Macromolecules **1993,** *26,* 3289–3294

Effect of Biaxial Drawing Conditions on Orientation and Structure of Poly(ethylene terephthalate)

Kwang Hee Lee[†] and Chong Sook Paik Sung[*]

Institute of Materials Science, Department of Chemistry, University of Connecticut,
97 North Eagleville Road, Storrs, Connecticut 06269-3136

Received October 5, 1992; Revised Manuscript Received March 22, 1993

ABSTRACT: The effects of biaxial drawing conditions on the molecular orientation and other molecular structure of poly(ethylene terephthalate) (PET) were investigated by using a new FTIR attenuated total reflection attachment for dichroism studies and thermal analysis. The angular profiles of IR absorbances for the transverse electric and the transverse magnetic polarization were collected at 16 different angles around a horizontal axis and used for the orientation analysis. The results show that the orientation and the structure in biaxially drawn PET is determined in a complex way by the drawing rate, drawing temperature, and draw ratio. At slower drawing rates, higher orientation is obtained at lower drawing temperature due to the slower chain relaxation. At faster drawing rates, crystallization rates become an important factor in the determination of orientation. The overall increase in the trans isomer content as a consequence of drawing plays an important role in the determination of the orientation.

Introduction

It is well-known that the properties of the polymers are influenced by the crystallinity and the orientation of the polymer chains. In fact, one can take advantage of such an influence in order to manipulate mechanical, optical, and electrical properties in a given polymer.

Poly(ethylene terephthalate) (PET) is a polymer widely used as fibers and films. Amorphous PET has lower strength and dimensional stability, requiring stretching and/or annealing above its glass transition temperature in order to increase molecular orientation and crystallinity for many commercial applications. The changes in orientation and crystallinity are strongly affected by such drawing conditions as drawing rate and temperature, prompting extensive research in PET since the early 1960s.[1–12] However, most of this research has addressed the uniaxial drawing process, rather than the biaxial drawing process.

In this paper, we studied the effects of biaxial drawing conditions on the molecular orientation and other molecular structure of PET by using FTIR attenuated total internal reflection (ATR) dichroism and thermal analysis.

Experimental Section

Materials. Biaxially drawn PET samples were provided by SKC, Ltd., of Korea. The viscosity molecular weight of PET was about 17 000 based on its intrinsic viscosity of 0.54 in *o*-chlorophenol at 25 °C. The undrawn PET films (dimensions of 10 cm × 10 cm with a thickness of 300 μm) were placed in a biaxial drawing device which was preheated at 60 °C. Biaxial drawing was carried out by further heating to 80, 87, or 94 °C with drawing speed of 2, 10, or 50 mm/s. Three draw ratios of 2 × 2, 3 × 3, and 4 × 4 were used. Samples were cooled quickly following drawing, in order to reduce chain relaxation and annealing effects.

FTIR ATR Setup

A truncated KRS-5 crystal with a specially made attachment was used to probe the surface of PET films. The angular profiles of IR absorbances around a horizontal axis were obtained from these surfaces. The details of the new crystal and attachment are described in a previous paper from our laboratory.[13] Figure 1 is the side view of the new truncated crystal, which also shows the multiple internal reflections in the crystal. Figure 2 is a schematic drawing showing the new ATR crystal, sample holder, and optical arrangement. The probing depth at 1000 cm^{-1} under the experimental condition was about 4 μm, since the incident angle to the crystal was 60°.

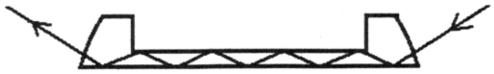


Figure 1. Schematic of the side view of a truncated ATR crystal with multiple reflection path illustrated.

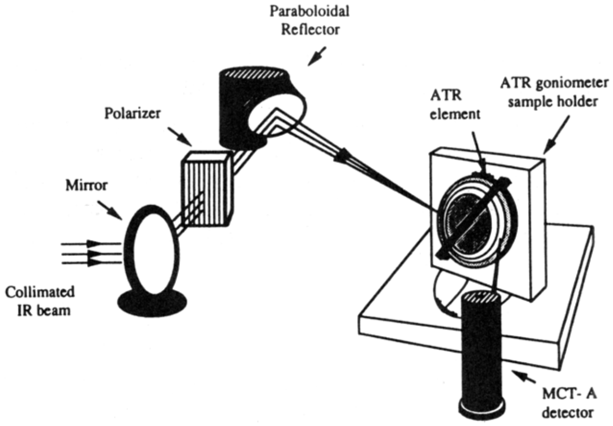


Figure 2. Schematic of the optical arrangement showing the new ATR crystal and its holder in a FTIR instrument.

ATR Analysis

The IR absorbancies (A_x, A_y, and A_x) along three coordinate axes are influenced by molecular orientation, crystallinity, and other structural factors in polymer films. According to Flournoy and Schaffers,[14,15] they are related to the ATR intensities for the transverse electric (A_{TE}) and the transverse magnetic (A_{TM}) polarization, according to eqs 1 and 2.

$$A_{TE} = \alpha A_x \tag{1}$$

$$A_{TM} = \beta A_y + \gamma A_z \tag{2}$$

In these equations, we define *x* and *y* as orthogonal biaxial draw directions on the film surface, while *z* is the thickness direction. The values of α, β, and γ are the constants

---

[†] Present address: High Performance Polymer Laboratory, Korea Institute of Science and Technology, 130-650, P.O. Box 131, Cheongryang, Seoul, Korea.

0024-9297/93/2226-3289$04.00/0 © 1993 American Chemical Society

Table I. Assignments of Infrared Bands Investigated in PET (References 2 and 16)

	band (cm^{-1})	assignment	polarization[a]
structure- and orientation-sensitive band	1042	gauche	π
	973	trans	π
	896	gauche	π
	848	trans	π
orientation-sensitive band	875		σ
internal thickness	795		–

[a] Key: π, parallel dichroism; σ, perpendicular dichroism; –, no dichroism.

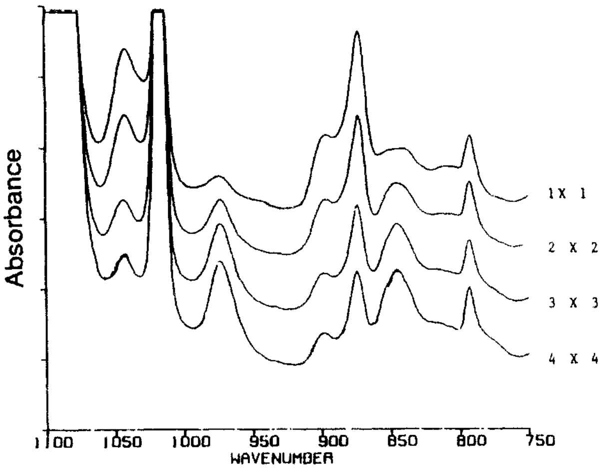


Figure 3. IR absorbance A_{TE} of PET films biaxially drawn at 87 °C and at 10 mm/s for different draw ratios.

determined by the refractive indices of the sample and the crystal and the angle of incidence.[14] In this study, we obtained many sets of A_{TE} and A_{TM} values from ATR spectra collected at 16 different angles. They were used in eqs 1 and 2 to estimate A_x, A_y, and A_z, as a function of drawing conditions.

Results and Discussion

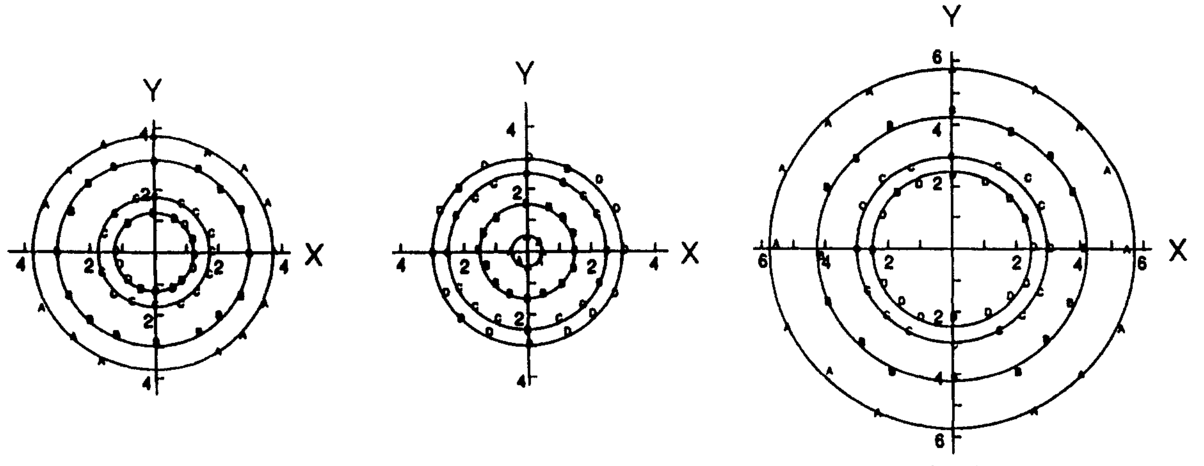
General Characteristics. In quenched thin PET films as were used in this study, the surface orientation and crystallinity as probed by ATR method are found to be comparable to the corresponding bulk characteristics when probed by thermal analysis and birefringence.[13] Therefore, we may assume that the surface layer probed by ATR method is representative of the changes in bulk structure in this study.

The IR spectra in the region of 750–1100 cm^{-1} contain two types of absorption bands for PET. One type is sensitive to structure as well as orientation while the other is sensitive only to the orientation.[2,16] The band either for the trans or the gauche isomer of the ethylene glycol unit of PET belongs to the first category, whose intensity depends on the concentration of the trans or the gauche structure. Table I summarizes the assignments of some IR bands investigated in PET. During drawing, some gauche isomer is converted to the trans isomer. Some of the converted trans isomer can crystallize, while uncrystallized trans isomer can relax back into the gauche form or it can remain as an amorphous oriented chain.[2-5]

Figure 3 shows a series of A_{TE} spectra in the region of 750–1100 cm^{-1} for biaxially drawn poly(ethylene terephthalate) films. It shows that higher draw ratios lead to the increase in the trans isomer peaks at 973 and 848 cm^{-1}, while the gauche isomer peaks at 1042 and 896 cm^{-1} have consequently decreased. Since both are parallel bands, these results support the trends described in the preceding paragraph. The band at 875 cm^{-1} is due to the out of plane deformation of the C–H bond in the benzene ring and represents the average orientation in PET films. Since it is a perpendicular band in regard to chain direction, its intensity decreased with draw ratio.

In order to see if the biaxial drawing leads to balanced orientation on the plane of the film surface, A_{TE} and A_{TM} spectra were taken by rotating the film about a horizontal axis for a full 360°. Spectra were recorded at 16 different angles. Figure 4 shows the angular profiles of the intensity values of A_{TE} at 1042, 973, and 875 cm^{-1} for films drawn at 87 °C with a drawing speed of 10 mm/s. These figures support a well-balanced orientation since the intensities of all three bands are quite independent of the angles about a horizontal axis. From these trends, we can conclude that A_x is equal to A_y. Similar circular profiles were obtained from A_{TM} intensities, indicating that film orientation is uniform in the xy plane of the film.

Orientation. IR dichroism has been frequently used as a method to investigate the anisotropy of the polymer.[2-6,17-21] Since the principles of IR dichroism are well established,[22,23] we will limit our discussions to the relationship between D_{xz} and the degree of orientation in biaxially drawn films. In these films, we can think of PET chains composed of some perfectly oriented ones and the rest as random chains. If we assume the fraction of perfectly oriented chains to be f along the x or y direction, the fraction of random chains becomes $(1 - 2f)$, since there



A_{TE} (1042)

A_{TE} (973)

A_{TE} (875)

Figure 4. Angular profile of IR absorbance A_{TE} for various IR bands for PET film biaxially drawn at 87 °C and at 10 mm/s: (A) draw ratio = 1 × 1; (B) draw ratio = 2 × 2; (C) draw ratio = 4 × 4.

is no directionally on the x–y plane of the film. In these cases, the IR absorption coefficient for the x, y, or z direction can be expressed[22] by eqs 3 and 4

$$k_x = k_y = NP^2[f\cos^2\theta + {}^1/_2 f\sin^2\theta + {}^1/_3(1-2f)] \quad (3)$$

$$k_z = Np^2[f\sin^2\theta + {}^1/_3(1-2f)] \quad (4)$$

In the above equations, N is the number of absorbing centers per unit volume, P is the magnitude of the transition moment vector of the absorbing group, and θ is the angle between transition moment and the chain axis. Since $D_{xz} \equiv A_x/A_z = k_x/k_z$, D_{xz} can be related to f by the following equations

$$D_{xz} = \frac{2 - f + 3f\cos^2\theta}{2 - 4f + 6f\sin^2\theta} \quad (5)$$

$$f = \frac{2D_{xz} - 2}{4D_{xz} - 6D_{xz}\sin^2\theta + 3\cos^2\theta - 1} \quad (6)$$

Equation 6 provides a way to estimate f from the experimentally determined value of D_{xz}, since

$$D_{xz} = \frac{\gamma A_{\mathrm{TE}}}{\alpha A_{\mathrm{TM}} - \beta A_{\mathrm{TE}}} \quad (7)$$

Equation 7 has been obtained from eqs 1 and 2 since $A_x = A_y$ in these PET films. As can be seen in eq 7, we need to know the values of α, β, and γ in order to determine D_{xz} from the experimental data of A_{TE} and A_{TM}. The calculation of α, β, and γ values assumes the material is isotropic.[14] Since these PET films are not isotropic and the IR refractive indices were not measured, we will attempt to estimate the ratio of α:β:γ, by using the experimental data where a certain value of f is assumed.

First, in the case of an undrawn PET film, D_{xz} is unity and A_{TE} was almost equal to A_{TM}. Therefore, we can obtain eq 8 in this isotropic case, by substituting the values in eq 7.

$$\alpha - \beta - \gamma = 0 \quad (8)$$

According to the previously reported values for highly oriented PET after uniaxial drawing, the fraction of perfectly oriented chains is about 0.62 for the 875-cm^{-1} band.[2,6,10] If we assume similar extent of orientation in highly biaxially oriented PET, the value of f in either x or y direction would be 0.31 for the 875-cm^{-1} band. We will use this band to represent the overall orientation of PET since it is known to be only dependent on the orientation and θ is known to be 86°.[6] Among the samples we have, the sample with 4 × 4 draw ratio drawn at 87 °C with a drawing rate of 50 mm/s was assumed to have f of a value of 0.31. By substituting f at a value of 0.31 and θ of 86°, D_{xz} was obtained from eq 5. The experimental values of A_{TE} and A_{TM} and the value of the obtained D_{xz} were substituted into eq 7, which led to the second relationship between α, β, and γ as in eq 9.

$$\alpha - 0.74\beta - 1.148\gamma = 1 \quad (9)$$

From eqs 8 and 9, we now can obtain the ratio of α:β:γ to be 1.54:0.54:1.0. These ratios can be substituted in eq 7 to determine D_{xz} from the experimental values of A_{TE} and A_{TM}.

Table II summarizes the values of D_{xz} as a function of drawing conditions. The higher the draw ratio, the smaller the values of D_{xz} since it is a perpendicular band. The drawing speed seems to have similar effects even though its effect is smaller than the draw ratio. Due to the assumptions made in the estimation of the ratio of α:β:γ, the absolute values of D_{xz} may not be very accurate. However, the trends observed in D_{xz} as a function of drawing condition will remain the same. From these D_{xz} values, we obtained the values of f from eq 6. Figure 5 illustrates an example when the draw temperature was 87 °C, as a function of draw ratio and drawing rate. In Figure 5, the orientation function f increases with draw ratio, as expected at all drawing rates. We also observe that the faster drawing rate results in greater values of f. This drawing rate effect is due to the reduced chain relaxation at a faster drawing rate. Similar trends have been observed when the draw temperature was either at 80 or at 94 °C.

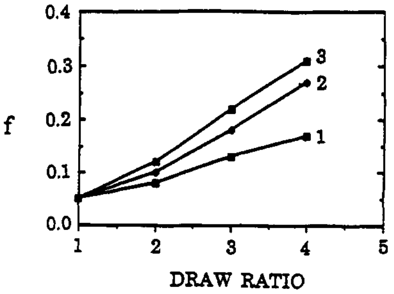


Figure 5. Orientation function, f, as a function of draw ratio at 87 °C and various drawing rates: (1) 2 mm/s; (2) 10 mm/s; (3) 50 mm/s.

Table II. Dichroic Ratio, D_{XZ}, at 875 cm^{-1} for Biaxially Drawn PET Films

drawing temperature (°C)	drawing speed (mm/s)	draw ratio 2 × 2	draw ratio 3 × 3	draw ratio 4 × 4
80	2	0.88	0.81	
	10	0.86	0.78	
	50	0.86	0.77	
87	2	0.89	0.83	0.78
	10	0.86	0.77	0.68
	50	0.84	0.73	0.65
94	2	0.92	0.85	0.82
	10	0.88	0.82	0.73
	50	0.86	0.74	0.62

We can investigate the effect of drawing temperature at a constant drawing rate, as illustrated in Figure 6. When the drawing rate is as slow as 2 mm/s, we observe a greater extent of orientation at a lower drawing temperature, as illustrated in Figure 6a. In contrast, orientation increases more rapidly after drawing at higher temperatures when the drawing speed is much faster, as shown in Figure 6c for 50 mm/s. These trends can be explained in view of the orientation rate, crystallization rate, and chain relaxation occurring during drawing. When PET is drawn, amorphous chains become oriented. Some of the oriented chains can crystallize, while some may relax back to unoriented chain or stay as oriented amorphous chain. At slow drawing rate, the chain relaxation becomes an important process reducing orientation in amorphous PET. Since the relaxation is slowest at 80 °C, orientation remains highest at this temperature. On the other hand, at fast drawing rate, relaxation is less important. Instead, crystallization rate becomes more important. At 94 °C, the rate of crystallization is faster than either at 87 or 80 °C, since the maximum rate of crystallization for PET is about 170 °C.[24] Therefore, the greater crystallinity at 94 °C contributes to the higher orientation, because not only crystallites themselves would have higher orientation but they may make chain relaxation more difficult in the amorphous region. In uniaxial drawing, it has been reported that lower draw temperatures can lead to higher orientation.[6,8] However, only relatively slow drawing speed was studied in previous uniaxial studies. At much faster drawing speed, we would expect similar trends as observed in this study for biaxial drawing.

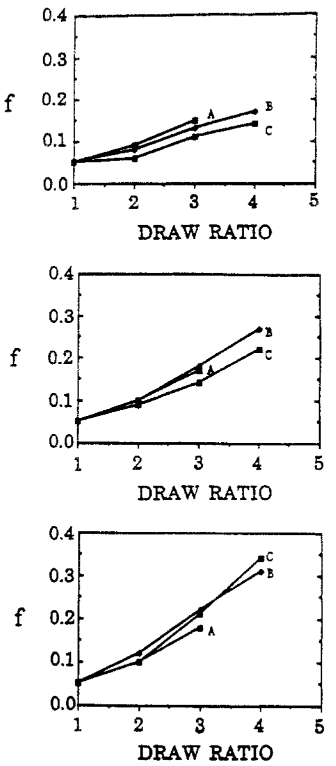


Figure 6. Orientation function, *f*, as a function of draw ratio at various drawing temperatures: (A) 80 °C; (B) 87 °C; (C) 94 °C. Drawing rates were (a, top) 2 mm/s; (b, middle) 10 mm/s; (c, bottom) 50 mm/s.

Molecular Structure. We can obtain information on molecular structure as a function of biaxial drawing conditions by estimation of the amount of the trans or gauche isomer in PET. Since the trans or gauche peak intensity is dependent on the orientation as well as its concentration, the so-called structural factor A_0 can be calculated with the knowledge of absorbance in three directions as shown below

$$A_0 = (A_x + A_y + A_y)/3 \tag{10}$$

This factor A_0 is thus independent of the orientation effect and will be only dependent on the concentration. In this study, we chose the 1042- and 973-cm^{-1} bands to represent gauche and trans isomer, respectively. Before we describe the results, it is worth noting that the trans isomer can exist in both crystalline and amorphous phases, while the gauche isomer exists only in the amorphous region. Schmidt has shown that the 973 cm^{-1} band intensity is mainly from the crystalline phase. In other words, its intensity is mainly a reflection of the change in crystallinity. Often, the structural factor is divided by an internal-thickness band such as the 795-cm^{-1} band in order to compare all the measurements on a common basis of thickness.[2-5] This ratio is called the reduced structural factor, A_0'.

Figure 7 illustrates the effect of the drawing rate at a drawing temperature of 87 °C. It is noted that the faster the drawing speed, the greater the reduced structural factor for trans peak and the smaller the reduced structural factor representing gauche isomer content. This is because a faster drawing rate creates more trans isomer. At other drawing temperatures, similar trends were observed, as far as the drawing speed is concerned.

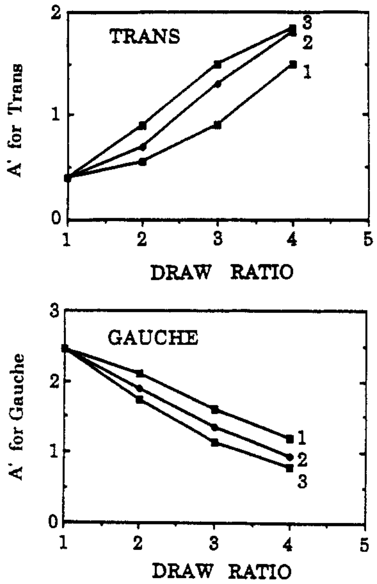


Figure 7. Reduced structural factor, *A*′, for trans and gauche isomer as a function of draw ratio at 87 °C and various drawing rates: (1) 2 mm/s; (2) 10 mm/s; (3) 50 mm/s.

The effects of the drawing temperatures can be seen in Figure 8. At slow speed of drawing, more trans isomer remains after drawing at lower draw temperature since the relaxation back to gauche is slower (see Figure 8a). However, as the drawing rate increases, the temperature effect becomes more complicated. The gauche isomer content shows the same trend regardless of the drawing rate; the gauche content is higher at high draw temperature, since the relaxation is faster. In contrast, the reduced structural factor for trans isomer appears to increase more after drawing at higher temperatures. For example, Figure 8c illustrates that drawing at 94 °C results in the greatest value for the reduced structural factor for trans isomer. Since the total amount of trans isomer and the gauche isomer should be constant, this trend as in Figure 8c may appear contradictory. However, as mentioned previously, the trans isomer intensity may be mainly determined by the crystalline isomer, whose content is greater at higher draw temperature due to faster crystallization rate following fast orientation at higher drawing speed.

In order to provide information on the trans isomer present in the amorphous phase, thermal analysis was used. Figure 9 shows differential scanning calorimetry thermograms for the PET sample biaxially drawn by 4 × 4 times. For a slowest drawing rate of 2 mm/s, DSC thermograms were almost the same regardless of the drawing temperature, as illustrated in Figure 9a. On the other hand, we observed a different trend in DSC thermogram, depending on the drawing temperature at much faster drawing rate (in Figure 9b. We can interpret these trends in the following way. As mentioned in the preceding sections, most of the trans isomer gets incorporated into the orientation induced crystalline region at the slowest drawing rate, leaving small amount of trans isomer in the amorphous region. Therefore, we do not see the endotherm due to the relaxation of the oriented trans isomer in the amorphous region. At the fastest drawing speed, apparently not all the trans isomers can be quickly crystallized. Thus, only a part of the trans isomer is converted to the crystalline region, leaving some trans isomer in the amorphous region. At the draw temperature of 87 °C, the crystallization rate is slower than that at 94 °C. Relatively larger amounts of the trans isomer must remain in the amorphous region at 87 °C than at 94 °C. Therefore, we can clearly observe an endothermic DSC peak near 90 °C for a sample drawn at 87 °C, as shown in Figure 9b, but not for a sample drawn at 94 °C. This result on the latter sample is due to the reduced amount of the trans isomer in the amorphous region, probably because of the greater

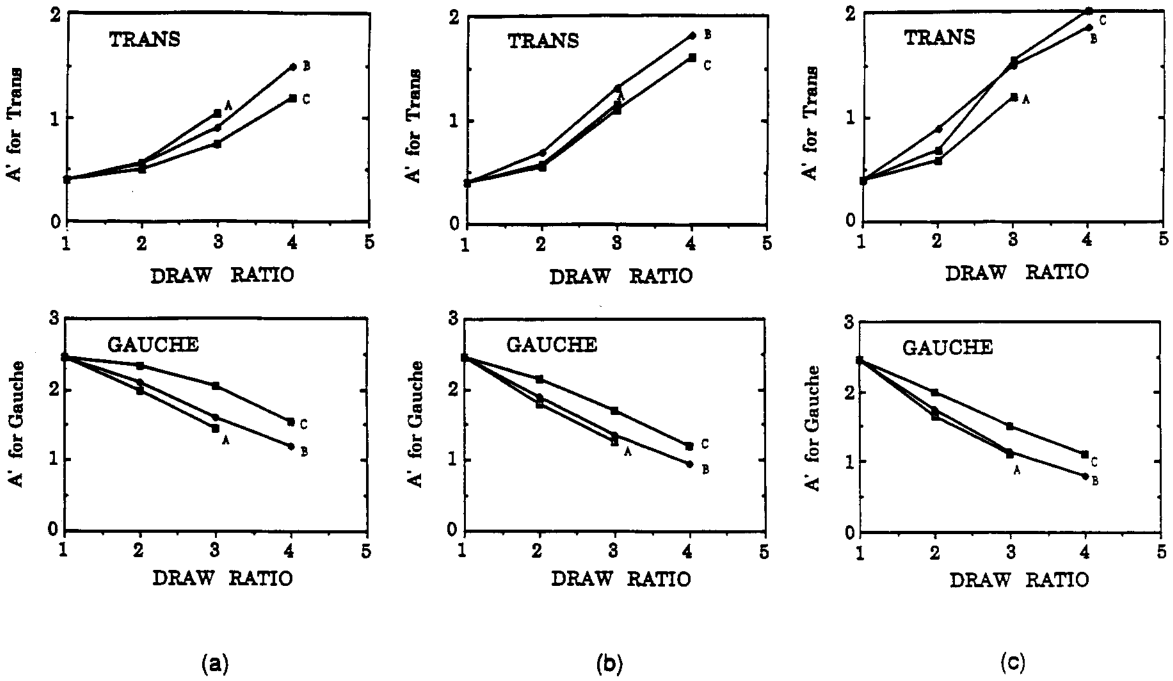


Figure 8. Reduced structural factor, A', for trans and gauche isomer as a function of draw ratio at various drawing temperatures: (A) 80 °C; (B) 87 °C; (C) 94 °C. Drawing rates: (a) 2 mm/s; (b) 10 mm/s; (c) 50 mm/s.

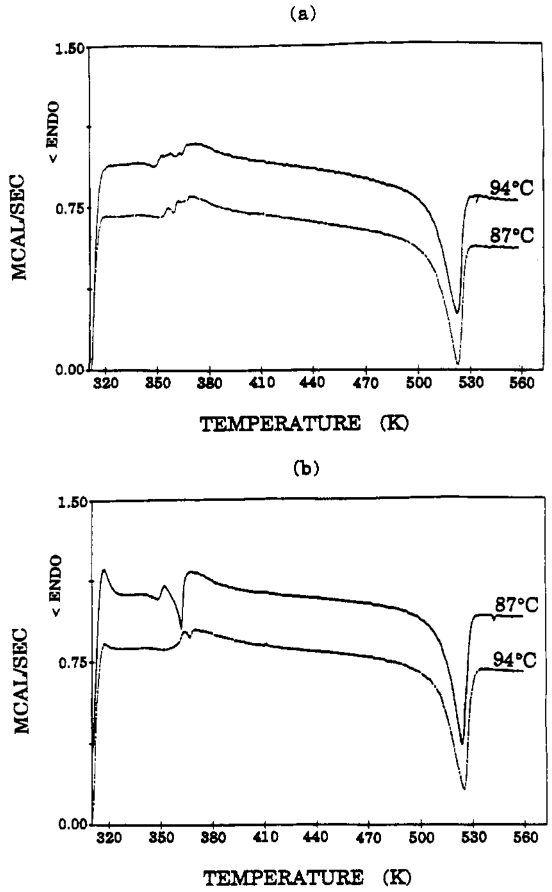


Figure 9. DSC thermograms of PET films biaxially drawn at 87 and 94 °C. Draw ratio was 4 × 4: (a) drawing rate at 2 mm/s; (b) drawing rate at 50 mm/s.

relaxation to the gauche isomer and of the greater transformation to the crystalline form at a higher temperature than at 87 °C.

Conclusion

The orientation and the structure in biaxially drawn PET are found to be determined by the rates of the drawing, chain relaxation, and the crystallization. When the drawing rate is slow, one can obtain higher orientation at lower drawing temperatures due to the slow chain relaxation. At faster drawing speed, crystallization rate becomes an important factor in determination of orientation. For example, we can obtain higher orientation and crystallinity at 94 °C than at 80 or 87 °C, when the drawing speed is 50 cm/s, presumably because the crystallization rate is greatest at 94 °C. The overall increase in the trans isomer content as a consequence of drawing plays an important role in the determination of the orientation.

Acknowledgment. This work was in part supported by the Office of Naval Research. K.H.L. is grateful for the postdoctoral fellowship from the Korean National Science Foundation, which made his stay at the University of Connecticut possible. We are grateful for the polymer samples provided by SKC, Ltd., of Korea.

References and Notes

(1) Farrow, G.; Ward, I. M. *Polymer* **1960**, *1*, 330.
(2) Schmidt, P. G. *J. Polym. Sci., Part A* **1963**, *1*, 1271.
(3) Koenig, J. L.; Hannon, M. J. *J. Macromol. Phys.* **1967**, *B1*, 119.
(4) Koenig, J. L.; Cornell, S. W. *J. Macromol. Phys.* **1967**, *B1*, 279.
(5) Koenig, J. L.; Cornell, S. W. *J. Polym. Sci., Part C* **1969**, *22*, 1019.
(6) Cunningham, A.; Ward, I. M.; Willis, H. A.; Zichy, V. *Polymer* **1974**, *15*, 749.
(7) Althen, G.; Zachman, H. G. *Macromol. Chem.* **1979**, *180*, 2723.
(8) LeBourvellee, G.; Monnerie, L.; Jarry, J. P. *Polymer* **1986**, *27*, 856.
(9) LeBourvellee, G.; Monnerie, L.; Jarry, J. P. *Polymer* **1987**, *28*, 1712.
(10) Sharma, S. K.; Misra, A. *J. Appl. Polym. Sci.* **1987**, *34*, 2231.
(11) LeBourvellee, G.; Beautemps, J. *J. Appl. Polym. Sci.* **1990**, *39*, 319.
(12) Mocherla, K. K.; Bell, J. P. *J. Polym. Sci., Polym. Phys.* **1973**, *11*, 1779.
(13) Yuan, P.; Sung, C. S. P. *Macromolecules* **1991**, *24*, 6095.
(14) Fluornoy, P. A.; Schaffers, W. J. *Spectrochim. Acta* **1966**, *22*, 5.
(15) Fluornoy, P. A. *Spectrochim. Acta* **1966**, *22*, 15.
(16) Boerio, F. J.; Bahl, S. K. *J. Polym. Sci., Polym. Phys.* **1976**, *14*, 1029.
(17) Hobbs, J. P.; Sung, C. S. P.; Krishnan, K.; Hill, S. *Macromolecules* **1983**, *16*, 193.

(18) Siesler, H. W. *Colloid Polym. Sci.* **1984**, *262*, 223.
(19) Amram, B.; Bokobza, L.; Quesel, J. P.; Monnerie, L. *Polymer* **1986**, *27*, 877.
(20) Pirnia, A.; Sung, C. S. P. *Macromolecules* **1988**, *21*, 2699.
(21) Sung, N. H.; Lee, H. Y.; Yuan, P.; Sung, C. S. P. *Polym. Eng. Sci.* **1989**, *29*, 791.
(22) Samuels, R. J. *Structured Polymer Properties*; Wiley-Interscience: New York, 1974.
(23) Siesler, H. W. *Adv. Polym. Sci.* **1984**, *65*, 1.
(24) Van Krevelen, D. W. *Properties of Polymers*, Elsevier: New York, 1976; Chapter 19.