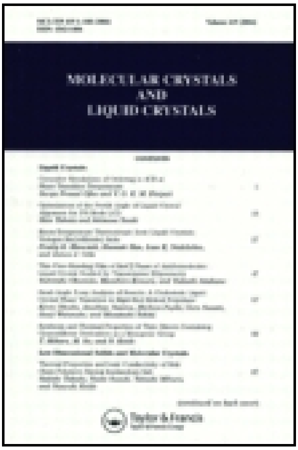

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A Polyester Forming a Thermotropic Cholesteric Phase

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Mesomorphic polyesters were synthesized from 4,4′-dihydroxy-α-methylstilbene and adipic acid (P-6) or (+)-3-methyl adipic acid (P-6M). P-6 forms a thermotropic nematic phase and P6-M a thermotropic cholesteric phase. The nematic phase of P-6 could easily be identified by optical microscopy. For both polymers we observed a biphasic region in which the isotropic and liquid crystalline phases coexist. Bright colors were obtained by increasing the pitch of P6-M by admixture with either a low molecular weight nematogen or with polymer P-6, and also by synthesizing a copolymer containing the two dibasic acids. The copolymeric cholesteric phase, which is stable between 199 and 282°C, had a predominately planar texture, and these features could be retained in the solid state by quenching to produce a film having a deep blue color at room temperature. The role of the degree of polymerization upon the development of organization, and parameters, of the mesophase is discussed.

The uniaxial alignment characteristic of a nematic phase is ideal for the production of high modulus fibers, since the resulting distribution of molecules about the fiber axis is very narrow. A perfect biaxial orientation, with every molecule lying parallel to a plane, would be the corresponding "ideal" orientation for a film. Such an ideal structure could be prepared as a composite from uniaxially oriented films by rotating the direction of preferred orientation of successive layers by a fixed angle. However, since each uniaxial film has highly anisotropic properties, it may be difficult to obtain the permanent adhesive bond necessary for such a composite. A molecular composite would

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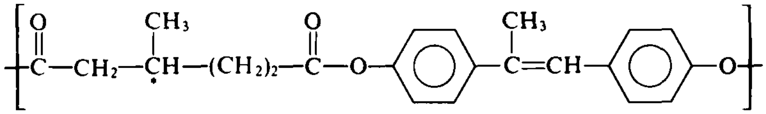
appear to offer a more attractive route to biaxially oriented films. A thin cholesteric mesophase with Grandjean texture would have all of the helical axes perpendicular to the plane. If such a texture could be conserved during solidification, the resulting film should have the optimum modulus if tested along any arbitrarily selected direction in the plane of the film.

Liquid crystalline behavior can arise from the presence of mesomorphic groups on the sidechain, or in the main chain. If the objective is to achieve a particular alignment of the molecules, only the latter is of interest. Materials exhibiting a cholesteric phase differ from nematogens in possessing resolved chiral centers. Cholesteric polymers have been described[1,2] in which a mesogenic sidechain contains an asymmetric carbon atom, while in other examples[3,4] these features are part of the main chain. Furthermore, a copolymer containing a monomer capable of forming a nematogenic homopolymer and a second, optically active monomer is expected to exhibit a cholesteric phase. Some of the present authors followed this route in preparing a predominantly aromatic polyamide having high chain extension, and exhibiting a cholesteric mesophase.[5] This involved a copolymer of *p*-aminobenzoic acid containing a small amount of *L*-valine units. While such a polymer is likely to exhibit high modulus properties typical of the highly extended aromatic polyamides, it shares with them a very high melting temperature and quite limited solubility. The advantage of ease of fabrication could be gained by lowering the melting point. For this purpose polyesters are preferable to polyamides since, as a class, their melting temperatures are lower. Nevertheless, a fully extended aromatic polyester, such as the homopolymer of *p*-hydroxybenzoic acid, only melts with decomposition. The thermotropic polyesters described by Wooten *et al.*[6] are random copolymers of extended units of the type just described and more flexible polyethylene terephthalate units. The melting point can also be reduced through introduction of flexible sidechains, as illustrated by Aharoni[7] with polyisocyanates. The most popular procedure to control the melting temperature involves a repeating unit consisting of an extended mesogenic unit followed by a flexible spacer, as suggested by De Gennes.[8] Examples of polyesters having flexible spacers in the repeating unit have been reported by Sirigu and coworkers,[9-12] Blumstein *et al.*,[13] Strzelecki and van Luyen,[14,15] and by Griffin and Havens.[16,17]

Turning to cholesteric polymers, van Luyen, Liebert, and Strzelecki[3] have recently reported thermotropic cholesteric polyesters obtained by transesterification of the diacetate of 4,4′-dihydroxy phenyl benzoate with mixture of pimelic and (+)-3-methyl adipic acids. Values of the pitch ranged upward from the visible wavelengths, depending upon the copolymer composition. Vilasagar and Blumstein[4] have also reported a thermotropic cholesteric phase in a copolymer of highly extended *p,p*′-azoxydiphenol with a mixture of tetradecanedioic acid and chiral (+)-3-methyl adipic acid, giving a melting temperature of 162°C.

While a larger reduction of the melting temperature can be achieved by increasing the length of the dibasic acid, we believe that better mechanical properties can be obtained by using dibasic acids having fewer methylene units, since this should give a more rigid and extended chain conformation. We therefore investigated homopolymers and copolymers of 4,4'-dihydroxy-α-methyl-stilbene with adipic acid and (+)-3-methyl adipic acid. Roviello and Sirigu[12] investigated nematic polyesters belonging to this family with the number of carbon atoms, *n*, in the dibasic acid ranging from 8 to 14 (6 to 12 methylene units). Clearly the nematic behavior is due to the extended stilbene moiety since both the low molecular weight dialkyloxy[18] and dicarboxy[19] derivatives exhibit enantiotropic mesophases. For these polymers, the temperature of the crystal-nematic transition decreases from 280°C to 160°C with increasing *n*, and also exhibits an odd-even effect. The temperature range of stability of the nematic phase increases from 25 to 50°C and *n* increases from 8 to 11, but decreases for the still higher members. We follow the nomenclature of Roviello and Sirigu in symbolizing the former copolymer as P-6, while the latter, designated as P-6M, has the repeating unit:



EXPERIMENTAL

The method of Zaheer *et al.*[20] was used to prepare 4,4'-dihydroxy-α-methylstilbene. The yield and purity of the crude product could be improved by testing the reaction mixture by thin layer chromatography (1:1 ethylacetate/CH_3OH) and terminating the reaction when it reached completion. A first crystallization from 1:1 ethanol/water gave a white crystalline product, and further recrystallization from $CHCl_3$/ethanol gave 60% yield of the final product melting at 188°C. The melting temperature reported by Zaheer *et al.* is 182–183°C. Adipoyl chloride was purchased from Eastman Chemical Company, and (+)-3-methyl adipoyl chloride was prepared from the corresponding acid and oxalyl chloride. Both acid chlorides were twice distilled before use.

The polyesters were prepared by interfacial polycondensation. In a typical example, a mixture of 0.01 mole of 4,4'-dihydroxy-α-methylstilbene and 0.02 mole of NaOH was dissolved in 100 ml of distilled water and placed in a blender. To this was added 0.5 g of benzyltrimethylammonium chloride in 10 ml of water. The diacid chloride (0.01 mole) in 50 ml of 1,2-dichloroethane was rapidly added with high speed stirring. After 5 minutes, the polymer was preciptated by the addition of *n*-hexane, washed thoroughly with water and water/ethanol mixture, and dried overnight in a vacuum oven at 60°C.

The polymers were obtained in the form of powders, and they were stored in a vacuum desiccator until used. Solid films were obtained by cooling the melt on a glass slide. Mechanical mixtures of P-6M with P-6 or *p*-azoxyanisole (PAA) were prepared by weighing the two components on a glass slide, covering with a cover slip, and heating on a hot stage until a single homogeneous phase was observed microscopically.

Inherent viscosities were measured with a Ubbelohde viscometer at 25°C using a polymer concentration of 0.5g/dl in *m*-cresol. The flow time of the solvent exceeded 100 sec, so no kinetic correction was applied. Microscopic observations were performed with a Bausch and Lomb polarizing microscope equipped with a Mettler FP52 hot stage. For microscopic examination, the samples were placed on a glass slide and covered with a cover slip. DSC measurements were performed with Perkin-Elmer DSC-1B using sample weights in the range 3–6 mg and a heating rate of 10°/min unless otherwise noted. Annealing was performed in a vacuum over for 24 hours at 150°C for P-6 and 70°C for P-6M. CD measurements were made at ambient temperature with a Jasco ORD/UV-5 spectrometer using polymer films approximately 20μ in thickness attached to a glass slide. These films were prepared by heating the polymer to 250°C and then quickly cooling to room temperature.

RESULTS AND DISCUSSION

The transition temperatures of these polymers were studied using both the polarizing microscope and DSC. The transition temperatures measured for virgin samples using a heating rate of 10°/min are collected in Table I. We begin with the results obtained microscopically. All of the systems exhibited a biphasic region in which the isotropic and liquid crystalline phases coexist. Hence we define t_a as the centrigrade temperature of the crystal-liquid crystal transition, and t_b as the lowest temperature, and t_c as the highest temperature,

TABLE I

Characteristics of samples investigated

Sample	η_{inh}(dl/g)	Mesophase	λ_0	t_a(°C)	t_b(°C)	t_c(°C)
P-6	0.14	nematic	—	176	220	>300
P-6M	0.13	cholesteric	<4,000	110	166	250
9:91 mixture P-6M + PAA	—	cholesteric	~5,500	108	137	152
20:80 mixture P-6M + P-6	—	cholesteric	~6,000	—	—	—
50:50 copolymer *co*-P-6/6M	0.40	cholesteric	4,000	199	282	>300

at which the system is biphasic. As the temperature is increased from t_b to t_c, the isotropic phase grows at the expense of the anisotropic phase. The observation of a biphasic region over a wide temperature range is not surprising for the copolymer or the mechanical mixtures listed in Table I, but it was unexpected for the homopolymers P-6 and P-6M. Hence, P-6M samples were tested by repeated heating and cooling cycles, using two heating rates, to investigate the possible effect of previous thermal history. The results are collected in Table II.

The samples were initially conditioned at 140°C for 3 minutes, cooled to ambient temperature, and then held at 100°C for 15 minutes before beginning the first heating cycle. Subsequent heating and cooling cycles were performed without any additional thermal treatment. The larger value of t_a observed during the first heating at either rate reflects the annealing during the thermal conditioning prior to that cycle. The values of t_a observed during the first heating at either rate reflects the annealing during the thermal conditioning prior to that cycle. The values of t_b marking the onset of the biphasic region are, apart from the first entry, largely unaffected by the previous history under the conditions adopted. Samples exposed to the higher temperatures for periods over an hour exhibited somewhat lower t_b values, probably indicating degradation. The maximum temperature of the biphasic region, t_c, exhibits a supercooling of approximately 40°C. This degree of supercooling was unexpected, and represents a departure from the behavior of low molecular weight mesogens. Finally, the results collected in Table II confirm the existence, for this homopolymer, of a rather broad temperature range over which the anisotropic and isotropic phases coexist.

TABLE II

Effect of thermal history on P-6M transitions

		A. Heating rate 10°/min		
Cycle		t_a(°C)	t_b(°C)	t_c(°C)
1	heating	141	182	260
	cooling		169	205
2	heating	120	165	250
	cooling		169	205
3	heating	109	160	240
	cooling		169	200
4	heating	109	160	240
	cooling		169	200
		B. Heating rate 1°/min		
1	heating	139	169	253
	cooling		173	208
2	heating	109	169	240
	cooling		169	205

Samples of a mesogenic polymer crystallized from a biphasic system would probably have inferior mechanical properties since the portions existing in the isotropic phase would not achieve the desired orientation. Thus, a biphasic region over a wide temperature range is undesirable. This can hardly be avoided for a random copolymer, which represents a disadvantage of this procedure for lowering the melting temperature. Under isobaric conditions the Gibbs phase rule does not permit the coexistence of two phases over a temperature range for a one component system. Of course, even homopolymers consist of many components of different molecular weight. However, if the number-average molecular weight is sufficiently high so that the transition temperatures of most of the components are nearly the same, the biphasic region may be restricted to a very narrow temperature interval. The inherent viscosities shown in Table I indicate that all of the polymers investigated are of very low molecular weight, providing an explanation for the low melting point and wide biphasic region observed for the two homopolymers. The coexistence of the anisotropic and isotropic phases over a range of temperature also affects the DSC measurements. The thermogram of a virgin P-6 sample shown in Figure 1 shows only a broad shoulder at about 170°C (corresponding to the crystal-nematic transition). Annealing at 150°C for 24 hours sharpens the melting endotherm at 170°C (t_a determined microscopically is 176°C), but no endotherm corresponding to the nematic-isotropic transition is observed. Corresponding scans for P-6M appear in Figure 2. The melting endotherm of the virgin sample appears at 108°C, while annealing for 24 hours at 70 or 90° increases this temperature to 110°C (in agreement with the t_a value measured microscopically). Sirigu and co-workers[10,11] reported the occurrence of crystalline polymorphs for higher members of this series, and the endotherms observed below 100°C in Figure 2 probably arise from polymorphic transitions.

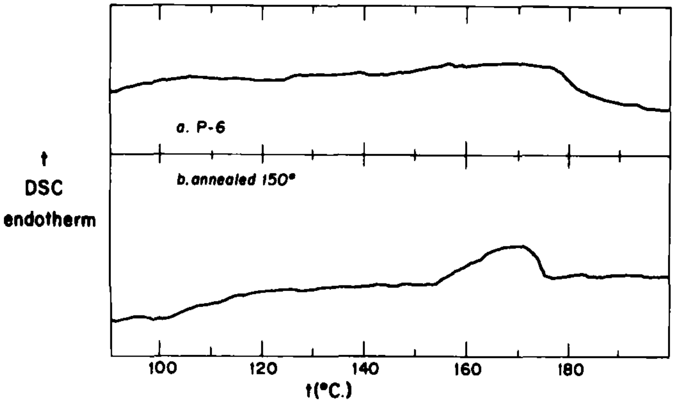


FIGURE 1 DSC scans for samples of P-6: a, virgin sample; b, sample annealed 24 hours at 150°C.

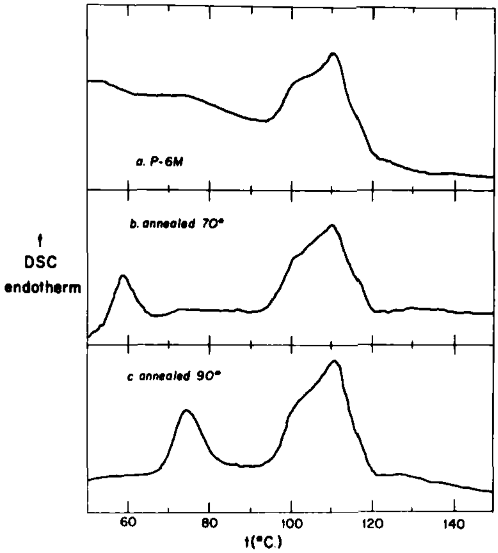


FIGURE 2 DSC thermograms for samples of P-6M: a, virgin sample; b, annealed 24 hours at 70°C; c, annealed 24 hours at 90°C.

As was observed for P-6, no endotherm marks the transition to the isotropic phase. The lack of this endotherm is due to the gradual transition over the range of the biphasic region. For this type of polymer the hot stage microscope is more informative.

As indicated by the inherent viscosity given for our P-6 sample in Table I, this polymer has a low molecular weight. Extrapolation of the results of Roviello and Sirigu[12] for the homologues having $n \geq 8$ leads to the expectation that t_a of P-6 should be above 300°C, which is 125°C above the value measured for our sample. Apparently this difference is due to the low molecular weight of our sample. Millaud, Thierry and Skoulios[21] have remarked that the transition temperature of oligomeric polyazomethines increases very rapidly with molecular weight for the lower members. Roviello and Sirigu[12] reported no biphasic region for their polymers and, from their results, the range of stability of the nematic phase for P-6 would be predicted to be less than 25°C. The nematic range for our P-6 sample is 44°C, and the biphasic region extends more than 80° above t_b. Evidently the primary effects of low molecular weight are to lower t_a and to introduce a wide biphasic region. The effect upon t_c appears to be much smaller.

We next consider the procedures used to characterize the mesophases. A photomicrograph of P-6 taken at a temperature between t_a and t_b appears in Figure 3. This sample exhibits the typical schlieren texture, and is therefore nematic. In this connection it should be noted that an earlier attempt to establish the nematic character of a polyester by microscopic examination gave mis-

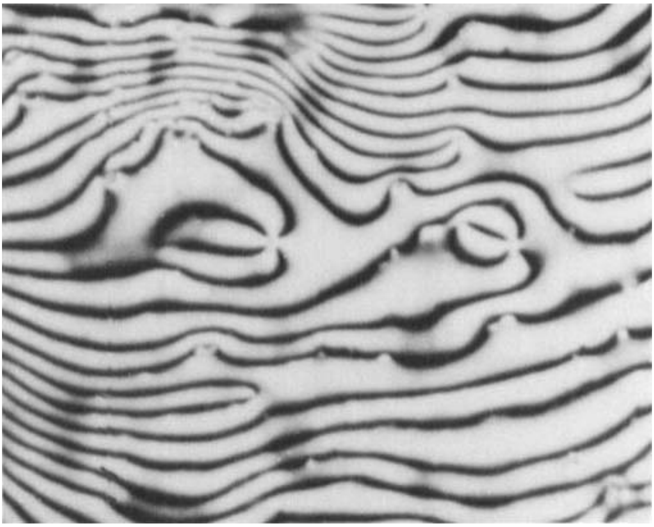


FIGURE 3 Photomicrograph of P-6 at 200°C. (original magnification 100X) illustrating schlieren texture.

leading results,[22] and no micrographs were shown to demonstrate that the polyesters synthesized by Roviello and Sirigu were nematogenic. The low molecular weight of our samples appears to facilitate the observation of the texture, probably due to the low viscosity.

A typical micrograph of P-6M taken at a temperature between t_b and t_c is illustrated in Figure 4. Dark isotropic inclusions in the bright background of the anisotropic phase indicate that at this temperature the sample is in the biphasic region. Initially we entertained some doubts about the cholesteric nature of the liquid crystal phase of P6-M, since we were unable to observe either the fingerprint pattern[23] or the bright colors expected if the helical pitch exceeds or approximates the wavelength of light.[24] After examining a number of samples at temperatures between t_a and t_b, we eventually observed fan-like structures as shown in the lower right of Figure 5. This suggests that P-6M may exhibit a cholesteric phase,[25] and the foregoing results can be explained if its pitch is considerably smaller than visible wavelengths.

With this information in hand, we investigated three procedures for bringing the pitch into the visible region. The first involved preparation of a mechanical mixture of P-6M with PAA, a low molecular weight nematogen. It is well known that the cholesteric pitch can be altered by adding a diluent. Our sample of PAA had *KN* 118°C and *NI* 134°C. A 9:91, w/w mixture of these components exhibited a bright yellow color at 120°C. The wavelength of maximum reflectivity, λ_0 is related to the pitch , p, by the de Vries relation:[26]

$$\lambda_0 = np \tag{1}$$

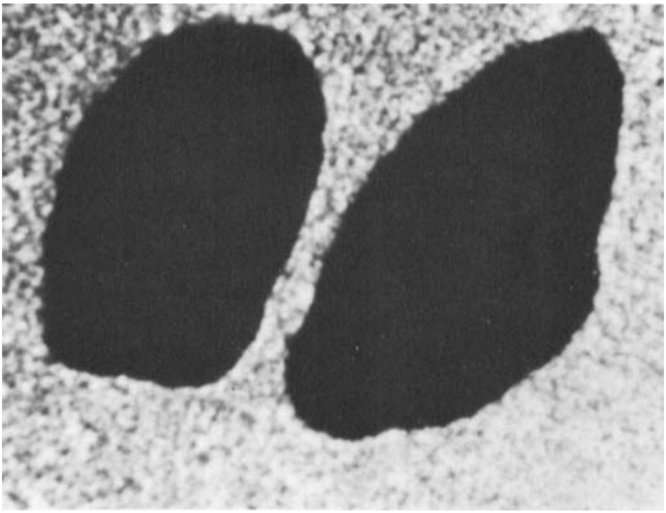


FIGURE 4 Coexistence of two phases in P-6M at 170°C (60×).

where n is the refractive index (approximately 1.5 for these polymers). As indicated in Table I, λ_0 is on the order of 5500 Å for this mixture. Figure 6 shows a photomicrograph of this sample taken at 120°. The uniform areas indicate a planar texture. Both the transition temperatures and λ_0 could be shifted by varying the proportion of PAA.

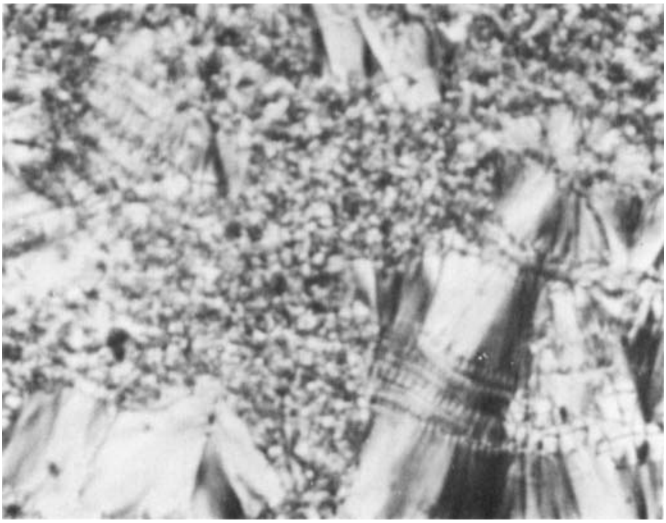


FIGURE 5 Fan-like texture in P-6M at 140°C (100×).

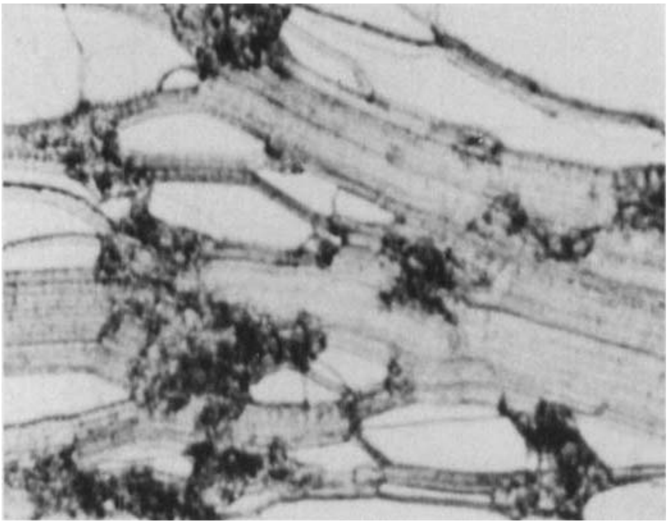


FIGURE 6 Planar cholesteric texture with oily streaks exhibited by 9:91 (w/w) mixture of P-6M and PAA at 120°C (60×).

A second procedure for increasing the cholesteric pitch involved preparation of mixtures of P6-M with the nematogenic polymer P-6. Figure 7 is a micrograph taken at 200°C of a 20:80 mixture of these polymers. The color in this case was bright red, indicating λ_0 is approximately 6000 Å for this mixture. Again, the uniform regions indicate a planar texture. A third procedure

FIGURE 7 Cholesteric texture of a 20:80 mixture of P-6M and P-6 at 200°C (100×).

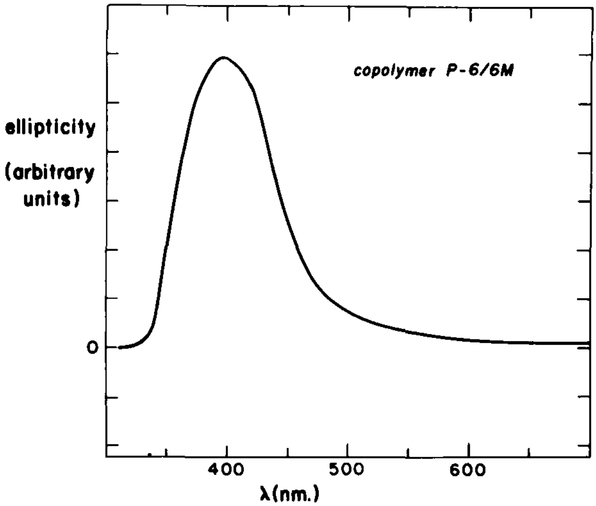


FIGURE 8 CD spectrum of a quenched film of *co*-P-6/6M at 25°C.

used by others[3,4] involves the preparation of a random copolymer. We prepared a copolymer containing an equal number of moles of (+)-3-methyl adipic acid and adipic acid which melted to form a cholesteric phase at 199°C. A photomicrograph of this copolymer taken at 250°C indicates a predominately Grandjean planar texture with maximum reflectance in the blue region ($\lambda_0 \sim 4000$ Å). To explore the possibility of retaining at ambient temperature the cholesteric texture observed at 250°C, films of this copolymer were quenched on a cold surface. It proved to be possible to produce a film having a deep blue color at room temperature providing the film was thin (allowing rapid quenching) and no stress was applied to the film. The CD spectrum of this solid film shown in Figure 9 indicates that the wavelength of maximum reflectivity is centered at 4000 Å, that the cholesteric helix is left-handed, and that this structure has been preserved in the solidified film.

CONCLUSIONS

We have demonstrated that thermotropic polyesters can be prepared which exhibit a cholesteric phase with planar texture, and that this texture can be retained in the solid film by quenching. Further considerations regarding the conservation of liquid crystalline textures in solid polymers have been presented elsewhere.[27] The demonstration that a polymeric cholesteric phase can readily be induced to adopt the planar texture is an important step toward the realization of the ideal biaxially oriented films described at the outset. The ability to control the pitch of a polymeric cholesteric phase by several different methods is also a significant step in the preparation of materials having novel properties. For example, it should be possible to prepare polymeric films in a range of colors without the need for added pigments or dyes. Finally, this study suggests the possibility of varying the transition temperatures by controlling the degree of polymerization. A low degree of polymerization avoids high transition temperatures and facilitates development of the desired texture. Occurrence of the biphasic region can be avoided by operating between the temperatures t_a and t_b. A low degree of polymerization may not be desirable for high tenacity applications; however, the procedure of post-polymerization in the solid state, which has already been described as a route to achieve high modulus polyesters,[28] might result in enhanced thermal and mechanical properties for polymeric cholesteric systems as well.

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