

# Preparation of Ultrahigh Modulus Isotactic Polypropylene by Means of Zone Drawing

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## Synopsis

Highly oriented isotactic polypropylene with ultrahigh modulus was prepared by means of the zone drawing method proposed by Kiho and Asai. This method features heating a limited portion of the sample. The maximum value of modulus attained was 15 GPa, which corresponds to about half the crystal modulus along the molecular axis evaluated by the x-ray method. Such an ultrahigh modulus was obtained for a sample of medium molecular weight by inducing necking in the heater and subsequently cooling the sample at lower temperature. The loss tangent peak with the initiation of micro-Brownian motion of amorphous chains became progressively smaller and broadened more at higher temperatures with increasing draw ratio. Orientation function of the crystal *c*-axis increased with draw ratio  $\lambda$  in the region below  $\lambda = 9$ , but reached a constant value, 0.995, in the region above  $\lambda = 9$ . The modulus increased with draw ratio in all ranges of the draw ratio.

## INTRODUCTION

The elastic modulus of a uniaxially oriented crystalline polymer is generally much lower than the one of crystals along the molecular axis. Oriented crystalline polymers consist of crystalline and amorphous regions which alternatively align along the molecular axis,<sup>1</sup> and therefore the latter with lower modulus mainly contributes to the decrease in modulus. But tie molecules, by which crystallites are connected, would be formed in amorphous regions and would cause the modulus to increase.<sup>1</sup> Therefore, if the fraction of tie molecules can be increased, that is, the fraction of fold chains decreases, we can obtain oriented polymers with moduli as high as the modulus of the crystals along the molecular axis.

Many techniques for increasing the elastic moduli of oriented crystalline polymers have been developed. Among them, Kiho and Asai<sup>2</sup> achieved an ultrahigh modulus of 70 GPa for linear polyethylene by means of zone drawing. This method is based on the principle that the necking part is locally heated by the heater, which shifts with regulated speed to harmonize with the progress of the necking zone. The modulus was about 30% of the crystal modulus along the molecular axis, which was observed by the x-ray method.<sup>3</sup> On the other hand, Ward et al.<sup>4</sup> and Porter et al.<sup>5</sup> also achieved the same value by cold drawing of carefully prepared samples and solid-state extrusion with an Instron capillary rheometer, respectively. For isotactic polypropylene, Ward et al.<sup>6</sup> succeeded in obtaining an ultrahigh modulus of 19 GPa by means of cold drawing. Clark et al.<sup>7</sup> also obtained an ultrahigh modulus of 22 GPa, which is about 65% of the crystal modulus of 34 GPa,<sup>3</sup> by means of two-step drawing.

According to Kiho and Asai,<sup>2</sup> advantages of the zone drawing compared with

the usual drawing method are as follows: (1) Drawn samples having the same draw ratio can be prepared under different drawing stresses, that is, various heater temperatures. The draw ratio value can be controlled by the ratio of the drawing rate to the shifting rate of the heater. (2) Annealing of the drawn sample can be avoided because the sample is immediately cooled to room temperature after being drawn in the heater. (3) Since a drawn sample with uniform cross-sectional area can be prepared and its draw ratio can be controlled, we can easily characterize the change in the superstructure of the drawn sample with increasing draw ratio.

In this work oriented isotactic polypropylene films with ultrahigh modulus were prepared with an improved zone-drawing apparatus which was constructed on the basis of the zone-drawing apparatus designed by Kiho and Asai.<sup>2</sup> The improved zone-drawing apparatus was equipped with cooling elements, by which a sample is cooled to a temperature lower than room temperature immediately after being drawn in the heater. On the other hand, the zone-drawing apparatus designed by Kiho and Asai was not equipped with cooling elements, and therefore the drawn sample could be cooled merely to room temperature. It was examined whether annealing of the drawn sample is more completely removed by the improved zone-drawing apparatus. Optimum conditions for the preparation of ultrahigh modulus-isotactic polypropylene were maintained.

## EXPERIMENTAL

### Preparation of Samples

The isotactic polypropylenes used in this work were MH-4 (Mitsubishi Yuka Co., Ltd.), MA-8 (Mitsubishi Yuka Co., Ltd.), Tokuso A (Tokuyama Soda Co., Ltd.), and a nonbrand sample (provided by Tokuyama Soda Co., Ltd.). The viscosity-average molecular weights  $\bar{M}_v$  of these samples were determined by the following equation<sup>8</sup>:

$$[\eta] = 1.10 \times 10^{-4} \bar{M}_v^{0.80}$$

where  $[\eta]$  is the intrinsic viscosity, which was measured in a dilute decalin solution at 408 K. Table I shows six original films employed for zone drawing which are different in molecular weight and the condition of preparation. The pellets of MH-4 were compression molded at 468 K between two brass plates in a nitrogen atmosphere to give a film about 0.5 mm thick, which was rapidly quenched by

TABLE I  
Viscosity-Average Molecular Weight  $\bar{M}_v$  and Conditions of Preparation of Isotactic Polypropylene Samples Used in this Work

Sample	Brand of sample	$\bar{M}_v$	Molding temperature, K	Annealing condition
A	MH-4	330,000	468	unannealed
B	MH-4	330,000	468	at 423 K for 6 hr
C	MH-4	330,000	493	unannealed
D	Tokuso A	440,000	493	unannealed
E	MA-8	510,000	493	unannealed
F	nonbrand	740,000	493	unannealed

plunging it into cold water immediately after removal from the press (sample A). This film was annealed at 423 K for 6 hr (sample B). Films of samples C, D, E, and F were prepared from the pellets of MH-4, Tokuso A, MA-8, and the nonbrand sample, respectively, by compression molding the pellets at 493 K and then quenching them in cold water. Specimens 1 mm wide cut out from the original films were zone drawn.

### Method of Zone Drawing

Figure 1(a) shows a schematic representation of the improved zone-drawing apparatus equipped with a tensile tester, Tensilon UTM-III-500 (Toyo Baldwin Co., Ltd.); Figure 1(b) shows the detailed construction of the heater and the cooler. The heater is a pillar of brass wound with nichrome wire, and the cooler is a thermoelectric cooling unit, SCU-7103 (Shin-nippon Denko Co., Ltd.). The exothermic side of the cooling unit was cooled by circulating ice water. The thickness of the heater was 10 mm, so that the heating zone was restricted to 10 mm along the drawing direction. The temperatures of the heater and the cooler were measured with thermocouples set very close to the sample. The samples were drawn at a drawing speed of 30 to 250 mm/min by the tensile tester. The ensemble of the heater and the cooler was shifted at appropriate rates so that the necking region was confined to the heater during extension.

### Characterization of Zone-Drawn Samples

The tensile complex modulus of zone-drawn samples was measured at room temperature at 3.5 Hz with a viscoelastometer, Rheovibron DDV-III (Toyo Baldwin Co., Ltd.). Temperature dependence of storage modulus  $E'$ , loss modulus  $E''$ , and loss tangent  $\tan \delta$  was measured at 110 Hz with a viscoelastometer, Rheovibron DDV-IIB (Toyo Baldwin Co., Ltd.). Orientation function of the crystal  $c$ -axis was evaluated from the (110) and (040) planes azimuthal intensity distributions of x-ray diffraction by the usual method.

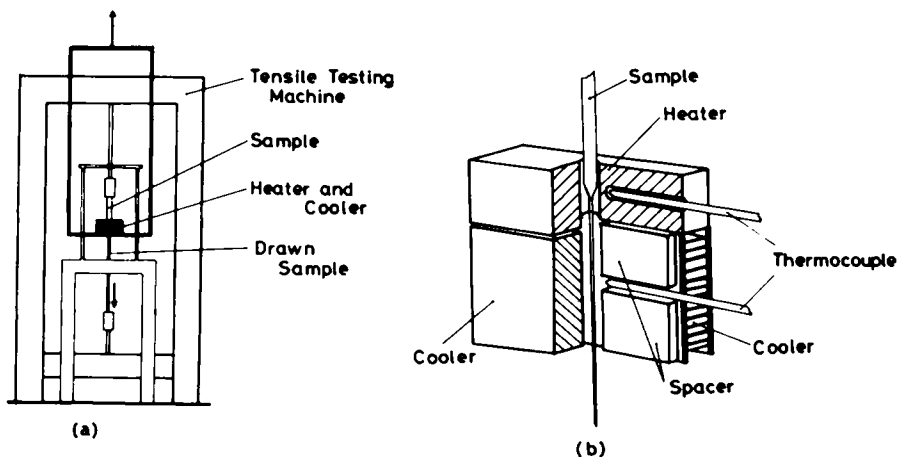


Fig. 1. (a) Schematic representation of zone-drawing apparatus equipped in a tensile tester and (b) detailed construction of heater and cooler.

## RESULTS AND DISCUSSION

## Effects of Various Testing Conditions and Molecular Weights on Modulus

**Testing Temperature.** Figure 2 shows the relationship between modulus and draw ratio for sample B, which was drawn at various heater temperatures,  $T_d$  with the cooler temperature  $T_q$  kept at room temperature. Draw ratio was determined from the cross-sectional area reduction. For each testing condition, modulus increased with draw ratio, but the ratio of its increase decreased at higher draw ratio. The highest modulus obtained under these testing conditions was 8.5 GPa when  $T_d = 403$  K. The optimum temperature to prepare the sample with maximum modulus may be located between 393 and 413 K when the results of Figure 2 are surveyed. At this region of temperature, crystals of isotactic polypropylene become viscoelastic since the crystalline relaxation temperature is located at about 390 K (138 Hz).<sup>9</sup> The drawing temperature at which Ward et al.<sup>6</sup> prepared the oriented isotactic polypropylene with the highest modulus by means of cold drawing was 383 K, which is lower than that in the present work. According to Clark et al.,<sup>7</sup> the optimum temperature for preparing the oriented isotactic polypropylene with the highest modulus was 403 K.

**Molecular Weight.** Figure 3 shows the relationship between modulus and draw ratio for  $T_d = 403$  K and  $T_q =$  room temperature for the quenched samples of different molecular weights. It can be seen that the relationship between modulus and draw ratio depends on molecular weight in a region of high draw ratio and that the higher the molecular weight, the higher the maximum modulus attained when molecular weight is below 510,000. When the molecular weight was 740,000, the highest modulus attained was 5 GPa at most.

**Drawing Stress.** Figure 4 shows the relationship between modulus and drawing stress for both quenched and annealed samples (samples A and B) drawn at various heater temperatures keeping  $T_q$  equal to room temperature. The drawing stress is determined by dividing the load in drawing by the cross-sectional area of the sample after being drawn. It is apparent that the relationship between modulus and drawing stress depends on neither the heater temperature nor the thermal histories of the original samples. Figure 5 shows the relationship between modulus and drawing stress for quenched samples with different molecular weights (samples C, D, E, and F). They were drawn at  $T_d = 403$  K and

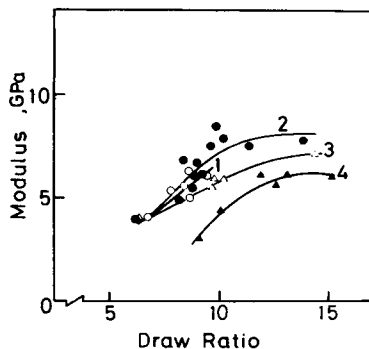


Fig. 2. Modulus vs draw ratio for sample B: 1,  $T_d = 393$  K (O); 2, 403 K (●); 3, 413 K (Δ); 4, 423 K (▲);  $T_q =$  room temperature.

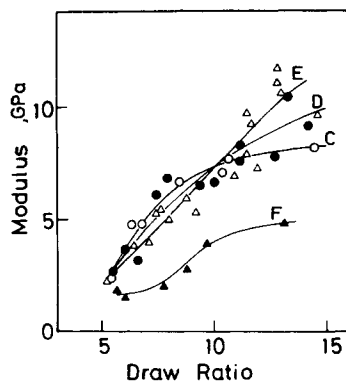


Fig. 3. Modulus vs draw ratio for samples C, D, E, and F.  $\bar{M}_v$ : 330,000 (○); 440,000 (●); 510,000 (△); 740,000 (▲).  $T_d = 403$  K;  $T_q =$  room temperature.

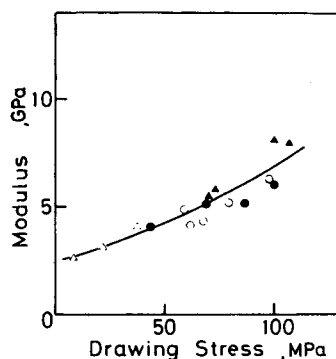


Fig. 4. Modulus vs drawing stress. Sample A (△):  $T_d = 403$  K and  $T_q =$  room temperature. Sample B:  $T_d = 383$  K (○), 393 K (●), and 403 K (▲);  $T_q =$  room temperature.

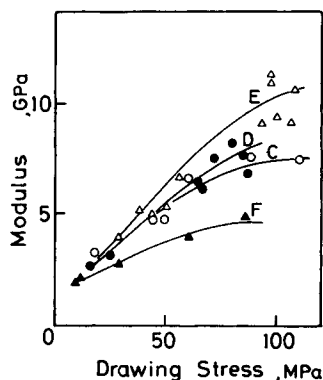


Fig. 5. Modulus vs drawing stress for samples C (○), D (●), E (△), and F (▲).  $T_d = 403$  K and  $T_q =$  room temperature.

$T_q =$  room temperature. The dependence of modulus on molecular weight became conspicuous in the region of higher drawing stress.

**Temperature of Cooling Zone.** Figure 6 shows the relationship between modulus and draw ratio for sample E at  $T_d = 410$  K and  $T_q =$  room temperature and 263 K. The modulus curve of  $T_q = 263$  K is always above that of  $T_q =$  room

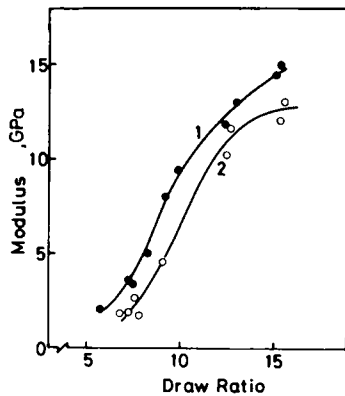


Fig. 6. Modulus vs draw ratio for sample E,  $T_d = 410$  K: 1,  $T_q = 263$  K (●); 2, room temperature (○).

temperature. When  $T_q = 263$  K, we could prepare an oriented isotactic polypropylene film with ultrahigh modulus of 15 GPa corresponding to about 44% of the crystal modulus of 34 GPa.<sup>3</sup>

### Viscoelastic Property and Superstructure of Zone-Drawn Sample

Figure 7 shows the temperature dependence of  $E'$ ,  $E''$ , and  $\tan \delta$  for sample E drawn at various draw ratios  $\lambda$  at  $T_d = 403$  K and  $T_q =$  room temperature. The  $\tan \delta$  peak located around 285 K corresponding to the primary relaxation is associated with the initiation of micro-Brownian motion of amorphous chains.<sup>9</sup> The  $\tan \delta$  peak became progressively smaller and broader at the higher temperature side with increasing draw ratio. Such depression and broadening of the  $\tan \delta$  peak might be ascribed to the increased number of tie molecules newly formed which hardly engage in micro-Brownian motion. The value of  $E'$  increased with increasing draw ratio over all ranges of temperature, as shown in Figure 7. It should be noted that reduction of  $E'$  above the primary relaxation temperature became less distinct for higher draw ratio samples. In the fiber structure displaying the small reduction of  $E'$ , the fraction of tie molecules seems to be increased as if the amorphous regions were included in the crystalline matrix.<sup>10</sup>

Figure 8 shows the relationship between the orientation function of crystal  $c$ -axis and draw ratio for sample E drawn at  $T_d = 410$  K and  $T_q = 263$  K. The orientation function of the crystal  $c$ -axis increased with a draw ratio below  $\lambda = 9$  and reached a constant value of 0.995 above  $\lambda = 9$ . In Figure 8 modulus is also plotted against draw ratio. The remarkable increase in modulus below  $\lambda = 9$  is attributable to the increase in the orientation function of the crystal  $c$ -axis. Above  $\lambda = 9$  the orientation function of the crystal  $c$ -axis scarcely changed with draw ratio, but the modulus nevertheless increased. It can be presumed that the increase of modulus above  $\lambda = 9$  should result from the formation of tie molecules. When a sample is further drawn over  $\lambda = 16$ , whitening of the sample was observed and the modulus abruptly decreased. The whitening of the sample may result from microvoids formed by preferential scission of strained tie molecules. The fact that the attainable draw ratio of  $T_d = 393$  K was lower than at higher  $T_d$  as shown in Figure 2 may be explained by scission of tie molecules at the final range of extension.

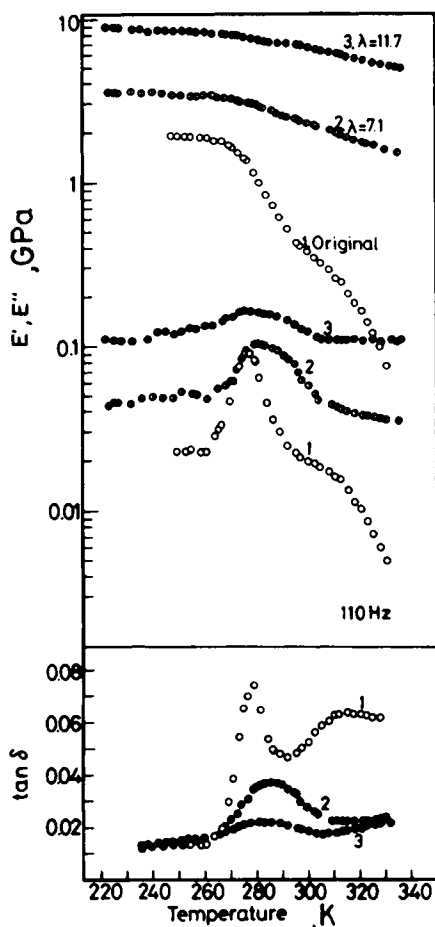


Fig. 7. Temperature dependence of  $E'$ ,  $E''$ , and  $\tan \delta$  for sample E drawn at  $T_d = 403$  K and  $T_q =$  room temperature.

When the drawn sample formed in the heater of the improved zone-drawing apparatus is cooled at  $T_q = 263$  K immediately after the drawn sample leaves the heater, it can be inferred that the drawn sample may be no longer deformed and structurally fixed in the cooler, especially when the primary relaxation is located above 263 K and the amorphous chains are completely frozen in at 263 K. If the folded chains of crystallites are largely unfolded at higher draw ratio, more tie molecules are formed by an increase of extended chains. Drawn sample having a higher fraction of tie molecules would be obtained when it is quenched to 263 K after being drawn in the heater, since loosening of the formed tie molecules should be prevented. This may explain the higher modulus when the cooling units are attached to the heater (refer to Fig. 6).

As shown in Figure 3, the modulus depends on the molecular weight, especially in the region of higher draw ratio. Up to  $\bar{M}_v = 510,000$  the higher the molecular weight, the higher is the modulus. The ends of extended chains, which are formed by being unfolded from the crystallites, form defects which give rise to formation and growth of microcracks when the sample is stretched. When the molecular weight is large, there are fewer such defective points and therefore

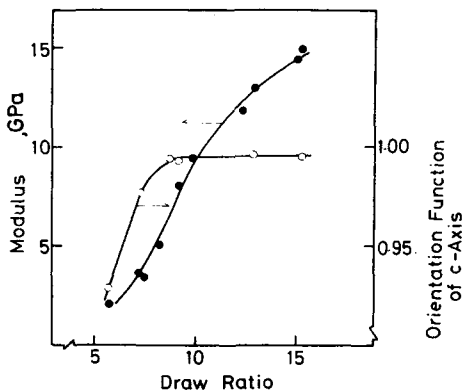


Fig. 8. Orientation function of crystal *c*-axis and modulus vs draw ratio for sample E drawn at  $T_d = 410$  K and  $T_q = 263$  K.

the process of extension for the original sample of larger molecular weight will be possible to more conspicuously unfold without formation of microcracks than with samples of lower molecular weight. It can therefore be presumed that up to  $\bar{M}_v = 510,000$  drawing stress should be more effectively generated on a sample of the higher molecular weight through unfolding of folded chains and depression of formation of microcracks. But for samples of  $\bar{M}_v = 740,000$ , where molecular chains are much larger, unfolding may be more difficult in extension, and scission may more easily take place during the unfolding process, and therefore the fraction of tie molecules does not increase so much. This inference would be supported by Figures 3 and 5.

### Fraction of Tie Molecules

The fraction of tie molecules will be quantitatively evaluated on the basis of the assumption that the modulus of a strained tie molecule is equal to that of crystal along the molecular axis, using the composite model composed of the series and parallel connection of crystalline region (C) and amorphous region (A) shown in Figure 9.<sup>10,11</sup> The modulus of drawn sample E is calculated on the basis of the above model by the following equation:

$$E = (1 - \xi)E_c + \xi[(1 - \phi)/E_c + \phi/E_a]^{-1} \quad (1)$$

where  $E_c$  is the crystal modulus along the molecular axis,  $E_a$  is the modulus of the amorphous phase except for tie molecules, and  $\phi$  and  $\xi$  are the measures of fraction of series and parallel connection of the amorphous phase.  $\xi\phi$  is equal to the volume fraction of the amorphous region,  $v_a$ . If  $\phi = v_a/\xi$  is substituted in eq. (1), we obtain

$$1 - \xi = \frac{v_a E (E_c - E_a) - E_a (E_c - E)}{v_a E_c (E_c - E_a) - E_a (E_c - E)} \quad (2)$$

Since  $E_c$  and  $E$  are<sup>3</sup> 34 GPa and 10–15 GPa, respectively, and  $E_a$  at room temperature higher than  $T_g$  might be of the order of  $10^{-2}$  GPa, eq. (2) is rewritten as follows:

$$1 - \xi = E/E_c \quad (3)$$

The fraction of tie molecules,  $1 - \xi$ , can be evaluated from eq. (3). The closed



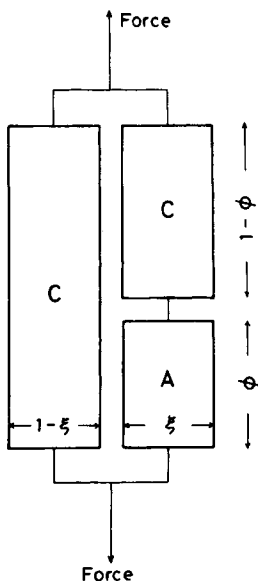


Fig. 9. Mechanical model of oriented crystalline polymers.

circles in Figure 10 show the relationship between the fraction of tie molecules and draw ratio for sample E drawn at  $T_d = 410$  K and  $T_q = 263$  K. The relationship is shown only in the region of draw ratio from 9 to 16, taking into account that change in modulus would depend on only the fraction of tie molecules because the orientation function of crystal  $c$ -axis does not change in this deformation region and reaches a maximum value, 0.995.

The relationship between the fraction of tie molecules and the draw ratio above a draw ratio of 9 may be represented by eq. (4) on the assumptions that (1) only the folded chains connected by tie molecules are unfolded in the heating zone and that (2) these tie molecules cannot be refolded because they pass through the cooler zone and are not broken down during zone drawing. Since according to the above assumptions the number of tie molecules at the cross section does

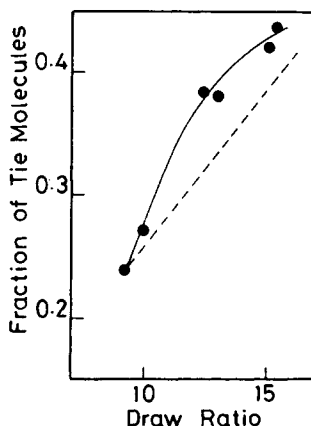


Fig. 10. Fraction of tie molecules vs draw ratio calculated from eq. (3) (●) and eq. (4) (broken line).

not change during zone drawing, we obtain

$$\frac{(1 - \xi)_\lambda}{(1 - \xi)_{\lambda_0}} = \frac{\lambda}{\lambda_0} \quad (4)$$

where  $\lambda_0$  is the draw ratio determined from the cross-sectional area reduction at which the orientation function of the crystal  $c$ -axis begins to level off, as shown in Figure 8;  $\lambda$  is a larger draw ratio than  $\lambda_0$ ; and  $(1 - \xi)_\lambda$  and  $(1 - \xi)_{\lambda_0}$  are the fractions of tie molecules at  $\lambda$  and  $\lambda_0$ , respectively. In Figure 10 the broken line shows the relationship represented by eq. (4) between the fraction of tie molecules and the draw ratio. It is located below the value evaluated from eq. (3). Thus, another origin for the increase in the fraction of tie molecules should be considered. Extending chains seem to be formed not only by unfolding of folded chains due to extension of the tie molecules but also by slipping between molecular chains in crystallites if the extended chains formed are not refolded and broken down. Therefore, the greater increase in the actual fraction of tie molecules at  $\lambda$ , as shown in Figure 10, can be explained by the deformation mechanism that the folded chains contained in undrawn sample are unfolded in the region of a draw ratio above 9 by both extension of tie molecules and slipping between the molecular chains in the crystallites.

### References

1. A. Peterlin, *Polym. Eng. Sci.*, **17**, 183 (1977).
2. H. Kiho and K. Asai, *J. Macromol. Sci.-Phys.*, in press.
3. I. Sakurada and I. Kaji, *J. Polym. Sci. C*, **31**, 57 (1970).
4. I. M. Ward and G. Capaccio, *Polymer*, **15**, 223 (1974).
5. N. E. Weeks and R. S. Porter, *J. Polym. Sci. Polym. Phys. Ed.*, **12**, 635 (1974).
6. D. L. M. Cansfield, G. Capaccio, and I. M. Ward, *Polym. Eng. Sci.*, **16**, 721 (1975).
7. W. N. Taylor and E. S. Clark, *Polym. Eng. Sci.*, **18**, 518 (1978).
8. J. B. Kinsinger and R. E. Hughes, *J. Phys. Chem.*, **73**, 2002 (1959).
9. S. Minami, Y. Tanoue, and M. Takayanagi, *Kogyo Kagaku Zasshi*, **830**, 68 (1965).
10. M. Takayanagi, K. Imada, and T. Kajiyama, *J. Polym. Sci. C*, **15**, 75 (1966).
11. M. Takayanagi, *Mem. Fac. Eng. Kyushu Univ.*, **23**, 1 (1963).

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