

열방성 액정공중합체의 물성에 미치는 화학구조의 영향

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Effects of Chemical Structure on Properties of Thermotropic Liquid Crystalline Copolymers

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요 약 : 단량체 *p*-acetoxybenzoic acid (*p*-ABA), terephthalic acid (TPA), low inherent viscosity (IV) poly(ethylene terephthalate) (PET) 및 2,7-diacetoxy naphthalene (2,7-DAN)을 사용하여 여러 조성의 열방성 액정고분자를 제조하여 화학조성이 그 성질에 미치는 영향을 조사하였다. IV가 1.6 이상이고 210~290℃에서 용융가능한 열방성 액정 공중합체를 얻었다. 얻어진 공중합체는 230℃에서부터 최소 320℃까지의 넓은 온도범위까지 nematic mesophase를 보였다. 유리전이온도 및 저장탄성율이 급격히 감소되는 온도는 mesogenic 단위 및 2,7-DAN 함량의 증가에 따라 현저하게 증가하였다.

Abstract : The thermotropic liquid crystalline copolymers were prepared by melt polymerization using *p*-acetoxybenzoic acid (*p*-ABA) and terephthalic acid (TPA) as mesogenic monomers, poly(ethylene terephthalate) (PET) to give a flexible linkage, and 2,7-diacetoxy naphthalene (2,7-DAN) as a dissymmetrical monomer. The composition of these monomers was varied as a means of manipulating thermal and dynamic mechanical properties. The polymers with inherent viscosities near or above 1.6 that were melt processible in the temperature range of 210~290℃ were obtained. Highly anisotropic melts were observed indicating the presence of a nematic mesophase. The glass transition temperature increased with increasing contents of mesogenic units and 2,7-DAN. The temperatures at which the storage modulus drastically dropped off increase with increasing mesogenic units and 2,7-DAN.

INTRODUCTION

We have recently described the preparation and properties of some linear nematic thermotropic liquid crystalline copolyesters¹⁻⁴. The relationships between structure and properties in the thermotropic liquid crystalline polymers were of principal interest in the investigations of these polymers. The application of thermo-

tropic liquid crystalline polyesters as high strength, high modulus materials, in fiber or thermoplastics, requires that they have reasonable melt-processing temperatures, which means that the normally high melting points characteristic of rigid wholly aromatic polyesters must be reduced below the temperature where degradation occurs.

It is generally recognized that melting temper

ature can be lowered by copolymerizing the rigid backbone moieties with controlled amounts of a moiety having flexible linkages and/or dissymmetrical units having bulky side groups or kinks.⁵⁻⁷ Copolymerizing mesogenic monomers with controlled amounts of monomers having flexible linkage and kink units is expected to broaden the molecule and make the spontaneous packing more difficult due to the irregularity and steric hindrances of the backbone. As a result, the decrease of transition temperatures should be encountered.

Hamb^{8,9} found that copolyesters could be prepared by the reaction of poly(ethylene terephthalate) (PET) with 4,4-isopropylidene diphenol diacetate and an equimolar amount of terephthalic acid. The proposed mechanism was an initial acidolysis of the PET followed by the condensation of carboxylic and acetate end groups to form high molecular weight polymers. In an attempt to increase the glass transition temperature of the PET, increase its flame resistance, and impart unusual physical properties, Jackson and Kuhfuss¹⁰ used a similar approach to prepare a series of copolyesters of PET and *p*-acetoxybenzoic acid. They reported that melts of copolyesters containing more than 30 mol% *p*-acetoxybenzoic acid exhibited liquid crystalline character. High moduli (~ 12 GPa) were observed for specimens injection-molded from these materials. A commercial name of the material is Rodrun LC-5000 made by Unitika Company.

In our earlier papers,¹⁻⁴ we have presented the effect of chemical composition and structure of monomers on the properties of thermotropic liquid crystalline copolymers prepared by melt polymerization using *p*-acetoxybenzoic acid and terephthalic acid as mesogenic monomers, PET to give a flexible linkage and a dissymmetrical monomer having bulky side groups or kinks.

This paper deals with the synthesis and properties of a series of thermotropic liquid crystalline copolyesters based on various combination of *p*-acetoxybenzoic acid (*p*-ABA), terephthalic acid (TPA), low inherent viscosity PET and 2,7-diacetoxy naphthalene (2,7-DAN). The chemical structure-property correlations for the series of materials is examined.

EXPERIMENTAL

p-Acetoxybenzoic acid (*p*-ABA), 2,7-diacetoxynaphthalene (2,7-DAN) were prepared using the acetylation reaction procedure described in our earlier paper. Terephthalic acid (TPA) and PET with an inherent viscosity of 0.36 dL/g were obtained from industrial sources and used without further purification. Sodium acetate was used as a reagent grade.

All the polymers were prepared in the same manner, utilizing an ester interchange reaction. PET (0.36 IV), TPA, 2,7-DAN, and *p*-ABA in the desired proportions plus 0.17wt% sodium acetate were added to a 250 mL three-neck round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet, and a distillation head/condenser. While keeping the flask temperature at 100°C, the reaction mixture were dehydrated under vacuum. Under a steady flow of nitrogen, the flask was heated at 250°C for 30 mins. The temperature was then raised to 317°C at the heating rate of 1.5°C/min. The nitrogen flow was halted and a vacuum connection attached at 320°C. The pressure was then rapidly reduced to less than 0.5 mmHg at 325°C. Under vacuum, the temperature was raised to 340°C and reacted for 10 mins. After the temperature was raised to 370°C for 20 mins, subsequently, the vacuum was released under nitrogen and the flask cooled.

Inherent viscosities were measured at 25°C in tetrachloroethane/*p*-chlorophenol (60/40 wt%) at a polymer concentration of 0.2g/100mL. Thermal behavior of as-polymerized samples was examined using a DSC (Seiko DSC 20) at a heating rate of 10°C/min. The optical texture was observed using a polarized microscope with a hot stage. Surface structure was observed

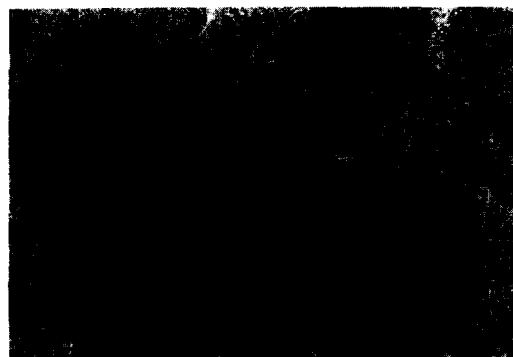
Table 1. Description of Thermotropic Liquid Crystalline Aromatic Copolyester Series

Designation	Composition (mol%) PET/2,7-DAN /TPA/ <i>p</i> -ABA	Content of mesogenic monomer	Inherent viscosity (dL/g)
LC-1	5/10/10/75	85	
LC-2	10/10/10/70	80	
LC-3	20/10/10/60	70	1.6
LC-4	30/10/10/50	60	1.7
LC-5	10/30/30/30	60	

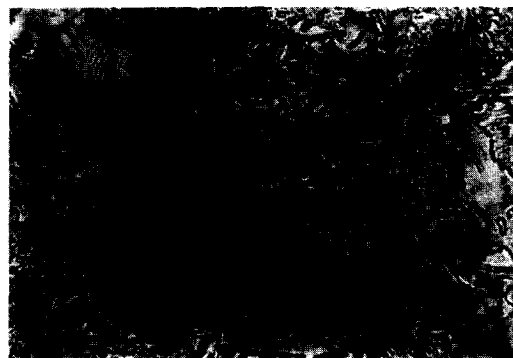
using a SEM (Jeol model JSM 5400). Viscoelastic properties, dynamic modulus (E' and E'') and $\tan \delta$ were determined from Rheovibron (Toyo Baldwin DDV-II). Measurements were made from 30°C to 210°C at 11Hz. x-ray diffraction patterns were obtained by using a x-ray diffractometer (Rigaku Denki Model D-MAX) whose source of radiation was copper with a nickel filter.

RESULTS AND DISCUSSION

Viscosity and Morphology. The sample designations, compositions and inherent viscosities (IV) are shown in Table 1. The highest IV values were obtained when strenuous precautions were taken to eliminate the effects of air and moisture on the reaction. LC-copolymers with IV near or above 1.6 were obtained. However, IV measurements could not be made for LC-1, LC-2, and LC-5, which contain less than 10 mol % of PET units. The morphological texture of a typical copolymer prepared in this study, LC-2, was studied as a function of temperature using a hot stage mounted on a polarizing optical microscope. Photomicrographs taken at different temperatures during the heating experiment are shown in Fig. 1. LC-2 exhibits a nematic mesophase in the broad temperature range of 230°C up to at least 320°C, apparent from the high birefringence under crossed polarizers. The domains (crystal aggregates) remained clearly dis-



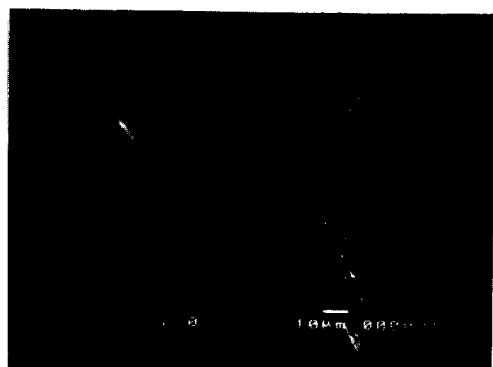
(a)



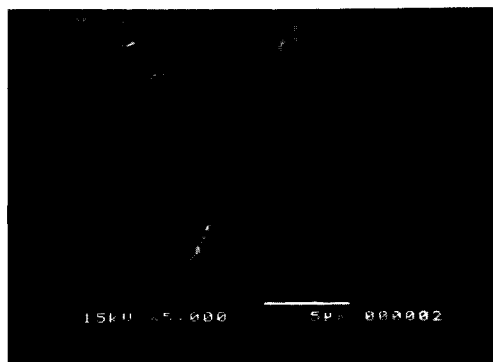
(b)

Fig. 1. Optical photomicrographs of LC-2 viewed between crossed polarizers at various temperature : (a) 230°C; (b) 320°C.

cernible and fused in the surrounding mesophase with increasing temperature. Highly anisotropic melts were observed indicating the presence of a nematic mesophase. A threaded texture of the nematic phase increased with increasing temperature (Fig. 1(a) and 1(b)). The fluidity of the melt decreased noticeably with the formation of the threaded texture. The melt processible temperatures of the copolyesters synthesized here were in the temperature range of 210~290°C. Fig. 2 shows fibrillar structure of fracture surface of as-polymerized sample. This indicated that the fibril was already formed during melt polymerization due to the arran-



(a)



(b)

Fig. 2. SEM microphotographs of the fractured surface of selected as-polymerized LC-copolyesters : (a) LC-2; (b) LC-5.

gement of molecules during agitation.

Thermal Characterization. Differential scanning calorimetry was used to obtain information about the thermal transition of LC-copolyesters. Fig. 3 shows initial DSC scans of the LC-copolyesters obtained at the heating rate of 10 °C/min. Glass transition temperature mainly depends on 2,7-DAN units and the ratio of flexible PET units to rigid mesogenic. By increasing the PET content from 5 to 30 mol% at the expense of a mesogenic monomer, *p*-ABA, the glass transition temperature is decreased from 124°C to as low as 89°C. The glass transition temperature increased with increasing rigid me-

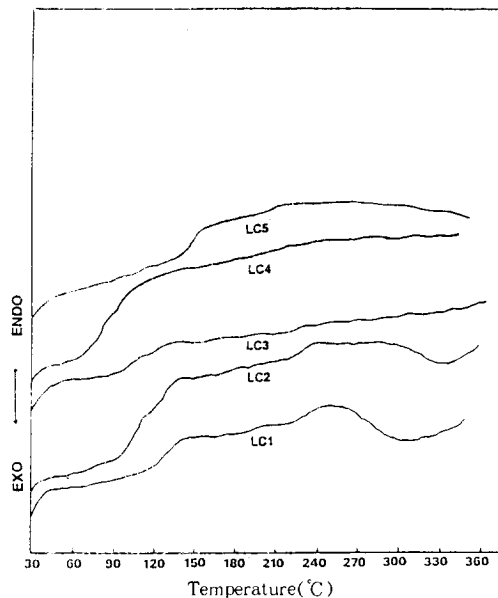


Fig. 3. DSC thermogram for the LC-copolyesters; first scans at 10°C/min.

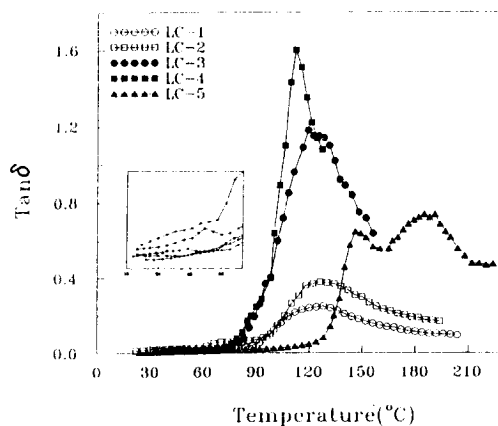


Fig. 4. Tan δ for the LC-copolyesters.

sogenic units. It was found that the glass transition temperature increased markedly with increasing rigid 2,7-DAN units. The higher glass transition temperature of LC-5 may be due to the effect of stiffness of 2,7-DAN units in the amorphous phase.

With increasing PET content, the melting en-

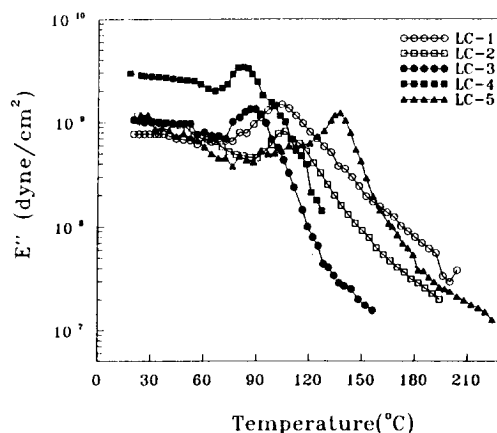
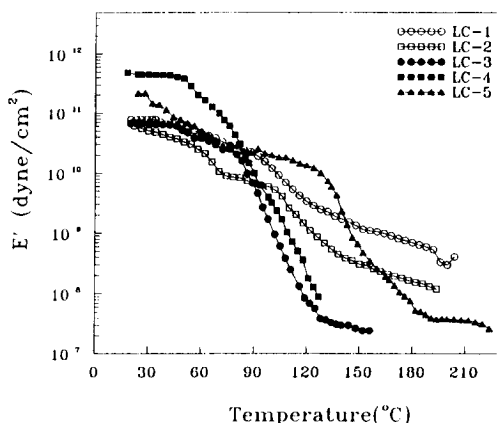
Table 2. Thermal and Dynamic Mechanical Properties

Description	Composition (PET/2,7-DAN/ TPA/ <i>p</i> -ABA)	Content of mesogenic units	T _g (°C) from DSC	T _g (°C) from Rheovibron (E'')	tan δ peak (°C)
LC-1	5/10/10/75	85	124	105	128
LC-2	10/10/10/70	80	115	103	126
LC-3	20/10/10/60	70	108	88	118
LC-4	30/10/10/50	60	89	81	111
LC-5	10/30/30/30	60	140	136	144, 187

dothrm peak weakens and moves to lower temperature because of classical copolymer melting point depression for LC-1 and LC-2 (see Fig. 3). The LC-1 has a melting temperature near 250°C. LC-3, LC-4 and LC-5 containing 20 mol % and above of PET or 2,7-DAN have not a distinct melting endotherm peak. A detailed assignment of indistinct melting endotherms for these copolyesters will not be attempted. But the five LC-copolyesters synthesized in this study exhibit turbid melts in the broad temperature range from 230°C up to at least 320°C.

Dynamic Mechanical Properties. The loss modulus (E''), loss factor ($\tan \delta$) and storage modulus (E') for the copolymers obtained at 11Hz are shown in the Figs 4, 5 and 6. In the series of samples from LC-1 to LC-4, the content of mesogenic units decreases as the content of PET units increased while the mole percentage of TPA and 2,7-DAN is held constant. As show in Figs 4 and 5, in the temperature range examined, several relaxation peaks which varied with composition of the copolyesters synthesized in this investigation are observed owing to the multiple microstructures of amorphous region.

The main loss modulus peak of 126°C for LC-1 shifted to a slightly lower temperature, but increased in intensity markedly as the content of PET units was increased. The rate of decline of the storage modulus (E') with temperature after the main relaxation increased rapidly as more PET units were added. It is believed that this behavior observed above the room tempera-

**Fig. 5.** Dynamic loss modulus (E'') for the LC-copolyesters.**Fig. 6.** Dynamic storage modulus (E') for the LC-copolyesters.

ture mainly reflects the relaxation of the PET component. This indicates that PET component is included primarily in the amorphous regions. And it is found that the relaxation phenomena were also dependent on the content of the dissymmetrical 2,7-DAN units. The 2,7-DAN content of LC-5 is higher than that of LC-2 while the PET content is the same. This effect is clearly seen by comparing the composition and relaxation peaks of LC-1 and LC-5 in Figs. 4 and 6. The higher relaxation temperature of LC-5 may be due to the effect of stiffness of 2,7-DAN units in the amorphous phase. In the polymer series LC-1 through LC-4, the main relaxation transition broadens, weakens in intensity and moves to higher temperature as the contents of mesogenic units increase. This with no doubt reflects the accompanying decrease in chain flexibility and the ordering of the chain as mesogenic units replace flexible PET units. Besides the main relaxation as discussed above, a small relaxation peak appeared near or below 60°C. Benson and Lewis¹¹ investigated the dynamic mechanical properties of a series of PHB/PET copolymer. They reported that the PHB/PET 60/40 exhibited α -, β - and γ -relaxation peaks at approximately 88, 62, and 45°C. The small relaxation peak of the copolyesters synthesized here is similar to β - or γ -relaxation of PHB/PET. A detailed assignment of these multiple relaxations will not be attempted.

The storage modulus of LC-copolyester synthesized here maintains almost its initial value until the main relaxation but drops rapidly after the main relaxation. The rate of decline of the storage modulus (E') with temperature after the main relaxation increase markedly as the contents of PET and 2,7-DAN units were increased. The temperatures at which the storage modulus drastically dropped off increase with increasing mesogenic units and 2,7-DAN. From the storage modulus data, it can be concluded that the LC-copolyesters containing more 2,7-DAN content are excellent materials for main-

taining its initial mechanical properties at higher temperatures.

X-ray Diffraction. Ecomony et al.¹² reported that the homopolymer based on *p*-hydroxybenzoic acid has two significant x-ray diffraction lines indicated as 220 ($2\theta=19.6^\circ$) and 006 ($2\theta=28.8^\circ$). The 220 peak represents the repeat distance between the hexagonally arranged double helices while the 006 peak defines the repeat distance of the chain.

Fig. 7 shows the x-ray diffraction patterns of five LC-copolyesters synthesized in this study (LC-1~5). Their significant peaks were found to be near $2\theta=19.6^\circ$ and $2\theta=28.8^\circ$. Peak sharpness of these LC-copolyesters increases with increasing the content of *p*-ABA unit, indicating that the LC-copolyester containing a higher *p*-ABA content has similar structure to the homopolymer based on *p*-hydroxybenzoic acid. The peak sharpness decreased with increasing the contents of PET and 2,7-DAN units. As a result of this investigation, it is concluded that the diffraction peak broadening effect is due to defects formed by the presence of several different monomeric components having flexible monomer PET units and dissymmetrical monomer 2,7-DAN units in the chains.

A peak at $2\theta=23.1^\circ$ has been identified as a conventional PET crystalline peak. Jackson et al.¹⁰ reported that the PET crystalline fraction decreased continuously as the *p*-hydroxybenzoic acid (PHB) content increased in the PET/PHB system and that PHB60 (PET(40)/PHB(60)) has very little PET crystallinity. The five LC-copolyesters synthesized in this study have not a distinct pure PET crystalline peak.

CONCLUSIONS

A series of thermotropic liquid crystalline copolymers were prepared by melt polymerization using *p*-acetoxybenzoic acid (*p*-ABA) and terephthalic acid (TPA) as mesogenic monomers, poly(ethylene terephthalate) (PET) to give a fl-

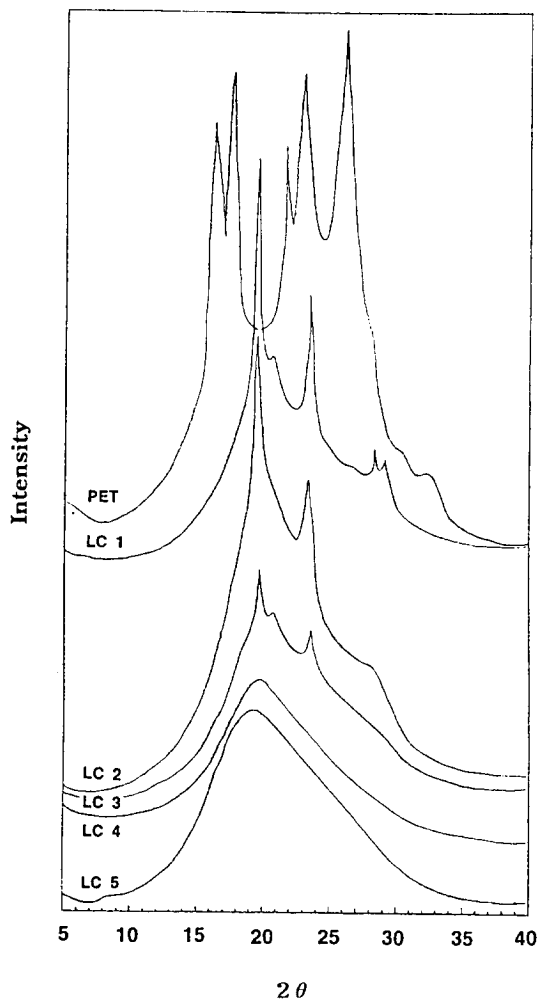


Fig. 7. X-ray diffraction pattern for LC-copolyesters.

exible linkage, and 2,7-diacetoxy naphthalene (2,7-DAN) as a dissymmetrical monomer. The effects of chemical structure on the properties of thermotropic liquid crystalline copolymers are as follows.

1. The copolymers with inherent viscosities

near or above 1.6 that were melt processible in the temperature range of 210~290°C were obtained.

2. The copolymers exhibit a nematic mesophase in broad temperature range of 230°C upto at least 320°C.

3. The glass transition temperature increases markedly with increasing mesogenic units and 2,7-DAN content.

4. The temperatures at which the storage modulus drastically drop increase with increasing mesogenic units and 2,7-DAN.

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