

## Liquid Crystal Polymers. V. Thermotropic Polyesters with Either Dyad or Triad Aromatic Ester Mesogenic Units and Flexible Polymethylene Spacers in the Main Chain

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(Received April 6, 1981)

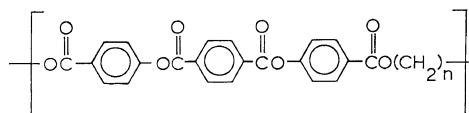
**ABSTRACT:** The thermal properties of two new series of thermotropic, liquid crystalline polyesters were studied by differential scanning calorimetry and on a hot-stage of a polarizing microscope. The first series contained an aromatic ester triad with a central terephthaloyl and two terminal oxybenzoyl units connected by a flexible polymethylene spacer containing from two to ten methylene units. The second series contained a head-to-head tail-to-tail aromatic ester dyad with one terephthaloyl and one oxybenzoyl unit and either a dimethylene or hexamethylene spacer. The melting temperatures and the transition temperatures for conversion from the mesophase to the isotropic phase (the clearing temperature) of the polyesters in the first series initially decreased in a zig-zag manner for polymers with up to nine methylene units but increased for the decamethylene polymer. The temperature ranges over which the mesophase formation occurred were generally broader for polymers containing an odd number of methylene units than for those with an even number of units. Most, if not all, of the polymers in both series formed nematic states on melting. The enthalpy and entropy changes for the clearing transition both increased with the length of the polymethylene spacer. Polymers of the second series possessed lower transition temperatures and narrower temperature ranges for mesophase formation, as would be expected for the shorter mesogenic unit.

**KEY WORDS** Liquid Crystal Polyesters / Thermotropic Polyesters / Mesogenic Dyads and Triads / Melting Points of Aromatic Polyesters / Clearing Temperatures of Thermotropic Polyesters / Melting Enthalpy and Entropy of Polyesters / Clearing Enthalpy and Entropy of Thermotropic Polyesters /

The thermotropic, liquid crystalline behaviour of polymers having rigid mesogenic units interconnected through flexible spacers along the main chain has been predicted theoretically and is well known experimentally from reports over the past several years.<sup>1-5</sup> We previously reported the synthesis and properties of several new series of polyesters having thermotropic liquid crystalline properties.<sup>6-8</sup> In this work, two new series of polymers have been prepared with the structures shown below.

The first series of polymers, Series I, was a group of linear polyesters having an alternating sequence containing a mesogenic triad unit with three

linearly-aligned aromatic rings, the bis(*p*-carboxyphenyl) terephthalate moiety, and a polymethylene flexible spacer of varying length, *n*, as follows:



Series I.

in which *n* was either 2, 3, 4, 5, 6, 7, 8, 9 or 10. Equimolar copolymers were also prepared in this series containing two different polymethylene spacers having paired sizes of either 2 and 7 or 2 and 10 methylene units, *n*.

Dewar and Goldberg, in their study on the effects

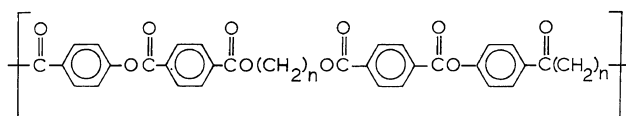
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of central and terminal groups on liquid crystalline properties of low molecular weight aromatic esters, reported that bis(*p*-ethoxycarbonylphenyl) terephthalate, which is basically the same as the mesogenic structural unit of the polymer in Series I with  $n=4$ , formed a nematic mesophase above its melting point.<sup>9</sup> They measured and interpreted the thermodynamic properties of the melting and clearing point of this compound, and one objective of the present investigations was to determine if the thermotropic liquid crystalline behavior of small organic compounds is directly related to the mesomorphic properties of polymers having equivalent structural components.

In relation to previous work in this laboratory, it

should also be noted that the structure of the polymer in Series I with  $n=2$  corresponds to one of the structural sequences expected to be formed in a random copolymer containing both oxybenzoate and ethylene terephthalate units.<sup>10</sup> This type of thermotropic copolyester has been under investigation in our laboratory for several years to find the effect of sequence distribution on physical properties.<sup>11</sup>

The aromatic mesogenic units in the polymers of Series II were arranged, in effect, in exactly an alternating sequence of head-to-head, tail-to-tail placements of terephthaloyl-oxybenzoyl mesogenic dyads separated by either of two different flexible polymethylene spacers as follows:



Series II.

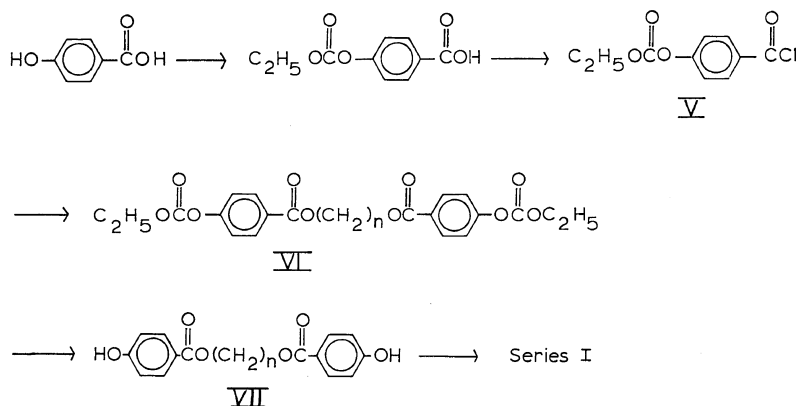
in which  $n$  was either 2 or 6. That is, in contrast to the fairly large number of polymers of Series I, in which either a single type of flexible polymethylene spacer or a random mixture of two different flexible spacers were used, those in Series II were based on only an  $n$  value of either 2 or 6. Within both series, the thermal behaviors of the polymers were investigated in relation to their structure, and a comparison could be made for the effects of the dyad vs. triad mesogenic units on physical properties. For Series II, it may be noted that the polymer

with  $n=2$  also had one of the many possible repeating units which can exist in a random poly(oxybenzoate-co-ethylene terephthalate),<sup>10,11</sup> and this relationship was an added incentive to us for its investigation as indicated above.

## RESULTS AND DISCUSSION

### Polymer Synthesis

The following reaction steps were followed for the synthesis of the polymers of Series I:

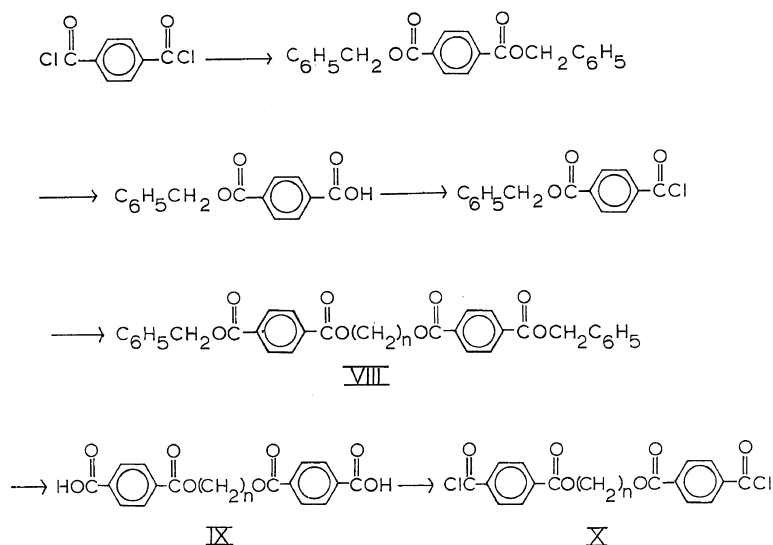


The preparations of the bisphenol monomers with  $n$  ranging from 2 to 6 has been described by Wilkinson and coworkers,<sup>12</sup> but higher homologous compounds have not been previously reported.

The polymers of Series I were prepared by a reaction of the  $\alpha,\omega$ -bis(4-hydroxybenzoyloxy)-alkane monomer, VII, (or in the case of the copolymers, an equimolar mixture of two monomers of this type) with terephthaloyl chloride in a 1,1,2,2-tetrachlorethane (TCE) solution at room temperature. Pyridine was used as the HCl acceptor

in this reaction. All polymers precipitated out of the reaction mixture while the polymerization proceeded. For the Series I copolymers, equimolar amounts of two bisphenol monomers were used with combinations of  $n$  of either 2 and 7 or 2 and 10.

The polymers of Series II were prepared by a reaction of the bisphenol monomer, as above, with a bis(acid chloride) in a TCE-pyridine solvent mixture. The bis(acid chloride), X, monomers were synthesized by the following route<sup>5</sup>:



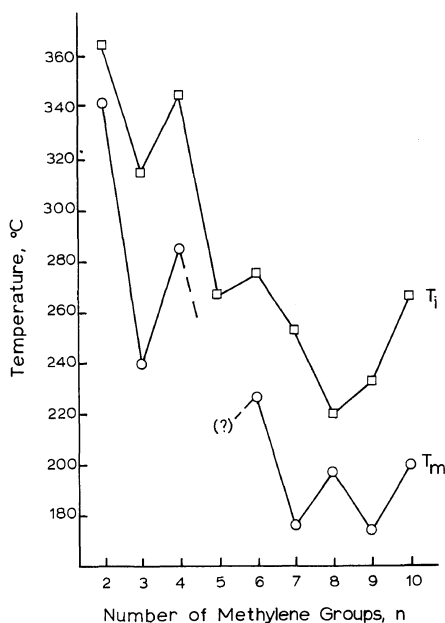
The general procedure used for the preparation of these monomers was the same as reported by Hässlin and coworkers,<sup>13</sup> although the intermediates with an  $n$  of 6 were not previously reported. The synthetic method used for the preparation of polymers in Series II was basically the same as for those in Series I.

#### Polymer Properties

The properties of the polymers of Series I are shown in Table I. In general, as expected for polymerization reactions with low product yields, the molecular weights of the polymers were relatively low as reflected by their low viscosities. The melting points of the polymers measured by DSC analysis decreased regularly in a zig-zag manner as  $n$  increased to 7 or 8 but then appeared to increase beyond that value. As commonly observed, the

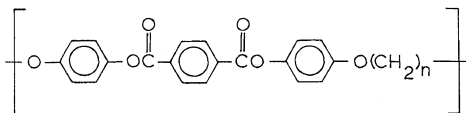
polymers with an even number of  $n$  methylene units showed higher melting points than those with odd number  $n$  as shown in Figure 1.

According to the cooling thermograms, polymers with short flexible spacer groups, especially those with odd  $n$  values such as 3 and 5, exhibited a higher degree of supercooling in crystallizing from melts. For example, at the same heating and cooling rate of  $20^\circ\text{C min}^{-1}$ , the crystallization exotherm in the cooling curve of the polymer with  $n=3$  occurred at a temperature  $110^\circ\text{C}$  below the melting endotherm. Another interesting observation was that the polymers of Series I did not show as distinct multiple melting transitions as those of the previously reported Series III shown below.<sup>8</sup> The latter series of polymers, which was described in an earlier report from this laboratory,<sup>8</sup> had ether instead of ester linkages between the mesogenic



**Figure 1.** Dependence of Series I polymer melting temperatures and clearing temperatures on spacer lengths.

units and flexible spacers:



**Series III.**

The equimolar copolymers of Series I having mixed polymethylene spacers, with the compositions presented in Table I as either  $n=2/7$  or  $2/10$ , apparently possessed a very low degree of crystallinity compared with their homopolymers, as expected. The  $2/7$  copolymer showed a broad and weak melting transition by DSC analysis, and the heat of melting,  $\Delta H_m$ , of this sample was much lower than those of the other polymers. For the  $2/10$  copolymer, no melting transition could be detected by DSC analysis, suggesting a completely amorphous nature for this composition. However, a solidification temperature of about  $200^\circ\text{C}$  was observed by microscopy at which the flow of the polymer melt stopped.

The Series II polymer with  $n=2$  (see Table II) was not soluble in the reaction mixture while that with  $n=6$  was soluble. The melting temperatures of both

polymers were much lower than those of the corresponding polymers of Series I having the same length flexible spacer. Hence, the effect of the length of the overall mesogenic unit (*i.e.*, an aromatic triad in Series I vs. a dyad in Series II) on the melting point can clearly be seen from this comparison.

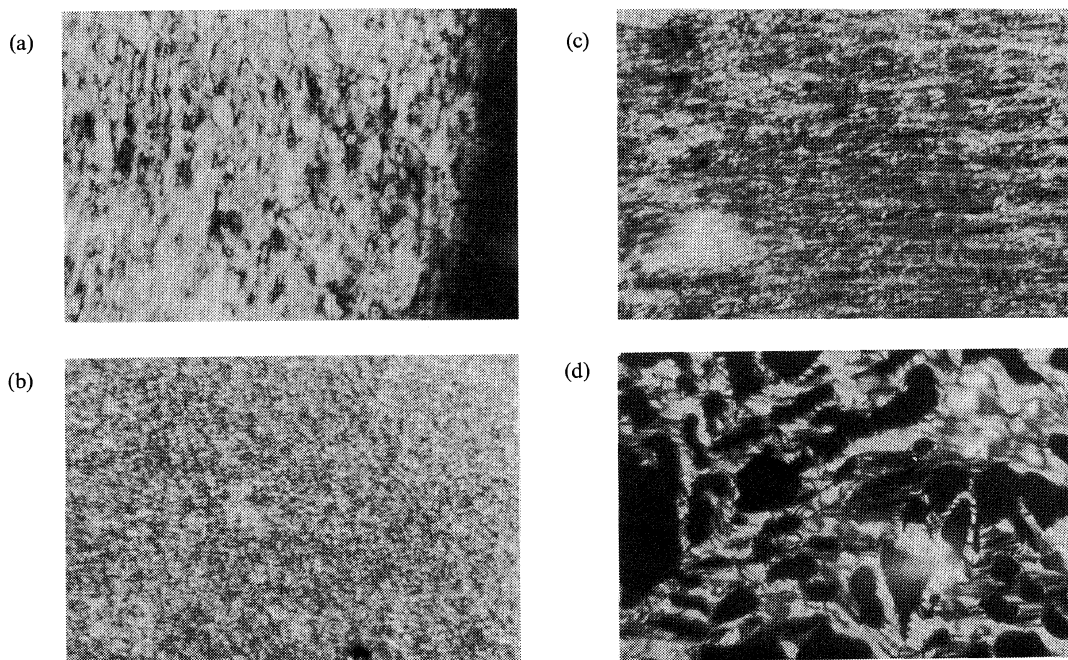
#### *Thermotropic Liquid Crystal Melts*

All the polymers and copolymers in both Series I and II formed turbid melts, and the melts exhibited strong stir-opalescence at temperatures up to their transition into the isotropic melt phase. Some of the optical textures of these polymers in the liquid crystal state, as observed with a hot-stage polarizing microscope, are shown in Figure 2. There is some indication that the polymers with spacer units up to  $n=8$  formed a nematic state, while those with  $n=10$  formed a smectic state, but this conclusion is still tentative and a further investigation on the nature of the mesophases is in progress.

The clearing temperatures,  $T_i$ , or the temperatures of the transition from the mesophase to the amorphous isotropic melt as measured by DSC analysis, showed a regular trend with a zig-zag decrease in values for polymers up to  $n=8$ , but  $T_i$  was higher than expected for 7 and increased for 9 and 10, as seen in Figure 1 and Table I. That is, the transition temperatures for the polymers with an even number for  $n$  were generally higher than those adjacent in the series with either higher or lower  $n$  values. As a result, the temperature range,  $\Delta T$ , over which the mesophase existed was consistently broader for the polymers with an odd  $n$ , as compared to that with an even  $n$ , as shown in Table I. This result can be attributed to the ability of the variation in length of the spacer groups to have a greater decreasing effect on  $T_m$  than on  $T_i$ , particularly among the polymers with odd-numbered polymethylene spacers. The transition temperatures for the first three polymers in Table I were determined visually by observing the disappearance of stir-opalescence of the melts. However, the reliability of these numbers is somewhat in doubt because of decomposition and discoloration of the polymers, which hindered visual observation.

Similar trends have been observed for many homologous series of low molecular weight organic compounds, which were known to be thermotropic.<sup>14-18</sup>

Quantitative as well as qualitative attempts have



**Figure 2.** Photomicrographs of the Series I polymers (each picture spans a sample width of  $440\ \mu\text{m}$  with a magnification of  $320\times$ ): (a)  $n=6$ , taken at  $250^\circ\text{C}$ ; (b)  $n=8$ , taken at  $205^\circ\text{C}$ ; (c)  $n=10$ , taken at  $250^\circ\text{C}$ ; (d)  $n=10$ , taken at  $T_i$ .

been made to explain such trends in thermal properties based on changes in either anisotropic molecular polarizability<sup>14,15</sup> or conformational alternation<sup>16-18</sup> caused by the lengthening of the flexible spacers and passing from an odd to an even number of  $n$ . All of these explanations have been made mainly for low molecular weight compounds. The phenomenon of the increase in  $T_i$  at  $n$  values of 9 and 10 after the decrease up to an  $n$  value of 8 as  $n$  increased has been attributed in the case of low molecular weight compounds to a conformational change from the fully extended *trans* conformation of the polymethylene spacer to that having a central *gauche* unit in the longer spacers which, through slightly energetically less favorable, would stabilize the mesophase order.<sup>16</sup> An alternate possibility for the unexpected trends in  $T_m$  and  $T_i$  for polymers with  $n=8$  and higher may be the formation of a smectic phase because of the presence of the long polymethylene spacers, but the existence of such a phase has not yet been observed in this work by other characterization methods.

The thermodynamic parameters for the isotropic transitions of the polymers in Series I are tabulated in Table I. As observed in previous investigations

on the polyesters of Series III,<sup>8</sup> the values of both  $\Delta H_i$  and  $\Delta S_i$  generally increased with  $n$  even though  $T_i$  steadily decreased (discounting the odd-even effect). Haller and coworkers, in a study on a homologous series of aldonitrones, made a similar observation that the change in entropy,  $\Delta S_i$ , between the mesomorphic and isotropic states of the *N*-(*p*-alkoxyphenyl)- $\alpha$ -(*p*-methoxyphenyl)nitrones increased smoothly with  $n$ .<sup>19</sup> The increase of  $\Delta S_i$  with  $n$  indicates that, for polymer molecules with longer polymethylene spacers, the conformations of these chains and the placement of the mesogenic units were increasingly more ordered for the mesophase relative to the isotropic phase.<sup>19</sup>

Distinct differences were observed in the thermal behavior of the mesophases of the polymers in Series I compared to the previously investigated polymers of Series III as follows: (1) the clearing point,  $T_i$ , was higher for the polymers of Series III having an odd value of  $n$  than for those with an even value of  $n$ , while the opposite was true for the polymers of Series I, and (2) the clearing points of the polymers in Series III steadily decreased with increasing  $n$  up to 10, while in Series I,  $T_i$  decreased only up to an  $n$  of 8 and then increased at  $n=9$

and 10. The former difference, however, may be attributable in some way to the fact that the polymethylene spacer in Series III is attached to an aromatic ring through an oxygen atom which is similar in geometrical effect to a methylene group, while the polymethylene spacer in Series I is attached through a carboxy group which imparts a considerably different spacial arrangement. As a result, an odd  $n$  in Series III would have the same effect on the mesophasic order as an even  $n$  in Series I.

The second difference listed above can be attributed to the intrinsic differences in structure-property relationships for the two different types of mesogenic units. For low molecular weight, liquid crystal organic compounds, it is well known that structural variations in the mesogenic units can give rise to substantial changes in the thermal behavior of the mesophases,<sup>16</sup> although the theoretical interpretation of such a dependence remains to be established.

For the copolymers of Series I, thermal transitions associated with the liquid crystal phases could not be clearly identified by DSC analysis. The molten polymers, however, showed a strong stir-palescence and readily identifiable nematic optical textures. They showed clearing points around 300°C (see Table I) when visually observed on a Fisher-

Johns, hot-plate melting point apparatus. The temperature ranges of the mesophases of the two copolymers were broader than those of homopolymers, apparently because of the high degree of lowering of the melting temperatures of the copolymers without diminishing their capability to form stable mesophases. This result has also been seen in unsymmetrical *p*-phenylene di-*p*-*n*-alkoxybenzoates where  $T_m$  decreased without a substantial decrease in  $T_i$ .<sup>20</sup>

The polymers of Series II, whose mesogenic groups consisted of only two consecutive aromatic ester units had, as expected, much lower melting points and clearing temperatures than those of Series I for corresponding lengths of polymethylene spacers; see Table II. The temperature ranges,  $\Delta T$ , of the mesophases were also narrower, probably due to an increased rotational as well as translational mobility in Series II, but thermodynamic parameters for these have not yet been determined.

The controlling effect of the length of the mesogenic unit on the thermal properties is clearly seen from the data in Tables I and II for the comparable polymers of Series I and II having the same length of polymethylene spacer unit. At  $n=2$ , the Series I polymer had a 107°C higher melting point and an 80°C higher clearing temperature, while at  $n=6$ , the differences were 57°C and 48°C, respectively. It is

Table I. Properties of Series I polymers

$n$	Yield	$\eta_{inh}$	$T_m$	$T_i$	$\Delta T$	$\Delta H_i^d$	$\Delta S_i^d$
	wt%		°C	°C	°C	kcal mol <sup>-1</sup>	cal mol <sup>-1</sup> K <sup>-1</sup>
2	80	0.178	342	365 <sup>e</sup>	23	—	—
3	94	0.262	240	315 <sup>a</sup>	75	—	—
4	91	0.228	285	345 <sup>a</sup>	60	—	—
5	62	0.139	— <sup>f</sup>	267	—	1.5	2.7
6	75	0.276	227	290	48	0.54	1.2
7	48	0.196	176	253	77	1.6	3.1
8	66	0.196	165	220	23	1.1	2.3
9	55	0.272	174	233	59	1.4	2.7
10	93	0.335	220	267	47	2.0	3.6
2/7 <sup>a</sup>	63	0.220	252	335 <sup>e</sup>	83	—	—
2/10 <sup>b</sup>	14	0.230	200 <sup>c</sup>	290 <sup>e</sup>	90	—	—

<sup>a</sup> Copolymer prepared from an equimolar mixture of monomers with  $n=2$  and  $n=7$ .

<sup>b</sup> Copolymer prepared from an equimolar mixture of monomers with  $n=2$  and  $n=10$ .

<sup>c</sup> Microscopically observed flow temperature, not verified as a melting point.

<sup>d</sup> Dash means property could not be measured accurately.

<sup>e</sup> Observed visually, not by DSC; actual  $T_i$  may be higher.

<sup>f</sup> No melting endotherm observed.

Table II. Properties of Series II polymers

$n$	Yield	$\eta_{inh}$	$T_m$	$T_i$	$\Delta T$
	wt%		$^{\circ}\text{C}$	$^{\circ}\text{C}$	
2	47	0.133	235	285	50
6	89	0.298	170	190	20

also of interest to note that the effect of changes in mesogenic unit size was greater on the  $T_m$  than on the  $T_i$ , but this differential effect of mesogenic unit size on properties was also considerably moderated by increasing the polymethylene spacer length.

Lengthening the polymethylene spacer between the mesogenic groups in Series II decreased  $T_m$ ,  $T_i$ , and  $\Delta T$ , as expected. The same trend has been observed for similar polymers which were reported by others for closely related polymers where the mesogenic units were connected to the flexible spacer through other linkages instead of ester linkages, as in the present polymers.<sup>3</sup>

## CONCLUSION

Two new homologous series, I and II, of polyesters having rigid mesogenic units and polymethylene spacers within the main chain were prepared and characterized for their thermal and liquid crystal properties. All the polymers in both series were found to have thermotropic liquid crystal properties by DSC and microscopy, and their values of  $T_m$ ,  $T_i$ , and  $\Delta T$  strongly depended on the length of the flexible spacers and on the nature of the mesogenic units. For the first series of polymers,  $\Delta H_i$  and  $\Delta S_i$  increased steadily with an increase in the length of the spacer,  $n$ , indicating the existence of a higher molecular order in the polymer melt with longer spacers. Copolymers derived from an equimolar mixture of two different diphenols having different length spacers had lower degrees of crystallinity and lower values of  $T_m$  but not lower values of  $T_i$ , which resulted in a broadening of the temperature range of the mesophases behaviour.

The polymers of the second series exhibited lower values of  $T_i$ ,  $T_m$  and  $\Delta T$  compared with those of the first series for the same polymethylene spacer length. This was expected, considering the longer, triad mesogenic structure of the latter compared to the dyad structure of the former.

## EXPERIMENTAL

### Synthesis of Series I Monomers and Polymers

*p*-Ethoxycarbonyloxybenzoic Acid. **IV**. This compound was prepared by adding ethyl chloroformate (50 ml) in three portions to a cool ( $5^{\circ}\text{C}$ ) stirred solution of *p*-hydroxybenzoic acid (60 g, 0.434 m) and sodium hydroxide (38.0 g, 0.955 m) in 900 ml of distilled water. The final mixture was acidified with 2 *N* HCl, and the precipitate was filtered and washed with excess water. The product was recrystallized without drying from an acetone-water mixture.<sup>12,21,22</sup> Yield, 95% (white needles); mp, 157–158°C.

*Polymethylene bis(p-ethoxycarbonyloxybenzoates)* **VI**. The *p*-carbonate ester substituted benzoic acid above was converted to the corresponding acid chloride, **V**, by a reaction with thionyl chloride in the presence of DMF.<sup>13</sup> On the assumption that a 90% yield for the acid chloride would be obtained, a 20% functional excess of thionyl chloride was used. Dry  $\alpha,\omega$ -alkanediol was then added to the solution of the acid chloride (20 g) in 50 ml of 1,2-dichloroethane. The mixture was refluxed with stirring for 4 hours, cooled, and poured into 300 ml of a 0.5 *N*-NaOH solution in ice water. The product was extracted into toluene. After drying with sodium sulfate, the product was isolated on a rotating evaporator, dried under vacuum, and recrystallized in ethanol.<sup>12</sup>

*Polymethylene Bis(p-hydroxybenzoates)*. **VII**. The carbonate ester intermediates, **VI**, were hydrolyzed to the corresponding phenols, following the literature method.<sup>12</sup> For the bisphenols, **VII**, not previously reported in which  $n=7, 8$ , and 10, the following recrystallization solvents (v/v) were used and melting points and elemental analyses were obtained:  $n=7$ , methanol-water (70:30), 138°C, *Anal.* Calcd: C 67.7%, H 6.5%; Found: C 67.3%, H 6.5%;  $n=8$ , ethanol-water (90:10), 185°C, Calcd: C 68.4%, H 6.8%; Found: C 68.3%, H 6.9%;  $n=10$ , ethanol-water (90:10), 165°C, Calcd: C 69.5%, H 7.3%; Found: C 69.3%, H 7.3%.

*Polymers*. The monomer was dissolved in a minimum amount of pyridine, and to this was added a solution of terephthaloyl chloride in 1,1,2,2-tetrachloroethane (about 2 g in 50 ml). The mixture was stirred at room temperature for 24 to 48 hours. The reaction mixture was poured into 300 ml of acetone or methanol, stirred for 1 hour, filtered,

and partly dried. This product was broken up and stirred in sodium carbonate solution for one-half hour, filtered, washed with dilute hydrochloric acid, water, and finally dried in a vacuum oven at 50°C. Two copolymers were prepared from equimolar mixtures of diphenols having  $n=2$  and 7 (2/7 in Table I) and  $n=2$  and 10 (2/10 in Table I) using the same method as described above for the preparation of homopolymers.

#### Synthesis of Series II Monomers and Polymers

*Polymethylene Bis(benzyl terephthalates)*. **VIII**. The acid chloride of the monobenzyl terephthalic acid was prepared by following a literature method,<sup>13</sup> and 21.6 g (0.078 m) was dissolved in 250-ml of dry dioxane. A solution of the diol (4.09 g, 0.035 m of 1,6-hexanediol, for example), excess pyridine, and dioxane (50 ml) were added dropwise with stirring. After addition, the mixture was refluxed for 4–5 hours, the product cooled and mixed into 1 l of dilute hydrochloric acid. The precipitate was washed with water after filtration, stirred in an aqueous sodium carbonate solution, filtered again, washed with water again and dried.<sup>13,23</sup> The yield, recrystallization solvent and melting point of the bisbenzyl ester based on 1,6-hexanediol, **VIII**  $n=6$ , were as follows: 80%, ethanol, 107°C. The diester was hydrolyzed to the diacid, **IX**, in trifluoroacetic acid with hydrobromic acid, and the yield, recrystallization solvent (v/v), melting point and elemental analysis of the compound with  $n=6$  were as follows: 80%, 75/25 dioxane–ethanol, 242°C, *Anal.* Calcd: C 63.5%, H 5.8%; Found C 63.4%, H 5.4%.

The diacid, **IX**, was converted to the bis(acid chloride) monomer, **X**, as described above for the Series I monomers. To the same diphenol monomers, **VII**, as those prepared for the polymers of Series I monomers. To the same diphenol monomers, **VII**, as those prepared for the polymers of the diacid chloride monomer dissolved in 1,1,2,2-tetrachloroethane. The mixture was stirred at room temperature for 24–48 hours. The polymer formed was separated, washed, and dried in the same way as described for the polymers of the first series with the results given in Table II.

#### Characterization of Polymers

The test for stir-opalescence of the polymer melts was performed by placing the polymer between two cover glasses and sliding the upper one over the

lower when the polymer was observed to be in a molten state on a Fisher-Johns melting point apparatus. The thermal behavior of the polymers were studied under a nitrogen atmosphere on a Perkin-Elmer DSC-1B at the heating and cooling rates of 20°C min<sup>-1</sup>. Peak maximum positions were taken as the transition temperatures. The optical texture of the polymer melts and their thermal behaviors were examined on a hot-stage (Mettler FP-2) on a polarizing microscope (Leitz). A magnification of 320 × was used throughout the study. Inherent viscosities were measured at 45°C on solutions of 0.5 g of polymer in 100 ml of *p*-chlorophenol with a Ubbelohde type viscometer.

*Acknowledgements.* The authors are grateful to the Office of Naval Research and to the NSF-sponsored Materials Research Laboratory of the University of Massachusetts for their support in this work. The financial support and permission provided by Korea University for J-I. Jin to come to the University of Massachusetts for his sabbatical leave, and the financial support by the Government of Canada to C. Ober for his NSERC Post-graduate Scholarship, are both gratefully acknowledged.

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