

Novel Aliphatic Polyketone Fiber by a Wet-Spinning Method Using Aqueous Composite Metal Salt Solutions

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ABSTRACT: Poly(1-oxotrimethylene), obtained by the perfectly alternating polymerization of ethylene and carbon monoxide, was successfully dissolved in composite metal salt solutions such as zinc chloride and calcium chloride aqueous solutions. Certain poly(1-oxotrimethylene) solutions exhibited a phase-separation point of 0°C or greater; the different phase-separation temperatures depended on the metal salt composition ratio, the polymer molecular weight, and the polymer concentration. When a solution with a phase-separation point was used for wet spinning, a coagulation temperature below the phase-separation point resulted in gelation of the filament, which was caused by a temperature jump during the coagulation process; this yielded a coagulated filament with a dense and homoge-

neous cross-sectional structure. The hot drawing of the coagulated fiber produced a high-performance polyketone fiber with high strength and high elastic modulus [tenacity = 18.5 cN/dtex (2.4 GPa); elongation = 5%; elastic modulus = 450 cN/dtex (59 GPa)]. With a solution that exhibited no phase-separation temperature, coagulation proceeded as the coagulant penetrated from the fiber surface into the filament inside, yielding a coagulated filament with a skin-core structure. The maximum tenacity achieved with this skin-core coagulated filament was as low as 15 cN/dtex (1.9 GPa). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1183–1189, 2004

Key words: fibers; strength; structure-property relations

INTRODUCTION

Poly(1-oxotrimethylene) [ECO; Fig. 1(A)], obtained by the perfectly alternating copolymerization of ethylene and carbon monoxide, is a quite attractive polymer because of its high mechanical and thermal performance and its utilization of inexpensive starting monomers. In particular, ECO is expected to form a high-strength and high-elastic-modulus fiber because of its planar zigzag conformation and because its smallest cross-sectional area is in the crystalline phase¹ [ultimate tenacity = 266 cN/dtex (34.7 GPa); crystal elastic modulus = 2770 cN/dtex (361 GPa)].

The development of polymerization processes for aliphatic polyketones such as ECO has been vigorously pursued by Shell Oil Co.² Because ECO tends to crosslink above its melting point, melt processing is difficult for industry. In 1995, therefore, Shell Oil developed a polyketone terpolymer [Carilon; Fig. 1(B)] through the copolymerization of ECO with propylene to lower the melting point and allow melt processing (melting point = 220°C).

Shell Oil also attempted the melt spinning of Carilon.³ However, because of the low molecular weight of Carilon, which renders it suitable for melt processing, and because of the increased cross-sectional area

occupied by each polymer chain on account introduction of the propylene group, the mechanical properties do not significantly differ from those of poly(ethylene terephthalate) (PET) fibers widely used as industrial materials.³ Gupta et al.⁴ reported the melt spinnability of ECO and a polyketone terpolymer in detail.

Wet-spinning methods have also been investigated for obtaining ECO fibers. Several organic solvents, such as hexafluoroisopropanol and phenol,^{5,6} have been used as solvents. However, attempts at commercial production with these organic solvent systems have been abandoned because of problems such as toxicity, poor dissolution during spinning, and the high cost of the solvents.⁷

Shell Oil subsequently found that a high-concentration zinc chloride (ZnCl₂) aqueous solution could be a suitable ECO solvent.⁸ Aqueous ZnCl₂ has low toxicity, is inexpensive, and has already been industrially used as a solvent for polyacrylonitrile. Therefore, it seemed promising as an industrial solvent for ECO. However, the properties of the resultant ECO fibers were equivalent to those of PET fibers, with a tenacity of 11.5 cN/dtex and an elastic modulus of 153 cN/dtex. In addition, the coagulated filaments were fragile, and this made it difficult to achieve stable spinning.

We studied aqueous solutions of various metal salts independently and concurrently with Shell Oil.^{9,10} We found that when a composite metal salt solution consisting of metal salts such as ZnCl₂ and calcium chlo-

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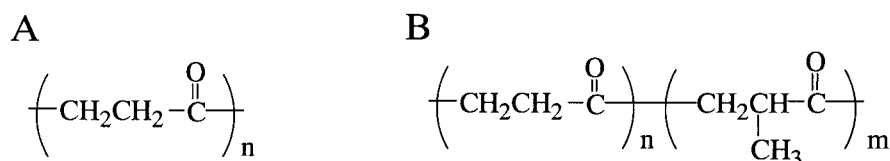


Figure 1 (A) ECO (melting point = 260°C) and (B) polyketone terpolymer (melting point = 220°C).

ride (CaCl₂) was used as a solvent, the polymer solution exhibited phase-separation behavior. These ECO solutions were used in wet-spinning methods to obtain high-performance fibers with high strength and high elastic modulus, a goal impossible to achieve with the Shell Oil technology. In this article, we discuss the properties of an ECO solution prepared from an aqueous composite metal salt solution containing ZnCl₂ and a wet-spinning process in which the solution was used.

EXPERIMENTAL

Materials

ECO was prepared as follows.^{11,12} 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 39.6 g of *p*-benzoquinone were added to the solution and dissolved.

One liter of methanol 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 the temperatures and for the times listed in Table I. After the reaction, the resulting polymer was washed several times with methanol and then dried.

The intrinsic viscosity ($[\eta]$) values, measured in hexafluoroisopropanol at 25°C, and the weight-average molecular weight (M_w) values, measured by the gel permeation chromatography/low-angle laser light scattering (GPC-LALLS) method with hexafluoroisopropanol, are listed in Table I.

TABLE I
Relationship of $[n]$ and M_w and the
Polymerization Conditions

Polymer	Reaction temperature (°C)	Reaction time (h)	$[\eta]$ (dL/g)	M_w
1	95	1.5	2.3	80,000
2	83	3.0	3.9	156,000
3	80	4.0	5.3	235,000
4	77	5.0	6.5	310,000
5	74	6.0	8.6	480,000
6	72	8.0	9.9	620,000

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 down to 0°C. The phase-separation temperature was defined as the temperature at which the transparent solution became clouded.

Spinning method

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

Measurement of the swelling

A 2-g sample of the coagulated fiber (G in 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 by the following formula:

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

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

The coagulated filament (G in Fig. 2) was wound and anchored onto a frame. This was then immersed in aqueous ethanol solutions of different concentrations in the following order: 50/50, 75/25, 90/10, 95/5,

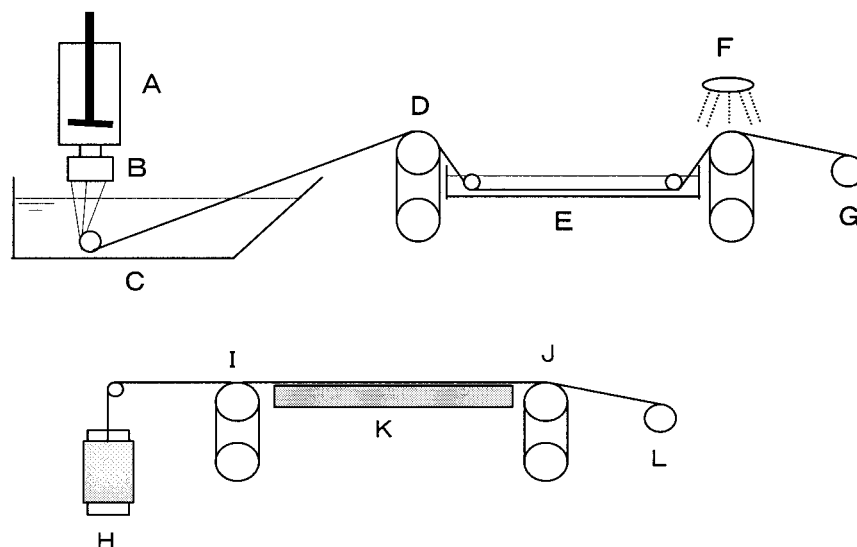


Figure 2 Schematic diagram of the spinning apparatus.

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 S5000 super-high-resolution SEM instrument (Tokyo, Japan) was used for the observation of the fiber cross section at an acceleration voltage of 1.0 kV.

Measurement of the fiber tensile strength and elastic modulus

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 in aqueous metal salt solutions

Table II shows the properties of an ECO solution obtained through the addition of 7.0 wt % ECO (poly-

mer 3) to aqueous metal salt solutions of different compositions.

ECO was dissolved in a simple ZnCl_2 aqueous solution with a salt concentration of 70–85 wt %. Soluble ECO had a wide range of $[\eta]$ values, and complete dissolution occurred even when $[\eta]$ was 15.6 dL/g ($M_w = 1,000,000$).

Mixing the other metal salts with ZnCl_2 significantly altered the ECO solution properties in a manner dependent on the type of metal salt. Upon the addition of 10 wt % sodium chloride (NaCl), CaCl_2 , or magnesium chloride to a 65 wt % ZnCl_2 solution for a total salt concentration of 75 wt %, a homogeneous ECO solution was obtained. However, homogeneous dissolution was not possible with potassium chloride. A major difference was found, in that the zero shear viscosity of the dissolved solution became low for NaCl or CaCl_2 but was high for magnesium chloride. However, dissolution occurred at 80°C with 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ or 32/27 (w/w) lithium chlo-

TABLE II
ECO Solubility and Solution Properties with Different Aqueous Metal Salt Solution Compositions

Aqueous metal salt solution composition w/w	Zero shear viscosity (Pa s/80°C)	Phase-separation point (°C)
$\text{ZnCl}_2/\text{H}_2\text{O} = 75/25$	100	Not observed
$\text{ZnCl}_2/\text{H}_2\text{O} = 65/35$	No complete dissolution	
$\text{ZnCl}_2/\text{NaCl}/\text{H}_2\text{O} = 65/10/25$	30	Not observed
$\text{ZnCl}_2/\text{CaCl}_2/\text{H}_2\text{O} = 65/10/25$	35	Not observed
$\text{CaCl}_2/\text{ZnCl}_2/\text{H}_2\text{O} = 40/22/38$	230	22
$\text{ZnCl}_2/\text{KCl}/\text{H}_2\text{O} = 65/10/25$	Not complete dissolution	
$\text{ZnCl}_2/\text{MgCl}_2/\text{H}_2\text{O} = 65/10/25$	220	Not observed
$\text{LiCl}_2/\text{ZnCl}_2/\text{H}_2\text{O} = 32/27/41$	50	32

Polymer 3 was used, with a concentration of 7.0 wt %. Dissolving conditions: 80°C, 3 h of stirring.

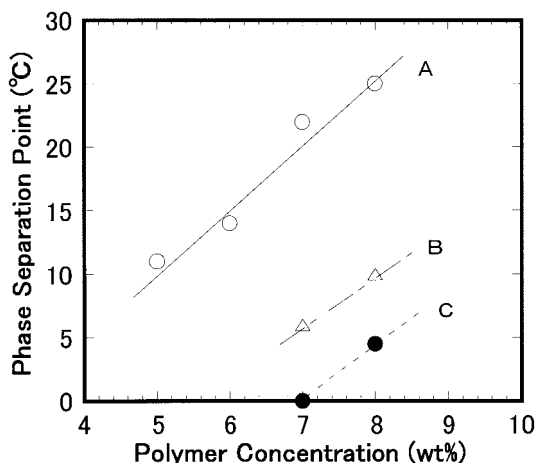


Figure 3 Phase-separation points versus the concentration of ECO (polymer 3). The solvents were (A) 40/22 (w/w), (B) 40/24 (w/w), and (C) 38/24 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solutions.

ride/ ZnCl_2 aqueous solutions, and a solution clouding phenomenon as the temperature was lowered (phase separation) was observed at a temperature of 0°C or greater. When these solutions were allowed to stand at a lower temperature than the phase-separation point, they lost fluidity and solidified into gels.

Properties of ECO solutions with aqueous $\text{CaCl}_2/\text{ZnCl}_2$ composite solutions

Figure 3 shows the phase-separation points versus the polymer concentration. The solid line represents the boundary line at which the phase separation of the solution occurred, above which a homogeneous solution was obtained and below which a cloudy nonhomogeneous solution resulted. A higher polymer concentration in the solution produced a higher phase-separation point. A different metal salt composition in the solvent also resulted in a marked shift in the phase-separation point. In particular, the phase-separation point was higher with a higher CaCl_2 content. Figure 4 shows the phase-separation points versus the ECO molecular weight. A higher ECO molecular weight yielded a higher phase-separation point. Clouding of the solution below the phase-separation point was thought to reflect nonuniformity of the polymer concentration, and the gel-like solidification of the solution was attributed to partial aggregation of ECO. The crosslinking points in the gel were points of molecular entanglement and microcrystals. These were heat-reversible because a homogeneous solution reappeared once the temperature was increased. The gelling was faster when the difference between the gelling point and the phase-separation point was greater.

Coagulated filament structure and fiber properties after hot drawing

We also investigated the relationship between the coagulated filament structure and fiber properties after hot drawing for wet spinning with two ECO solutions with and without a phase-separation point. The solvent with a phase-separation point was a 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution. A representative solvent without a phase-separation point was a simple ZnCl_2 aqueous solution. However, because it produced a coagulated fiber of weak strength, which made it difficult to achieve prolonged stable spinning, a 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution was instead used.

Solutions obtained through the dissolution of ECO (polymer 4) in these solvents were discharged from a spinneret into a water coagulation bath for wet spinning, producing the results described later. The polymer concentration in the 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution was 6.5 wt %, and the phase-separation point of the solution was 22°C . The polymer concentration in the 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution was 9 wt %, and no phase-separation point was observed.

Figure 5 shows the maximum tenacity after hot drawing versus the coagulation temperature. The hot draw ratio for these measurements was approximately 17. With the 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution, the tenacity increased drastically as the coagulation temperature fell below the phase-separation point, with a coagulation temperature of 2°C yielding a high-strength and high-elastic-modulus polyketone fiber with properties comparable to those of high-performance fibers [i.e., a tenacity of 18.5 cN/dtex (2.4 GPa), an elongation of 5%, and an elastic modulus of

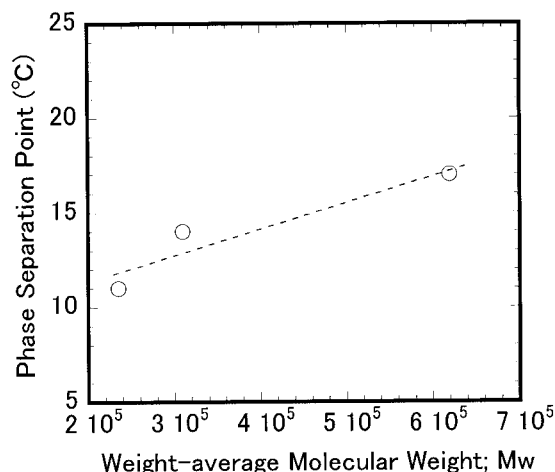


Figure 4 Phase-separation points versus the molecular weight of ECO (polymer 3, 4, 6). The solvent was a 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution, and the polymer concentration was 5 wt %.

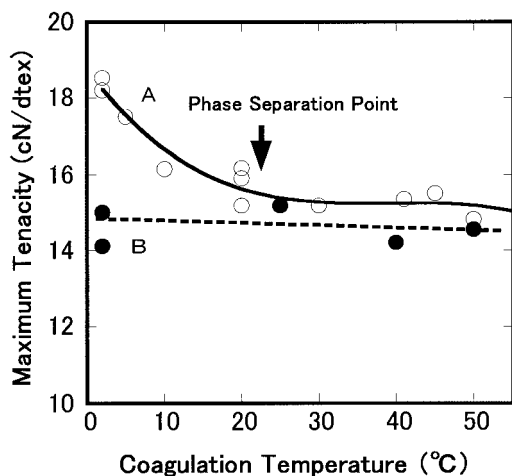


Figure 5 Maximum tenacity versus the coagulation temperature: (A) 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution and (B) 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution. The arrow indicates the phase-separation point of solution A.

450 cN/dtex (59 GPa)]. With the 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution, however, the tenacity was roughly consistent at a low level of about 15 cN/dtex, even when the coagulation temperature was changed.

Figure 6 shows the changes in the tenacity versus the draw ratio at a coagulation temperature of 2°C. With the 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution, the tenacity increase versus the draw ratio was higher than with the 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution.

We then conducted wet spinning by discharge into a 2°C water coagulation bath from spinnerets with different spinning apertures, and we examined the effects on the tenacity due to differences in the cross-

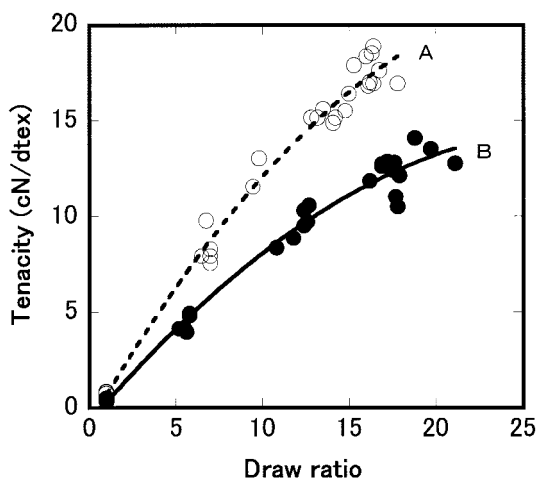


Figure 6 Tenacity versus the draw ratio: (A) 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution and (B) 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution. The coagulation temperature was 2°C.

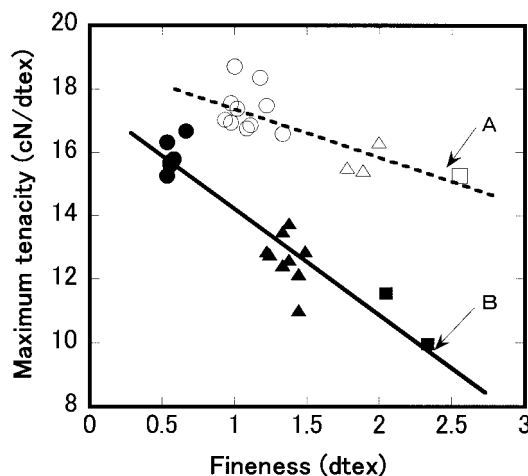


Figure 7 Maximum tenacity versus the filament fineness: (A) 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution [(○) 0.15, (△) 0.20, and (□) 0.25 mm] and (B) 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution [(●) 0.10, (▲) 0.15, and (■) 0.20 mm]. The coagulation temperature was 2°C.

sectional area of the coagulated filament. Figure 7 shows the maximum tenacity versus the filament fineness for hot drawing at a ratio of about 17. Because the draw ratio was approximately the same, the filament fineness after drawing was roughly proportional to the cross-sectional area of the coagulated filament. Increasing tenacity with smaller fineness is a phenomenon commonly observed with high-strength and high-elastic-modulus fibers,¹³ but the 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution was less affected by the filament fineness than the 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution.

The following discussion focuses on the reasons that the ECO solutions with a phase-separation point yielded high-strength and high-elastic-modulus polyketone fibers by coagulation at a temperature lower than the phase-separation point.

Figure 8 shows the degree of swelling versus the coagulation temperature, with the coagulation temperatures varied as shown in Figure 5. The degree of swelling is primarily due to the amount of water present inside a coagulated filament. It may be considered to reflect the coagulated denseness. With the 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution, the degree of swelling decreased drastically as the coagulation temperature fell below the phase-separation point, presumably indicating a dense coagulated state. However, with the 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution, very little change in the degree of swelling with respect to the coagulation temperature was observed. The degree of swelling remained high even with a low coagulation temperature.

Figure 9 shows a cross-sectional SEM photograph after the freeze drying of a filament coagulated in

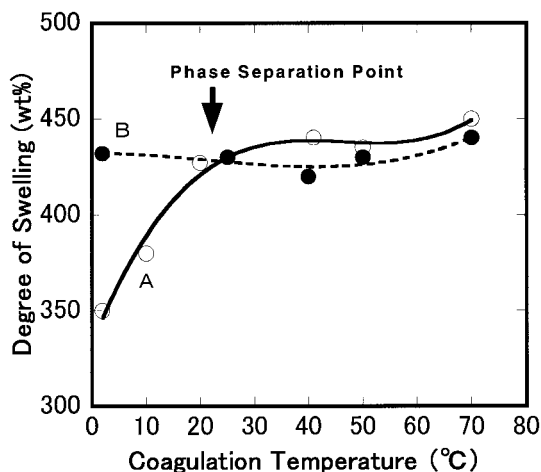


Figure 8 Degree of swelling versus the coagulation temperature: (A) 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution and (B) 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution. The arrow indicates the phase-separation point of solution A.

water at 2°C. When the 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution was used as the solvent, the filament cross section presented a relatively uniform structure. However, when the 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution was used as the solvent, the filament cross section was a dense skin-core structure with a sparse center and a dense exterior.

With the 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution, the 80°C polymer aqueous solution discharged from the spinneret exceeded the phase-separation point (22°C) and rapidly cooled upon entering the coagulation bath at 2°C (temperature jump). The polymer solution, therefore, gelled throughout the entire filament interior at the instant of entering the coagulation bath, and this resulted in a dense and homogeneous structure. After gelling,

the metal salt began to diffuse to the outside of the filament because of water penetration through the surface, but the gelled structure was almost completely maintained. It was presumed that a coagulated filament with a dense and homogeneous cross-sectional structure suffered minimal defects during hot drawing and that the orientation of the ECO molecules in the fiber axis direction proceeded in a uniform manner in the fiber cross section; this resulted in an ECO fiber with high strength and high elastic modulus.

With the 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution, however, the structural formation of the polymer solution in the coagulation bath proceeded because of the penetration of the coagulant (water) from the fiber surface to the interior of the filament; this produced a difference in the coagulating rates between the surface and interior, resulting in a non-uniform structure. The resultant coagulated filament, therefore, possessed a skin-core structure and exhibited low tenacity even after hot drawing because of voids and other defects. This tendency was more pronounced with greater filament fineness, as for the 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution shown in Figure 7, in which the maximum tenacity is shown to decrease with greater filament fineness.

Even with solutions exhibiting a phase-separation point, such as the 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution, only coagulant-induced structure formation occurred as long as the coagulating bath temperature was higher than the phase-separation point. The coagulated filament structure, therefore, was a skin-core type, and the maximum tenacity was approximately the same as that with the 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution (Fig. 5).

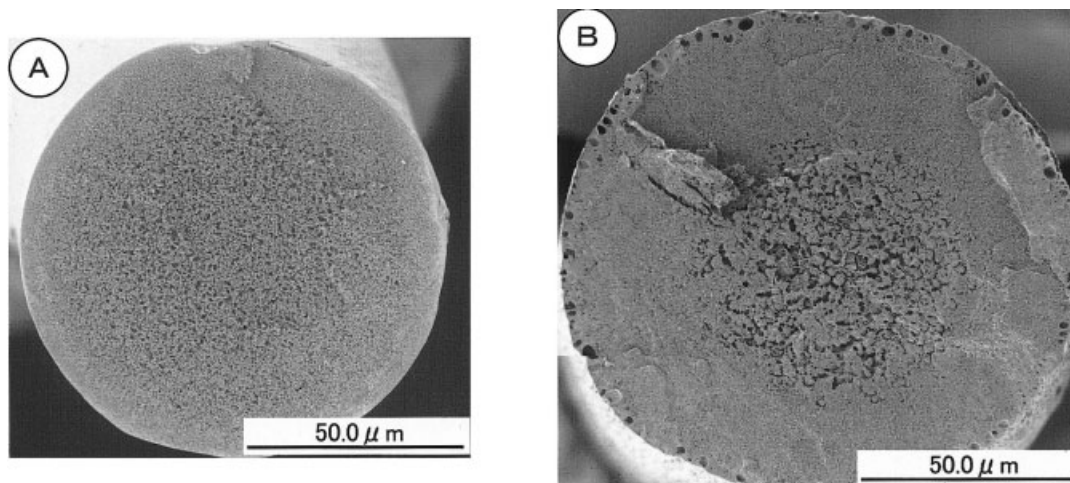


Figure 9 Cross-sectional SEM photographs of freeze-dried coagulated filaments (800 \times): (A) 40/22 (w/w) $\text{CaCl}_2/\text{ZnCl}_2$ aqueous solution and (B) 65/10 (w/w) $\text{ZnCl}_2/\text{NaCl}$ aqueous solution.

CONCLUSIONS

ECO dissolved in aqueous composite metal salt solutions combining metal salts such as $ZnCl_2$ and $CaCl_2$, and some ECO solutions exhibiting a phase-separation point higher than $0^\circ C$ were successfully prepared through the selection of the metal salt composition. The rapid cooling of these solutions from a temperature above the phase-separation point to a temperature below the phase-separation point (temperature jump) formed a gel. For example, discharge of a 40/22 (w/w) $CaCl_2/ZnCl_2$ aqueous solution with a phase-separation point of $22^\circ C$ from a spinneret above the phase-separation point and coagulation in a coagulation bath below the phase-separation point produced a coagulated filament that had a lower degree of swelling, greater density, and a more uniform cross-sectional structure than a coagulated filament obtained from an ECO solution with no observed phase-separation point. The drawing of this superior coagulated filament produced a polyketone fiber with tensile properties equivalent to those of high-performance fibers [tenacity = 18.5 cN/dtex (2.4 GPa); elongation = 5%; elastic modulus = 450 cN/dtex (59 GPa)] by a

wet-spinning method using an aqueous composite metal salt solution.

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