

## Effect of the Rigid Units Content on Tensile Properties of the Thermotropic Liquid Crystalline Polyesteramides

Youn Cheol KIM<sup>†</sup>

Advanced Materials Division, Korea Research Institute of Chemical Technology,  
P.O. Box 107, Yusong, Taejeon 305-600, Korea

(Received June 27, 1997)

**ABSTRACT:** The effects of the rigid units content on tensile properties of thermotropic liquid crystalline (TLC) polyesteramides with bulky side group were investigated by wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), and tensile measurements. The LC phase and relaxation times of TLC polyesteramides were largely dependent on the amount of rigid units. The as-spun fiber of the copolyesteramide ( $X=0.7$ ) having large amount of rigid units exhibited higher tensile properties than that of the homopolyesteramide ( $X=1.0$ ). The high tensile strength of copolyesteramide could be explained by the longer relaxation time and better LC property due to the increase of the amount of rigid unit in the molecular chain. The tensile strengths decreased by annealing at 220°C spun fiber, the decrease of tensile strength became dominant in high draw ratio region. It may be attributed to the relaxation of molecular orientation by long time annealing at 220°C.

**KEY WORDS** Thermal History / Rigid Unit / Thermotropic Liquid Crystalline Polyesteramides / Tensile Properties /

Over the past twenty years a number of technologies have emerged for producing highly oriented polymeric materials.<sup>1,2</sup> These successful approaches fall into two distinct classes: 1) the careful manipulation of conventional polymers into extended chain structures of near perfect molecular orientation in the solid state and 2) the design of rod-like molecules which exhibit nematic liquid crystalline behavior in the melt or solution and transform easily into the orientation structure. Thermotropic liquid crystalline (TLC) polymers which exhibit nematic LC phase in molten state produce a high degree of molecular orientation during melt processing and are able to maintain this orientation after solidification due to their longer relaxation time. The characteristic of the LC polymers to maintain the molecular orientation in the solid state yields superior mechanical properties such as tensile modulus and strength. Moreover, TLC polymers show high softening and melting temperature due to their rod-like structure. This is why TLC polymers are prime candidates for high performance polymers and reinforcement of flexible polymers.<sup>3-7</sup> Generally, the tensile strength of the TLC polymers strongly depends on the molecular structure, molecular orientation, processing conditions, and heat treatment. A number of studies<sup>8-12</sup> have been reported on the effect of processing condition, molecular orientation, and heat treatment on the mechanical properties of TLC polymers, but there are few studies on the relationship between molecular structure and mechanical properties of TLC polymers. The present article describes the effect of the rigid units content on tensile properties of new TLC polyesteramides controlled the rigid units content and obtain some detailed information about the relationship between molecular structure, molecular orientation and tensile properties. The difference in tensile properties was interpreted in terms of the molecular orientation and relaxation time in molten state observed by means of the

X-ray diffraction, the dynamic viscoelasticity, and the stress relaxation measurements.

### EXPERIMENTAL

#### Materials

As shown in the previous paper,<sup>13</sup> the polyesteramides were synthesized from sebacoyl chloride, terephthaloyl chloride and 1,4-bis(4-aminobenzoyloxy)-2-phenylbenzene by Schotten-Baumann type reaction in a cold mixture of *N,N*-dimethyl acetamide (DMAc) with 5 wt% of LiCl.<sup>14</sup> The purity and the chemical structures of monomers were confirmed by the elemental analysis and by the Fourier transform infrared spectroscopy (FT-IR) and the <sup>1</sup>H NMR, respectively. The molecular structure of polyesteramides is shown in Figure 1. And the characteristics are summarized in Table I.

**Fiber Preparation.** The fibers were prepared by spinning the polymer through a capillary rheometer at an apparent shear rate of 12.7 s<sup>-1</sup> (Instron Model 3211,  $L/D=40$ ,  $D=0.1235$  cm) at 280°C. In order to investigate the effect of draw ratio (DR, take-up speed/extrusion speed) on the molecular orientation, the extrudate was elongated by take-up apparatus located 60 cm below the capillary rheometer. Annealing of the fibers was

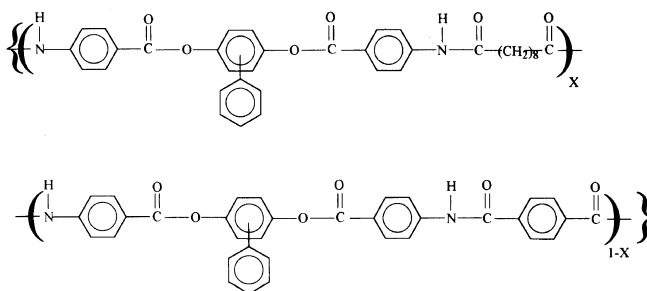


Figure 1. Chemical structure of the polyesteramides.

<sup>†</sup> Present address: Department of Materials Science & Engineering, University of Illinois at Urbana-Champaign, 1304W Green Street, Urbana, Illinois 61801, U.S.A.

**Table I.** The characteristics of the polyesteramides

Polymers ( $X$ -value)		$T_g/^\circ\text{C}^b$	$T_m/^\circ\text{C}^b$	$\Delta H_m/\text{J g}^{-1}{}^b$	$M_n \times 10^{-4}{}^c$	$M_w/M_n{}^c$
Theoretical	Calculated <sup>a</sup>					
1.00	1.00	164	238	6.35	2.6	1.36
0.70	0.72	170	229	1.78	2.8	1.85

<sup>a</sup> Calculated value of  $X$  were obtained from FT-IR. <sup>b</sup> Thermal properties of the polyesteramide fibers were measured in the first heating (rate =  $20^\circ\text{C min}^{-1}$ ). <sup>c</sup> Average molecular weights were measured by gel permeation chromatography (Waters-150).

performed for fixed time ( $t_a$ ) at  $220^\circ\text{C}$  in a nitrogen atmosphere for fixed length of 6 cm.

### Measurements

**Thermal Analysis.** DSC measurements were carried out with du Pont 910 thermal analyzer to study the effects of annealing on the fiber properties. For the annealing experiments, the following thermal history was applied: the sample was heated to  $220^\circ\text{C}$  at a scan rate of  $20^\circ\text{C min}^{-1}$ , held for a certain period of annealing.

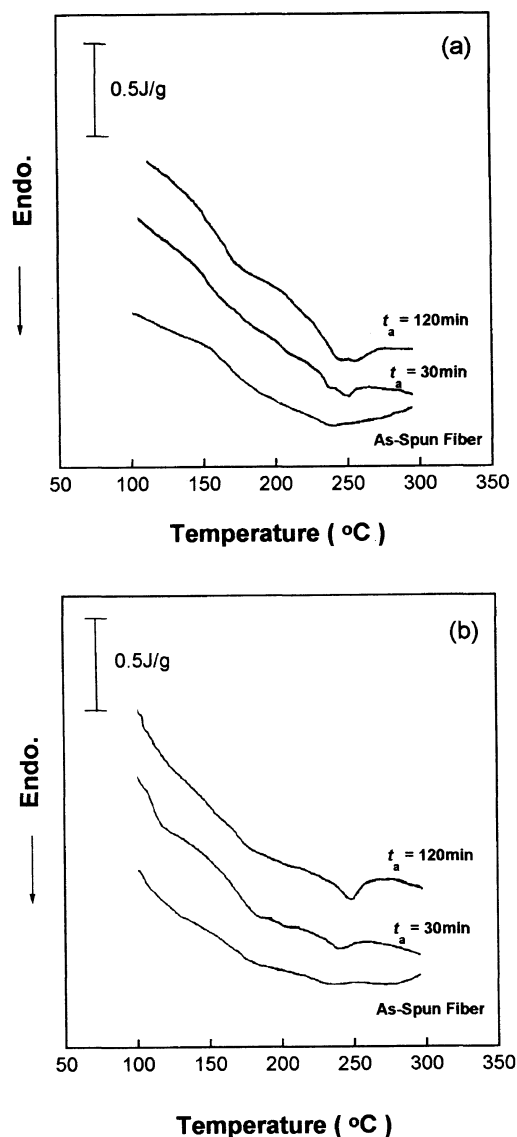
**Optical Measurement.** The photographic observation of the TLC polyesteramide powder was carried out by using a cross polarized light microscope (Carl Zeiss Laborrux 12 Pols) with a heating stage and an automatic camera. The heating rate was about  $20^\circ\text{C min}^{-1}$ .

**Wide-angle X-ray diffraction (WAXD)** was measured by an X-ray generator (Rigaku Co.). The point focus beam was monochromatized by using  $\text{Cu-K}\alpha$  target with a graphite crystal. The scan speed was fixed at  $4^\circ\text{ min}^{-1}$ . The conditions were room temperature, 40 kV, and 100 mA for the exposure time of 2 h. Specimens for X-ray fiber diagrams were prepared by making a bundle of 50 fibers. The  $d$ -spacing were calibrated with silicon powder (325-mesh size).

**Scanning Electron Microscopy (SEM).** The morphology of the fibers was analyzed by using SEM (SEM 515, Philips Co.). Fractured surfaces were coated with gold for the microscopy.

Tensile measurements were carried out by using an Instron (Model 4201) tensile tester with gauge length of 30 mm and cross-head speed of  $50\text{ mm min}^{-1}$  at room temperature. All presented results were obtained from tensile tests and based on the average of 6 measurements.

Rheological properties of the polyesteramides were measured using a Rheometrics Mechanical Spectrometer (Rheometrics Inc., RMS 800) in a cone-and-plate type of geometry (12.5 mm in radius and 0.1 radian in con angle) and a dynamic viscometer (Physica, Rheo-Lab MC 120) in a parallel plate type of geometry (12.5 mm in radius and 1.0 mm in gap size). The disk-shaped samples were molded at the temperature  $20^\circ\text{C}$  higher than the respective melting points by a laboratory hot press, and had the diameter of 25 mm and the thickness of 2 mm. The sample was hot-pressed under about 10 metric tons and dried in a vacuum oven for 24 h before the test. The polyesteramides showed the linear viscoelasticity below 0.1 of strain. In this study the strain was fixed at 0.05.

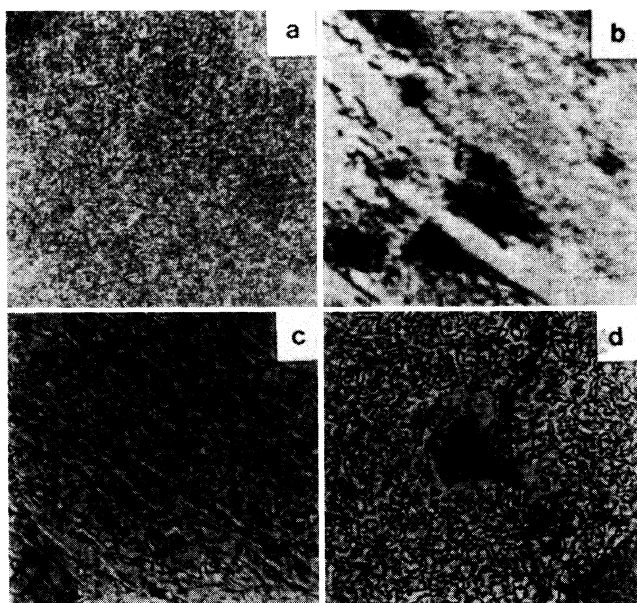


**Figure 2.** DSC thermograms of the polyesteramide fibers at DR = 15 as a function of annealing time ( $t_a$ ): (a)  $X = 1.0$  and (b)  $X = 0.7$ .

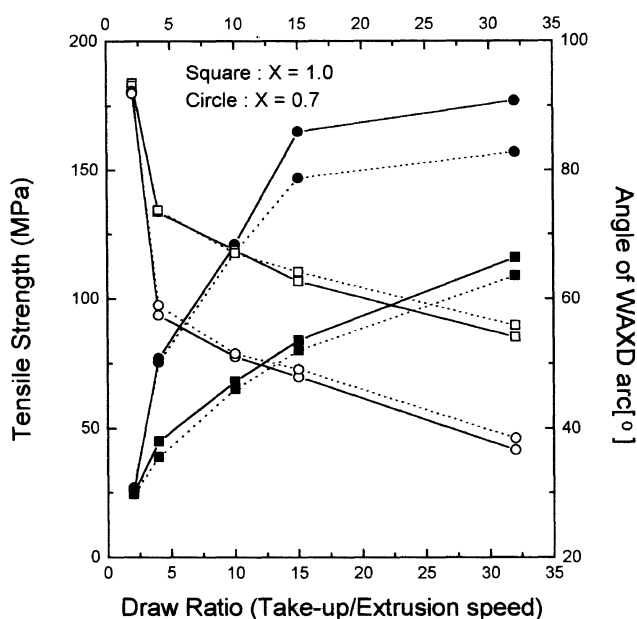
## RESULTS AND DISCUSSION

### LC Characteristics and Tensile Properties of the Polyesteramides

Figure 2 shows the DSC thermograms of the as-spun polyesteramide fibers measured at a heating rate of  $20^\circ\text{C min}^{-1}$ . Compared to DSC thermograms of powder samples, the endothermic peaks of the polyesteramide fibers were very small. These results suggest that the crystallization process is prevented by rapid cooling in extrusion process due to the strong steric



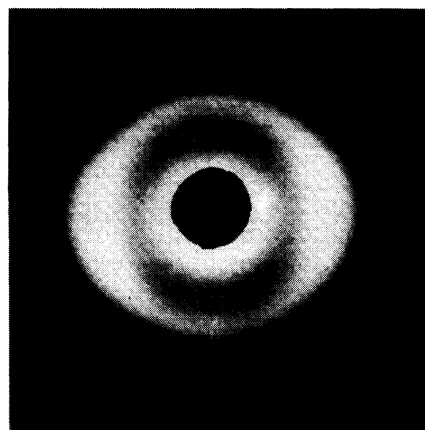
**Figure 3.** Liquid crystalline textures of the polyesteramides observed by polarized optical micrograph ( $\times 320$ ): (a)  $X=1.0$ , (c)  $X=0.7$  at  $280^\circ\text{C}$  and (b)  $X=1.0$ , (d)  $X=0.7$  at  $350^\circ\text{C}$ .



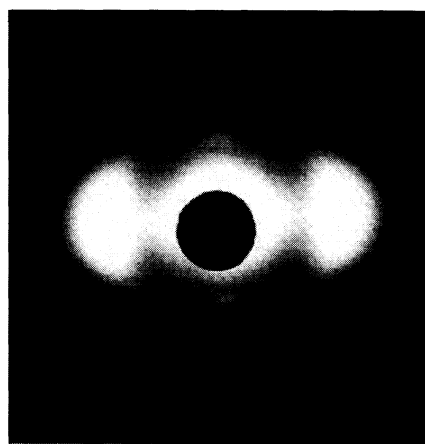
**Figure 4.** Tensile strength and orientation angle of the polyesteramide fibers: a solid line is as-spun fiber, a dotted line is annealed fiber, and open symbol is orientation angle.

hindrance of the polyesteramides. As shown in Table I, the homopolyesteramide shows a slightly higher endothermic peak than that of the copolyesteramide. For the copolyesteramide little amount of heat of fusion might be because the destruction of chain regularity by random copolymerization inhibits normal crystallization caused by rapid cooling.

Figure 3 shows the optical textures of the polyesteramides. Polarized micrograph reveals that the polyesteramides prepared have a nematic mesophase above melting temperature and keep the nematic state up to  $350^\circ\text{C}$ . The photographs of copolyesteramide ( $X=0.7$ ) showed more developed and stable nematic LC texture than the homopolyesteramide ( $X=1.0$ ), which



(a)



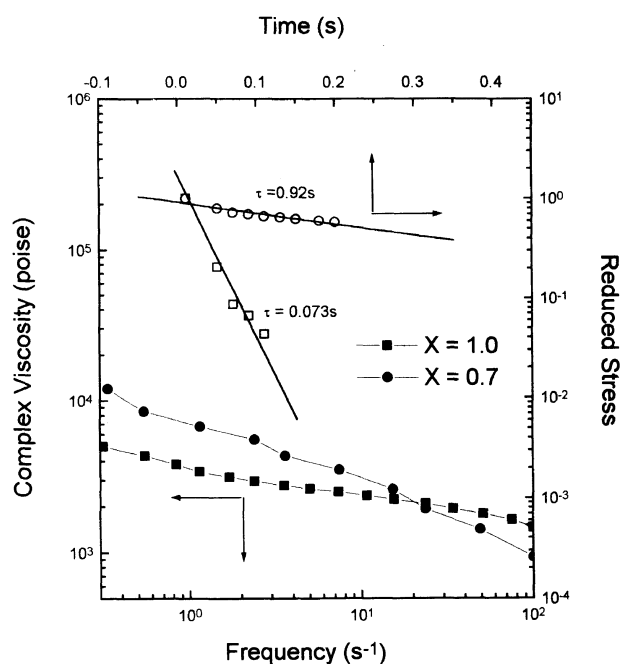
(b)

**Figure 5.** WAXD patterns of the polyesteramides at DR=15: (a)  $X=1.0$  and (b)  $X=0.7$ .

may be an evidence of the easier molecular orientation in molten state due to the increase of chain rigidity.

The draw ratio dependence of the tensile strength and orientation angle of the polyesteramide fibers are displayed in Figure 4. The tensile strength increased as the draw ratio increased in both samples. In the whole draw ratio region, the copolyesteramide fiber with  $X=0.7$  had higher tensile strengths than those of the homopolyesteramide fiber with  $X=1.0$ . These results can be explained by the increase of the molecular orientation and the relaxation time in molten state owing to the increase of chain rigidity.

WAXD patterns were used to characterize qualitatively the relative molecular orientation of the polymeric fiber. Many researches<sup>5,11,12</sup> were performed for the relationship between the mechanical properties and the molecular orientation measured by WAXD patterns. The researchers reported that the tensile strengths at high DR have higher value than those at low DR due to the enhancement of the molecular orientation by the extensional flow field. From the WAXD patterns it is well known that the angle of WAXD arc indicates the degree of molecular orientation. Figure 5 shows WAXD patterns of the polyesteramides at DR=15. The as-spun fiber of copolyesteramide had a smaller angle than



**Figure 6.** Complex viscosity versus frequency (left versus bottom axis) and stress relaxation patterns versus time after stop the motion (right versus top axis) of the polyesteramides at 280°C.

that of the as-spun fiber of homopolyesteramide, which indicates they have higher degree of orientation owing to the chain rigidity. The angles of the diffraction arc on the WAXD diffraction patterns were displayed in Figure 4 as a function of DR. The angles decreased with the increase of DR. It can be clearly recognized that the chains are highly oriented in high DR. These molecular orientation result in the increase of tensile properties.

The molecular orientation generated in the melt flow will be substantially relaxed before the solidification if the relaxation takes place very rapidly by the thermal motion. However, a series of relaxation experiments<sup>15,16</sup> revealed that the liquid crystalline polymer (LCP) melts possessed long relaxation times at various temperatures comparing with those of ordinary flexible polymers. Figure 6 shows the frequency dependence of the complex viscosity and the stress relaxation patterns after cessation of the steady shear flow for the polyesteramides. In the low frequency region, the homopolyesteramide ( $X=1.0$ ) had lower complex viscosity than the copolyesteramide with  $X=0.7$ . On the other hand, the copolyesteramide have lower complex viscosity than that of the homopolyesteramide in the high frequency region, which is similar to the result of Jackson and Kuhfuss<sup>17</sup> for poly(ethylene terephthalate)/4-(hydroxy benzoic acid) (PET/HBA) (X7G). This behavior could be associated with the existence of the ordered region in the nematic state. That is, the structural change of the ordered region may reduce the melt viscosity of the thermotropic LCPs. In this work, the stress relaxation after the cessation of steady shear was also studied. The disk was rotated at a constant rate to generate the shear rate of  $0.5\text{ s}^{-1}$  at 280°C. After reaching to the stationary state, the motion of cone was abruptly halted and the stress decay was registered as a function of time through a transducer connected to the shaft of plate. The stress decay curves showed simple straight line charac-

**Table II.** The viscosity ratio and relaxation time of the polyesteramides

Polyesteramide	Ratio of complex viscosity <sup>a</sup>	Relaxation time ( $\tau$ ) <sup>b</sup> /s	Correlation coefficients <sup>b</sup>
$X=1.0$	2.34	0.073	0.94130
$X=0.7$	7.27	0.920	0.98186

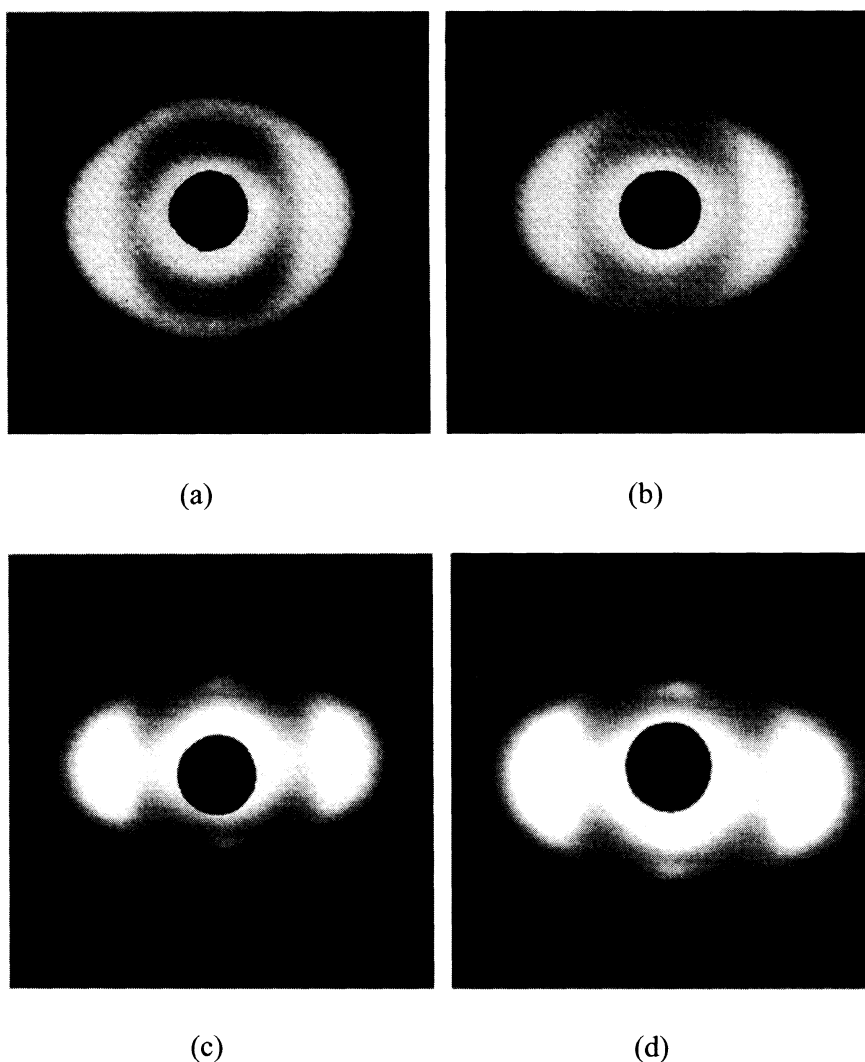
<sup>a</sup> Ratio of the complex viscosities at 1 and  $100\text{ s}^{-1}$ . <sup>b</sup> Maxwell-type relaxation of the polyesteramides at 280°C.

terizing Maxwell-type relaxation. The relaxation time ( $\tau$ ) is determined from the slope of these straight lines. The stress relaxation patterns of the polyesteramides are plotted against time at short time interval as shown in Figure 6 and values of the relaxation time of the polyesteramides are summarized in Table II. The relaxation time increased as the amount of rigid units increases in the molecular structure. This may be due to the particular behavior of rigid molecules whose segmental motion is restricted within very narrow limits even at 280°C. The fact that the tensile strength and molecular orientation increase with the amount of rigid unit could be related to that the chain rigidity of the polyesteramide might lead to the higher relaxation time and molecular orientation.

#### Heat Treatment of the Polyesteramide Fibers

The annealing of the as-spun fibers were carried out for 120 min at 220°C. The tensile strengths of the annealed fibers spun at a low DR showed almost same value compared to the as-spun fiber as shown in Figure 4. On the other hand, the tensile strengths of annealed fibers decreased slightly in high DR. In order to investigate the molecular weight effect on the tensile properties, the inherent viscosities of the polyesteramides fiber were measured by using Cannon-Fenske viscometer with  $0.5\text{ g dl}^{-1}$  solution in DMAc containing 5 wt% of LiCl at 30°C. There was no remarkable change in the inherent viscosity with the data of  $0.554\text{ dl g}^{-1}$  ( $X=1.0$ ) and  $0.583\text{ dl g}^{-1}$  ( $X=0.7$ ) for the as-spun fiber at DR=15 and  $0.559\text{ dl g}^{-1}$  and  $0.586\text{ dl g}^{-1}$  for the annealed fiber at 220°C. These results suggest that the molecular weight can be ruled out from the interpretation of the decrease of tensile properties for the annealed fiber. The decrease of the tensile strength may result from the relaxation of molecular orientation which is caused by easy molecular motion by long time annealing at 220°C. Uryu *et al.*<sup>18</sup> reported that the chain conformation transforms from trans to gauche by long time annealing for the TLC polymer with the flexible spacers. The change of conformation occurs the relaxation of molecular orientation.

In order to investigate the change of molecular orientation by annealing WAXD was used in the polyesteramide fibers before and after annealing. WAXD patterns of the annealed fibers at DR=15 were shown in Figure 7 as a function of annealing time. The angle of WAXD diffraction arc increased slightly by annealing at 220°C for the fiber made at DR=15. As shown in Figure 4, the angles of WAXD diffraction are almost same for the fibers before and after annealing in low DR region while the angles increase slightly by anneal-



**Figure 7.** WAXD patterns of the polyesteramides as a function of annealing time at DR = 15: (a) 0 min, (b) 120 min of  $X=1.0$ , and (c) 0 min, (d) 120 min of  $X=0.7$ .

**Table III.** Heat of fusion of the polyesteramides

Polyesteramide		Heat of fusion of as received sample/ $J g^{-1}$	Heat of fusion annealed <sup>c</sup> sample/ $J g^{-1}$
$X=1.0$	Powder <sup>a</sup>	12.41	30.83
	Fiber <sup>b</sup>	6.35	19.23
$X=0.7$	Powder	2.01	3.67
	Fiber	1.78	2.92

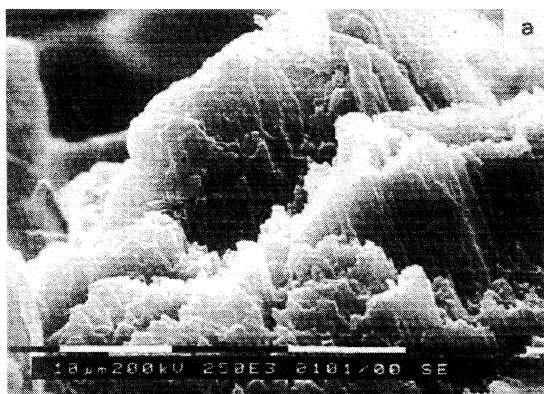
<sup>a</sup> Thermal properties of the polyesteramide powder were measured in the second heating (rate =  $20^{\circ}C min^{-1}$ ). <sup>b</sup> Thermal properties of the polyesteramide fibers were measured in the first heating (rate =  $20^{\circ}C min^{-1}$ ). <sup>c</sup> Thermal properties of the polyesteramides were measured in first heating (rate =  $20^{\circ}C min^{-1}$ ) of the sample after annealing for 120 min at  $220^{\circ}C$ .

ing in high DR region. And DSC thermograms of the TLC polyesteramide fibers as a function of annealing time were shown in Figure 2. As the annealing time at  $220^{\circ}C$  becomes longer, the melting temperature of the polyesteramide fibers shifted higher value and the heat of fusion became more distinct. The fact that the melting temperature and heat of fusion increase with the annealing time could explain that the slow crystallization process might lead to the more ordered packing,

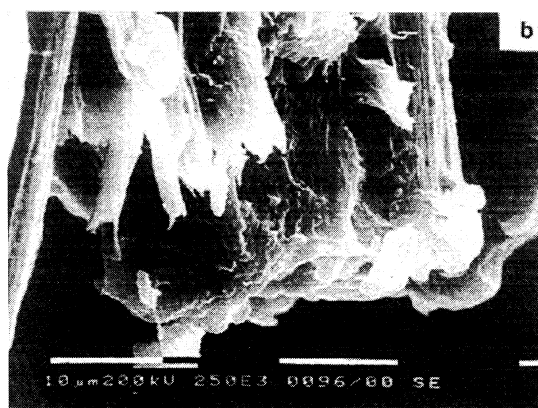
which was discussed in previous paper.<sup>13</sup> However, compared to heat of fusion of the fiber made at DR = 15, the heat of fusion of powder showed pretty high value as shown in Table III. From these results it can be analogized that the molecular orientation is almost same in low DR region since the molecular packing and molecular relaxation occurs competitively while the molecular orientation decreases because the molecular motion process becomes more effective in case of high oriented molecular chain in high DR region.

Figure 8 shows the tensile fractured surface of the fiber. The as-spun fiber of the copolyesteramide ( $X=0.7$ ) made at DR = 15 seemed to show fibrous structure indicated the good molecular orientation compared to the homopolyesteramide fiber ( $X=1.0$ ) made at DR = 15. It can be inferred that the copolyesteramide fibers with  $X=0.7$  maintain high molecular orientation in solid state since they show good nematic texture in the molten state and represent the long relaxation time.

From above results, we may conclude that an increase of the rigid unit content in the molecular chain improves the tensile properties owing to the enhancement of molecular orientation and the longer relaxation time to keep the orientation during solidification of the



(a)



(b)

**Figure 8.** Fractured surface of the polyesteramide fibers with draw ratio of 15: (a)  $X=1.0$  and (b)  $X=0.7$ .

fiber. Also, for the fiber made at high DR the decrease of tensile strength was attributed to the relaxation of molecular orientation causing from easy molecular motion by long time annealing at 220°C.

### CONCLUSION

The polyesteramides prepared in this work showed a

nematic texture above melting temperature and the nematic mesophase becomes more apparent as the rigid unit content increases. Since an increase of the amount of rigid unit in the molecular structure results in good nematic texture and long relaxation time in the molten state, the copolyesteramide ( $X=0.7$ ) fiber showed higher tensile strength and molecular orientation than the homopolyesteramide ( $X=1.0$ ). Due to the relaxation in molecular orientation of the polyesteramides, annealing process influences the tensile properties of the polyesteramides. The tensile strength of annealed fibers at 220°C had lower value than that of the as-spun fiber. The weakening of tensile strength may be evidence of the relaxation of molecular orientation causing from easy molecular motion by long time annealing.

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