

메소겐 단위와 격자의 연결기의 결합순서가 주사슬 액정 폴리에스테르의 열적 성질에 미치는 영향

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(1985년 7 월 5 일 접수)

Effect of the Order of Linkages Between Mesogenic Units and Spacers on the Thermal Properties of Main-Chain Thermotropic Polyesters

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(Received July 5, 1985)

1. Introduction

Recently we critically discussed various structural variables which influence the thermal and liquid crystalline properties of thermotropic polyesters containing flexible spacers¹. Structure and length of the mesogenic and spacer units and substituents on them are the most important factors exerting profound effects not only on thermal properties of the polymers but also on the nature of mesophases formed by them.

In addition, comparison of the results reported by different research groups indicates a subtle dependence of mesomorphic properties of the polymers on the bonding order of the linking

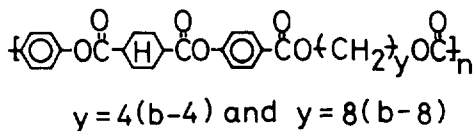
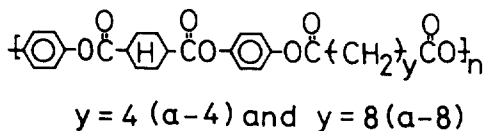
groups between mesogenic units and flexible

$$\begin{array}{c} \text{O} \qquad \text{O} \end{array}$$

spacers¹. An example is M-O-C-S vs. M-C-O-S, where M stands for a mesogenic unit and S for a spacer. In order to provide a further experimental evidence on this point we have prepared following polymers whose structural difference lies only on the order of the linking ester groups between the mesogenic units, bis-p-phenylene-trans-1,4-cyclohexane dicarboxylate, and the spacers, tetra or octamethylene units.

Thermal properties of the polymers were examined on a differential scanning calorimeter (DSC). The nature of the mesophases formed by the polymers were identified by their optical tex-

tures observed on a polarizing microscope equipped with a hot-stage.



2. Results and Discussion

The bisphenols I and III prepared following the literature methods^{2,3} were reacted at room temperature with the dichloride of trans-1,4-cyclohexane dicarboxylic acid II.

1,1,2,2-Tetrachloroethane (TCE) was used as a reaction medium and pyridine as an HCl acceptor.

The polymer yields together with other properties are summarized in Table 1. The yields as well as the inherent viscosities of the polymers were reasonably high. All of the four polymers were found to be enantiotropically thermotropic by DSC analysis and by the observation on a microscope. With the exception of polymer *a-4* they all showed definite melting (T_m) and isotropization (T_i) endotherms on the DSC heating curves and the corresponding exotherms on cooling. The positions of the endothermic peak maxima are shown in Table 1. As explained later polymer *a-4*

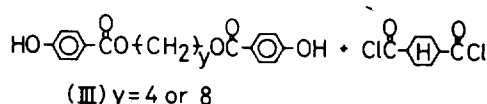
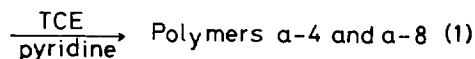
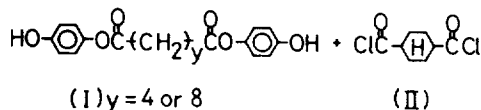


Table 1. Yields and Properties of Polymers

Polymers	Yield, wt. %	η inh ¹⁾	T_m , °C	T_i , °C
<i>a-4</i>	87	0.372	275	335 ²⁾
<i>a-8</i>	84	0.662	234	288
<i>b-4</i>	94	0.331	247	318
<i>b-8</i>	89	0.417	182	227

1) Measured on 0.5g/dl solution in TCE/phenol (80/20 by wt.) at $30 \pm 0.1^\circ\text{C}$.

2) Obtained on a Fisher-Johns apparatus.

did not exhibit a isotropization endotherm on DSC analysis probably due to thermal decomposition.

Upon melting the polymers exhibited strong stir-opalescence and threaded schlieren optical textures typical to nematics. At T_i 's the polymer melts ceased to show stir-opalescence and they became isotropic. On cooling the isotropic melts, reappeared nematic mesophases. Such transitional behavior confirms that the polymers are enantiotropic.

Comparison of the transition temperatures of the polymers shown in Table 1 leads us to the following two points: 1) Lengthening the spacer reduces T_m as well as T_i and 2) The values of T_m and T_i of the polymers *a-4* and *a-8* are significantly higher than those of counterparts *b-4* and *b-8*. The effect of the length of spacers on the transition temperatures of thermotropic polymers is very well documented and discussion on this point can be found elsewhere¹. However, the second observation deserves a comment.

As pointed out earlier, the polymers *a-4* and *a-8*

have oxycarbonyl groups (M-O-CO-S) between the mesogenic units and spacers, while the correspon-

ding polymers *b-4* and *b-8* carboxy (M-CO-O-S) linkages. Our present conjecture for the difference observed in the thermal properties of the

polymers *a*'s and *b*'s is that M-O-CO linkage allows conjugation to extend from M to C=O. This type of conjugation would result in a greater rotational

energy barrier around the single bonds, M-O and O-C=O, which in turn would increase the rigidity

of $\begin{array}{c} \text{O} \\ || \\ \text{-M-O-C-} \end{array}$ moieties leading to lengthened mesogenic units.

On the other hand, the similar conjugation is

less efficient in $\begin{array}{c} \text{O} \\ || \\ \text{M-C-O-S} \end{array}$ linkages and conformational freedom around -O- is much higher. There-

fore only $\begin{array}{c} \text{O} \\ || \\ \text{M-C} \end{array}$ part should be considered to belong to the rigid, mesogenic unit. Accordingly, the longer mesogenic structure of the polymers *a-4* and *a-8* would exhibit higher T_m 's and T_i 's, as observed in the present and other investigations⁴, than the polymers *b-4* and *b-8* whose mesogenic unit is shorter. One can arrive at the same conclusion by considering the influence of conjugation to the effective spacer length. The extension of conjugation in the mesogenic units of polymer *a*'s leads us to take only alkylene groups as spacers, while in polymer *b*'s the longer oxyalkyleneoxy groups as spacers. It is well known that longer spacers usually result in lower T_m and T_i ¹. Although structural effect must certainly be very important, we believe that this could be only a part of the reason for the difference observed. Other factors such as molecular weight, molecular weight distribution and intermolecular attraction should be also taken into account. Unfortunately quantitative informations on these points are not presently available.

3. Experimental

3-1. Synthesis of Polymers

The compounds I and III were prepared following the literature methods^{2,3}. Since all of the polymers were prepared in the same way, only a representative procedure is given: trans-1,4-Cyclohexane dicarboxylic acid (1g: 5.8 m mole) was dissolved in 10 ml of thionyl chloride containing 2 drops of DMF and the mixture was refluxed

for 5 hours. Excess thionyl chloride was distilled off under a reduced pressure. The white solid, diacid dichloride II, was dissolved in 10 ml of dry 1,1,2,2-tetrachloroethane (TCE). This solution was added dropwise to a solution of bis (p-hydroxyphenyl) adipate (1.914g; 5.8 m mole) dissolved in 10 ml of dry pyridine.

The polymerization was allowed to proceed for 5 hours at room temperature under a nitrogen atmosphere. And then, the reaction mixture was poured into large excess of methanol. The precipitate was washed with methanol, water, dilute sodium bicarbonate solution, dilute hydrochloric acid, and finally again with water. The yield of the polymer *a-4* thus obtained was 87% of calculated value.

4. Characterization of Polymers

The solution viscosities of the polymers were measured at $30 \pm 0.1^\circ\text{C}$ using a Ubbelohde type viscometer. A mixture of TCE and phenol (80/20 by wt.) was used as a solvent. Thermal properties of the polymers were examined on a DSC analyzer (du Pont model 910) under a nitrogen atmosphere and on a Fisher-Johns melting point apparatus. Heating rate for DSC analysis was $10^\circ\text{C}/\text{min}$. The optical textures of the polymer melts in mesophases were observed on a hot-stage (Mettler FP-2) attached to a polarizing microscope (Leitz, Ortholux). The isotropization temperature of the polymer *a-4* was determined by observing the disappearance of stir-opalescence of the polymer melts on the preheated Fisher-Johns apparatus. DSC analysis of this polymer did not provide a clear-cut isotropization transition temperature due to thermal degradation.

Acknowledgement: Authors are grateful to the Korea Science & Engineering Foundation for the support of this work

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