

열방성 주축 액정 Polyester와 Copolyester들의 기계적 성질

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The Mechanical Properties of Thermotropic Main Chain Liquid Crystalline Polyesters and Copolyesters

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요 약: 4,4'-Dihydroxy- α -methyl stilbene이나 4,4'-dihydroxy-2,2'-dimethyl azoxybenzene을 이용하여 합성된 열방성 주축 액정 Polyester와 Copolyester들을 이용하여 이들의 Film과 Fiber들을 제조 하였다. 이때 Film은 액정 고분자 용액을 Casting 해서 제조 하였으며, Fiber는 액정 고분자를 Mesophase에서 녹여서 하는 Melt spinning 방법을 이용해서 제조 하였다. 이들 제조된 Film과 Fiber들의 기계적 성질들(Modulus, Tenacity)을 연구하였다. Elongation ratio에 따른 Film들의 Modulus들을 연구 하였으며 이때 Film의 Modulus는 Elongation ratio에 따라서 증가 하였다. Film과 Fiber들의 Modulus가 온도에 따라서는 어떻게 변하는가 또한 연구하였다. Orientation 되지않은 Film의 Modulus는 온도증가에 따라서 큰 폭으로 감소하는데 반해서 Orientation이 된 Film이나 Fiber의 Modulus는 유리전이 온도 이상에서도 크게 감소하지 않았다.

Abstract: Thermotropic liquid crystalline polyesters and copolyesters based on the 4,4'-dihydroxy- α -methyl stilbene(DYS-00, DYS-50, DYS-70) or 4,4'-dihydroxy-2,2'-dimethyl azoxybenzene(AZA-9 and DDA-9) were processed to obtain films and fibers; The films of these polymers were prepared by the casting of polymer solutions in chloroform and fibers of them were prepared by the melt spinning in their mesophases. The mechanical properties of these films and fibers such as moduli and tenacity were studied. The variation in the moduli of the films as a function of elongation ratio was studied; The moduli of films were increased with elongation ratio. The effect of the temperature on the moduli of the films and fibers was also studied; The moduli of unoriented films decreased in relatively large scale with increasing temperature, but those of oriented films and fibers did not decrease much even above glass transition temperatures.

Keywords: liquid crystal, film, fiber, mechanical properties.

INTRODUCTION

Thermotropic liquid crystal main chain poly-

mers have been considered as high performance polymer materials due to their ease in melt processing and expected good mechanical proper-

ties, which suggest potential application as high modulus fibers and films.¹⁻³ High performance polymer materials require the creation of a proper supermolecular structure: maximal orientation of macromolecules, perfect crystallites built up by extended chains, and a relatively high molecular weight of polymer.

The orientation of molecular chains, which is very important for good mechanical properties, can be obtained by several different ways such as cold or hot drawing,^{3,4} solid extrusion,^{4,5} rapid drawing from melts or solutions,^{4,6} and extrusion at the mesophase of thermotropic liquid crystal polymers.^{1,2} These mechanical and/or thermal treatments produce fibrillar structure from the isotropic one. The high mechanical properties of liquid crystal polymers were resulted from the supramolecular organization (maximal alignment of parallel molecular chain).

In this paper, in order to study the temperature dependence of the mechanical properties of oriented films or fibers of thermotropic liquid (LC) crystalline polymers, the films and fibers were made from the LC polyesters and copolyesters. The mechanical properties of them were measured by using an Instron tensile tester and a dynamic mechanical analyzer under different temperature conditions.

EXPERIMENTAL

Materials. Thermotropic liquid crystalline polyesters and copolyesters based on the 4,4'-

dihydroxy- α -methyl stilbene (DYS-00, DYS-50, DYS-70)³ or 4,4'-dihydroxy-2,2'-dimethyl azoxybenzene (AZA-9 and DDA-9)² prepared in our laboratory were used. The chemical structures and physical properties^{2,3} of these LC polymers are shown in Fig. 1 and Table 1, respectively. Chloroform was used as solvent of the LC polymers.

Film preparation. The liquid crystalline polymer films were prepared by casting the polymer solutions in chloroform on Teflon plates. Film thicknesses were about 50 μ m.

Orientation and heat treatment of films. In order to obtain the oriented films, a cold drawing method of the nematic glassy films was used. Before the cold drawing, the films were annealed at the nematic mesophases for 5 minutes and quenched to 0°C to make them nematic glass. The obtained nematic glassy films were elongated to the elongation ratio $\lambda=2$ or 3 at room temperature and oriented films were prepared.

For the heat treatment of the elongated films,

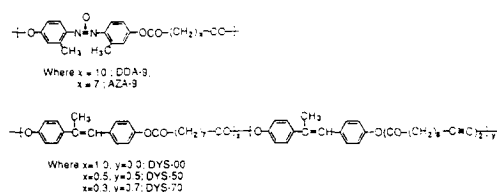


Fig. 1. Chemical structures of the liquid crystal polymers.

Table 1. Physical Properties of Thermotropic Liquid Crystalline Polyesters and Copolyesters

Polymer	M_n (g/mole)	T_g (°C)	Transition temperature (°C)	
			Heating	Cooling
DYS-00	56,500	40.5	C 174.5 N 215.4 I	I 200.6 N 138 C
DYS-50	45,000	35.0	C 13 N 161 I	I 150 N 92 C
DYS-70	13,000	35.0	C 113.9 N 142.9 I	I 129.7 N 85.7 C
DDA-9	18,100	18.9	C 123.2 N 166.2 I	I 154.9 N 73.8 C
AZA-9	19,100	21.7	C 90.6 N 160.6 I	I 151.4 N 84.2 C

* Heating and cooling rates of DSC were 100°C/min.

** Transition temperatures were obtained from the 2nd scans of DSC.

*** Glass transition temperatures (T_g) were obtained from the 2nd heating scans of DSC.

a hot stage equipped with a calibrated thermometer was used. The oriented films were positioned on the hot-stage, heated up to their mesophase, annealed for 5 minutes, and cooled down slowly to room temperature.

Fiber spinning. For the fiber spinning, a melt spinning method with a monofilament spinneret developed for a small experimental sample scale were used.² Around 2g of polymers, DDA-9 and AZA-9, were placed in the melting chamber and melted at their nematic mesophases, 142°C for DDA-9 and 92°C for AZA-9, and extruded. The diameters of spun fibers were approximately 45 μm . The spun fibers were stored at the low temperature(-5°C).

Dynamic mechanical analysis. Dynamic mechanical properties of films(unoriented and oriented) were measured by a Dynamic Mechanical Analyzer(model:Dupont, DMA 983). The sample dimension was as follow:(Width;2 mm) \times (Length;10mm) \times (Thickness;0.05mm). The gap distance between the sample holders was 1mm. The frequency was fixed at 1 Hz and amplitude(p-p) was 1.5mm. The temperature range was from 20°C to just below the melting point($T_m-10^\circ\text{C}$) of polymers and heating rate was 2°C/min.

Tensile testing. The tensile testings of the fibers were carried out at four different temperatures(-64, 0, 25, and 40°C). The tenacities and moduli of fibers were obtained by means of an Instron tensile tester(model TTC) under conditions as follows: The initial specimen length was 12" at the gauge length of 5", a strain rate of 2"/min, and a chart speed of 10"/min at four different temperatures.

Wide angle X-ray diffraction. X-Ray diffraction patterns of oriented films were obtained from a Laue camera mounted on a Rigaku generator operating at 40 KV and 25 mA using nickel filtered Cu-K alpha radiation with wavelength as 1.54 Å.

RESULTS AND DISCUSSION

Effect of orientation. In order to study the effect of orientation on the mechanical properties of the LC polymers, the films of two polymers with relatively high molecular weights, DYS-00 ($M_n = 56,500$) and DYS-50 ($M_n = 45,000$) were used. The oriented films were prepared by the elongation of the nematic glass films as explained in the experimental part. The Fig. 2. that is the wide angle x-ray diffractograms of the elongated film of DYS-00 is indicating very good orientations of the macromolecules in the elongated film. The oriented films with different elongation ratio showed different moduli. Table 2 shows the moduli of those films.

The flexural storage moduli (E') of the films were increased with orientation of the macromolecules (see Table 2). The flexural storage modulus (E') of oriented DYS-00 film (7.098 GPa) was comparable to that of Vectran HC-100C (8.02 GPa), which is the commercially available high modulus high strength fiber from Vectra by Hoechst-Celanese. The high moduli of the oriented films can be explained by the great number of macromolecules bearing the external mechanical strain and the presence of strong molecular interactions. In other words,

Table 2. The Influences of Orientation (Elongation) on the Flexural Storage Moduli(E') for Films of Liquid Crystal Polymers Based on the 4,4'-dihydroxy- α -methylstilbene

Polymer	Modulus(E')(GPa)		
	Unoriented cast film	Oriented film (100% elongtn)	Oriented film (200% elongtn)
DYS-00	0.50	-	7.10
DYS-50	0.36	10.2	6.38
DYS-70*	0.20	-	-
Vectran-HC 100C**		8.01	

All data were obtained at 25°C.

* Because of the relatively low molecular weight films of DYS-70 could not be oriented by elongation.

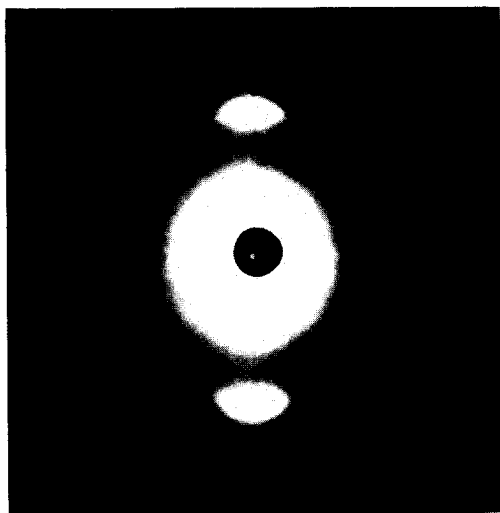


Fig. 2. The wide angle x-ray diffraction pattern of a DYS-00 film oriented by the cold drawing with a elongation ratio, $\lambda=3$, at room temperature.

with orientation, macromolecules in random coil state can be stretched along the elongation direction and stretched macromolecules can get together easily. Consequently, the oriented films can have higher number of macromolecules in the unit area as well as the increased intermolecular interactions. This high number of macromolecules per unit area and increased intermolecular interaction will produce high modulus of the film. From this result, it can be suggested that flexible main chain liquid crystalline polymers under suitable orientation can achieve moduli similar to rigid macromolecules such as Vectra.

Effect of temperature.

Fims : The study on the mechanical properties behavior as a function of temperature was carried out with films (unoriented and oriented) of DYS-00 and DYS-50. The temperature dependence of dynamic flexural storage moduli E' of unoriented films are shown in Fig. 3. The dynamic flexural storage modulus (E') of unoriented film of DYS-00 at 25°C was 0.5 GPa and decreased with increasing temperature (0.1 GPa at 80°C). Almost 80% decrease in E' occurs when passing from a glassy to rubbery

state. A similar temperature dependence of E' was found for an unoriented DYS-50 film. The decrease in E' was 86% (0.37 GPa at 25°C as compared to 0.05 GPa at 80°C). The decrease in moduli above T_g is probably due to the increase of segmental motion associated with T_g .

The temperature dependence of dynamic flexural storage moduli (E') of oriented films of DYS-00 and DYS-50 is shown in Fig. 4. In this work, three differently oriented films were used (DYS-00 film with $\lambda=3$, DYS-00 film with $\lambda=4.5$, and DYS-50 film with $\lambda=3$). The E' values at 25°C (below T_g) of oriented films of DYS-00 and DYS-50 were as a follow; 7.10 GPa (DYS-00 film with $\lambda=3$), 9.74 GPa (DYS-00 films with $\lambda=4.5$) and 6.3 GPa (DYS-50 films with $\lambda=3$). These E' values gradually decreased with increasing temperature to 50°C. After 50°C, E' did not change much. From the Table 3 one can find that decreases in E' of oriented films (below and above T_g) are much less than those of unoriented films. This phenomenon may be due to the orientation of macromolecules because high orientation does not allow rapid relaxation and conformational changes of oriented macromolecules. It is even more pronounced in the case of fibers (see Fig. 5).

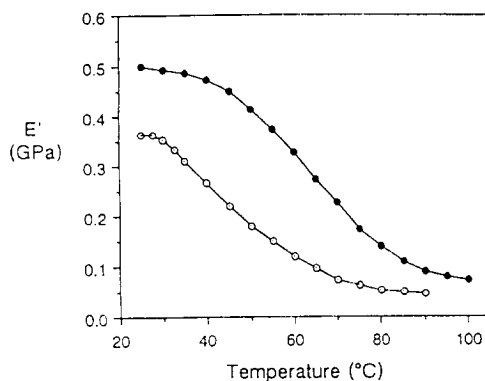


Fig. 3. The flexural storage moduli of solution cast films(unoriented) of liquid crystal polyesters as a function of temperature; DYS-00 (●) and DYS-50 (○).

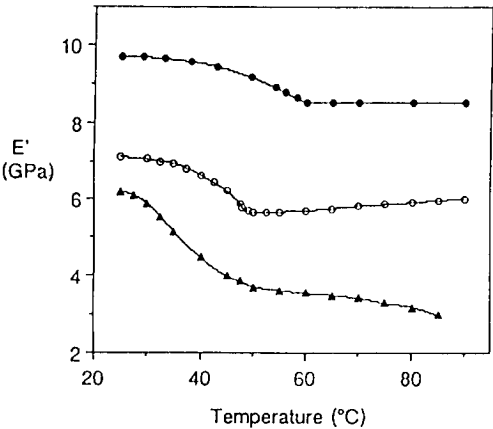


Fig. 4. The flexural storage moduli of oriented films with different elongation ratios of liquid crystal polyesters as a function of temperature; DYS-00 ($\lambda=3$)(\circ), DYS-00 ($\lambda=4.5$)(\bullet), and DYS-50 ($\lambda=3$)(\blacktriangle).

Table 3. The Effects of Temperature on the Flexural Storage Moduli (E') of Liquid Crystal Polymer Films with Different Extension Ratios (λ)

Polymer	Extension ratio (λ)	Modulus (E')(GPa)	
		25 °C	80 °C
DYS-00	0	0.50	0.10
	3	7.10	5.90
	4.5	9.74	8.45
DYS-50	0	0.37	0.05
	3	6.30	3.3

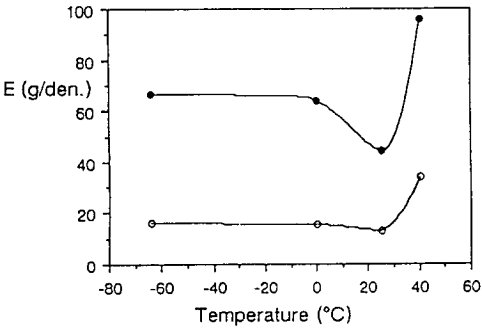


Fig. 5. Young's moduli (E) of thermotropic liquid crystal polyesters fibers, as a function of temperature; DDA-9 (\bullet) and AZA-9 (\circ).

Fibers : The mechanical properties of oriented fibers as a function of temperature were studied with fibers of AZA-9 and DDA-9 spun from the nematic mesophases. The tensile properties such as tenacity and modulus (E) of liquid crystalline polyester fibers spun at their mesophase are shown in Table 4 and Fig. 5. The tenacities and moduli of these fibers were unchanged in the temperature range from -64°C to 0°C but decreased gradually with an increase in temperature from 0°C to 25°C through glass transition temperatures of these polymers shown in Table 2. When the tensile moduli of these fibers at two temperatures such as 0°C (below T_g) and 25°C (above T_g) are compared, the differences are also very small and similar to the differences observed in E' of oriented films. For example, 70 percent (44.66 g/den) of tensile modulus of DDA-9 at 0°C (64.26g/den) remained at 25°C and 85 percent (13.3g/den) of tensile modulus of DDA-9 at 0°C (15.7g/den) remained at 25°C . This is remarkable, given the usual drop of the tensile modulus of

Table 4. The Influence of the Testing Temperatures on the Young's Moduli (E) and Tenacities of Thermotropic Liquid Crystalline Polyesters Fibers Spun from their Nematic Mesophase; 142°C for DDA-9 and 94°C for AZA-9

DDA-9		
Temperature* ($^{\circ}\text{C}$)	Tenacity (g/den.)	Modulus(E)** (g/den.)
-64	2.02	66.49
0	1.80	64.26
25	1.20	44.66
40	1.60	95.97
AZA-9		
Temperature* ($^{\circ}\text{C}$)	Tenacity (g/den.)	Modulus(E)** (g/den.)
-64	0.78	16.03
0	0.30	15.70
25	0.18	13.30
40	0.23	33.89

* Mechanical testing temperature with Instron
** Young's modulus

10~100 fold at T_g . The small change in moduli and tenacity at T_g of liquid crystalline fibers can be only due to the high orientation of macromolecules forming the fibers obtained from the nematic mesophase.

The tensile moduli at 40°C obtained from the annealed fibers of DDA-9 and AZA-9 at 40°C for 3 hours were very high. The value E at 40°C of annealed DDA-9 fiber was 95.97g/den, which was 2.2 fold of that obtained at 25°C. Also, the value E at 40°C of annealed AZA-9 fiber was 33.89g/den, which was 2.55 fold of that obtained at 25°C. These high increase in the tensile moduli of fibers also may be due to the crystallization of the oriented molecular chains at the temperature above T_g . The remarkable result of this study is the rather small drop in E on passing from below to above T_g .

The high orientation of LC main chain polyesters macromolecules obtained by the spinning from the nematic mesophase is responsible for this. This high orientation does not allow the rapid relaxation and conformational changes of the oriented macromolecules.

CONCLUSION

High orientations of macromolecules of liquid crystalline polymers can be obtained by the spinning at the nematic mesophase or by the elongation. The high orientation does not allow the easy relaxation and conformational changes of the oriented macromolecules, responsible for the decrease in mechanical properties, in the

moderate temperature range used in this experiment. Because of the uneasy relaxation and conformational change, the moduli of oriented fibers and oriented films are not changed with the temperature change from below to above T_g . The orientation also decrease the free volume in the fibers of films and increase the interactions between the oriented macromolecules. The increased interaction and stereoregularity of molecular chains are favorable for the formation of crystals, which is corresponding to the high increase in the moduli of annealed fibers at temperature above glass transition. Highly oriented fibers and films of liquid crystalline polyesters have very good mechanical properties due to the great number of chains bearing the external mechanical strain and to the presence of strong molecular interaction.

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