

# Study of the Coagulated Structure and Fiber Strength with Wet Spinning of Aliphatic Polyketone with Aqueous Composite Metal Salt Solutions

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Received 5 May 2004; accepted 16 August 2004

DOI 10.1002/app.21547

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Poly(1-oxotrimethylene) (ECO) was dissolved in aqueous calcium chloride ( $\text{CaCl}_2$ )/zinc chloride ( $\text{ZnCl}_2$ ) composite metal salt solutions, and the solutions had phase-separation temperatures greater than  $0^\circ\text{C}$ . A higher proportion of  $\text{CaCl}_2$  with respect to  $\text{ZnCl}_2$  increased the phase-separation temperature of the ECO solutions. When wet spinning was carried out with a coagulation bath at  $2^\circ\text{C}$ , an ECO solution with a higher phase-separation temperature tended to produce greater ECO fiber strength. Therefore, a higher phase-separation temperature resulted in coagulated filaments with a denser and more homogeneous cross-sectional structure. When the metal salt concentration of the coagulation bath was increased with an ECO

solution with a phase-separation temperature of  $22^\circ\text{C}$  and a coagulation-bath temperature of  $2^\circ\text{C}$ , the strength of the ECO fibers tended to be lower. Although little difference was observed in the uniformity of the fiber cross sections, a higher metal salt concentration in the coagulation bath facilitated greater spherical growth of the coagulated particles. Large, spherical coagulated particles promoted defects during drawing and thus lowered the strength of the ECO fibers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1250–1258, 2005

**Key words:** fibers; strength; structure-property relations

## INTRODUCTION

Poly(1-oxotrimethylene) (ECO; Fig. 1) has been obtained through the perfectly alternating copolymerization of ethylene and carbon monoxide. It is expected to form a high-strength and high-elastic-modulus fiber because of its planar zigzag conformation and its smallest cross-sectional area in the crystalline phase<sup>1</sup> [ultimate tenacity = 266 cN/dtex (34.7 GPa), crystal elastic modulus = 2770 cN/dtex (361 GPa)].

The melt spinning of aliphatic polyketones such as ECO has been studied.<sup>2,3</sup> However, the mechanical properties of the melt-spun fibers do not significantly differ from those of poly(ethylene terephthalate) fibers widely used as industrial materials.

Wet-spinning methods have been investigated to obtain ECO fibers. Several organic solvents, such as hexafluoroisopropanol and phenol,<sup>4,5</sup> have been used as solvents. The hot drawing of coagulated fibers produces high-performance polyketone fibers with high strength and high elastic modulus [tenacity = 20 cN/dtex (2.6 GPa), elongation = 6.6%, elastic modulus = 230 cN/dtex (30 GPa)]. However, attempts at com-

mercial production with these organic solvent systems have been abandoned because of toxicity, poor desolvation during spinning, and high solvent costs.

We have studied aqueous solutions of various metal salts, such as zinc chloride ( $\text{ZnCl}_2$ ), calcium chloride ( $\text{CaCl}_2$ ), and sodium chloride ( $\text{NaCl}$ ).<sup>6,7</sup> Aqueous solutions have low toxicity and are inexpensive, and aqueous  $\text{ZnCl}_2$  solutions have been industrially used as solvents for polyacrylonitrile. Therefore, they seem promising as industrial solvents for ECO.

We previously reported that ECO fibers with high strength and high elastic modulus [tenacity = 18.5 cN/dtex (2.4 GPa), elastic modulus = 450 cN/dtex (59 GPa)] could be obtained via wet spinning with an ECO solution consisting of ECO dissolved in an aqueous 40/22 (w/w)  $\text{CaCl}_2/\text{ZnCl}_2$  solution, followed by superdrawing.<sup>8</sup> The ECO solution exhibited a phase-separation temperature greater than  $0^\circ\text{C}$ , solidifying to a gel below the phase-separation temperature. Wet spinning with a coagulation bath at a temperature below the phase-separation temperature of the ECO solution was a key point, and it yielded high-strength ECO fibers, with a lower coagulation-bath temperature yielding higher strength. The temperature jump during the coagulation process solidified the ECO solution into a gel, and this gave the coagulated filament a dense, uniform structure. The superdrawing of the coagulated filament produced an ECO fiber with ten-

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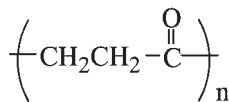


Figure 1 ECO.

sile properties equivalent to those of high-performance fibers.

In this article, we discuss the wet spinning of ECO with aqueous  $\text{CaCl}_2/\text{ZnCl}_2$  solutions as the solvents, focusing on the effects on the coagulated structure and fiber strength and using ECO solutions with different phase-separation temperatures and aqueous solutions with different metal salt concentrations as the coagulation baths.

## EXPERIMENTAL

### Materials

ECO was prepared as follows.<sup>9,10</sup> A solution of 1.210 g of 1,3-bis[di(2-methoxyphenyl)phosphino]propane in 500 mL of acetone was mixed with a solution of 0.412 g of palladium acetate in 500 mL of acetone. The mixture was stirred for 1 h. Trifluoroacetic acid (4.18 g) and *p*-benzoquinone (39.6 g) were added to the solution and dissolved.

Methanol (1 L) and 36.5 mL of the prepared catalyst solution were placed in a 2-L autoclave; a 1:1 mixed gas of ethylene and carbon monoxide was injected to a pressure of 5.5 MPa, and the reaction was conducted at 80°C for 4.5 h. After the reaction, the resulting polymer was washed several times with methanol and

then dried. The intrinsic viscosity ( $[\eta]$ ), measured in hexafluoroisopropanol at 25°C, was 5.6 dL/g.

### Phase-separation temperature

An ECO solution was placed in a cylindrical glass bottle with a 40-mm inner diameter. With the temperature controlled by a thermostat, the temperature was gradually lowered from the dissolution temperature at a rate of 10°C/h to 0°C. The phase-separation temperature was defined as the temperature at which the transparent solution became clouded.

### Spinning

With a plunger extruder (Fig. 2), an ECO solution was extruded from a spinneret with fifty 0.15-mm-diameter holes at a solution temperature of 80°C through a 10-mm air layer into a coagulation bath at a spinning speed of 3 m/min. The coagulated fiber was picked up onto a Nelson roll at 3 m/min and then was passed through an aqueous 0.5 wt % hydrochloric acid bath, washed with a washing roll, and wound up at a speed of 3 m/min. The wound coagulated fiber was heat-dried with a 1-m hotplate at 230°C with drawing rolls at a speed of 1 m/min. The obtained undrawn fiber was heated on a 1-m hotplate at 240–270°C and was hot-drawn at various speeds by the drawing rolls. The obtained drawn fiber was wound into a cheeselike package.

### Observation of the coagulated filament cross section by scanning electron microscopy (SEM)

The coagulated filament (Fig. 2) was wound and anchored onto a frame. This was then immersed in aque-

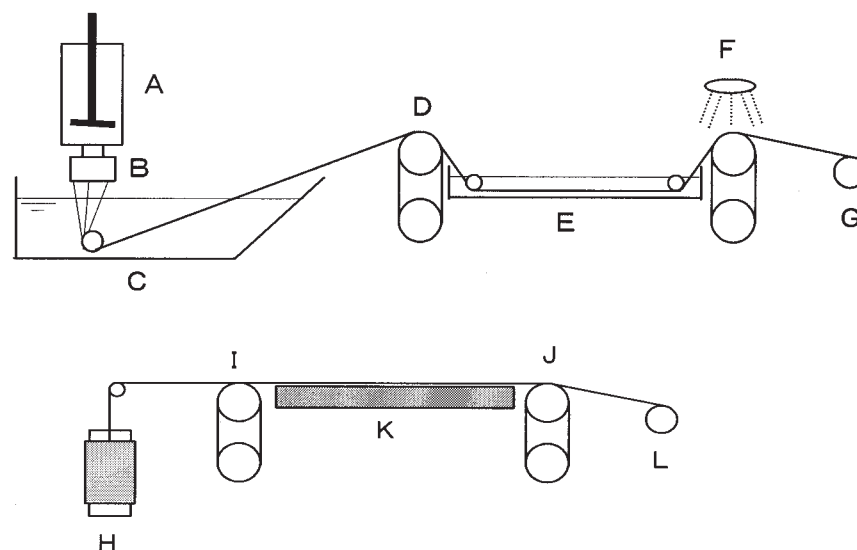
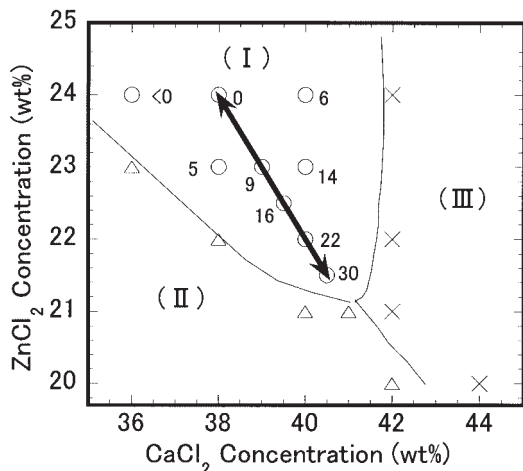


Figure 2 Schematic diagram of the spinning apparatus: (A) plunger extruder, (B) spinneret, (C) coagulation bath, (D) Nelson roll, (E) aqueous 0.5 wt % hydrochloric acid bath, (F) washing roll, (G) wound coagulated fiber, (H) undrawn fiber, (I, J) drawing rolls, (K) 1-m hotplate, and (L) drawn fiber.



**Figure 3** Solubility of ECO with aqueous  $\text{CaCl}_2/\text{ZnCl}_2$  solutions of different compositions: (O) homogeneously dissolved ECO, ( $\Delta$ ) nonhomogeneously and incompletely dissolved ECO, and ( $\times$ ) incompletely dissolved metal salt in water. The polymer concentration was 7 wt %, and the dissolution conditions were 80°C and 3 h of stirring.

ous ethanol solutions of different concentrations in the following order: 50/50, 75/25, 90/10, 95/5, 99/1, and 100/0 (w/w) ethanol/water. The water in the fiber was thus replaced with ethanol, and the fiber was then freeze-fractured with liquid nitrogen. It was subsequently immersed in *t*-butyl alcohol, for the substitution of the ethanol in the fiber, and then freeze-dried for use as a sample. The sample was Pt/Pd-coated for 40 s, and a Hitachi (Tokyo, Japan) S5000 super-high-resolution SEM instrument was used for the observation of the fiber cross section at an acceleration voltage of 1.0 kV.

### Measurement of the swelling

A 2-g sample of the coagulated fiber (Fig. 2) was subjected to 10 min of centrifugal separation at a centrifugal force of 1000g to remove the water adhering to the fiber surfaces. After the fiber weight ( $W_1$ ) was measured, the fiber was dried at 105°C for 5 h, and the weight of the dried fiber ( $W_2$ ) was then measured. The degree of swelling was recorded as the value calculated with the following formula:

$$\text{Swelling (wt \%)} = (W_1 - W_2)/W_2 \times 100$$

### Measurement of the fiber strength

A UCT-10T Tensilon (Orientech, Inc., Tokyo, Japan) was used with a fiber length of 20 cm and a pull rate of 20 cm/min.

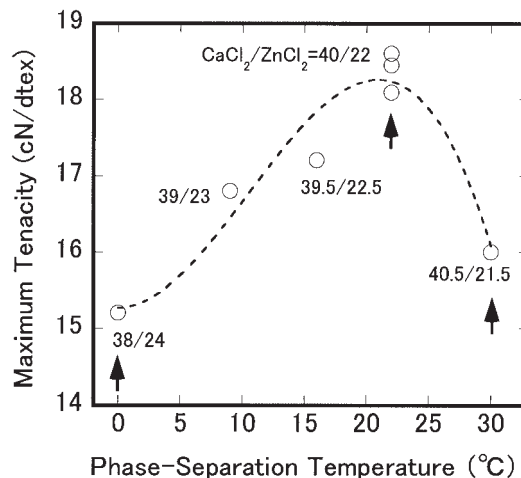
## RESULTS AND DISCUSSION

### Solubility of ECO and fiber properties based on the composition of the aqueous $\text{CaCl}_2/\text{ZnCl}_2$ solutions

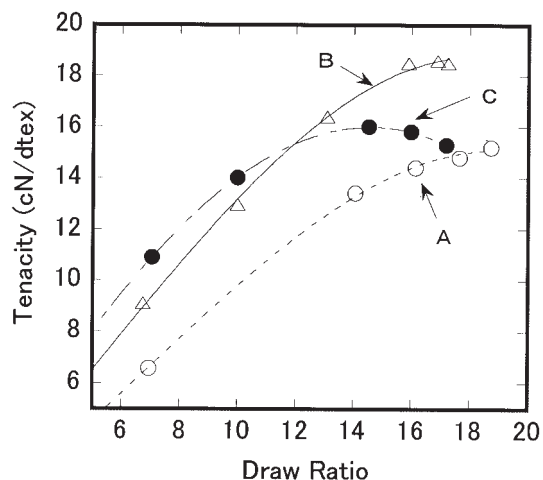
Figure 3 shows the solubility of ECO in aqueous metal salt solutions with different  $\text{CaCl}_2/\text{ZnCl}_2$  weight ratios. Region I represents a composition of the aqueous metal salt solution such that ECO with  $[\eta] = 5.6 \text{ dL/g}$  can be completely dissolved at a concentration of 7 wt % at 80°C. Region II represents a composition of the aqueous metal salt solution such that ECO cannot be completely dissolved under the previous conditions. Region III represents a composition such that the metal salt does not dissolve in water at 80°C. The numerals next to the circles in region I indicate the phase-separation temperatures of the ECO solutions with the respective aqueous metal salt solutions as solvents.

The ECO solution is homogeneous and transparent at 80°C, but at temperatures below the phase-separation temperature, the solution loses fluidity and solidifies into a gel. Because the solution returns to homogeneity if the temperature is increased above the phase-separation temperature, the gel crosslinking points are molecular entanglements or microcrystals. The arrow line shown in Figure 3 represents a metal salt concentration of 62 wt % in the aqueous metal salt solution. A higher proportion of  $\text{CaCl}_2$  raises the phase-separation temperature of the ECO solution and reduces its ability to dissolve ECO.

Figure 4 shows the maximum tenacity of the ECO fiber after hot drawing versus the phase-separation temperature for the spinning of five ECO solutions with different phase-separation temperatures shown on the arrow line in Figure 3, with 2°C water as the coagulation bath. Up to a phase-separation tempera-



**Figure 4** Maximum tenacity versus the phase-separation temperature for the spinning of ECO solutions with different phase-separation temperatures.

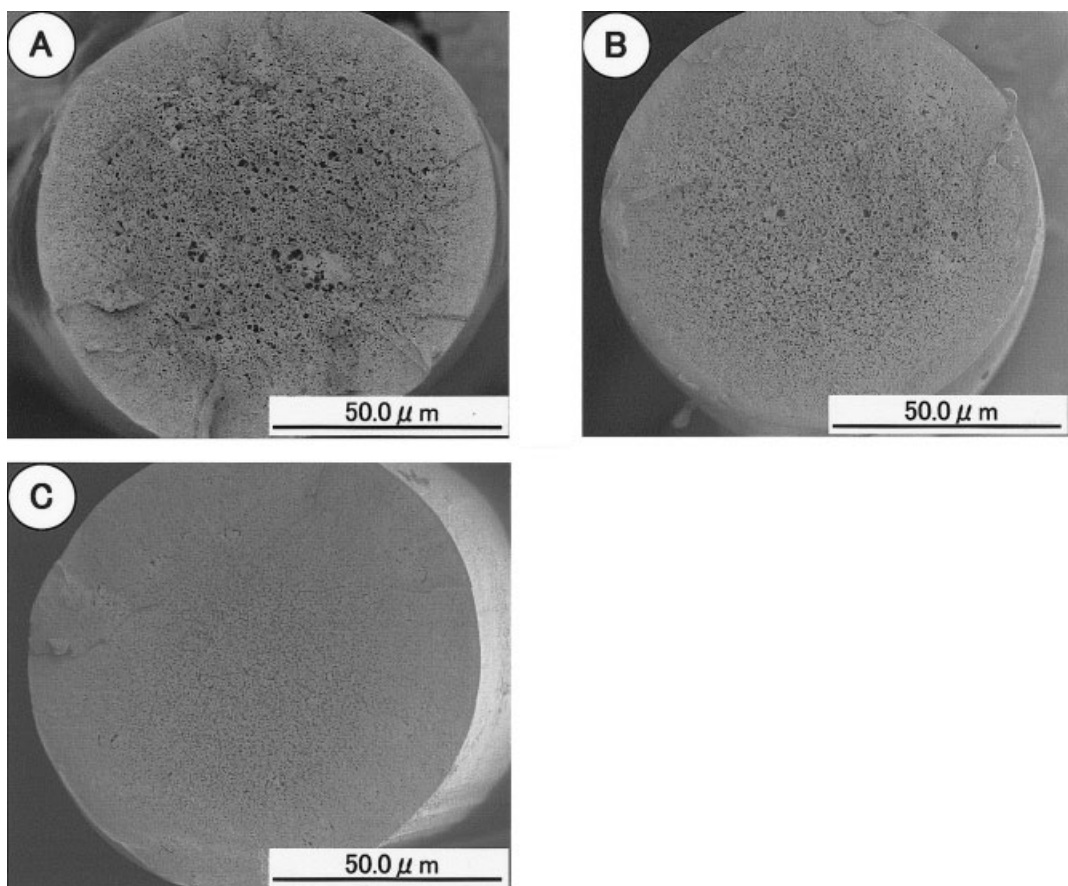


**Figure 5** Tenacity versus the draw ratio: (A) aqueous 38/24 (w/w)  $\text{CaCl}_2/\text{ZnCl}_2$  solution, (B) aqueous 40/22 (w/w)  $\text{CaCl}_2/\text{ZnCl}_2$  solution, and (C) aqueous 40.5/21.5 (w/w)  $\text{CaCl}_2/\text{ZnCl}_2$  solution.

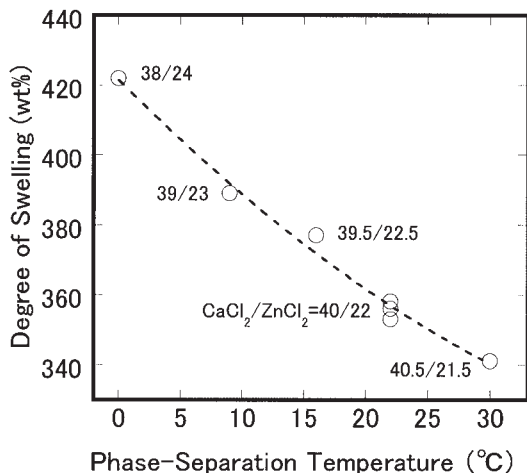
ture of 22°C, a higher phase-separation temperature tends to yield ECO fibers with greater tenacity. The tenacity tends to be lower, however, above a phase-separation temperature of 22°C. Figure 5 shows the

change in the tenacity versus the draw ratio in the hot-drawing process for the ECO fibers indicated by the arrows in Figure 4. With a higher phase-separation temperature, a tendency can be observed toward higher tenacity with respect to the draw ratio. However, when the solvent is an aqueous 40.5/21.5(w/w)  $\text{CaCl}_2/\text{ZnCl}_2$  solution with the highest phase-separation temperature, the tenacity with respect to the draw ratio is highest up to a draw ratio of about 10, but the tenacity decreases with a higher draw ratio.

Figure 6 shows cross-sectional SEM photographs after the freeze drying of coagulated filaments wet-spun under conditions given in Figure 5. A lower phase-separation temperature results in more voids at the central area of the cross section; therefore, a nondense, nonhomogeneous structure can be observed. Figure 7 shows the degree of swelling of the coagulated filament versus the phase-separation temperature of the ECO solution. The degree of swelling is primarily due to the amount of water present inside the coagulated filament and reflects the coagulated denseness. A higher phase-separation temperature results in a smaller value for the swelling, and this correlates with the cross-sectional SEM photographs.



**Figure 6** Cross-sectional SEM photographs of freeze-dried coagulated filaments (see Fig. 5 for descriptions of parts A–C).



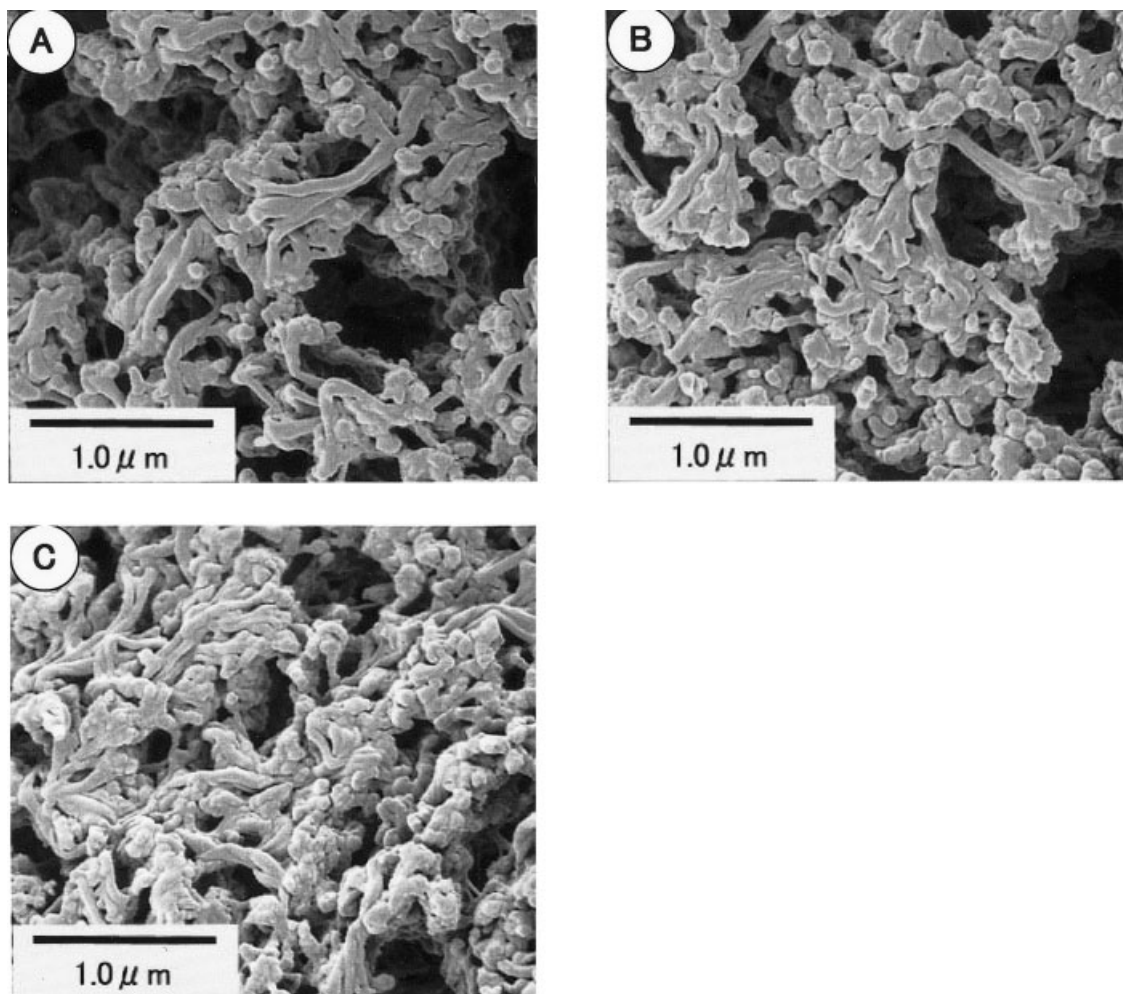
**Figure 7** Degree of swelling of the coagulated filaments versus the phase-separation temperature of the ECO solutions.

Figure 8 shows magnified views of the central areas of the cross-sectional photographs in Figure 6; the coagulated particle aggregates are connected in a

cordlike fashion. There is almost not a difference in the size of the coagulated particle under the different conditions.

Because the temperature of the coagulation bath is constant (2°C), a higher phase-separation temperature leads to more rapid solidification into a gel. The structure of the fiber tends to become more dense and homogeneous. On the other hand, a low phase-separation temperature slows the progression of gelling, so that the major coagulation is due to the diffusion of the nonsolvent water from the fiber surfaces, and this results in a nonhomogeneous structure.

When the cross-sectional structure of the coagulated filament is dense and homogeneous, fewer defects should occur during drawing, and so higher strength ECO fibers should be obtained. However, although using an aqueous 40.5/21.5(w/w) CaCl<sub>2</sub>/ZnCl<sub>2</sub> solution as the solvent results in the highest phase-separation temperature, the maximum tenacity is low. Because this solvent composition is near the solubility limit for the salt or ECO, as shown in Figure 3, the



**Figure 8** Magnifications of the center areas of the SEM photographs shown in Figure 6.

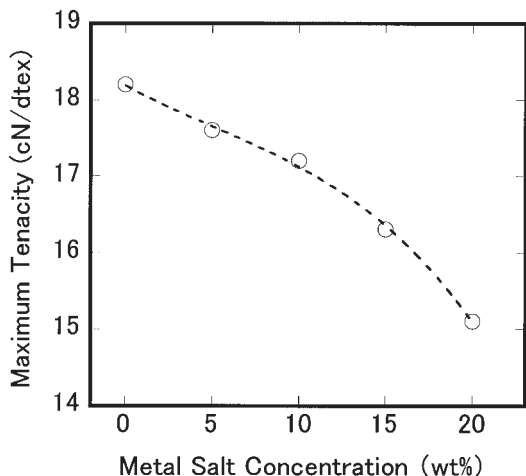


Figure 9 Maximum tenacity after hot drawing versus the metal salt concentration of the coagulation bath.

state of dissolution may be somewhat nonhomogeneous and may produce defects in the fibers, thus inhibiting high strength.

**Changes in the coagulated structure based on the metal salt concentration of the coagulation bath and effects on the strength of the drawn fiber**

For the industrial production of ECO fibers with an aqueous CaCl<sub>2</sub>/ZnCl<sub>2</sub> solution as the solvent, the recovery of CaCl<sub>2</sub> and ZnCl<sub>2</sub> extracted in the coagulation bath and their reuse in the solvent are essential for economic and environmental reasons. In this respect, it is best to use a coagulation bath obtained by the dilution of the solvent with water. Because the proportions of CaCl<sub>2</sub> and ZnCl<sub>2</sub> in the solvent are the same as those of the coagulation bath, the solvent can be obtained by the concentration of the coagulation

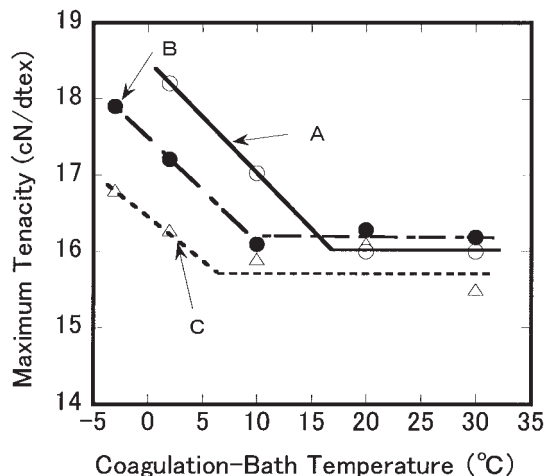


Figure 11 Maximum tenacity after hot drawing versus the coagulation-bath temperature at different metal salt concentrations: (A) 0, (B) 10, and (C) 15 wt %.

bath. When the concentration costs are considered, it is better for the coagulation bath to have a high metal salt concentration, but for the efficient extraction of the metal salt from the coagulated fibers, the metal salt concentration of the coagulation bath should be lower. Therefore, an optimum metal salt concentration exists.

Figure 9 shows the maximum tenacity after hot drawing versus the metal salt concentration of the coagulation bath when the coagulation bath has the same metal salts as the solvent. The ECO solution used for spinning is a solution of ECO with  $[\eta] = 5.6$ , dissolved at 7 wt % in an aqueous 40/22(w/w) CaCl<sub>2</sub>/ZnCl<sub>2</sub> solution, and the phase-separation temperature is 22°C. The temperature of the coagulation bath is 2°C. A higher metal salt concentration of the coagulation bath tends to result in a lower maximum tenacity after hot drawing.

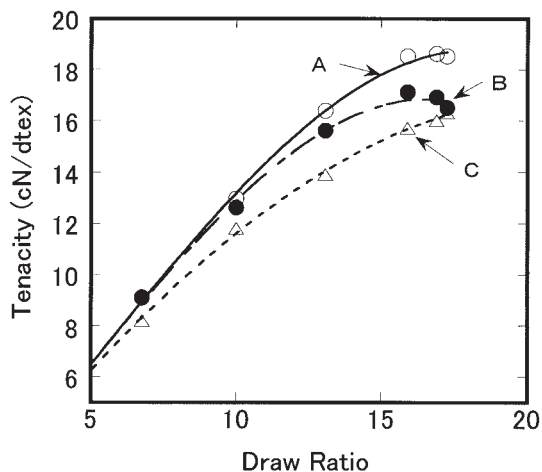


Figure 10 Tenacity versus the draw ratio for the different metal salt concentrations: (A) 0, (B) 10, and (C) 15 wt %.

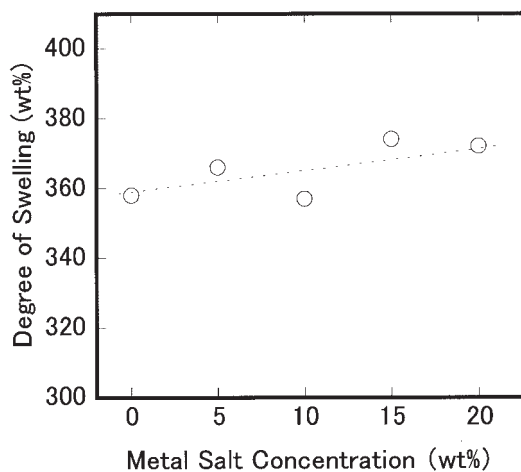
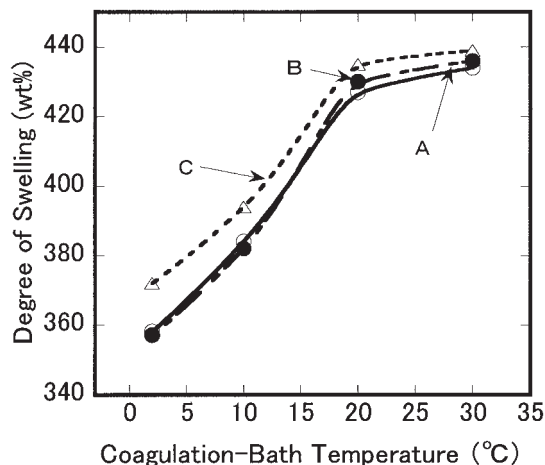


Figure 12 Degree of swelling of the coagulated filament versus the metal salt concentration of the coagulation bath.



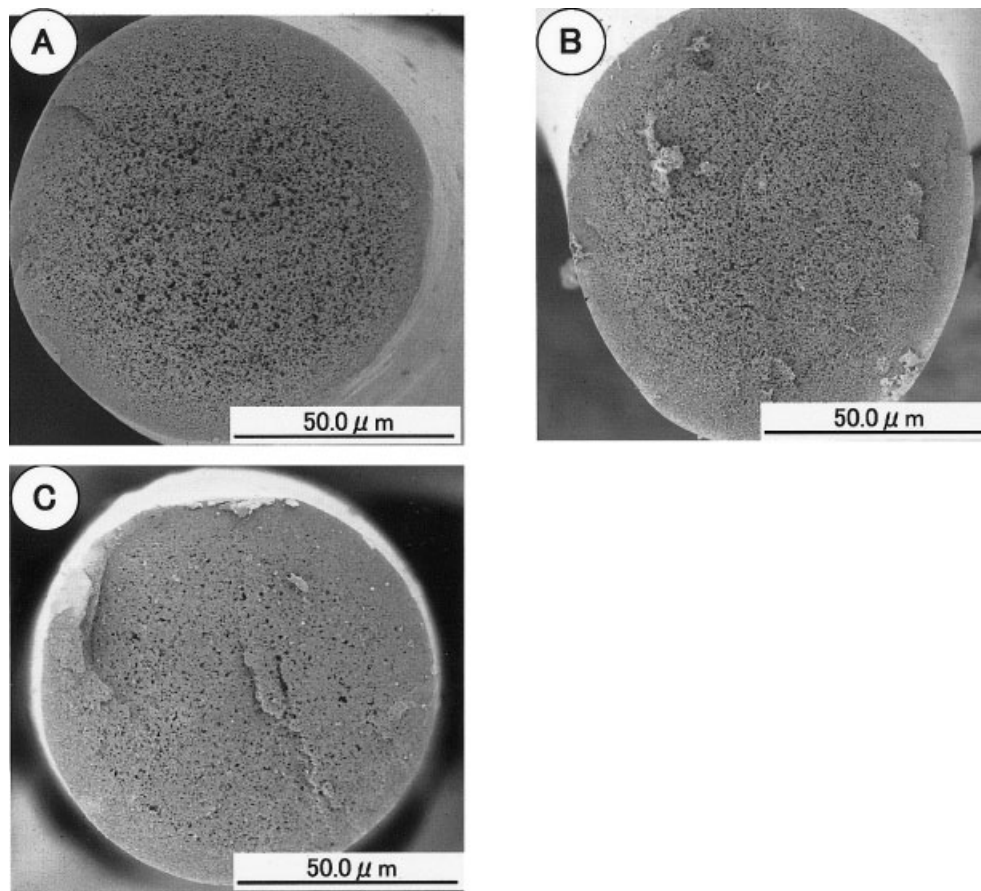
**Figure 13** Degree of swelling of the coagulated filament versus the coagulation-bath temperature at different metal salt concentrations: (A) 0, (B) 10, and (C) 15 wt %.

Figure 10 shows the changes in the tenacity versus the draw ratio in a hot-drawing process for the previously discussed ECO fibers. A higher metal salt concentration of the coagulation bath results in lower tenacity with respect to the draw ratio.

Figure 11 shows the maximum tenacity after hot drawing versus the coagulation-bath temperature for the different metal salt concentrations (0, 10, and 15 wt %) of the coagulation bath. The composition of the ECO solution is the same as that for Figure 9. With a coagulation-bath metal salt concentration of 10 wt %, the tendency toward increased maximum tenacity with a lower coagulation-bath temperature is the same as that with a 0 wt % concentration, but the maximum tenacity increases from a lower temperature. With a coagulation-bath metal salt concentration of 15 wt %, maximum tenacity is achieved from an even lower temperature of the coagulation bath.

It is believed that differences in strength after drawing based on the metal salt concentration of the coagulation bath affect the coagulated filament structure, as is the case with differences in the phase-separation temperature, as previously described.

Figure 12 shows the degree of swelling of the coagulated filament versus the metal salt concentration of the coagulation bath. Figure 13 shows the degree of swelling of the coagulated filament versus the coagulation-bath temperature for different metal salt concentrations (0, 10 and 15 wt %) of the coagulation bath. As previously mentioned, a smaller degree of swelling



**Figure 14** Cross-sectional SEM photographs of freeze-dried coagulated filaments (see Fig. 10 for descriptions of parts A–C).

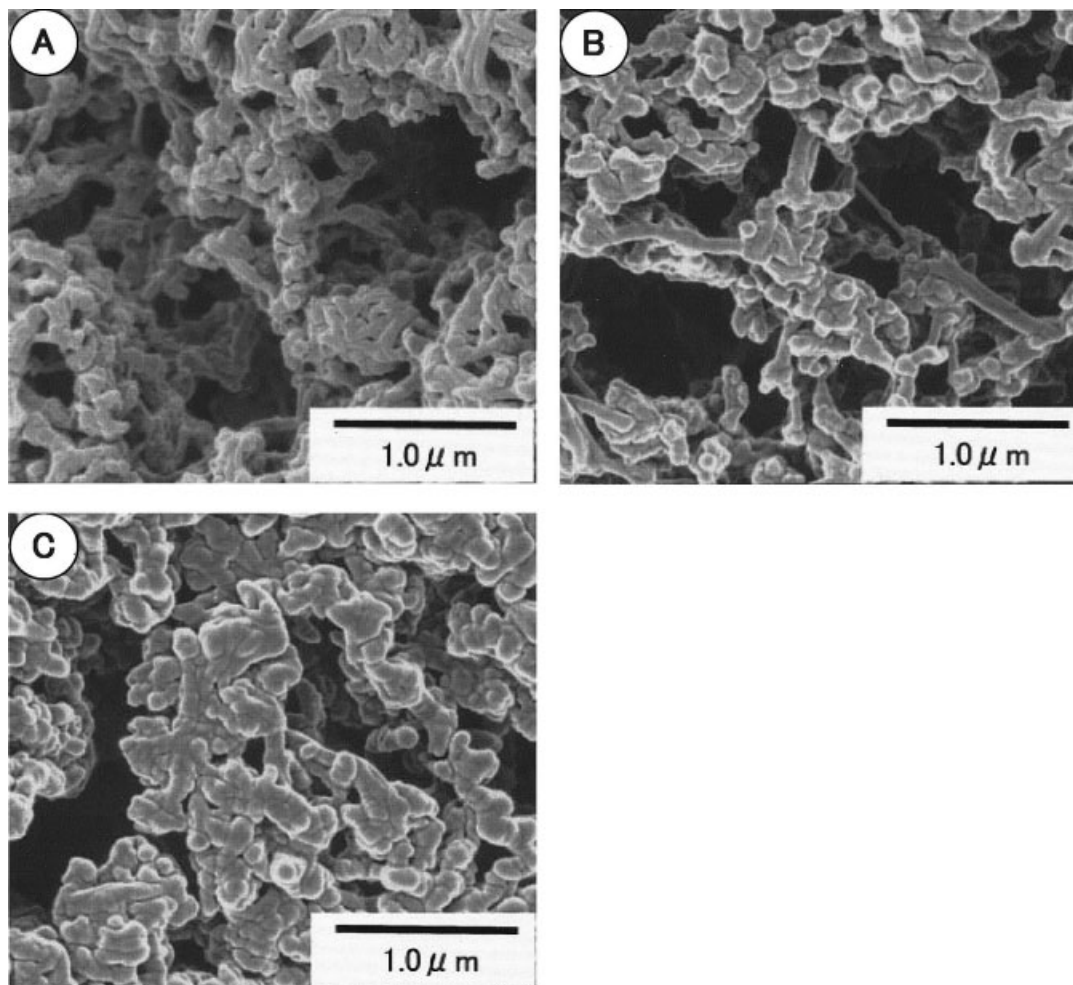


Figure 15 Magnifications of the center areas of the SEM photographs shown in Figure 14.

of the coagulated filament represents a denser structure. Although Figure 12 indicates a tendency toward a slightly higher degree of swelling with a higher metal salt concentration of the coagulation bath, the effect is smaller than the change due to different coagulation-bath temperatures, as shown in Figure 13. Figure 14 shows cross-sectional SEM photographs after the freeze drying of coagulated filaments wet-spun under the conditions given in Figure 10. No significant difference can be observed in comparison with the aforementioned difference in the cross-sectional structure because of differing phase-separation temperatures of the ECO solutions. Consequently, there is no significant change in the denseness or homogeneity of the cross-sectional structure of the coagulated filaments with differences in the metal salt concentration of the coagulation bath, in contrast to the trend of change in the maximum tenacity of the ECO fibers.

Figure 15 shows magnified views of the central areas of the cross-sectional photographs in Figure 14. The coagulated particle aggregates are connected in a cordlike fashion. A higher metal salt concentration of

the coagulation bath tends to produce larger coagulated particles. In particular, a coagulation-bath concentration of 15 wt % tends to yield coagulated particles as isolated particles. The increased frequency of defects during hot drawing is responsible for a lower attained strength.

At the instant the ECO solution enters the coagulation bath, the temperature jump of passing through the phase-separation temperature causes gelling because of the partial aggregation of the ECO molecules and, therefore, consolidates the overall structure of the fiber. Afterwards, the diffusion of the coagulation bath into the filament interior and the diffusion of the metal salt in the filament into the coagulation bath reduce the metal salt concentration in the filament, and this promotes aggregation of the ECO molecules because of the reduced solubility or, in other words, the formation of coagulated particles. A higher metal salt concentration of the coagulation bath slows the rate of coagulated particle formation, and this results in large spherical growth of the coagulated particles.



### CONCLUSIONS

During the wet spinning of ECO solutions with a coagulation-bath temperature of 2°C, a higher phase-separation temperature tends to result in a denser, more homogeneous structure of the coagulated filament. The denser, homogeneous structure occurs because the higher phase-separation temperature causes temperature-jump-induced gelling to proceed to the fiber interiors more rapidly. The dense, homogeneous coagulated structure results in a lower occurrence of defects during drawing, and so higher strength ECO fibers are obtained.

When the phase-separation temperature of the ECO solution and the temperature of the coagulation bath are constant and the metal salt concentration of the coagulation bath is increased, the gelling speed due to the temperature jump is unchanged, and so there is no difference in the homogeneity of the cross-sectional structures of the coagulated fibers, but the large spherical growth of the coagulated particles is promoted.

This leads to a greater frequency of defects during hot drawing and, therefore, lower attained strength for the ECO fibers.

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