_g^2 \rangle_z^{1/2}$  is similar to that of polystyrene with a similar chain length in good solvent, which shows that the segmented copolymer chain is still very flexible, even though it contains the PET segments. This flexibility is mainly due to the flexible ether linkages in the main copolymer chain. The relatively small values of  $\langle R_g^2 \rangle_z^{1/2}$  and  $A_2$  in butanone show that butanone as a solvent is not very good. By using Eq. (1) and  $\nu$ ,  $\nu_{PET}$ , and  $\nu_{PCL}$  in Tables I and II, we determined not only the absolute weight-average molecular weight ( $M_w = 6.58 \times 10^4$  g/mol) but also the *estimate* values of both  $P$  and  $Q$ . It is interesting to note that  $P$  has a negative value, which implies that the species with less ET content are weighted more in the distribution  $W_i M_i$ . If  $P$  and  $Q$  in Eq. (1) is divided by  $\sum_i W_i M_i$  (i.e., divided by  $M_w$ ), we have

$$\frac{P}{M_w} = \frac{\sum_{i=1}^N W_i M_i x_i}{M_w - \langle x \rangle} = \langle x \rangle_z - \langle x \rangle \quad (7)$$

and

$$\frac{Q}{M_w} = \frac{\sum_{i=1}^N W_i M_i (x_i - \langle x \rangle)^2}{M_w} = \mu_2(x) \quad (8)$$

By using the known values of  $\langle x \rangle$ ,  $M_w$ ,  $P$ , and  $Q$ , we were able to calculate  $\langle x \rangle_z$  and  $\mu_2(x)$  on the base of Eqs. (7) and (8), which are  $1.01 \times 10^{-1}$  and  $1.88 \times 10^{-1}$ , respectively. The ratio of  $\mu_2(x)/\langle x \rangle_z^2$  ( $\approx 18.5$ ) characterizes the distribution width, which shows that the composition distribution ( $x_i$ ) in the  $W_i M_i$  space is broad. This is why the correction of  $M_{w,app}$  to  $M_w$  is as high as 20%, which is quite significant.

## CONCLUSION

We have accomplished laser light-scattering characterization of the segmented ET-CL copolymers in chloroform, butanone, and tetrahydrofuran. In the characterization process, we have shown that a different method can be used to solve the problem of measuring the specific refractive index increments of both the PET and PCL segments in each of three chosen solvents, wherein the specific refractive index increments of two or more segmented copolymers with different ET content were used. In principle, this method can also be useful for the characterization of a random copolymer. With such obtained specific refractive index increments, we will be able to estimate the segment composition of an unknown segmented PET-PCL copolymer sample.

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## REFERENCES

1. W. H. Stockmayer, L. D. Jr. Moore, M. Fixman, and B. N. Epstein, *J. Polym. Sci.*, **16**, 517 (1955).

2. W. Bushuk and H. Benoit, *Can. J. Chem.*, **36**, 1616 (1958).
3. M. Leng and H. Benoit, *J. Polym. Sci.*, **57**, 263 (1962).
4. J. Prud'homme and S. Bywater, *Macromolecules*, **4**, 543 (1971).
5. J. G. Zilliox, J. E. L. Roovers, and S. Bywater, *Macromolecules*, **8**, 573 (1975).
6. T. Tanaka, T. Kobata, and H. Inagaki, *Macromolecules*, **9**, 561 (1976).
7. B. Chu, Q. C. Ying, D. C. Lee, D. Q. Wu, *Macromolecules*, **18**, 1962 (1985).
8. B. Chu, *Laser Light Scattering*, Academic Press, New York, 1974.
9. X. Lau, D. Z. Ma, and D. Z. Du, *J. Univ. Sci. Tech. China*, **3**, 280 (1986).
10. C. Wu and K. Q. Xia, *Rev. Scient. Instrum.*, to appear.

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