Liquid crystal polymers: 19. Cholesteric main chain polyesters with triad aromatic ester mesogenic units and chiral polyalkylene spacers

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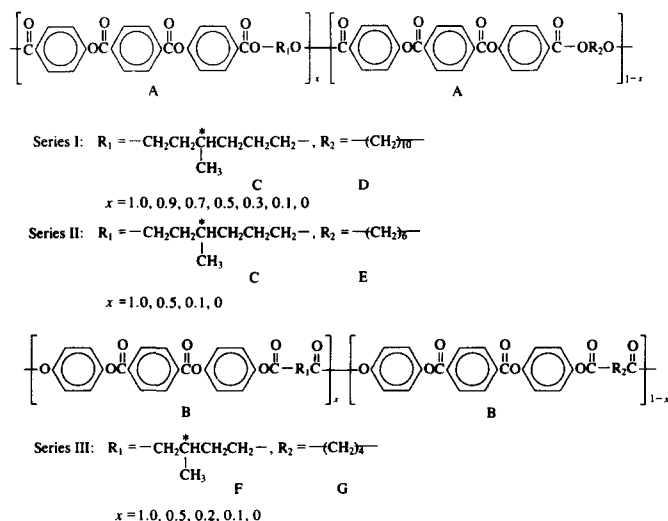
Three series of thermotropic, main chain polyesters and copolyesters which formed cholesteric mesophases were prepared and characterized. These polymers contained triad aromatic ester mesogenic units and chiral polyalkylene spacers. Differential scanning calorimetry and observations on a polarizing microscope were used to examine the thermal properties and the nature of mesophases of these polymers. The dependence of the wavelength of reflected light for some of the cholesteric polymer melts on temperature and composition was measured spectrotrophotometrically.

INTRODUCTION

The thermotropic behaviour of main chain polyesters having alternating mesogenic units and flexible spacers is of ever-increasing interest. We have reported on the synthesis and properties of many different types of polyesters which formed either nematic or smectic liquid crystalline phases, or both, in previous publications in this series[1-5]. The present report is concerned with the structure–property relationships of thermotropic polyesters which form cholesteric mesophases. Three different series of main chain polyesters and copolyesters, which have triad aromatic ester mesogens and chiral polyalkylene spacers, were prepared for this study. Two different triad mesogenic groups, A and B, and five different flexible spacers, C–G, were evaluated in these polymers, as follows:


Series I: $R_1 = -CH_2CH_2\overset{*}{C}HCH_2CH_2CH_2-$, $R_2 = -(CH_2)_{10}-$
      CH_3
        C   D
   $x = 1.0, 0.9, 0.7, 0.5, 0.3, 0.1, 0$

Series II: $R_1 = -CH_2CH_2\overset{*}{C}HCH_2CH_2CH_2-$, $R_2 = -(CH_2)_6-$
      CH_3
        C   E
   $x = 1.0, 0.5, 0.1, 0$

Series III: $R_1 = -CH_2\overset{*}{C}HCH_2CH_2-$, $R_2 = -(CH_2)_4-$
      CH_3
       F   G
   $x = 1.0, 0.5, 0.2, 0.1, 0$

Two of the spacers, C and F, contained chiral centres, and each was obtained from monomers of high optical purity.

Vilsager and Blumstein[6] recently reported on similar cholesteric polyesters having an azoxy group in the mesogenic units. For their polymers, which had the same chiral flexible spacer as our Series III polymers (Spacer F) obtained from optically pure 2-methyladipic acid, they observed typical cholesteric optical textures on examination by a polarizing microscope, and coloured reflected light was observed from films of the polymers. Other cholesteric main chain polymers have also been reported earlier by Van Luyen and coworkers[7] and by Krigbaum and coworkers[8].

EXPERIMENTAL

The polymerization reactions applied to the preparation of the Series I and II polymers were as follows:
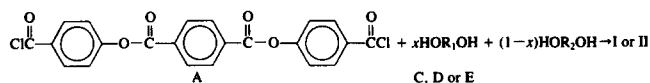
The glycol monomers used for these polymerization reactions were either (+)3-methyl-1,6-hexanediol, C, 1,12-dodecanediol, D, or 1,6-hexanediol, E, for the homopolymers ($x = 1.0$ or 0) or mixtures of two of these for the copolymers according to the molar compositions ($1.0 > x > 0$) indicated.

The Series III polymers were obtained by the following polymerization reactions:
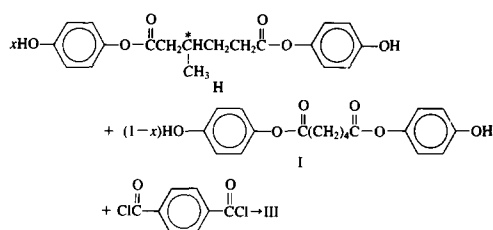
Synthesis of monomers

Bis(p-chloroformylphenyl)terephthalate, A. The dibenzyl ester derivative of this monomer was prepared and converted to the diacid form by following the known literature procedures[5,9,10], and the latter was refluxed in an excess of thionyl chloride for 4 h. At the end of the reaction, the excess thionyl chloride was distilled off at a reduced pressure, quantitative conversion to the *bis*(acid chloride), A, was assumed, and the product was directly used in the synthesis of Series I and II polymers.

(+)3-Methyl-1,6-hexanediol, B. Optically pure (+)3-methyladipic acid (6.4 g, 0.04 mole) was dissolved into 54 ml of dry THF, and the solution was added dropwise to a mixture of 150 ml of borane-THF complex (1 M) in 150 ml of THF. The temperature of the reaction mixture was maintained between 0°C and 5°C during the addition.

The mixture was allowed to stand at room temperature for 48 h, water (50 ml) was added to destroy the excess borane, the solution was saturated with potassium carbonate, and the THF layer was separated. After distilling off the THF, the product was dissolved in ether and washed with aqueous sodium bicarbonate solution, followed by washing with water. The ether layer was dried over anhydrous sodium sulphate, and a liquid product was obtained by distilling off ethyl ether. The monomer was obtained, by distillation under a reduced pressure, with a yield of 4.3 g (81.5%); specific rotation measured in dioxane solution was $(\alpha)_D^{20} = +1.98°$. Analysis, calculated for $C_7H_{16}O_2$: C, 63.63; H, 12.12%; found: C, 64.03; H, 12.27%.

Synthesis of Series I and II polymers

Monomer A, 2.215 g, 0.005 M, was dissolved in 100 ml of dry dichloroethane. The solution was heated to 60°C, and to it was added dropwise with stirring a solution of the glycol monomer, C, D or E, 0.005 M, or a mixture of two of these dissolved in 10 ml of dry pyridine. The reaction mixture was stirred under a nitrogen atmosphere for 1 h at 60°C and left at room temperature for 48 h, after which about one-half of the solvent was distilled off. Acetone was added to the concentrated reaction mixture, and the precipitated polymers were filtered and thoroughly washed with an aqueous sodium bicarbonate solution, dilute hydrochloride acid, water and finally with acetone. The yields and properties of polymers of Series I and II are listed in *Tables 1* and *2*.

1,4-Bis(p-hydroxyphenyl)-3-methyladipate, H, and 1,4-bis(p-hydroxyphenyl) adipate, I. The preparative methods for these two monomers were the same so only the procedure for the synthesis of the monomer I is given below. Adipoyl chloride, 6.86 g, 0.034 m, prepared from adipic acid and thionyl chloride, was dissolved in 100 ml of dry 1,2-dichloroethane, DCE, and the solution was added dropwise at room temperature to a solution of hydroquinone, 12 g, 0.11 M, in 50 ml of dry pyridine. Vigorous stirring was maintained through the reaction, and the reaction mixture was stirred at room temperature for an additional 48 h. The mixture was washed with water and aqueous sodium bicarbonate solution, and the crude product was obtained by removing DCE by distillation, extraction with toluene and evaporation of the solvent. The final product was obtained by recrystallization from either toluene for H or an ethanol–water mixture for I after treatment with decolourizing charcoal. The yields were 57 and 65% for monomers H and I, respectively. Monomer H melted at 113°C while I melted at 174°C. Analysis calculated for $C_{19}H_{20}O_6$, H: C, 66.28; H, 5.81%; found, C, 66.21; H, 5.96%; calculated for $C_{18}H_{18}O_6$, I: C, 67.08; H, 5.45%; found, C, 67.14; H, 5.42%.

Synthesis of Series III polymers

Terephthaloyl chloride, 2.93 g, 0.01 M, was dissolved in dry DMF (200 ml), and a solution of either monomer H or I or their mixtures, 0.01 m dry pyridine (30 ml), was added dropwise at room temperature to the acid chloride solution with vigorous stirring. The mixture was stirred at room temperature for 48 h under nitrogen atmosphere, poured into water, and the precipitate was thoroughly washed with an aqueous sodium carbonate solution, dilute hydrochloric acid, water, and then acetone. The yields and the properties of these polymers are listed in *Table 3*.

Characterization of polymers

The structure of polymers was confirmed by i.r. and n.m.r. analysis. The solution viscosities of the polymers

Table 1 Yield and properties of polymers of Series I with C and D spacers

Chiral spacer, C mole fraction	Polymer yield, (wt%)	$\eta_{inh}{}^a$	$T_m (°C)^b$	$T_i (°C)^b$
1.0	87	0.181	173	327
0.9	53	0.358	158	325
0.7	90	0.346	146	302
0.5	89	0.324	145	258
0.3	64	0.546	151	231
0.1	80	0.189	160	238
0ᶜ	94	0.480	212	245

^{a} Inherent viscosity measured on 0.5 g/dl solution in *p*-chlorophenol at 45°C
^{b} Peak of d.s.c. endotherm
^{c} Reference

Table 2 Yield and properties of polymers of Series II with C and E spacers

| Chiral spacer, C mole fraction	Polymer yield, (wt%)	$\eta_{inh}{}^a$	$T_m (°C)^a$	$T_i (°C)^b$
1.0	87	0.181	173	327
0.5	79	0.142	171	325
0.1	82	0.150	203	302
0ᶜ	94	0.158	227	275

^{a} See footnotes in *Table 1*
^{b} Estimated by observation on a Fisher–Johns melting point apparatus
^{c} Reference

Table 3 Yield and properties of polymers of Series III with F and G spacers

Chiral spacer, F mole fraction	Polymer yield, (wt%)	$\eta_{inh}{}^a$	$T_m (°C)^a$	$T_i (°C)^a$
1.0	92	0.215	233	350
0.5	88	0.145	268	340
0.2	96	0.227	276	340
0.1	83	0.140	279	346
0	91	0.157	294	347

^{a} See footnotes in *Table 1* and text
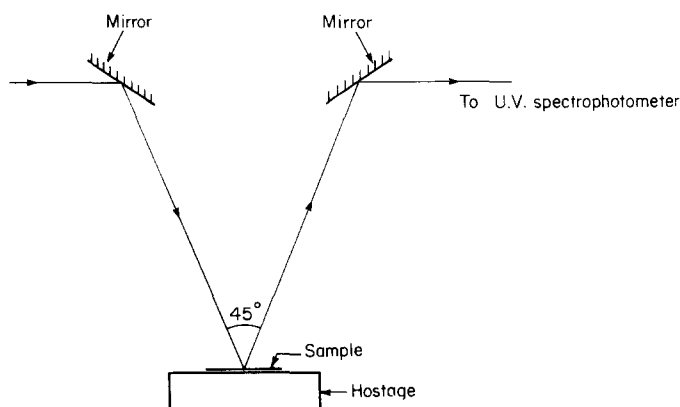
Figure 1 Schematic presentation of spectrophotometer cell for measuring the wavelength of reflected light

were measured with a Cannon–Ubbelhode type viscometer in a constant temperature bath. The thermal behaviour of the polymers was studied under a nitrogen atmosphere by d.s.c. on a Perkin-Elmer DSC-II instrument with heating and cooling rates of 20°C/min. The samples with high clearing temperatures in Series II and III were examined for their liquid crystal-to-isotropic liquid transitions, T_i, on a Fisher–Johns melting point apparatus. The disappearance of stir-opalescence of the polymer sample between two microscope cover glasses was taken as T_i. Optical textures were observed on the Mettler FP-52 hot stage placed on a polarizing microscope, Leitz, Ortholux, at a magnification of 320×.

The wavelengths of reflected light from polymer melts were measured spectrophotometrically using a Varian II spectrophotometer as shown in *Figure 1*. A small amount of polymer sample was placed on a thin quartz plate which was heated on a hot-stage. The assembly was placed in the cell compartment of the spectrophotometer. Two mirrors were located above the sample in such a way that incident and reflected lights made an angle of 45°. The temperature of the polymer melt was measured using a thermocouple. The wavelength of the reflected light was measured by the spectrohotometer in its transmission mode.

RESULTS AND DISCUSSION

Properties of Series I polymers

The general properties of the polymers of Series I are listed in *Table 1*. The molecular weights of the polymers were relatively low as indicated by their low solution viscosities. All of the polymers were crystalline and showed clear melting transition by d.s.c. analysis (see *Figure 2*). The melting temperatures of the chiral homo-

polymer ($x = 1$) in this series decreased continuously as the content of the non-chiral comonomer units, D, increased reaching a minimum at approximately the 50 mole percent composition ($x = 0.5$) as shown in *Figure 3*. All of the polymers formed turbid melts that exhibited strong irridescent colours over the temperature range from the melting temperature, T_m, to the clearing temperature, T_i. The d.s.c. thermograms of all polymers showed two endotherms in the heating cycle and two exotherms on cooling as illustrated in *Figure 2*.

Visual examination of the samples on the hot-stage of a polarizing microscope verified that the transitions of the lower temperature endotherms corresponding to melting and those of the higher temperature endotherms to clearing transitions. All of the compositions containing chiral spacers, from $x = 1.0$ to $x = 0.1$, had cholesteric textures as seen in the photomicrographs of *Figures 4a* and *4b*. The photomicrograph of *Figure 4a* of the Series I homopolymer shows regular spaced retardation lines, which are characteristic of the cholesteric phase. The photomicrograph of *Figure 4b* of the Series I copolymer with $x = 0.9$ shows the 'oily-streak' texture frequently
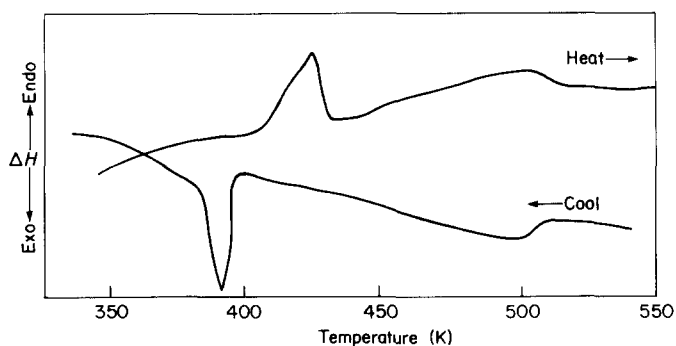
Figure 2 D.s.c. thermograms on Polymer I, $x = 0.7$; heating and cooling rates were 20°C/min
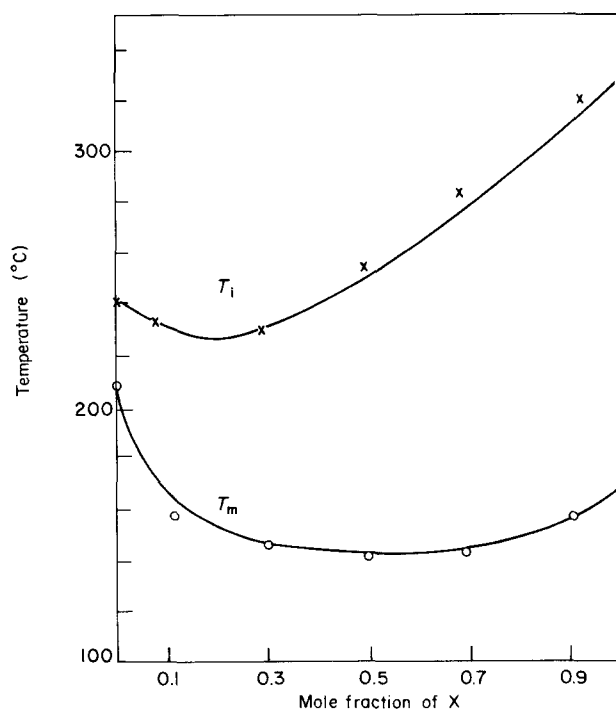
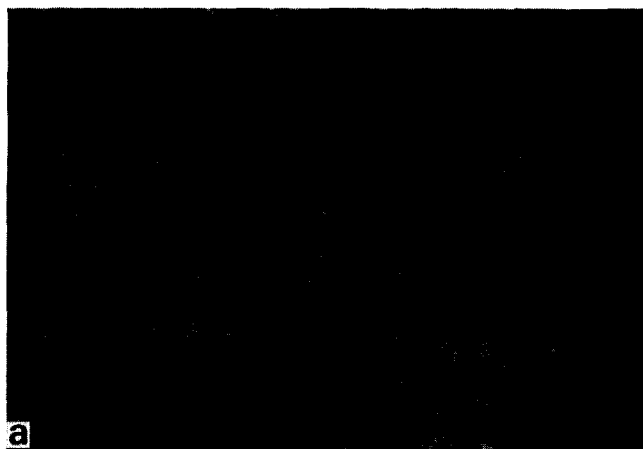**Figure 3** Dependence of T_m and T_i on the compositions of Series I polymers

Figure 4 Photomicrograph of: (a) Polymer I, $x = 1.0$, taken at 232°C, and (b) Polymer I, $x = 0.9$, taken at 270°C (magnification of 320×)
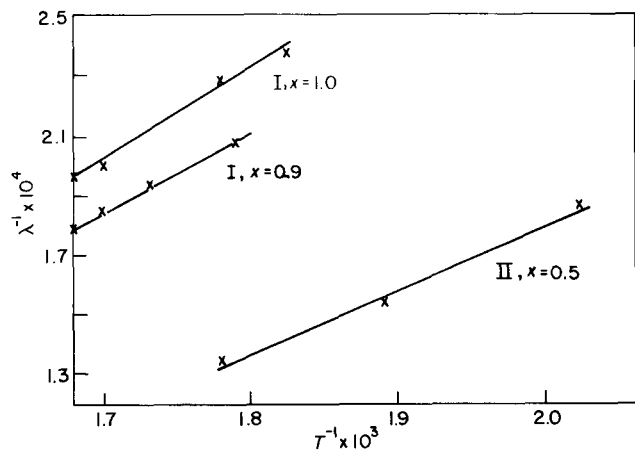

Figure 5 Dependence of wavelength of the reflected light from polymer melts on temperature

Figure 6 Dependence of T_m and T_i on the composition of Series II polymers

Figure 7 Photomicrograph of: (a) Polymer II, $x = 0.5$, taken at 205°C, and (b) Polymer II, $x = 0.1$, taken at 260°C (magnification of 320×)

observed for a cholesteric mesophase. The homopolyester of Series I with the dodecamethylene spacer ($x = 0$) was previously reported to form a smectic mesophase[2]. As seen from the data in *Table 1* and *Figure 3*, T_i decreased with increased content of the dodecamethylene unit, D, in the copolymers and apparently passed through a minimum, as did T_m. The mesophase temperature range, T_i-T_m, was significantly wider for the copolymers con-
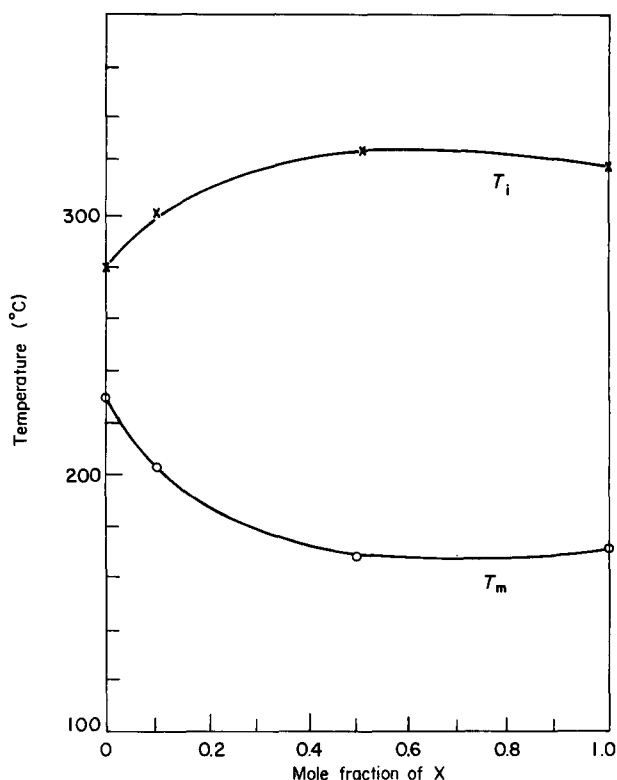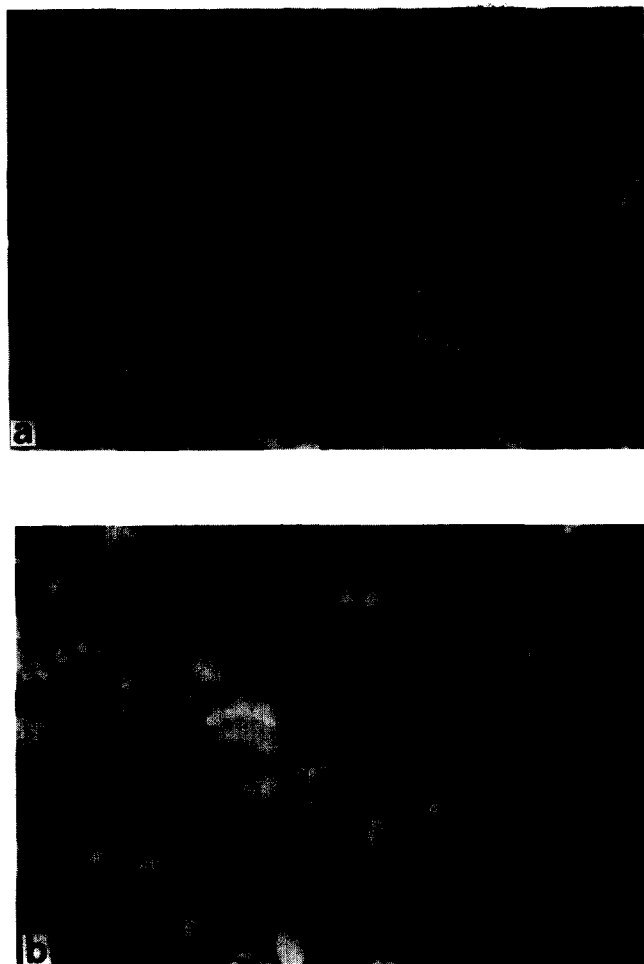
Figure 8 Photomicrograph of: (a) Polymer III, $x=0.5$, taken at 269°C, and (b) Polymer III, $x=0.1$, taken at 288°C (magnification of 320×)

taining higher concentrations of the chiral spacer, C, which is shorter than the achiral spacer, D.

The dependence of the wavelength of irridescent light on both temperature and polymer composition was also studied by visually observing the colour of reflected light on a Fisher–Johns melting point apparatus. The wavelength of reflected light from a cholesteric phase, λ, is determined directly by the pitch of helix, P, by the deVries equation: $\lambda = nP^8$. For the Series I homopolymer, a wide range of irridescent colours from violet to yellow ($\lambda = 4000$–5900 Å) was observed as the temperature was increased from T_m up to T_i. The melt of the Series I copolymer with $x=0.9$ did not reflect visible light up to a temperature of about 265°C, at which point it started to show violet irridescence. As the temperature was further increased the irridescent light changed from violet (4500 Å) to blue, to green, to yellow, to orange, and finally to red (6300 Å) at about 325°C, at which point the melt became colourless because of its phase transition to the isotropic phase.

The mesophase of the copolymer with $x=0.7$ also exhibited a broad range of irridescent colours. From T_m up to a temperature of about 250°C, the irridescence changed from a very weak violet to blue, to green, and then became pale yellow. Above this temperature the colour changed from yellow, to orange, and then to red when the polymer was heated to 295°C, from which point

the colour slowly disappeared as the temperature approached T_i.

The next copolymer in this series, $x=0.5$, showed an extremely weak irridescent below T_i, and the colour change on heating could not be followed visually. The mesophases of the copolymers with $x=0.3$ and 0.1 did not show irridescence in the visible region, possibly because either the helical pitch was too wide or the reflected light was of too low an intensity, or a combination of both.

The copolymers containing increasing contents of the achiral spacer, as described above, reflected light of longer wavelength as the amount of this spacer increased, presumably because of an increased pitch distance in the cholesteric phase. The intensity of irridescent light also decreased as the content of achiral unit increased, possibly because of a decrease in the amount of the cholesteric phase. *Figure 5* shows the temperature dependence of the wavelength of reflected light by the melts of Series I polymers with $x=1.0$ and 0.9. The wavelength was measured, as described in the Experimental section, using an assembly of a hot-stage, two mirrors and a spectrophotometer, and the observation angle was 45° with respect to the incident light. The upper two lines of *Figure 5* clearly verify that the wavelength of reflected light of the cholesteric phase increased in a regular manner with temperature, as was visually observed.

Finkelman and Stegemeyer[11] made a detailed study of the temperature dependence of the intrinsic pitch of low molecular weight cholesteric systems induced in a nematic host by the presence of chiral guest compounds. They observed that the pitch of the helically-stacked layers increased with increasing temperatures and as the content of the chiral compounds decreased, which agrees with our present observations. The dependence of the pitch on either the content of achiral spacer units or on the presence of external additive was recently qualitatively described for main chain polyesters by other investigators, and their observations are also in accord with our results[6,8]

Properties of Series II polymers

The flexible spacer units of the Series II copolymers consist of combinations of two different six-carbon atom units, the residues of ($+$)3-methyl-1,6-hexanediol, C, and 1,6-hexanediol, E. The general properties of this series of polymers are presented in *Table 2*. The dependence of the thermal properties of the copolymers on composition is somewhat different from that of the previous series. The homopolymer of Series II with $x=1.0$, C spacer homopolymer, had a significantly lower melting temperature than the homopolymer of Series II with $x=0$, the E spacer homopolymer. The presence of a methyl group on a chiral centre in the spacer of the former resulted in a decrease in T_m of 54°C compared with the latter, which had the same length spacer unit. In contrast, the clearing temperatures of the polymers in this series, as determined visually on a Fisher–Johns melting point apparatus, were found to decrease continuously as the content of chiral spacer decreased, see *Figure 6*. Hence, the presence of methyl side groups in the spacer greatly enhanced the thermal stability of the mesophases of these copolymers, but the reason for this effect is unknown at present. The T_m and T_i values of the copolymers in this series, in general, were higher than those in Series I because of the shorter length of the achiral spacer, a hexamethylene unit for the former

compared with dodecamethylene unit for the latter. Two copolyesters of Series II with $x = 0.5$ and 0.1 showed typical cholesteric optical textures as shown in *Figure 7a* and *7b*. The mesophase for the homopolymer of Series II with $x = 0$, which had only a hexamethylene spacer in the chain, was earlier identified to be nematic[2].

Copolymer II with $x = 0.5$ showed a weak irridescence in the mesophase. From T_m up to a temperature of 220°C, the melt showed a change from very weak violet, to blue, to green as the temperature increased. At higher temperatures the colour changed from yellow to orange, to red (6900 Å), and then began to fade at a temperature of about 290°C before reaching T_i. The quantitative dependence of the wavelength of the reflected light from the polymer melt on temperature is shown in *Figure 5*. The irridescence of copolymer II with $x = 0.1$ was too weak to be observed.

Properties of Series III polymers

This series of polymers is structurally different from the two previous series in that, for Series III, the spacers were derived from combinations of (+)3-methyladipic acid, F, and adipic acid, G, and the mesogenic units were based on the *bis*(hydroquinone)terephthalate moiety, B. The general properties of the polymers are summarized in *Table 3*. The melting points of the polymers of this series are considerably higher than those in both Series I and II as seen by the data in *Table 3*. All of the polymers, with the exception of the achiral homopolymer ($x = 0$), formed cholesteric mesophases as judged by their optical textures observed on a polarizing microscope. Photomicrographs of these textures are shown in *Figures 8a* and *8b*.

The clearing temperatures of the polymers were also much higher than those of the polymers of the previous two series. Because of the occurrence of decomposition reactions during visual observations on a Fisher–Johns melting temperature apparatus, the T_i values recorded in *Table 3* are only approximations, and the true values of T_i of these polymers are probably higher than those shown in the Table.

The chiral homopolyester of this series ($x = 1.0$) exhibited a violet (4000 Å) irridescence upon melting at 280°C. The violet colour persisted up to 320°C, at which temperature it changed to a bluish violet colour (4500 Å), which remained up to T_i. Apparently, therefore, the pitch distance of this polymer was the shortest among all of the polymers prepared in this study. The copolymer with $x = 0.5$ showed a bluish-green irridescence upon melting, and its colour gradually changed from bluish-green, to greenish-yellow, to yellow, to orange and finally to red (7000 Å) at about 325°C. The results again show that with increasing the amount of the achiral unit, and with increasing the temperature of the sample, the cholesteric pitch in the mesophase increased.

CONCLUSIONS

The following conclusions can be drawn from this investigation:

(1) All of the polymers having chiral spacers prepared in the present study exhibited thermotropic cholesteric properties.

(2) The phase transitions from the solid crystalline to the cholesteric phase, and from the cholesteric state to the isotropic phase, were fully reversible; that is, the polymers are enantiotropic.

(3) The T_m and T_i transitions of the copolyesters in all three series showed a continuous dependence on the contents of the two structural units.

(4) The wavelength of irridescent light observed for the cholesteric phase increased with temperature indicating an increase in the cholesteric pitch.

(5) The wavelength of reflected light from the cholesteric phase increased with the content of the achiral units in the copolymers indicating that the pitch distance also increased with achiral unit composition.

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