Study of *a*-axis orientation in drawn and annealed poly(ethylene terephthalate) film*

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The morphologies of poly(ethylene terephthalate) (PET) films annealed at various temperatures after drawing to various extents were studied by measurements of density and birefringence, wide-angle X-ray analysis, electron microscopy and measurement of the contraction on annealing. It is proposed that a new type of texture with *a*-axis orientation is formed when the resultant films have negative birefringence. Namely, thin lamellae, in which polymer molecules are folded, are aligned preferentially along the original drawing direction, which means that polymer molecules are oriented preferentially perpendicular to the drawing direction. It is suggested that, on annealing a drawn film with a slight positive birefringence and very low crystallinity, crystallites or a similar conformation of molecules (nuclei) with *c*-axis orientation may rotate, the extent depending on that of the frozen elongation of the amorphous tie-chains between the crystallites or nuclei, so as to make the tie-chains relax, giving rise to the texture in question.

(Keywords: poly(ethylene terephthalate); crystallization; drawing; annealing; *a*-axis orientation)

INTRODUCTION

In our previous paper[1], we dealt with a particular flow process of amorphous poly(ethylene terephthalate) (PET), in which neither crystallization nor molecular orientation takes place[2–4]. We have proposed the following mechanism for this particular flow process.

In a certain temperature range above T_g, the polymer molecules are deformed and oriented on drawing as usual, 'intermolecular linkage' playing an important role in the transmission of the applied force. In this temperature range, the resulting molecular orientation may induce crystallization[5]. When the intermolecular linkage is broken down by the applied force above a certain critical temperature, on the other hand, the polymer molecules may slip past each other and flow individually, exhibiting a large deformation inducing neither molecular orientation nor crystallization, just like in the flow of simple liquids.

It is of interest to see how the texture obtained by this sort of drawing affects the following crystallization induced by annealing. It is known that when non-crystalline PET films are drawn and annealed under certain conditions, the resultant films exhibit negative birefringence and *a*-axis orientation in X-ray studies[6,7]. *Figure 1* shows our results. It is seen that negative birefringence always results when drawn films with small positive birefringence are annealed, irrespective of the drawing temperature. Zachmann *et al.*[8] explained this particular phenomenon in terms of lamellar twisting.

The objective of this paper is to propose the formation of a new type of crystalline texture with *a*-axis orientation in films with negative birefringence and to discuss the underlying mechanism, in the light of various measurements on the changes in the texture occurring during annealing.

EXPERIMENTAL

Samples

The glassy 'amorphous' PET sheet was kindly provided by Teijin Co. The density at 25°C was 1.3376 g cm^{-3}. Strips of the sheet were drawn in water at various temperatures in the range from 64 to 90°C. The rate of drawing was mainly 25% of the original length per minute. The drawn samples were quenched into ice/water at fixed length. The effect of relaxation immediately after drawing at the drawing temperature was also studied. Similarly, the drawn films were treated by aqueous solutions of phenol with various concentrations, washed and dried. These samples were annealed at 160 and 225°C, respectively, mainly for 1 h.

Density

The density of the samples were measured at 25°C by titration of a mixture of two liquids of different composition, until the sample remained suspended in the mixed liquids. Heptane (density 0.700 g cm^{-3}) and carbon tetrachloride (density 1.580 g cm^{-3}) were used. The crystallinity of the sample was determined from the density measured, assuming a crystalline density[9] of 1.455 g cm^{-3} and an amorphous density[9] of 1.330 g cm^{-3}.

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Birefringence

The birefringence of the drawn strips of PET and those annealed after drawing were obtained from the retardation measured by a Berek compensatory at room temperature.

X-ray diffraction study

Wide-angle X-ray diffraction patterns were taken on a Rigaku Denki apparatus mainly for the samples drawn and annealed. In order to obtain the orientation function of each crystalline axis, the diffraction intensity was also measured along the azimuthal angle for the (1 0 0) and (0 1 0) reflections. The calculation of the orientation functions of the three crystalline axes was based on the method used by Wilchinsky[10]. The orientation function f_a, for example, is defined as:

$$f_a = (3\overline{\cos^2 \alpha} - 1)/2$$

where α is the angle between the *a*-axis and the draw direction.

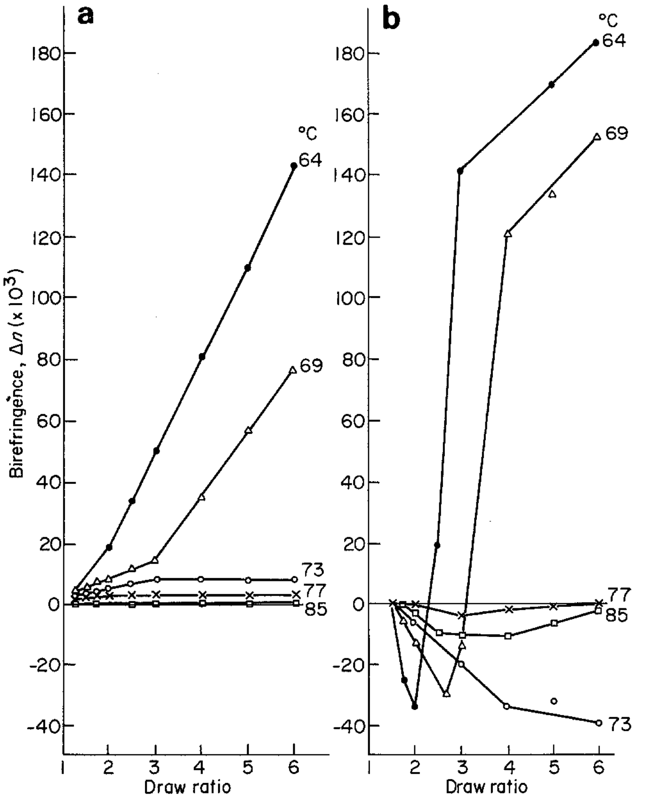

Figure 1 (a) The birefringence of films drawn at various temperatures (shown on the curves) and (b) that after annealing at 160°C for 1 h, plotted against the draw ratio

The contribution of the crystalline region to the total birefringence, Δn_c, was calculated from the above X-ray data, using the usual method. Next, making use of the crystallinity obtained from the density, the contribution of the non-crystalline region, Δn_a, was obtained, assuming additivity of the two components of the birefringence.

Electron microscopy

Electron micrographs were taken by a replica method through use of a Nihon Denshi apparatus. The annealed films were etched by monoethylamine for 1 h. Electron diffractions were obtained from the fragments that remained during the replication.

Measurement of the contraction of the drawn film on annealing

The samples drawn under various conditions were annealed for 1 h at 160°C and their lengths (along the draw direction) were measured before and after annealing.

RESULTS AND DISCUSSION

Figure 2 shows the contributions of the crystalline and non-crystalline regions to the total birefringence, Δn_c and Δn_a, respectively, plotted against the draw ratio for samples drawn at various temperatures and annealed at 160°C for 1 h.

It is evident from Δn_c (*Figure 2a*) that the negative birefringence of the samples shown in *Figure 1* is due to

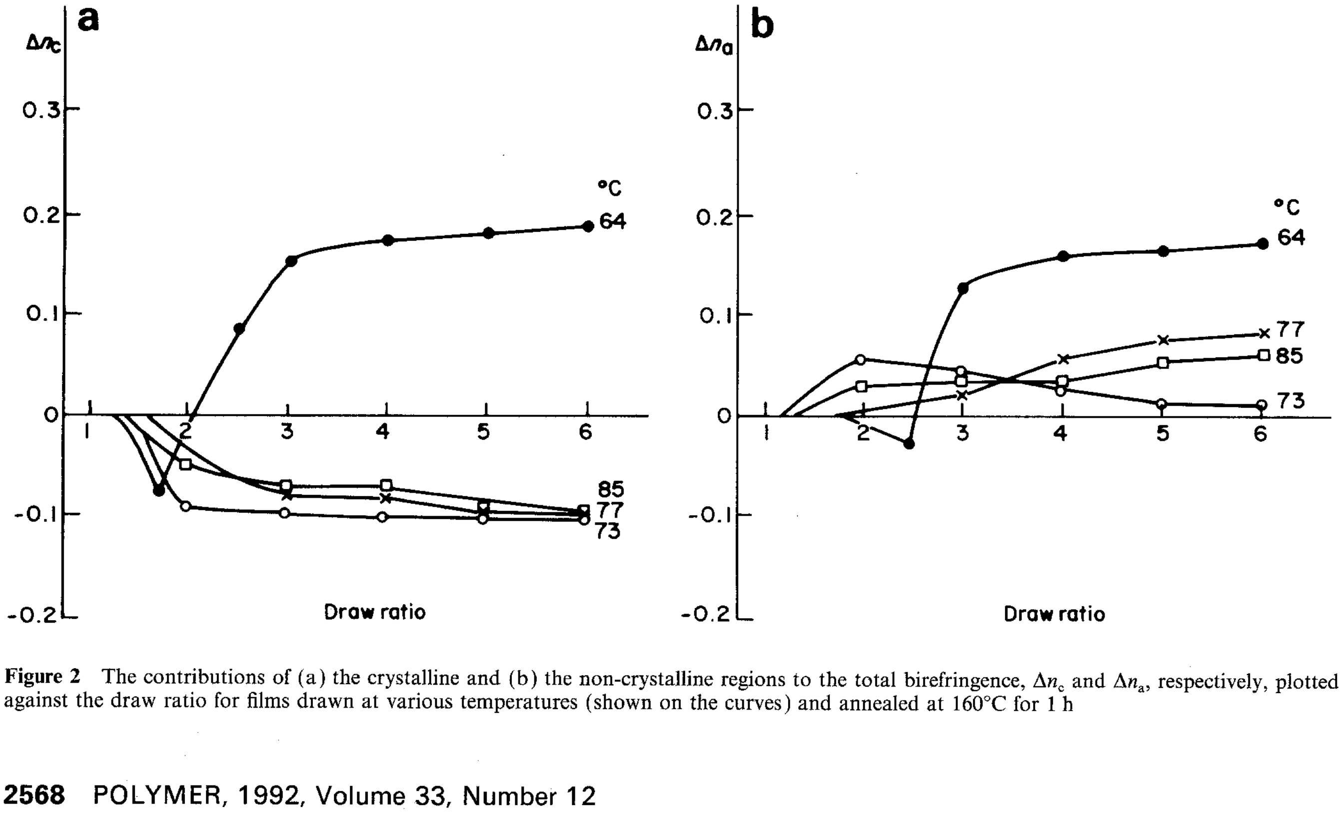

Figure 2 The contributions of (a) the crystalline and (b) the non-crystalline regions to the total birefringence, Δn_c and Δn_a, respectively, plotted against the draw ratio for films drawn at various temperatures (shown on the curves) and annealed at 160°C for 1 h

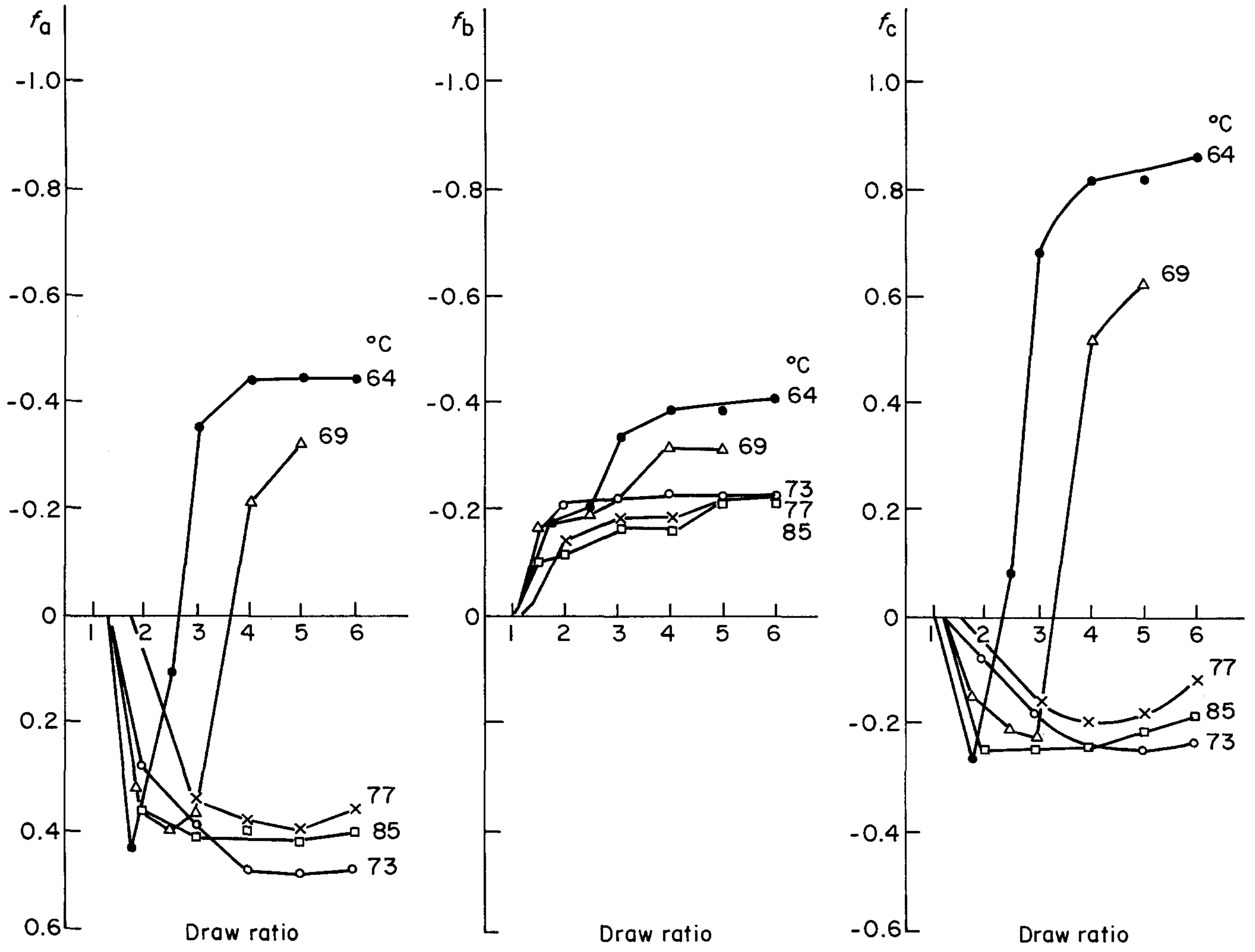

Figure 3 The orientation functions of the *a*, *b* and *c* crystalline axes, respectively, plotted against the draw ratio for films drawn at various temperatures (shown on the curves) and annealed at 160°C for 1 h

the formation of crystallites with molecular orientation preferentially perpendicular to the direction of drawing.

For the samples with positive total birefringence, Δn_c is also positive. X-ray photographs of these films (though not shown here) showed that all the samples with negative birefringence exhibit *a*-axis orientation, whereas the samples with positive birefringence showed *c*-axis orientation. The orientation of the amorphous chains as revealed by *Figure 2b* is positive in all the cases studied and larger in the films with *c*-axis orientation than in those with *a*-axis orientation of the crystallite.

In *Figure 3* are shown the orientation functions of the *a*, *b* and *c* crystalline axes, respectively, plotted against the draw ratio for various annealed samples at different drawing temperatures. On annealing, the orientation function of the *a*-axis, f_a, becomes positive and reaches values in the range of 0.3–0.5 for samples with negative birefringence, whereas it becomes negative for samples with positive birefringence. Just the opposite tendency is seen with the orientation function of the *c*-axis (the molecular axis). Namely, f_c is negative and reaches values near 0.2 for samples with negative birefringence, whereas it becomes positive for samples with positive birefringence. The orientation function of the *b* axis, f_b, is negative for all the samples and (negatively) larger for samples with *c*-axis orientation than for those with *a*-axis orientation. These results for the orientation function are entirely consistent with those of *Figures 1* and *2*.

Figure 4 shows X-ray photographs of a film drawn to 4 times at 77°C (at a rate of 250% min^{-1}), quenched into ice/water at fixed length and annealed at 225°C for 1 h in the free state (*Figure 4a*), compared with that of a film drawn and annealed under the same conditions but relaxed immediately after drawing (*Figure 4b*). It is seen that the (1 0 0) reflection arcs lie on the meridian, indicating *a*-axis orientation in the former, whereas they are in the middle between the meridian and equator in the latter.

The same applies when drawn films are treated by aqueous solutions of phenol, washed, dried and annealed, as compared with those just annealed. *Figure 5* shows X-ray photographs of films drawn to 2.63 times at 69°C, treated by various concentrations of phenol, washed, dried and annealed at 225°C for 1 h. The original sample (drawn and just annealed in the same conditions, though not shown here) and that treated by 0.4% phenol show *a*-axis orientation, but the (1 0 0) reflection arc becomes split as the phenol concentration increases, and finally shows *c*-axis orientation beyond 1.6% of phenol. This implies that internal stress due to the elongation of the amorphous chains induced by the stretching affects the resultant texture produced by annealing.

The transition from *a*-axis orientation to *c*-axis orientation was clearly realized on annealing the films drawn at 69°C by changing the draw ratio. *Figure 6* shows the rotation angle, θ, of the (1 0 0) arc from the equator,

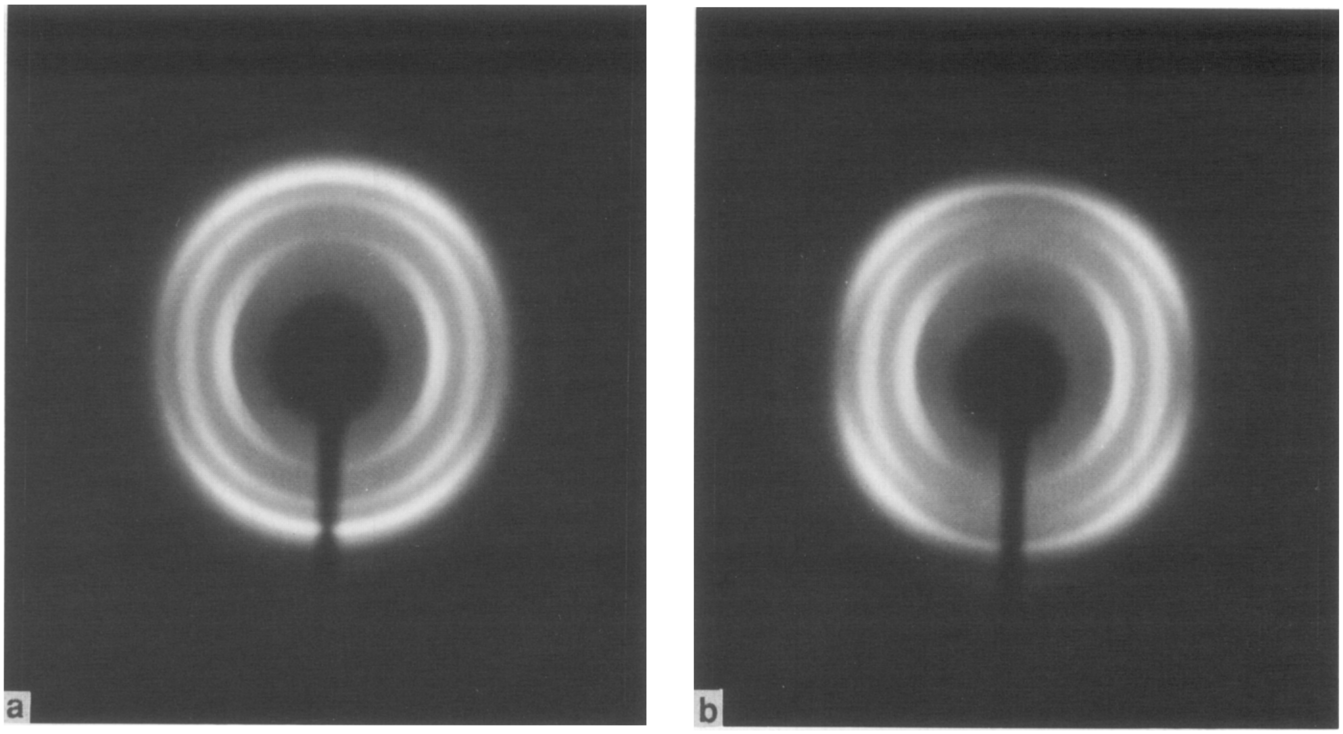

Figure 4 (a) X-ray photograph of a film drawn to 4 times at 77°C (at a rate of 250% min^{-1}), quenched into ice/water at fixed length and annealed at 225°C for 1 h in the free state, compared with (b) that of a film drawn and annealed under the same conditions but relaxed immediately after drawing. The draw direction is vertical

obtained for films drawn at 69°C at a rate of 25% min^{-1} and quenched into ice/water at fixed length and those annealed at 225°C for 1 h in the free state, plotted against the draw ratio. Namely, θ is the angle between the line connecting the centre of the (1 0 0) arc with the centre of the whole X-ray photograph and the equator, and is zero for complete *c*-axis orientation and 90° for complete *a*-axis orientation. Crystallization during drawing occurred appreciably above the draw ratio of 3.2 but always gave crystallites with preferentially *c*-axis orientation, as seen in the figure. On annealing these drawn films, the texture formed changes continuously from *c*-axis orientation (very low values of θ) to *a*-axis orientation (higher values of θ) in the range of draw ratios from 5 to 3.

The following mechanism may be suggested from all the above results on this particular crystallization under molecular orientation. Even slight molecular orientation induced by drawing may induce crystallization into the *c*-axis orientation, just like in the case of polyethylene[11,12], as seen in *Figure 7b*. Even when crystallization did not occur at all on drawing, this slight molecular orientation would give a similar molecular arrangement of the nuclei. (The particular flow process in which neither crystallization nor molecular orientation occurs completely is only realized under a very much restricted condition[1].)

On annealing the drawn film, crystallites or similar conformations of molecules mentioned above may rotate, the extent depending on that of the frozen elongation of the amorphous tie-chains between the crystallites or the nuclei mentioned above, so as to make the tie-chain relax, as seen in *Figure 8*. This may account for the formation of crystallites with *a*-axis orientation shown in *Figure 7a*. We propose this texture (*Figure 7a*) for the *a*-axis orientation in this particular case. In fact, this model was first proposed by Stein *et al.*[13] for the oriented crystallization of polyethylene, but was denied by many later experimental results at least for polyethylene.

The reason why this sort of texture was formed in this particular case may be as follows. First, this is not crystallization from the melt but crystallization from the solid state (i.e. annealing), where movements of the polymer molecules are restricted. Secondly, the growth of the crystallites may not be so fast as compared with the case of polyethylene, and thus the crystallites or nuclei can rotate during crystallization. The crystallinity attained in this case is also lower (ca. 40%)[14] than that generally attained in the case of polyethylene (ca. 80%). In fact, when high molecular orientation is attained by drawing, even in this study, larger amounts of crystallites with *c*-axis orientation have already been formed, which severely restrict such rotation as mentioned above, resulting in further crystallization into the *c*-axis orientation on annealing. Anyway, this sort of peculiar texture of *a*-axis orientation may happen under very restricted conditions.

In order to prove this texture, electron microscopy has been carried out on these samples. *Figure 9* shows an electron micrograph of the surface of a film drawn to 6 times at 77°C and annealed at 225°C for 1 h, which showed a typical *a*-axis orientation by the X-ray study. It is seen that row structures are aligned perpendicularly to the drawing direction. This may be indicative of the texture proposed in *Figure 7a*.

Figure 10 shows an enlarged photograph of a part of *Figure 9* (*Figure 10a*) and the electron diffractions from it (*Figure 10b*). Although the (1 0 0) reflection is very weak, the (0 1 0) (the outer in this pattern) and $(0\bar{1}1)$ (the inner) reflections can be seen.

Figure 11 shows an electron micrograph of a film drawn to 5 times at 64°C and annealed at 225°C for 1 h, which showed a typical *c*-axis orientation (*Figure 11a*), and the

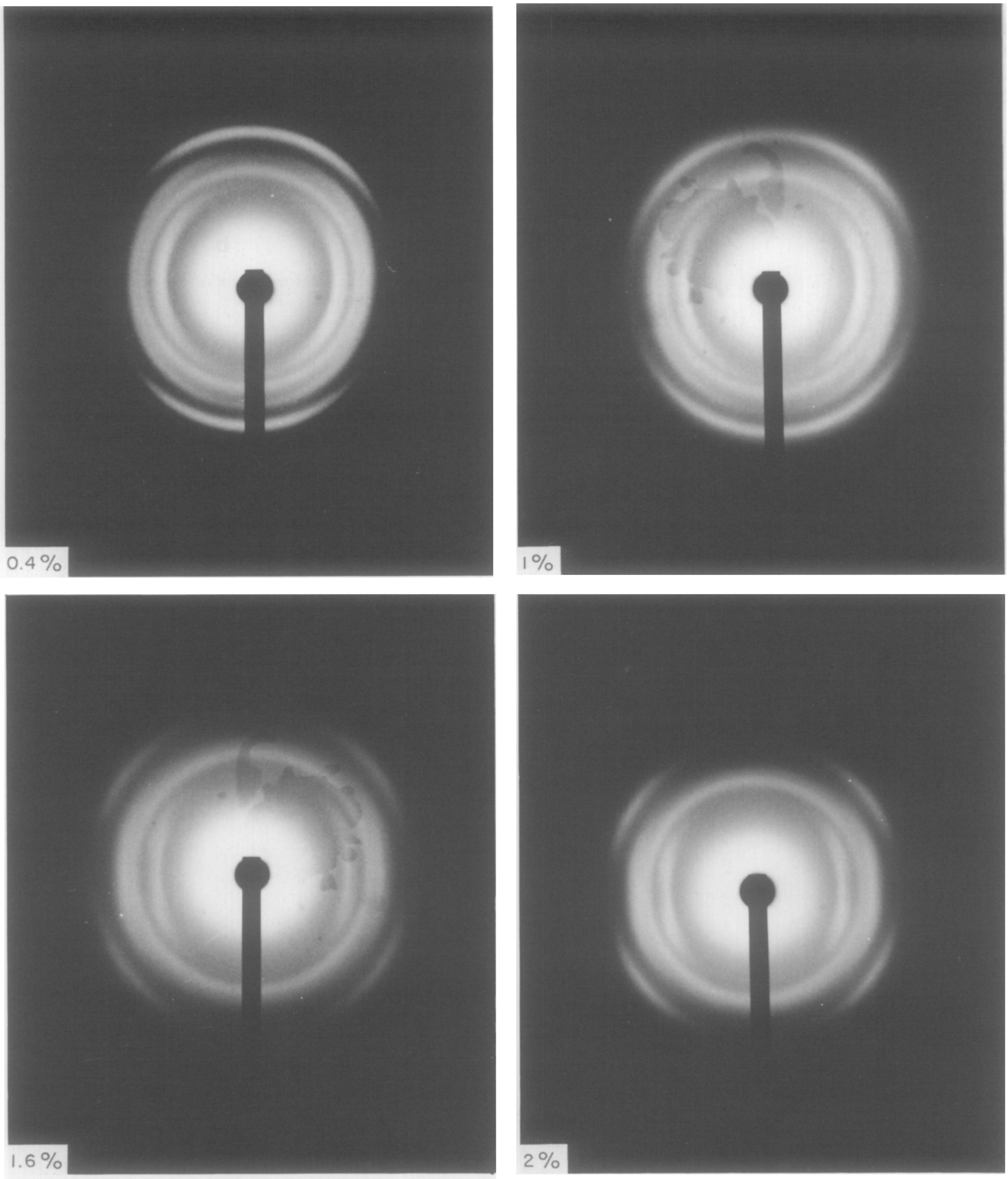

Figure 5 X-ray photographs of films drawn to 2.63 times at 69°C, treated by various concentrations of phenol (shown), washed, dried and annealed at 225°C for 1 h. The draw direction is vertical

electron diffractions from it (*Figure 11b*). Here, the row structures are aligned parallel to the drawing direction, as expected from usual crystallization under molecular orientation[11,12] (*Figure 7b*). The electron diffraction patterns (*Figure 11b*) naturally correspond to the *c*-axis orientation of the crystallites. As compared with *Figure 10b*, it may be said at least that the polymer molecules in the crystallites are perpendicular to the drawing direction in the case of the *a*-axis orientation. It must be mentioned from our studies of electron microscopy that the texture of the *a*-axis orientation in question is not so uniform throughout the sample as in *Figure 9* and the model of *Figure 7a*. However, this is quite reasonable in the light of the mechanism proposed above.

Finally, it is of interest to see the contraction behaviour on annealing the samples drawn at various temperatures.

Figure 12 shows the contraction of these samples on annealing at 160°C for 1 h plotted against the draw ratio. In the cases of the samples drawn at 69°C, the transition from the a-axis orientation (and negative birefringence) to the c-axis orientation (and positive birefringence) in

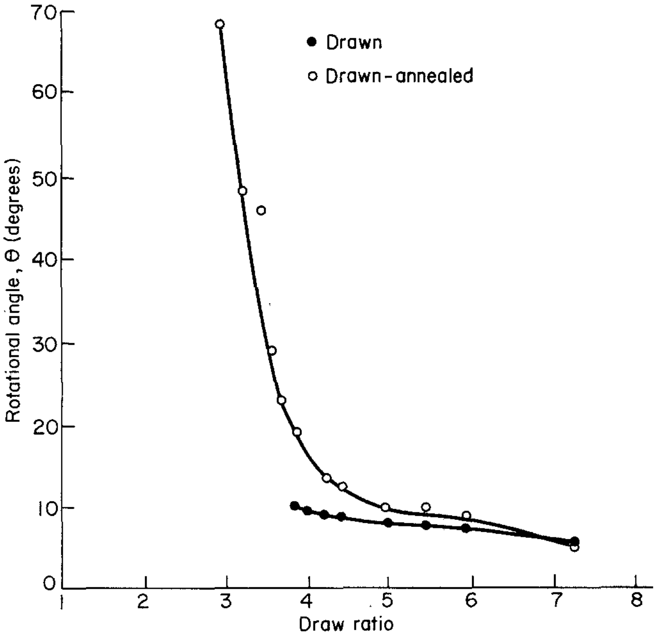

Figure 6 The rotational angle, θ, between the line connecting the centre of the (1 0 0) arc with the centre of the whole X-ray photograph and the equator, for films drawn at 69°C, quenched into ice/water at fixed length and those annealed at 225°C for 1 h in the free state, plotted against the draw ratio

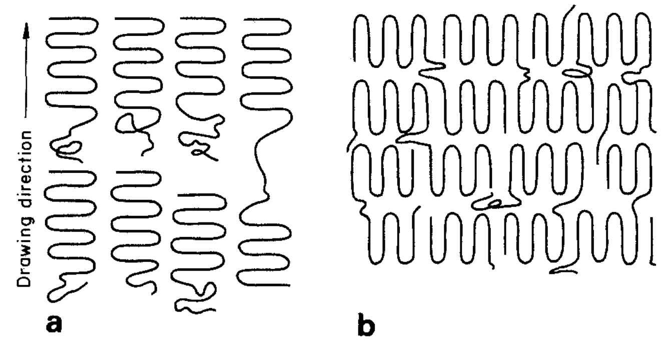

Figure 7 Illustration of the textures of (a) the a-axis orientation and (b) the c-axis orientation

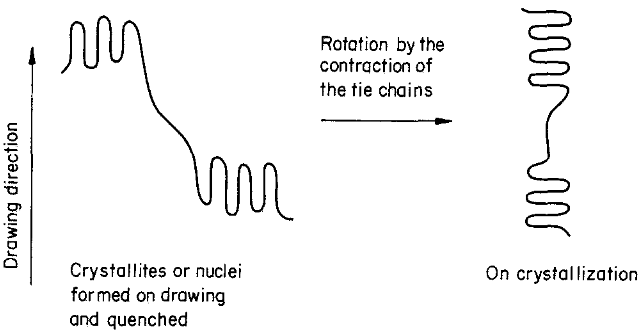

Figure 8 Illustration of the rotation of the crystallite or nucleus during annealing

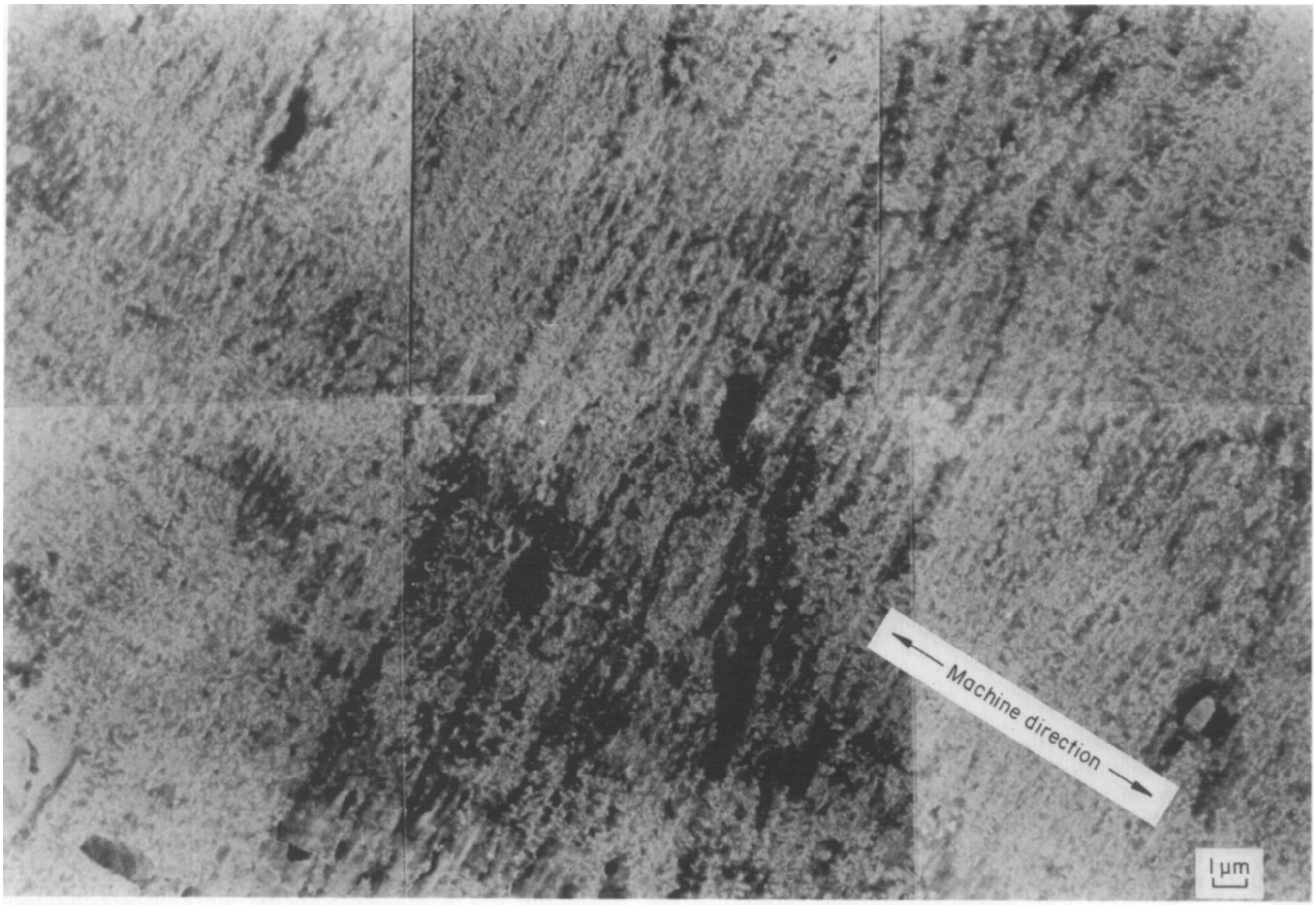

Figure 9 Electron micrograph of the surface of a film drawn to 6 times at 77°C and annealed at 225°C for 1 h (the a-axis orientation)

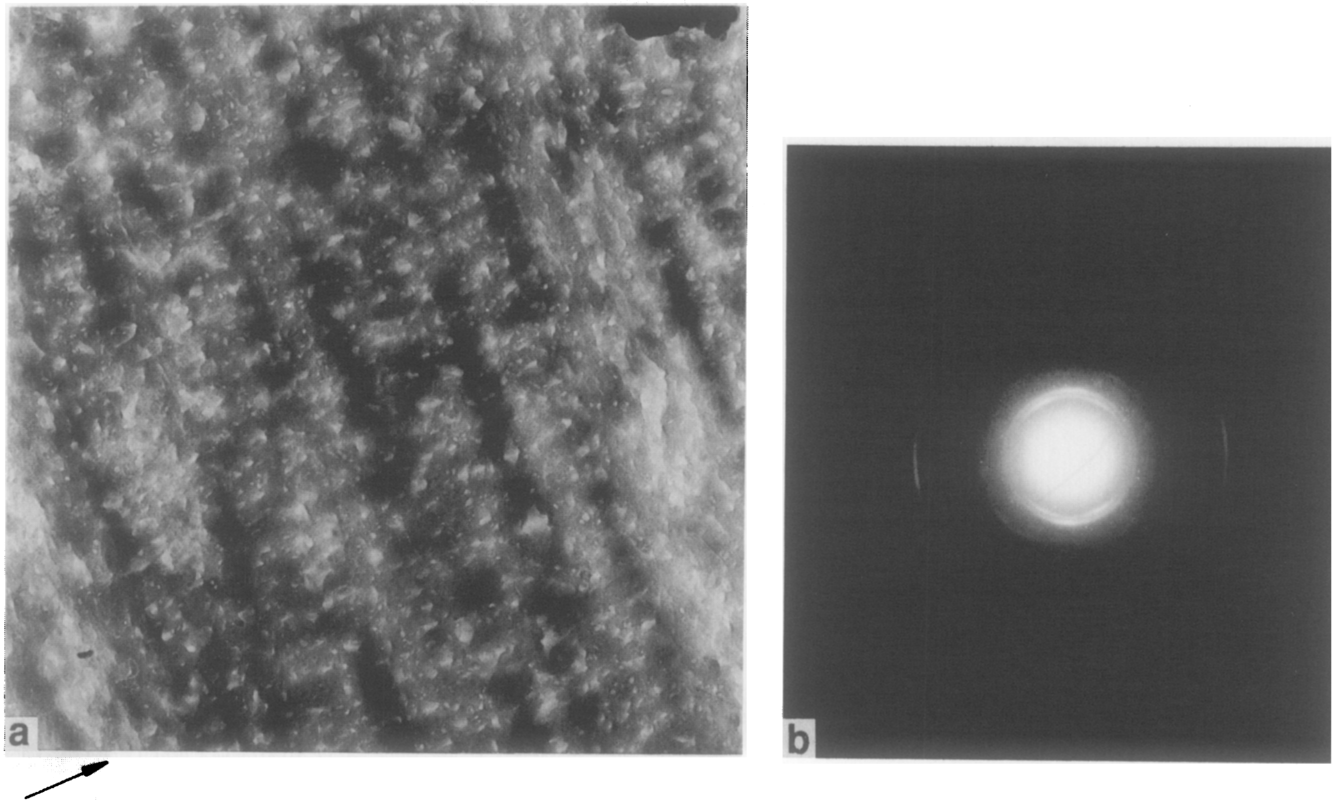

Figure 10 (a) Enlarged photograph of a part of *Figure 9* (×20000) (the machine direction is indicated) and (b) the electron diffractions from it (the machine direction is vertical)

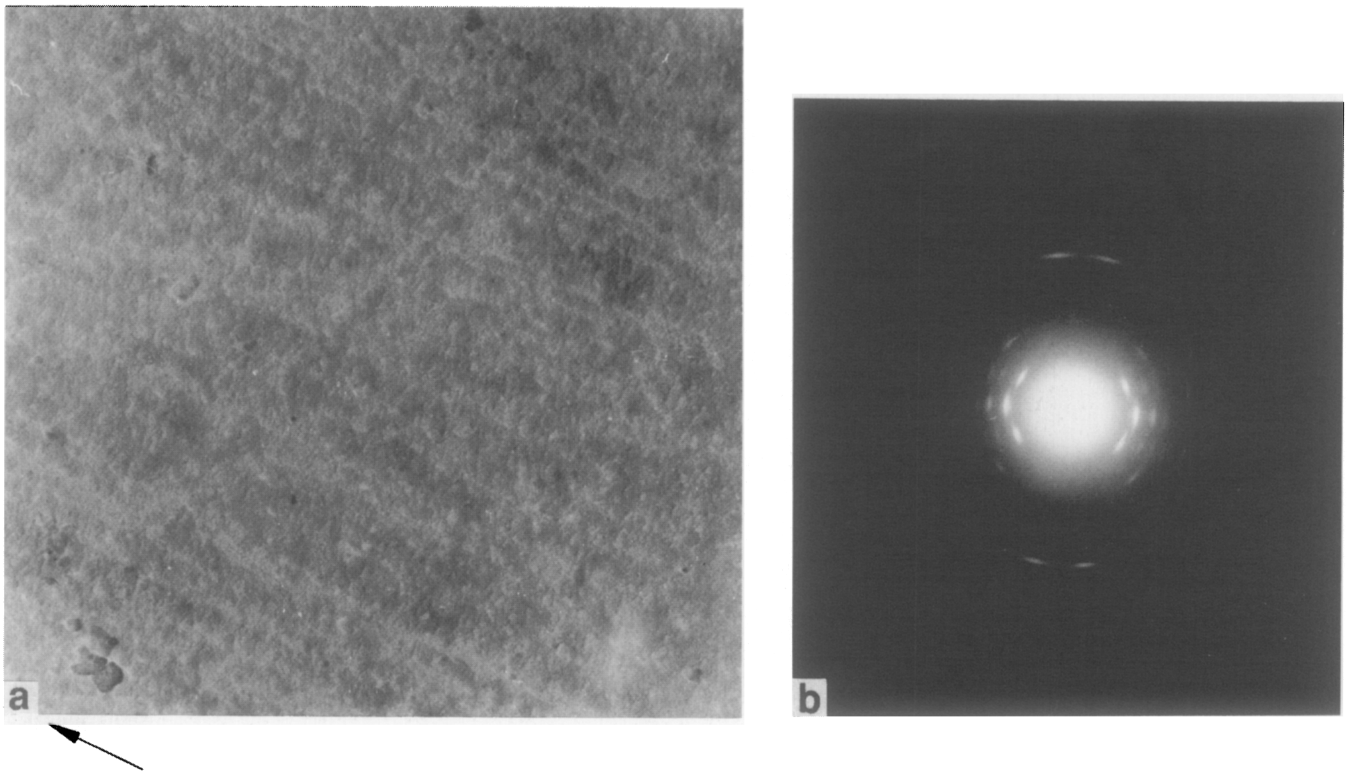

Figure 11 (a) Electron micrograph of a film drawn to 5 times at 64°C and annealed at 225°C for 1 h (the *c*-axis orientation) (the machine axis is indicated) and (b) the electron diffractions from it (the machine direction is vertical)

the annealed samples as the draw ratio increases seems to be clearly reflected in the contraction behaviour, which shows a maximum at a draw ratio of 2.5–3.0. This implies that the formation of crystallites with *a*-axis orientation gives rise to much higher contraction of the sample, compared with that with *c*-axis orientation. This is again consistent with the mechanism proposed above on the formation of the *a*-axis orientation (*Figures 7a* and *8*).

In fact, the films drawn at 73 and 77°C show larger contraction on annealing as the draw ratio increases.

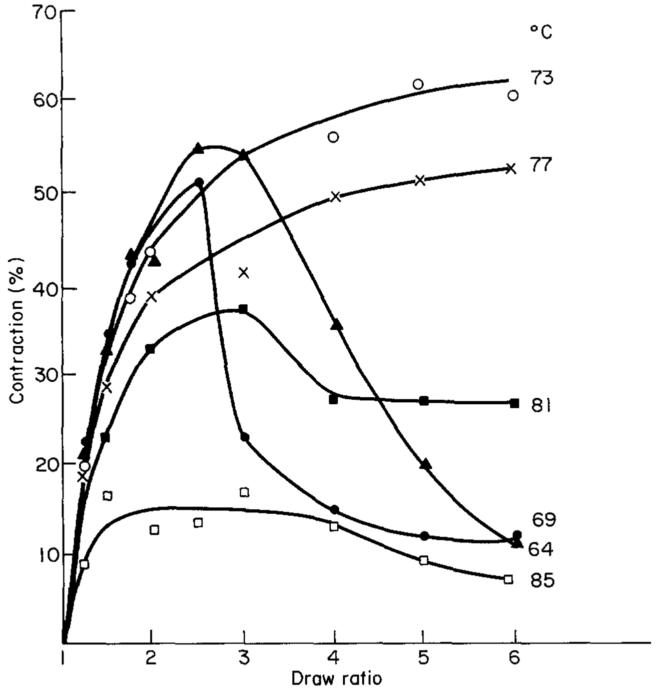

Figure 12 The contraction of films drawn at various temperatures (shown on the curves) on annealing at 160°C for 1 h, plotted against the draw ratio

These films showed slight positive birefringences on drawing and negative birefringences after annealing (*Figure 1*), indicating the *a*-axis orientation of the crystallites therein. The results on the samples drawn at 81 and 85°C seem to correspond to very low negative birefringence of the annealed samples. Crystallization on drawing occurs very slightly for these samples at higher draw ratios[3,15].

It may thus be concluded on the formation of *a*-axis orientation that crystallites with *c*-axis orientation or similar conformations of molecules prior to crystallization are formed first on drawing, and are rotated by the internal contractive force along the drawing direction on annealing, as seen in *Figure 8*, giving rise to the *a*-axis orientation or the intermediate between *a*-axis and *c*-axis orientations, depending on the frozen state of the amorphous tie-chains before annealing.

The above situation is, however, restricted to the cases where the overall molecular orientation and the degree of crystallinity prior to annealing are rather low. The lower molecular weight, and accordingly lower density of entanglements, compared with vinyl polymers and polyolefins may also play a role in the formation of the *a*-axis orientation mentioned above.

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REFERENCES

1 Sasano, H. and Kawai, T. *Makromol. Chem.* 1983, **184**, 217
2 Heffelfinger, C. J. and Schmidt, P. C. *J. Appl. Polym. Sci.* 1965, **9**, 2661
3 Koeniz, J. K. and Mele, M. D. *Makromol. Chem.* 1968, **118**, 128
4 Thompson, A. B. *J. Polym. Sci.* 1959, **34**, 741
5 Kawai, T. *Kobunshi* 1966, **15**, 898
6 Dulmage, W. J. and Geddes, A. L. *J. Polym. Sci.* 1958, **3**, 499
7 Kuriyama, I. and Shirakashi, K. *J. Soc. Fiber Sci. Technol. Japan* 1964, **20**, 56
8 Biangardi, H. J. and Zachmann, G. *Makromol. Chem.* 1976, **177**, 1173
9 Dauberg, R. P. and Bunn, C. W. *Proc. R. Soc.* (*A*) 1954, **226**, 521
10 Wilchinsky, Z. W. 'Advances in X-ray Analysis', Plenum Press, New York, 1963, Vol. 6
11 Keller, A. and Machin, M. J. *J. Macromol. Sci.* (*B*) 1967, **1**, 41
12 Kawai, T., Iguchi, M., Tonami, H. and Matsumoto, T. *Kolloid Z. Z. Polym.* 1967, **221**, 28
13 Stein, R. S. and Judge, J. T. *J. Appl. Phys.* 1961, **32**, 2357
14 Sasano, H., Ogawa, Y. and Kawai, T. *J. Soc. Fiber Sci. Technol. Japan* 1977, **33**, T-575
15 Sasano, H., Komoto, T. and Kawai, T. *J. Soc. Fiber Sci. Technol. Japan* to be published