

# Mechanical Properties of Nylon 6 Fibers Gel-Spun from Benzyl Alcohol Solution

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## SYNOPSIS

The drawing behavior and mechanical properties of gel-spun nylon 6 fibers were investigated in relation to the growth rate and morphology of gels. The sol-gel transition temperature of a nylon 6/benzyl alcohol solution increased with polymer concentration and, at higher concentration, appeared with gel melting. From the measurements of gelation time, the growth rate of gels was estimated assuming an Arrhenius type of gelation rate. It was found that gel growth of nylon 6 in benzyl alcohol was nearly three-dimensional, evidenced by the presence of spherical gels observed in the scanning electron microscope. A draw of as-spun fibers was performed at one-stage or two-stage hot drawing. Modulus and tenacity increased with increase of the draw ratio and were nearly independent of the draw temperature. A two-stage draw was more effective to obtain a higher modulus than that of the one-stage draw and it was ascribed to the difference in the molecular orientation mechanism. However, it was difficult to obtain a higher modulus than 6.2 GPa by the gel-spinning of nylon 6 in this study and it was regarded as a result of the presence of spherical gels which hindered the sample to elongate to a higher draw ratio. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Recently, many attempts have been made for developing high-modulus, high-strength polymer fibers.<sup>1,2</sup> The achievement of high-strength polymers is based on the concept of perfect chain orientation by the unfolding of flexible polymer chains from a crystal through ultrahigh drawing or by designing rigid and linear backbone chains. The highest modulus obtained in highly drawn ultrahigh molecular weight polyethylene is close to its theoretical range of 240–340 GPa.<sup>3,4</sup> However, it is still difficult to produce high-strength and high-modulus fibers of common polyesters and polyamides which have the merit of having a high melting temperature and high molecular rigidity in comparison with polyethylene.

Many investigators have devoted attempts to increase the modulus of nylon 6 fibers which are widely used, e.g., as tire yarns. The highest reported

modulus of nylon 6 is 19 GPa,<sup>5</sup> which is much lower than its theoretically calculated value of 263 GPa.<sup>6</sup> The difficulty of the ultradrawing of nylon 6 is largely due to the presence of intermolecular hydrogen bonding between adjacent amide groups in nylon 6. Some methods have been suggested to facilitate the deformation of nylon 6 by relieving hydrogen bonding during processing. Solid-state coextrusion of nylon 6 reversibly plasticized with anhydrous liquid ammonia increased the modulus to 13 GPa.<sup>7</sup> Anhydrous liquid ammonia as a plasticizer plays a role of temporarily disrupting hydrogen bonds in the amorphous phase of nylon 6 and making a draw easier. As the reversible plasticizer, iodine has been used to enter both the amorphous and crystalline phases, where a considerably high draw ratio was obtained, but the modulus was only 6 GPa because of chain slip within the nylon 6-iodine complex formed.<sup>8</sup> Also, dry-spinning<sup>9</sup> of nylon 6 from formic acid/chloroform cosolvent mixtures resulted in an enhanced modulus up to 19 GPa. On the other hand, solution-spinning of nylon 6 with a relative viscosity of 6.5

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in formic acid led to a high modulus of 5.2 GPa and tenacity of 1.2 GPa.<sup>10</sup> Melt-spinning of nylon 6/lithium bromide mixtures followed by drawing also led to fibers with a modulus up to the range of 9–13 GPa.<sup>10</sup>

As another potential approach, gel-spinning has been used to increase the modulus of fibers since its development by Kalb and Pennings<sup>11</sup> as a technique for solution-spinning of ultrahigh molecular weight polyethylene. It has been also applied to other flexible polymers such as polypropylene<sup>12</sup> and poly(vinyl alcohol).<sup>13</sup> Matsuo et al.<sup>14,15</sup> studied the deformation mechanism of nylon 6 films prepared by gelation/crystallization from solutions with cosolvent mixtures of formic acid–chloroform in comparison with the deformation of a melt film. However, they obtained a relatively low modulus of 4 GPa and poor drawability with a maximum draw ratio of  $\sim 4$ . It was ascribed to the preferential orientation of the *b*-axis with respect to the stretching direction by the rotation of crystallites around the *c*-axis without significant crystal transformation from a folded to a fibrous type. Chuah and Porter<sup>8</sup> tried to produce a nylon 6 gel by cooling a nylon 6 solution with benzyl alcohol from 165°C to room temperature. The resultant partially dried gel film was drawn by coextrusion with polyoxymethylene in an Instron rheometer. The modulus obtained was about 5.7 GPa at a draw ratio above 3.7.

In this study, mechanical properties of nylon 6 fibers prepared by gel-spinning from a benzyl alcohol solution were investigated with the growth index and morphology of the gels. A comparison was also made between the tensile properties of nylon 6 fibers drawn at one-stage and two-stage.

## EXPERIMENTAL

### Materials

Nylon 6 chips with an intrinsic viscosity of 1.54 dL g<sup>-1</sup> (Tongyang Nylon Co., South Korea) were used. Benzyl alcohol was used as a solvent of the polymer. A Canon-Fenske viscometer was used for the determination of intrinsic viscosity,  $[\eta]$ , of the polymer in formic acid at 25°C. Molecular weight was estimated to be  $4.7 \times 10^4$  according to the following formula<sup>16</sup>:

$$[\eta] = 22.6 \times 10^{-3} \times M_w^{0.82} \quad (1)$$

### Determination of Sol–Gel Transition Temperature, Gelation Time, and Gel Melting Temperature

The sol–gel transition temperature was determined by investigating the state of the solution by the test-tube tilting method after the hot solution was kept for 24 h at a fixed temperature. A test-tube tilting method was also used for measuring the gelation time,  $t_{\text{gel}}$ , which was defined as the time taken from the instant when the test tube was put in the bath at a fixed temperature to the gelation. The gel melting temperature,  $T_m^g$ , was determined from the peak temperature of the endothermic curve measured by differential scanning calorimetry using a liquid sample pan at the heating rate of 10°C/min.

### Gel-spinning

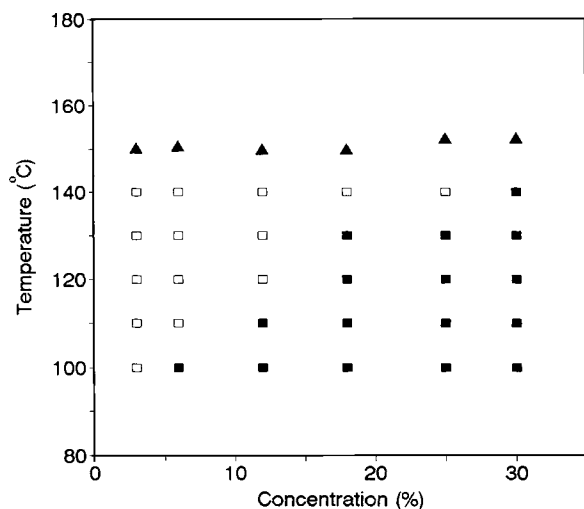
The spinning solutions were prepared by dissolving nylon 6 in benzyl alcohol at 160°C. The concentration of the polymer in the spinning solutions was 70 w/v %. Prior to the dissolution procedure, the polymer was dried for 24 h at 60°C in a vacuum oven. After complete dissolution occurred, the solution was transferred to a fiber extrusion device and spun at 160°C through a conical die. The as-spun fibers were quenched to room temperature to form a gel fiber. The gel fiber was then dried at ambient conditions. No residual solvent was recognized in the infrared spectra of the dried gel fibers. The x-ray diffraction pattern measured in the gel-spun fibers showed the crystal structure of the monoclinic  $\alpha$  phase.<sup>17</sup>

### Drawing Methods

The draw of the dried gel fibers was carried out by two methods, i.e., one-stage and two-stage draws. In the one-stage draw, the sample was drawn at a temperature region of 130–200°C in a hot-air oven as in the conventional draw. In the two-stage draw, the first-stage draw was done at 130°C to twice the original fiber length. Then, it was followed by the second-stage draw at 200°C to various draw ratios. The draw ratio was determined by measuring the displacement of ink marks on the sample before and after drawing.

### Measurements of Properties of Samples

The fiber morphology was characterized using an scanning electron microscope (SEM). The mechan-

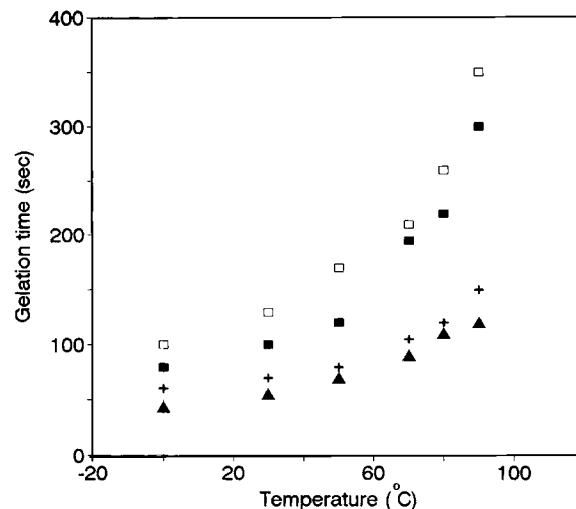


**Figure 1** Phase diagram of nylon 6/benzyl alcohol solution: (▲) gel melting temperature; (■) gel state; (□) sol state.

ical properties of nylon 6 fibers were measured at room temperature using an Instron tensile tester at a crosshead speed of  $2.54 \text{ mm min}^{-1}$ . The length of samples was 20 mm. The birefringence was measured by a Nikon polarizing microscope equipped with a Senarmont compensator. Densities were measured by the floating method using mixtures of carbon tetrachloride and toluene. The volume-fraction crystallinity,  $\chi$ , was calculated from the density,  $\rho$ , of the samples according to the relation

$$\chi = (\rho - \rho_a)/(\rho_c - \rho_a) \quad (2)$$

where  $\rho_a$  and  $\rho_c$  are the densities of the amorphous and crystalline regions, respectively. The values of  $\rho_a$  and  $\rho_c$  were taken as 1.08 and 1.23  $\text{g/cm}^3$ , respectively.<sup>18</sup>



**Figure 2** Plot of gelation time against gelation temperature for various polymer concentrations: (□) 12%; (■) 18%; (+) 25%; (▲) 30%.

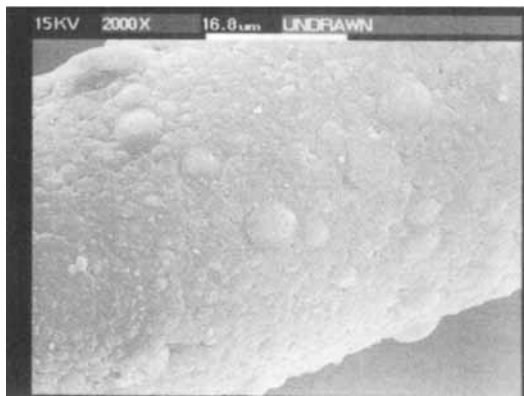
## RESULTS AND DISCUSSION

### Gelation Behavior

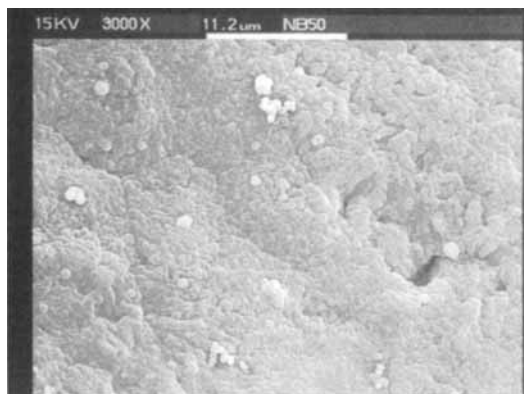
Figure 1 shows the temperature-concentration phase diagram of the nylon 6/benzyl alcohol solution. The sol-gel transition temperature increases largely with increase of the polymer concentration, and at a high polymer concentration of 30 wt % or more, the sol-gel transition appears with gel melting. The gel melting temperature is at the level of about  $150^\circ\text{C}$  and does not largely change with the polymer concentration. Figure 2 shows the gelation time of the solution as a function of temperature and polymer concentration. Gelation time increases with increase of temperature and its temperature dependence is higher in the higher temperature region. As the polymer concentration increases at a given gelation temperature, the gelation time decreases markedly.

**Table I** Supercooling Temperature Dependence of the Apparent Activation Energy in Various Polymer Systems

Polymer System	Type	Activation Energy
Polyethylene in xylene <sup>21</sup>	Crystallization	$(T_m^g - T)^{-1}$
Poly(vinyl alcohol) in water <sup>19</sup>	Gelation	$(T_m^g - T)^{-2}$
At-polystyrene in $\text{CS}_2$ <sup>19</sup>	Gelation	$(T_m^g - T)^{-2.8}$
Poly(vinylidene fluoride) in $\gamma$ -butyrolactone <sup>20</sup>	Gelation	$(T_m^g - T)^{-1.6}$
Nylon 6 in benzyl alcohol	Gelation	$(T_m^g - T)^{-1.7}$



(a)



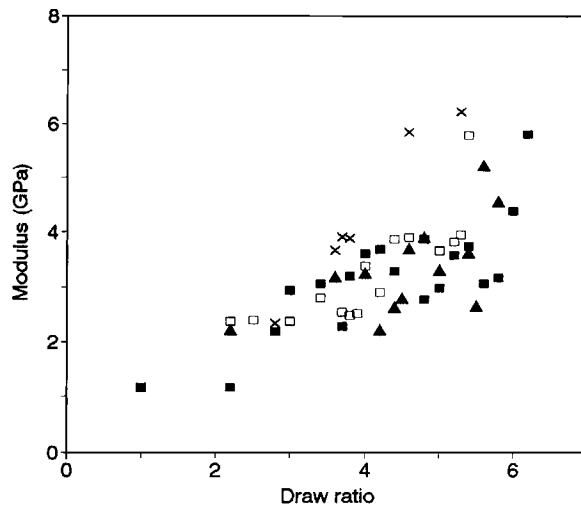
(b)

**Figure 3** SEM pictures of (a) gel-spun nylon 6 fiber and (b) dried gel film.

Assuming that the gelation rate, i.e., the inverse of gelation time, obeys an Arrhenius relationship, the following equation can be written<sup>19,20</sup>:

$$1/t_{\text{gel}} = \text{constant} \times \exp(-\Delta E/RT) \quad (3)$$

where  $T$  and  $\Delta E$  are the gelation temperature and an apparent activation energy for the gelation, respectively. Because of the nonlinearity of the apparent activation energy to temperature,<sup>19</sup> the apparent activation energy should be represented as a

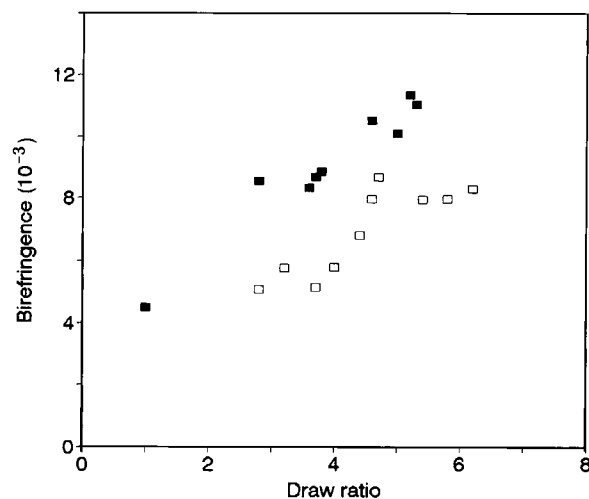


**Figure 4** Dependence of modulus on the draw ratio of nylon 6 fibers for one-stage draw: (■) 180°C; (□) 190°C; (▲) 200°C; and (×) two-stage draw.

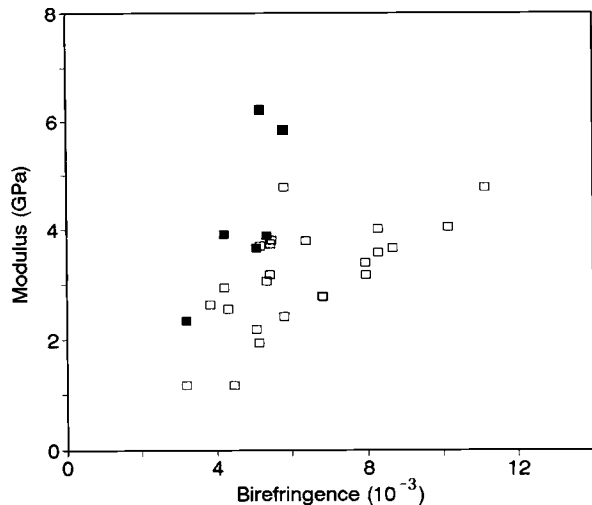
function of the supercooling temperature,  $\Delta T$ , i.e.,  $T_m^g - T$ , as in eq. (4):

$$\Delta E = B/(T_m^g - T)^n \quad (4)$$

where  $n$  and  $B$  are constants and  $n$  is defined as a growth index of the gels. With eqs. (3) and (4), the  $n$  value can be determined using the data of gelation time. The  $n$  value in this study was estimated as 1.7 from the data of Figure 2. It indicates that the nylon 6 gels grow nearly three-dimensionally. Table I represents some comparisons of  $n$  values for various polymer systems including this work. It was reported



**Figure 5** Birefringence vs. draw ratio of nylon 6 fibers: (□) one-stage draw at 180°C; (■) two-stage draw.

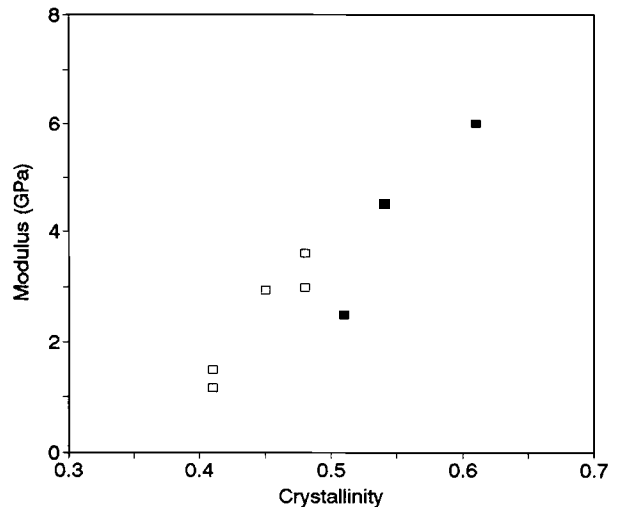


**Figure 6** Modulus vs. birefringence of nylon 6 fibers: (□) one-stage draw at 180°C; (■) two-stage draw.

that a poly(vinyl alcohol) aqueous solution<sup>19</sup> and a poly(vinylidene fluoride)/ $\gamma$ -butyrolactone solution<sup>20</sup> have three-dimensional gel growth. Three-dimensional growth of nylon 6 gels may be evidenced by SEM observation. The surface morphology of as-spun nylon 6 gel fiber indicates the presence of spherical gels as shown in Figure 3(a), i.e., nylon 6 gels seem to grow spherically on cooling the solution of benzyl alcohol. The distribution of gel size is also shown in Figure 3(a), which is likely to result from the difference of cooling rate due to the temperature variation within a fiber in nonisothermal gel-spinning. However, in gels formed under an isothermal condition, relatively uniform gels were observed as shown in Figure 3(b).

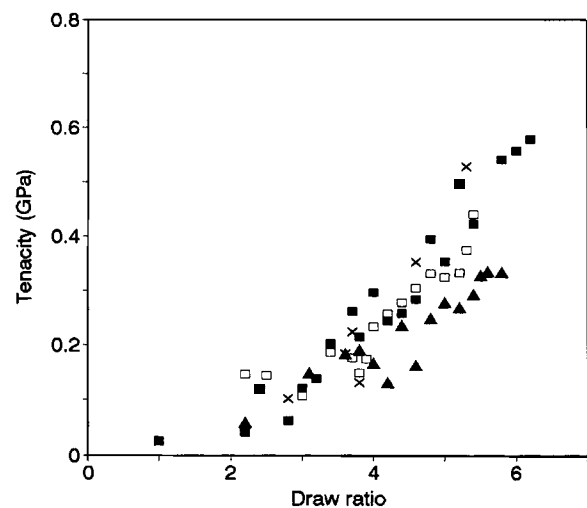
#### Drawing Behavior and Mechanical Properties

As-spun fibers could be drawn to a draw ratio of 5–6 in the one-stage or two-stage draw. Figure 4 shows the relationship between the modulus and draw ratio of samples drawn at one-stage and two-stage. The modulus tends to increase with increase of the draw ratio. An effect of draw temperature at the one-stage draw on the modulus was not clearly recognized. However, the modulus increases more steeply with increase of draw ratio for the two-stage draw than for the one-stage draw. It indicates that the two-stage draw is more effective to obtain a high modulus than is the one-stage draw. As well known, nylon 6 is a difficult material to elongate to a high draw ratio due to the presence of intermolecular hydrogen bonding between adjacent amide groups. Regarding

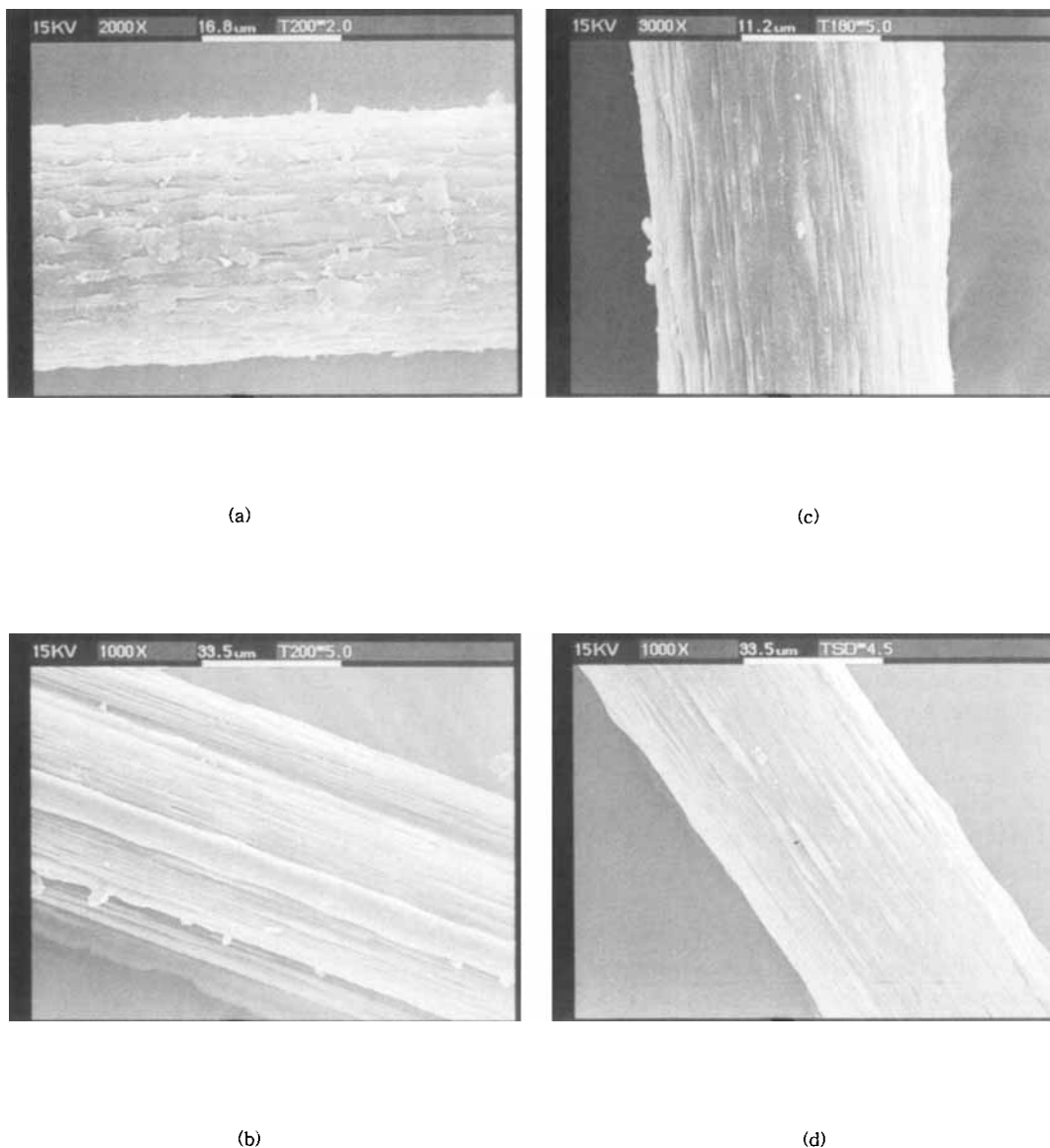


**Figure 7** Modulus vs. crystallinity of nylon 6 fibers for (□) one-stage draw at 180°C and (■) two-stage draw.

that the hydrogen bonding may act more strongly within crystals than in the amorphous region, defolding of lamella on drawing is more difficult to be made than is the orientation of amorphous chains. Therefore, it may be preferable to draw a nylon 6 sample having a low crystallinity to obtain a high draw ratio. On the basis of this viewpoint, it is considered that the two-stage draw in this study is a more effective method to obtain a high modulus than is the one-stage draw, because the first-stage draw in the two-stage draw is done at a relatively low draw temperature, i.e., 130°C, although the second-



**Figure 8** Dependence of tenacity on the draw ratio of nylon 6 fibers for one-stage draw: (■) 180°C; (□) 190°C; (▲) 200°C; and (×) two-stage draw.



**Figure 9** SEM pictures of drawn nylon 6 fibers with the draw ratio of (a) 2.0 at 200°C, (b) 5.0 at 200°C, and (c) 5.0 at 180°C for one-stage draw and (d) 4.5 for two-stage draw.

stage draw at 200°C follows it. The maximum draw ratio achieved in this study was 6.2 with the sample drawn at the one-stage at 180°C. The highest modulus obtained was 6.2 GPa for the sample drawn in the two-stage at 5.3 times.

Figure 5 shows the relationship between birefringence and draw ratio for the one-stage and two-stage draws. Birefringence increases with increase of the draw ratio for both drawing methods. The effect of the draw ratio on birefringence is higher for the two-stage draw than for the one-stage draw. It reflects well the relationship between modulus and draw ratio shown in Figure 4. However, the birefringences

of the drawn gel fibers in this study are relatively low in comparison with the values reported by other investigators.<sup>22</sup> It may be due to the imperfect defolding of crystals or the presence of surface defects that appeared in the drawn nylon 6 sample, which will be discussed in the next SEM observation. However, it should be noted that one-stage and two-stage draws may give rise to a difference in molecular orientation of the samples. Figure 6 shows the relationship between the modulus and birefringence of the samples. Modulus increases almost linearly with increase of the birefringence for both two-drawing methods, but its increasing rate is steeper

for the two-stage draw than for the one-stage draw. At this point, the difference in the slope between two lines may be ascribed to the result due to the difference of crystallinity of the samples. However, it is difficult to attribute it to the difference of crystallinity, while the crystallinity of sample by the two-stage draw is higher than that by the one-stage draw as shown in Figure 7. This is because the difference of crystallinity should give rise not to the difference in the slope of two lines but to two parallel lines. Therefore, the different slopes in the relationship between modulus and birefringence shown in Figure 6 should be interpreted in terms of the following molecular orientation mechanism. In the case of the two-stage draw, molecular orientation in the amorphous region is well developed between the crystal blocks interlocked each other. However, the one-stage draw does not give the continuous linkage structure of crystal blocks, leading to the low orientation of amorphous molecules. Sakai et al.<sup>23</sup> reported that such a molecular mechanism can be developed in zone-drawing. According to them, such linkages are formed when the crystallinity is higher than 77% in the case of polyethylene.

On the other hand, Figure 8 shows the relationship between the tenacity and draw ratio for one-stage and two-stage draws. Tenacity increases with increase of the draw ratio similarly as the modulus does. However, the tenacity of the samples by the two-stage draw does not show a superior value significantly in comparison with that by the one-stage draw. It may be ascribed to the surface characteristics of samples due to the gel-spinning. In general, the fiber strength is related to the microstructure and the presence of impurities, defects, and surface flaws. According to the concept of a surface flaw of Pennings et al.,<sup>24</sup> tensile strength has a relation to fiber diameter as in the following equation:

$$\sigma_b^{-1} = K(D - D_0)^{1/2} + \sigma_0^{-1} \quad (5)$$

where  $\sigma_b$  and  $\sigma_0$  are the tensile strength of the measured and flawless fibers;  $D$  and  $D_0$ , the diameters of the measured and flawless fibers, respectively; and  $K$ , a constant. Noting that the gels formed in fiber-spinning consist of spheres, the presence of such spherical gels may lower the fiber strength because of the rough surface morphology due to the three-dimensional gel growth. However spherical gels were extended by drawing the sample. Figure 9 shows that the spherical gels change to a fibrillar structure as the draw ratio increases. However, the surface of the drawn fiber is still not smooth, leaving many

flaws along the fiber length on the surface of fiber, although the surface flaws are diminished to a small extent in highly drawn samples. In contrast with it, it was reported that SEM observation of ultrahigh molecular weight polyethylene gel-spun from a decalin solution showed a fibrillar texture like spongy tissue and its drawn sample had nearly perfectly extended chains.<sup>25,26</sup> For the sample having such a gel morphology, an elongation to a high draw ratio up to about 300 could be achieved. The presence of spherical gels in this study are likely to hinder the fiber to elongate to a high draw ratio and to make many flaws appear on the surface of the fiber in the drawn samples. Therefore, in spite of the two-stage draw, the increase of tenacity with draw ratio does not make a dominant difference in comparison with the one-stage draw, dissimilarly as in the increase of the modulus with the draw ratio. This is because the effect of surface flaws due to the presence of spherical gels on the tenacity is significantly large. Consequently, it is considered that the mechanical properties of nylon 6 gel fiber are dependent on the spherical morphology of the gels, molecular orientation, and crystallinity.

## CONCLUSIONS

From the investigation of the gelation of nylon 6/benzyl alcohol solution and mechanical properties of gel-spun and hot-drawn fibers, the following conclusions were obtained. The sol-gel transition temperature increased with increase of polymer concentration and gel melting temperature did not change markedly with the concentration. It was found that gels grew three-dimensionally on the basis of the growth rate of gels estimated from the data of gelation time. Such a spherical gel morphology could be observed by SEM. Modulus and tenacity increased with increase of the draw ratio irrespective of draw temperature. In the drawing of as-spun fibers, the two-stage draw was more effective than was the one-stage draw because the two-stage draw could give the sample a higher modulus for the same draw ratio than for the one-stage draw. It could be explained by the difference of the orientation mechanism between the two drawing methods, i.e., in the two-stage draw, the molecular orientation in the amorphous region is developed between the continuous linkage structure of crystal blocks interlocked with each other, whereas the one-stage draw does not give a continuous link of crystal blocks. The mechanical properties of the nylon 6 gel fiber were

dependent on the spherical morphology of gels, molecular orientation, and crystallinity. The maximum draw ratio and modulus obtained in this study were 6.2 and 6.2 GPa, respectively.

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