액정 중합체 (제10보). 혼합폴리에틸렌 격자나 메소젠 단위를 갖고 있는 새로운 주사슬 혼성폴리에스테르의 합성 및 성질

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Liquid Crystal Polymers (X). Synthesis and Properties of New Thermotropic Main Chain Copolyesters with Either Mixed Polymethylene Spacers or Mixed Mesogenic Units

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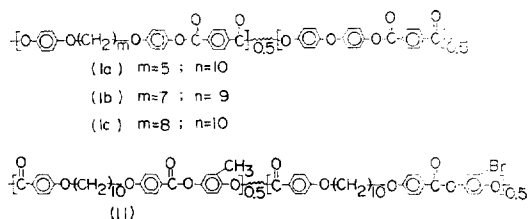*Massachusetts, Amherst, Mass. 01003, U. S. A.*
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요 약. 새로운 혼성 폴리에스테르 4가지를 합성하여 액정성을 DSC 및 편광 현미경을 사용하여 조사, 연구하였다. 세가지 혼성 폴리에스테르는 같은 메소젠 단위를 갖고 있으나 폴리메틸렌 유연 격자중 메틸렌기 수가 기수-우수, 기수-기수 및 우수-우수의 조합으로 되어 있는점이 다르며, 또 하나의 혼성 폴리에스테르는 양단에 *p*-옥시벤조일기가 결합하고 있는 메틸-및 브로모히드로 퀴논 단위가 데카메틸렌 격자에 결합하고 있는 구조를 갖고있다. 이들 폴리에스테르는 모두 녹는점 및 그 이상의 온도에서 네마틱 액정상을 형성함을 알았으며 네마틱→등방성 액체간의 상변환이 가역적으로 일어남을 DSC 및 현미경으로 관찰할 수 있었다. 액정→등방성액체의 상변환에 수반되는 열역학적 성질을 중합체의 구조와 관련시켜 고찰하였다.

ABSTRACT. Four new thermotropic copolyesters were prepared and their liquid crystal properties were investigated by differential scanning calorimetry and on a hot-stage of a polarizing microscope. Three copolyesters had same mesogenic unit, triad aromatic ester structure, interconnected through a random combination of either odd-even, or odd-odd, or even-even number of methylene groups in the polymethylene flexible spacers. Another random copolyester consisted of mesogenic units of 1 : 1 mixture of central methyl- and bromohydroquinone moieties with two flanking *p*-oxybenzoate units connected by decamethylene spacer. All of the polyesters formed nematic liquid crystal phase upon melting. The transitions for melting and nematic→isotropic transformations could be reversibly observed by DSC as well as by microscopic study. The thermodynamic properties for their liquid crystal→isotropic phase transitions were diucussed in relation to their chemical structures.

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INTRODUCTION

As a contiued effort to delineate the structure–property relationships for the thermotropic liquid crystalline polyesters having mesogenic units and spacers in the main chain[1~5], we have prepared several new random copolyesters having the following structures and their liquid crystal properties were investigated by differential scanning calorimetry (DSC) and on a hot-stage of a polarizing microscope:

(Ia) m=5 ; n=10
(Ib) m=7 ; n= 9
(Ic) m=8 ; n=10

(II)

The copolyesters of the Series(I) consist of the same mesogenic unit, but their flexible spacers are of different 1 : 1 odd–even combinations in the number of methylene groups of polymethylene flexible spacers. The copolyester(II) is composed of equimolar mesogenic units of different substituents and decamethylene spacer along the main chain.

Thermotropic liquid crystal properties and thermodynamic analysis of the phase transitions for the homopolymers corresponding to (I) and (II) were earlier reported by us.[1,2] Except fully aromatic copolyesters, there are not many reports on the thermotropic liquid crystal properties of the copolyesters which have the structural features described in this study[3,4]. According to the results of our and others' earlier works,[1~10] in general, the longer the rigid mesogenic unit and the shorter the flexible spacer, the higher was the thermal stability of the mesophase of a polymer. Moreover, minor structural alternation in the structure of mesogenic units could lead to a significant change

in the thermal properties of the mesophase. In light of these observations, it should be interesting to investigate the effect of mixed spacer length and mesogenic units on the liquid crystal properties of the resulting copolyesters.

EXPERIMENTAL

Preparation of Polymers. For the synthesis of the polymers of Series (I), the starting diphenols(4,4′-dihydroxy-α,ω-diphenoxyalkane: HO—⬡—O-(-CH$_2$-)$_n$-O—⬡—OH)were prepared from hydroquinone and α,ω-dibromoalkanes following the method of Griffin and Havens[7]. Equimolar mixture of diphenols with different n's was polymerized with terephthaloyl chloride in 1,1,2,2-tetrachloroethane (TCE) at room temperature. Pyridine was used as an HCl acceptor. Detailed preparation and isolation procedures of the polymers were described in a earlier report by us[1].

For the preparation of copolyester (II), 4,4′-dichloroformyl-1,10-diphenoxydecane

$$\text{(ClC}\overset{\overset{\text{O}}{\|}}{-}⬡\text{-O-(-CH}_2\text{-)}_{10}\text{-O-}⬡\overset{\overset{\text{O}}{\|}}{-}\text{CCl)}$$

was prepared following Griffin and Havens' method[7]. This diacid dichloride was polymerized with an equimolar mixture of bromohydroquinone and methylhydroquinone in a TEC–pyridine mixture at room temperature. Polymerization procedure can be found in our earlier report[1].

Polymer Characterization. Inherent solution viscosity numbers (η_{inh}) of the polymers were measured using a Cannon–Ubbelohde type viscometer in a constant temperature bath. Thermal properties were examined under a nitrogen atmosphere on a Perkin–Elmer DSC-1B instrument. Heating ratet was maintained constant at 20°C/min for all of the runs. The maximum temperature of the endotherm was taken as the transition temperature.

A Leitz Ortholux polarizing microscope equipped with a Mettler FP-2 hot-stage was employed for visual examination of phase changes and optical textures of polymer melts. The structure of polymers was verified by their IR spectra obtained by a JASCO 720 spectrophotometer and by elemental analysis. Elemental analysis confirmed that actual copolymer compositions were practically the same as the feed compositions.

RESULTS AND DISCUSSION

Copolyesters of Series(I) with Mixed Length of Flexible Spacers. General properties of the copolymers of Series(I) are presented in *Table* 1. The molecular weights of the polymers were relatively low as reflected by their solution viscosity numbers. The polymers showed low solubilities in various solvents such as chlorinated hydrocarbons, phenol-TCE mixtures, and trifluoroacetic acid. However, all of them were soluble in *p*-chlorophenol and trifluoromethane sulfonic acid.

The crystalline melting temperatures(T_m) of these copolyesters were significantly lower than those of corresponding homopolymers with a single flexible spacer component[2]. Melting point depression by copolymerization was the highest when the flexible spacer was of an odd-odd combination in m and n. Copolymer (Ib) melted at 166°C. The melting temperatures of the corresponding homopolymers with $m=7$ and 9 were 237 and 229°C, respectively. The

degree of melting point depressions was less profound for the other two. This is considered due to the well-known least effective intermolecualr packing for the copolymer with an odd-odd combination in the number of methylene groups of the spacer.

Multiple melting transitions were observed for all of these polymers on DSC thermograms, as shown in *Fig.* 1. Such multiple melting transitions were earlier observed by us[2] and others[9] for other thermotropic liquid crystal polymers. Since annealing treatment did not much change the melting characteristics, it is possible that these polymers are polymorphic.

As shown in *Fig.* 1, all of the polymers, after the melting endotherms, exhibited another broad endothermic peaks at a higher temperature region indicating the occurrence of a second phase transition. When the polymers were looked at on a hot-stage of a polarizing microscope, they produced birefringent melts upon melting and became isotropic over the temperature range corresponding to the second endotherms on their DSC thermograms.

The melts showed the optical textures, see *Fig.* 2a~2c, typical to nematic mesophase. When visually observed, the melts were turbid and strongly stir-opalescent, and became clear at the same temperature range where the second endotherm appeared on thermogram. This clearly demonstrates that the second endotherm is for nematic→isotropic phase transition. This transition could be reversibly observed on coo-

Table 1. Properties and thermodynamics for the isotropic transitions of the polymers of series(I)

Polymers	m/n	Yield, wt. %	η^*_{inh}	T_m, °C	T_i, °C	ΔH_i kcal/mol	ΔS_i cal/mol·°K
Ia	5/10	80.3	0.171	215	256	0.23	0.43
Ib	7/9	81.8	0.175	166	277	0.23	0.41
Ic	8/10	82.3	0.203	208	297	1.65	2.9

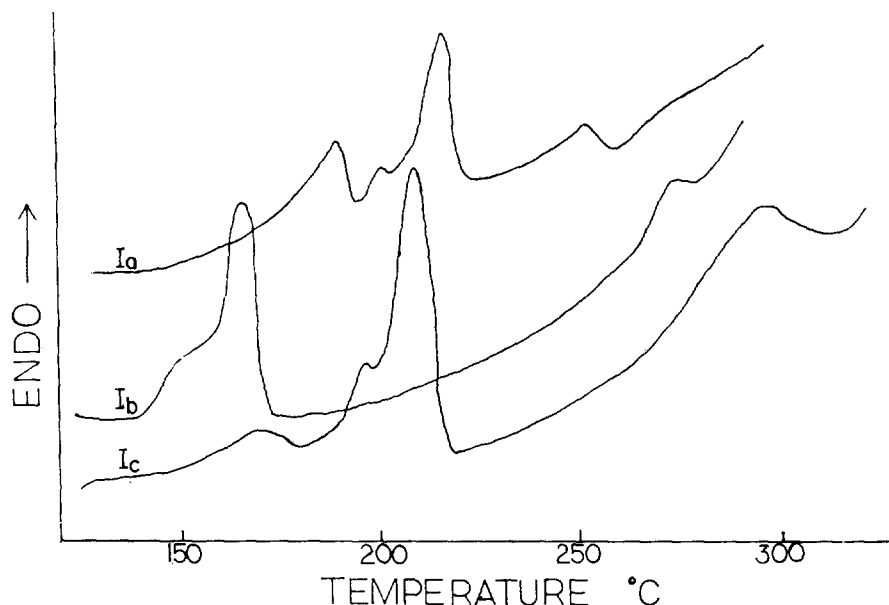*Measured on 0.2wt. % of polymer in *p*-chlorophenol at 45°C.

Fig. 1. DSC thermograms of the polymers of series(I).

ling indicating the formation of enantiotropic mesophase from these polymers. The nematic ⊢→isotropic phase transition temperature(T_i) was the highest, 297 °C, for Polymer(Ic), although its spacer was the longest compared with those for the other two, see *Table* 1.

The enthalpy ΔH_i and the entropy ΔS_i for the transition shown in *Table* 1 suggest that intermolecular attraction and the degree of order in the mesophase are the greatest for Polymer (Ic) among the three. Comparison of these values with those of corresponding homopolymers[2] did not lead to any direct correlation between the stability of the mesophases of homopolymers and copolymers, presumably due to significant difference in their molecular weights.

Copolyester (II) with Mixed Mesogenic Units. This copolyester showed better solubility in organic solvents than the copolymers of Series(I) and was soluble in TCE. The inherent viscosity of the polymer measured on a TCE solution at 40°C was 0.518. T_m and T_i

determined by DSC were 168° and 283°C, respectively. Both values are a little higher than those for corresponding homopolymers, whose properties were earlier reported by us[2]. This seems to be due to fact that the present polymer has significantly higher molecular weight than those of homopolymers, as reflected by their viscosity values. However, the temperature range, ΔT, over which mesophase of the copolymer existed was comparable to those of homopolymers.

This copolyester also showed a nematic liquid crystal texture upon melting and the texture disappeared at T_i. The formation of the mesophase was reversible. The values of ΔH_i and ΔS_i were 2.0kcal/mol and 3.7cal/mol·°K, respectively, both of which are slightly lower than those of homopolymers. This indicates slightly reduced intermolecular attraction and lower degree of molecular order in the mesophase of the copolymer, probably due to its structural irregularity compared with homopolymers. However, as pointed out for
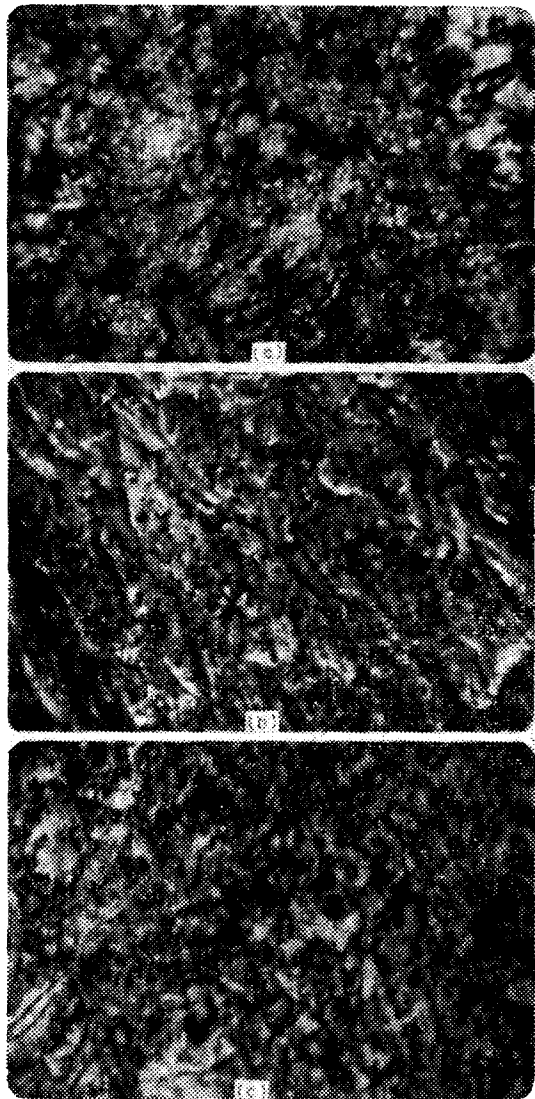
Fig. 2. Photomicrographs of polymer melts of series (I). (The photographs span a sample length of 440 μm): (a) photomicrograph of Polymer(Ia) taken at 235°C (magnification 320X) ; (b) Photomicrograph of Polymer (Ib) taken at 200°C (magnification 320X); (C) Photomicrograph of Polymer (Ic) taken at 220°C (magnification 320X).

the polymers of Series(I), conclusive remark can not be made because of the difference in their molecular weights. Study on the dependence of thermal behavior of liquid crystal polyesters on their molecular weights is pre-

sently in progress.

CONCLUSION

The following conclusions can be drawn from this work:

(1) All of the copolyesters described in this paper, having either mixed flexible spacers or mixed mesogenic units, exhibited enantiotropic thermotropic liquid crystal properties.

(2) Only nematic liquid crystal textures were observed for all of the copolyesters.

(3) Copolyester(Ic) with the combination of even–even numbered polymethylene spacers led to more highly ordered mesophase, judged by thermodynamic data for mesophase→isotropic phase transition, than those with odd–odd or even–odd combination.

(4) Thermodynamic stability of a liquid crystal phase seems to heavily rely on the molecular weight of the polymer.

(5) Copolyester(II) with mixed mesogenic units appears to have less ordered mesophase than corresponding homopolymers.

ACKNOWLEDGEMENT

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