

Thermal Degradation Study of Poly(1-oxotrimethylene) in Aqueous Composite Metal Salt Solutions

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ABSTRACT: Poly(1-oxotrimethylene) (ECO) was dissolved in an aqueous composite metal salt solution, and the ECO solution was heated at different temperatures and then used for wet spinning. Within a certain heating time, ECO fibers with a tenacity of 17.6 cN/dtex (2.3 GPa) or greater were successfully produced through hot drawing 16–17 times after drying. Over a certain heating time, however, the strength of the ECO fibers drastically decreased. A higher heating temperature shortened the heating time at which the drastic decrease in the maximum tenacity began. On the basis of ultraviolet measurements of the undrawn fibers,

heating ECO in the aqueous composite metal salt solution promoted the thermal degradation of ECO because of aldol condensation or Paal–Knorr furan synthesis. The thermal degradation due to these intermolecular or intramolecular crosslinking reactions was resistant to the molecular orientation of ECO by the hot drawing of the undrawn fibers and reduced the strength of the ECO fibers by producing defects in the filament. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3358–3363, 2006

Key words: degradation; fibers; strength

INTRODUCTION

Poly(1-oxotrimethylene) (ECO; Fig. 1), obtained by the perfectly alternating copolymerization of ethylene and carbon monoxide, 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.¹ Because the starting monomers, ethylene and carbon monoxide, are inexpensive, it offers excellent cost performance and is expected to become widely used as a novel industrial material fiber.

The melt spinning of aliphatic polyketones such as ECO has been studied.^{2,3} However, the mechanical properties of melt-spun fibers are not significantly different from those of poly(ethylene terephthalate) fibers, which are widely used as industrial materials.

Wet-spinning methods have been investigated for obtaining ECO fibers. Several organic solvents, such as hexafluoroisopropanol and phenol derivatives, have been used as solvents.^{4,5} The hot drawing of coagulated fibers produces high-performance polyketone fibers with a 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 commercial production with these organic solvent systems have been abandoned because of tox-

icity, poor dissolution during spinning, and high solvent costs.

We have examined aqueous solutions of metal salts such as zinc chloride (ZnCl₂) as ECO solvents.^{6,7} Metal salt aqueous solutions have low toxicity and cost, and aqueous ZnCl₂ solutions are already used as solvents for wet spinning in the industrial production process for polyacrylonitrile fibers.

We previously reported that ECO fibers with a 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 a 40/22 (w/w) calcium chloride (CaCl₂)/ZnCl₂ aqueous solution, followed by hot drawing.⁸ The ECO solution exhibited a phase-separation temperature greater than 0°C, solidifying to a gel below the phase-separation temperature and returning to a solution form above 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 yielded high-strength ECO fibers, whereas a lower coagulation bath temperature yielded a higher strength. The temperature jump during the coagulation process solidified the ECO solution into a gel, giving the coagulated filament a dense, uniform structure. The hot drawing of the coagulated filament produced an ECO fiber with mechanical properties equivalent to those of high-performance fibers.

ECO has carbonyl groups in the main chain and, therefore, has poor thermal stability, and the thermal

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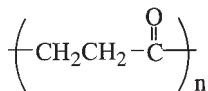


Figure 1 ECO.

degradation strongly affects the strength of the ECO fibers. A thermal degradation study of ECO was carried out by Xu and Chien⁹ and De Vito and coworkers^{10,11} and elucidated the mechanism of the molecular weight reduction due to cleavage of the ECO molecules and intermolecular or intramolecular crosslinking reactions. De Vito et al.¹¹ also reported the thermal degradation of ECO in aqueous solutions of acids or bases.

We have discovered that the thermal degradation of ECO proceeds even in aqueous composite metal salt solutions and that extensive thermal degradation is resistant to hot drawing, which makes it impossible to obtain high-strength ECO fibers. Optimizing the heating temperature and heating time for the ECO dissolution step will be a crucial point for the industrial production of high-strength ECO fibers. In this article, we report the thermal degradation rate of ECO with respect to the dissolution conditions when it is dissolved in aqueous composite metal salt solutions and the changes in the tenacity resulting from the thermal degradation.

EXPERIMENTAL

Materials

ECO was synthesized by the following method.^{12,13} A solution of 1.210 g of 1,3-bis[di(2-methoxyphenyl)

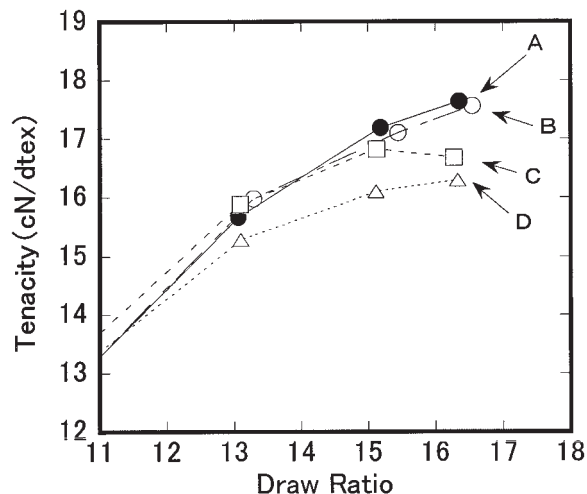


Figure 3 Tenacity versus the draw ratio: results of spinning and hot drawing with ECO solutions with dissolution times of (A) 3, (B) 5, (C) 7, and (D) 9 h.

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.

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 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.

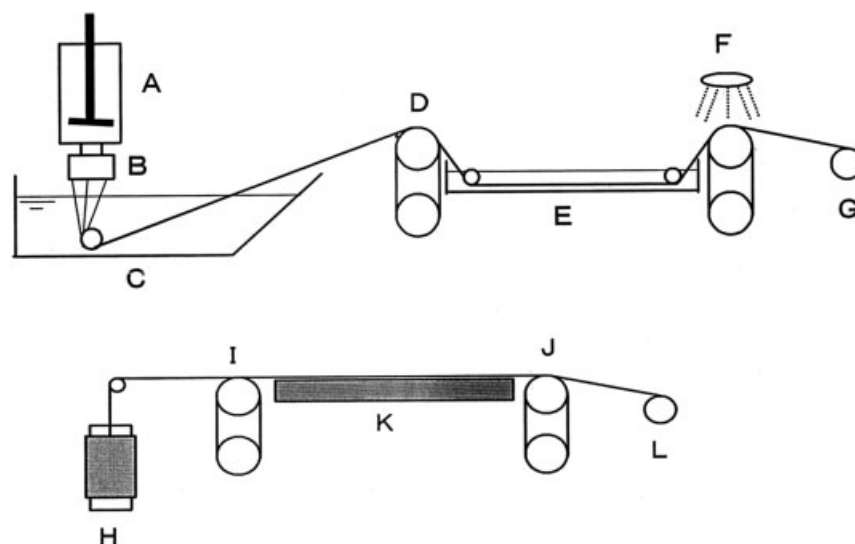
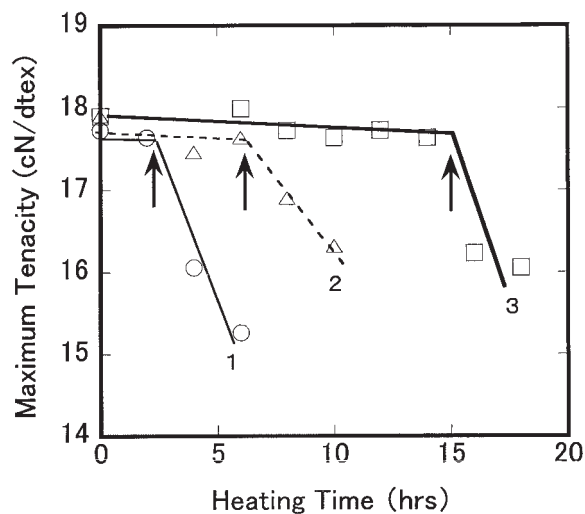
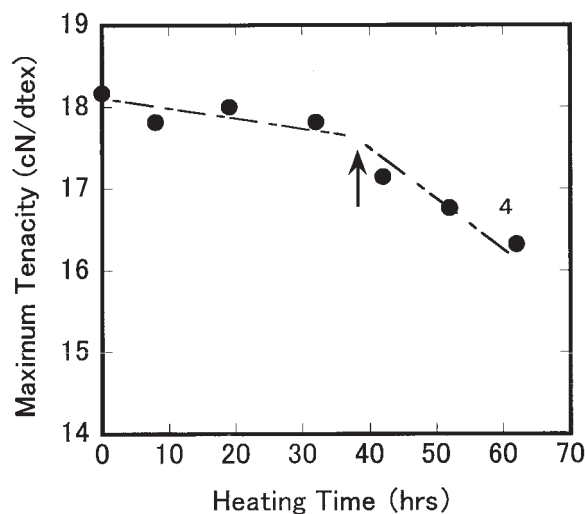


Figure 2 Schematic diagram of the spinning apparatus: (A) plunger extruder, (B) spinneret, (C) coagulation bath, (D) Nelson roll, (E) 0.5 wt % aqueous hydrochloric acid bath, (F) washing roll, (G) wound-coagulated fiber, (H) undrawn fiber, (I, J) drawing rolls, (K) 1-m hotplate, and (L) cheeselike package.



(a)



(b)

Figure 4 Maximum tenacity of ECO fibers versus the heating time: results of spinning and hot drawing with ECO solutions obtained (A) by dissolution at 80°C for 3 h followed by heating at (1) 80, (2) 70, and (3) 60°C and (B) by dissolution at 80°C for 3 h followed by heating at (4) 50°C.

Spinning

With a plunger extruder (see Fig. 2), the 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 containing water at 2°C. The coagulated fiber was picked up onto a Nelson roll at 3 m/min and then passed through a 0.5 wt % aqueous 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 while it was hot-drawn at various speeds by the drawing

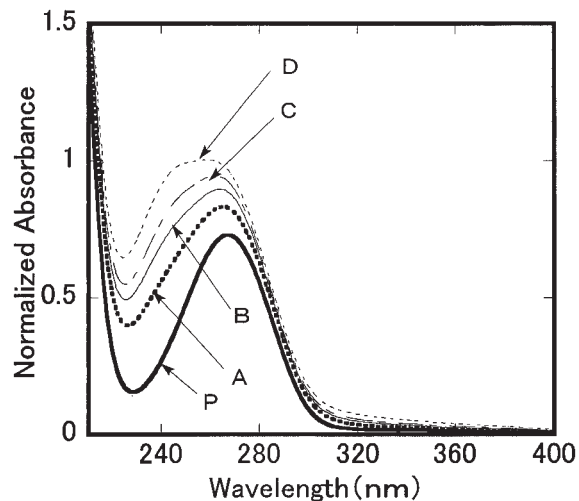


Figure 5 UV spectra for the ECO polymer and undrawn fibers: (A–D) UV spectra for undrawn fibers of Figure 3 (A–D) and (P) UV spectra for the ECO polymer.

rolls. The obtained drawn fiber was then wound into a cheeselike package.

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.

Measurement of the ultraviolet (UV) absorption spectrum of the filament

After 100 mg of the ECO filament was stirred in 100 g of hexafluoroisopropanol at 25°C for 3 h to dissolu-

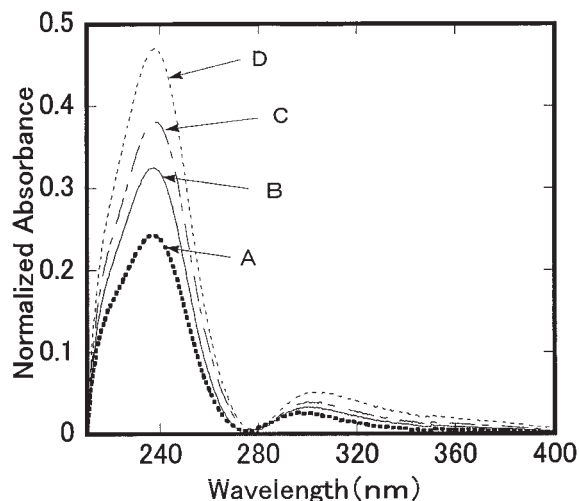


Figure 6 Difference spectra of the undrawn fibers of Figure 5 (A–D) with respect to Figure 5 (P).

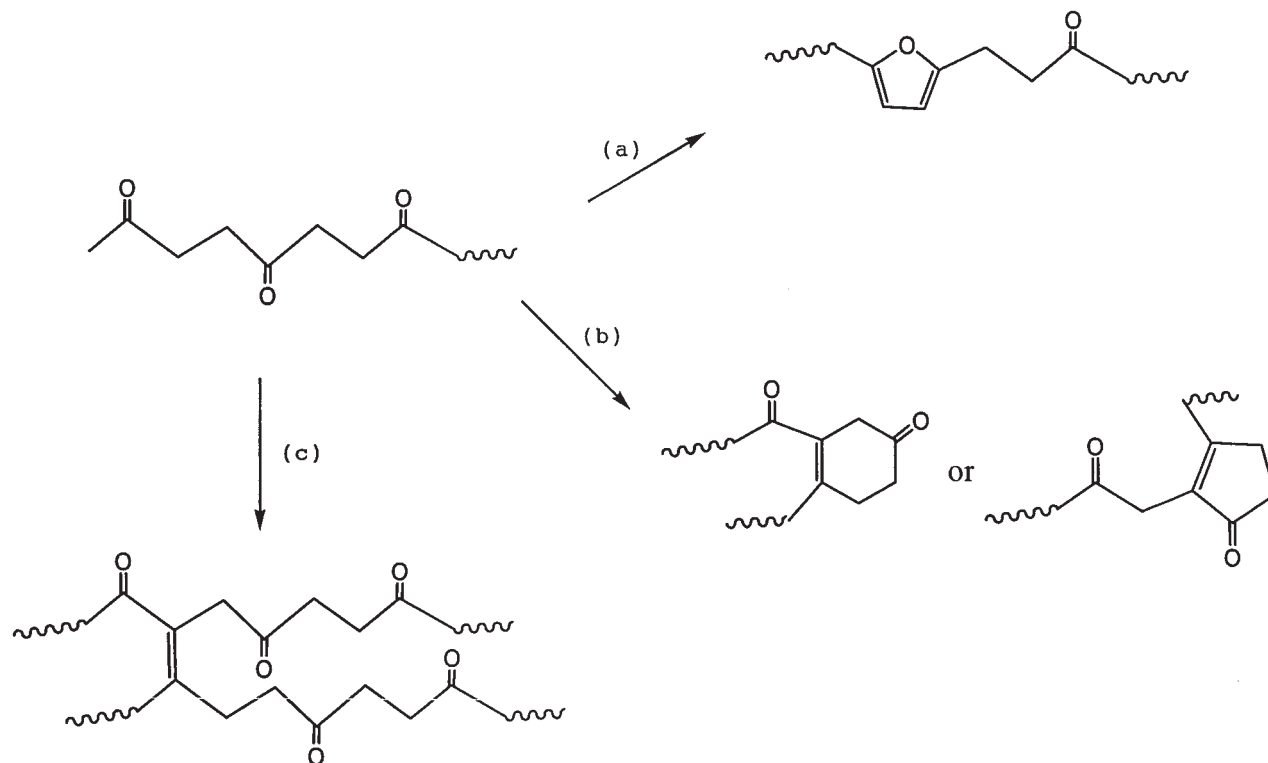


Figure 7 Thermal degradation of ECO predicted from absorption peaks of UV spectra in Figure 6: (a) Paal-Knorr furan synthesis, (b) Aldol condensations (intramolecular), and (c) Aldol condensations (intermolecular).

tion, the solution was placed in a quartz glass cell, and a V-530 ultraviolet-visible photospectrometer (Jasco Co., Ltd., Tokyo, Japan) was used for measurement at a scanning speed of 200 nm/min.

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

Dissolving conditions of ECO in aqueous composite metal salt solutions and fiber properties

ECO ($[\eta] = 5.6$ dL/g) was dissolved to a polymer concentration of 7 wt % in an aqueous composite metal salt solution consisting of CaCl_2 , ZnCl_2 , and lithium chloride (LiCl ; $\text{CaCl}_2/\text{ZnCl}_2/\text{LiCl}/\text{H}_2\text{O} = 30/22/10/38$ w/w) as the solvent. The ECO solution exhibited a phase-separation temperature of 45°C . The ECO solution was uniform and transparent at temperatures higher than 45°C , but at temperatures below 45°C , the ECO solution became cloudy, lost fluidity, and solidified into a gel state. This ECO solution was used for wet spinning for solidification into a gel in 2°C water, as shown in Figure 2, followed by drying and hot drawing 16–17 times.

Figure 3 shows the relationship between the tenacity and the draw ratio for different dissolution times (3, 5, 7, and 9 h) at 80°C . A longer dissolution time reduced the maximum tenacity. The longer dissolution time also reduced the tenacity at a lower draw ratio. The ECO solution, dissolved at 80°C for 3 h, was then heated at different temperatures, and the ECO solution was used to obtain a ECO fiber. Figure 4 shows the maximum tenac-

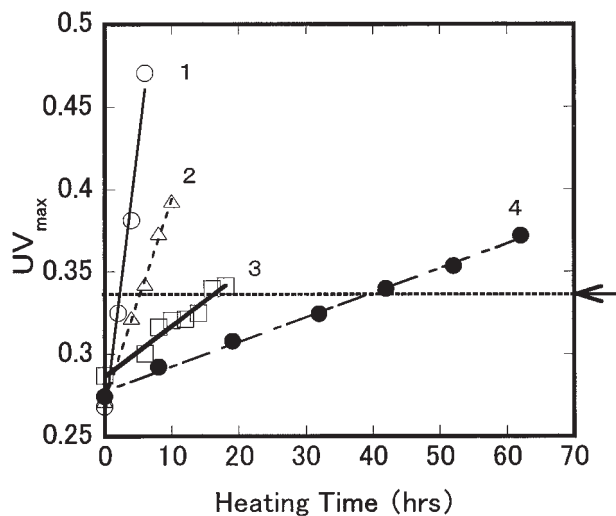


Figure 8 UV_{max} versus the heating time at different heating temperatures: (1) 80°C , (2) 70°C , (3) 60°C , and (4) 50°C .

ity versus the heating time. The maximum tenacity gradually decreased with the heating time at each temperature, and there was a drastic reduction in the maximum tenacity when the prescribed heating time had passed. Also, a higher heating temperature shortened the time at which the drastic reduction of the maximum tenacity began.

Thermal degradation of ECO in aqueous composite metal salt solutions

Figure 5 shows the UV spectra for the undrawn fibers of Figure 3(A–D). In the graph, P is the UV spectrum for the ECO polymer. Figure 6 shows the difference spectra of Figure 5(A–D) with respect to P. The absorbance of the peak observed at 230–250-nm wavelengths and 300–310 nm-wavelengths increased with the dissolution of ECO. When heated with an acid as the catalyst, ECO underwent an aldol condensation or Paal–Knorr furan synthesis, as shown in Figure 7, producing α,β -unsaturated carbonyl compounds or furans.¹⁴ The peak observed in the wavelength range shown in Figure 6 is characteristic of α,β -unsaturated carbonyl compounds, suggesting that this reaction proceeded in the presence of the Lewis acid $ZnCl_2$.

Figure 8 is a plot of the maximum values for the strong absorption peak (hereafter UV_{max}) observed at the wavelengths of 230–250 nm versus the heating time, from the difference spectra with respect to the ECO polymer, obtained by the measurement of the UV spectra of the dried undrawn fibers in Figure 4. There is a linear relationship between UV_{max} and the heating time, and the slope represents the thermal degradation rate for ECO. A higher heating temperature increased the slope. Figure 9 shows the results of an Arrhenius plot of the thermal degradation rate versus the heating temperature. The

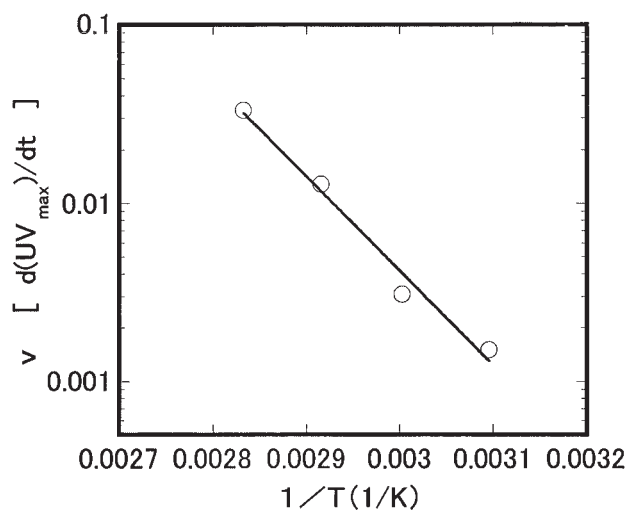


Figure 9 Arrhenius plot (T = heating temperature; v = thermal degradation rate).

TABLE I
Comparison of t_s and t_{uv}

	Heating temperature ($^{\circ}C$)			
	80	70	60	50
t_s (h)	2.3	6.0	15.0	38.0
t_{uv} (h)	2.3	5.5	15.5	38.0

plot indicates a good linear relationship, and the activation energy of the reaction, as determined from the slope, was 24.2 kcal/mol.

Table I shows the heating times at which a drastic reduction in the maximum tenacity begins to occur in Figure 4 (t_s 's) and the heating times at which a UV_{max} value is represented by an arrow in Figure 8 (t_{uv} 's). The t_s and t_{uv} values approximately match. Thus, the reduction in the maximum tenacity shown in Figure 4 is caused by the thermal degradation of ECO due to Paal–Knorr furan synthesis or aldol condensation in the ECO solution.

Figure 10 shows the changes in the zero shear viscosity of an ECO solution; the ECO solution, obtained by dissolution at 80 $^{\circ}C$ for 3 h in the same manner as described previously, was heated at 80 and 50 $^{\circ}C$. Although virtually no change was observed at 50 $^{\circ}C$ for up to 30 h, the zero shear viscosity increased at 80 $^{\circ}C$. This indicated that the molecular weight of ECO increased by intermolecular aldol condensation, as shown in Figure 7(c).

Consequently, the drastically reduced maximum tenacity shown in Figure 4 is due to a certain level of thermal degradation of ECO such as intermolecular crosslinking or intramolecular cyclization, which is resistant to hot drawing, thus producing defects in the filaments.

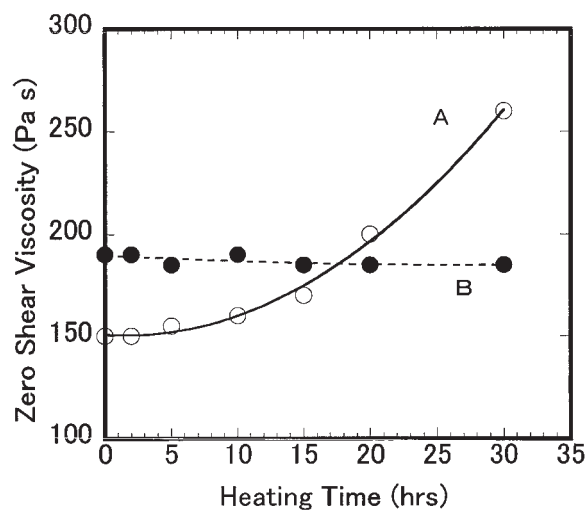


Figure 10 Zero shear viscosity of ECO solutions versus the heating time at (A) 80 and (B) 50 $^{\circ}C$.

CONCLUSIONS

During wet spinning with ECO solutions in aqueous composite metal salt solutions, it is possible to obtain ECO fibers with a strength comparable to that of superfibers. Inhibiting the thermal degradation of ECO in the solution is an important point for producing such a high strength. During the industrial production of ECO fibers, the thermal degradation of ECO can occur during the dissolution, degassing, and filtering processes. Such processes should be carried out at temperatures as low as possible to inhibit thermal degradation, but because an ECO solution solidifies below its phase-separation temperature, the process must be carried out at temperatures higher than the phase-separation temperature. Consequently, it will be important to develop techniques that minimize the residence time in these processes, such as shortening the dissolution time by powdering the ECO polymer or stirring with a significant shearing stress.

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