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CHOLESTERIC, THERMOTROPIC POLYMERS WITH MESOGENIC MOIETIES AND FLEXIBLE SPACERS IN THE MAIN CHAIN

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ABSTRACT

The synthesis of a new type of thermotropic soluble cholesteric polymer is described. The polymer contains nematogenic moieties separated by flexible spacers with an asymmetric center in the backbone. The polymer gives spontaneously characteristic Grandjean texturers when heated above its transition temperature between slide and cover slip. Selective reflection of light in the visible ($\lambda \sim 5000\text{-}5600\text{Å}$) occurs for a co-polymer containing pp'-azoxyphenol/dodecanedioic acid and (+)3-methyladipic acid units.

Low molecular weight thermotropic cholesteric liquid crystals because of their helicoidal structure exhibit, when suitably oriented, unique optical properties the most remarkable of which is iridescence. This phenomenon due to selective reflection of discrete wavelength of light is directly related to the helicoidal pitch of the cholesteric structure by the relation:

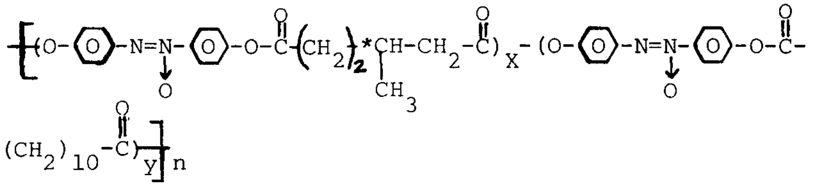
$$\lambda_p = \bar{n}\, p$$

where p is the pitch, $\bar{n}$ the average index of refraction and λ_p the reflected wavelength of light (1).

The pitch of the helix is very sensitive to temperature, pressure, electric or magnetic fields and to the chemical environment. This in turn leads to applications of cholesteric liquid crystals as transducers, sensors, memory devices in industry and medicine (2).

Because similar applications may be expected for polymers displaying thermotropic cholesteric mesophases with the added advantages specific to polymeric materials, the synthesis of such polymers is of great interest. Polymers in which a cholesteric moiety is directly attached to the vinyl backbone such as cholesteryl acrylate or cholesteryl methacrylate were shown to lead to lamellar (smectic) organization of macromolecules "locked in" below the T_g of the polymer (3) rather than to cholesteric arrangements of mesogenic side groups. The main chain of the macromolecule hinders the formation of such arrangements. By decoupling the mesogenic moiety from the convoluted backbone a number of nematic and smectic thermotropic polymers were prepared (4,5). Recently Finkelmann et al, (6) described the synthesis of what appears to be the first thermotropic cholesteric polymers. Such polymers are obtained through copolymerization of two vinyl monomers containing the mesogenic group at the end of a flexible spacer of different length. In addition one of these monomers contains a chiral center. The cholesteric polymers form spontaneously cholesteric Grandjean textures when heated in thin layer between slide and coverslip.

In this paper we would like to report about a different route leading to thermotropic, soluble cholesteric polymers. In our approach the mesogenic and chiral units were incorporated into the main chain of the polymer which also contained in its backbone long and flexible sequences of methylene units. Such polymers are known to display on heating mesomorphic behavior (7,8) of smectic and nematic type. By introducing an asymmetric center into the flexible spacer we have succeeded in synthesizing thermotropic cholesteric polymers. The polymers are polyesters of azoxyphenol (this mesogenic group being denoted no. 8 in our mesogenic series) with dodecanedioic acid (DDA) and (+)3-methyladipic acid (MAA*). The repeat unit is as follows:



Three polymers are described below:

(a) X = 0; y = 1
(b) X = 1; y = 0
(c) X =.5; y =.5

p,p' -Azoxyphenol was prepared according to literature procedures (9,10). The compound was recrystallized from aq. ethanol to give fine yellow needles melting at 224.2±0.1°C with decomposition. The acid chlorides of MAA* and DDA were prepared from corresponding acids with thionyl chloride. The polyesterification was carried out in dichloroethane. The polymer was precipitated in methanol, separated and purified by extraction with methanol. It was vacuum dried at 60°C.

Elemental Analysis:

	Calculated:			Found:		
Polymer	C	H	N	C	H	N
(a) DDA-8	67.90	6.65	6.60	67.64	6.87	6.43
(b) MAA*-8	64.40	5.12	7.91	64.30	5.20	7.84
(c) MAA*/DDA-(50/50)-8	66.31	5.95	7.19	66.13	6.18	6.98

Textures of polymers were studied between slide and coverslip using a Leitz Ortholux polarizing microscope equipped with a hot stage and a Mettler FP-52 temperature programmer. The polymers were characterized by intrinsic viscosity in 1:1 m-cresol:chloroform at 30°C.

In our previous work we have shown that polyesters containing aromatic Schiff base, diphenyl or stilbene moieties separated by flexible methylene sequences of sebacic acid units have a tendency to form rather well organized layered (smectic) mesophases (8). It is known that the presence of azoxy groups favors the formation of nematic mesophases in low molecular compounds, thus the diacetate of pp'-azoxyphenol is nematic (11) and its analogue containing a chiral center between two pp'-azoxyphenol units displays a cholesteric (twisted nematic) mesophase (11). We have therefore as a first step synthesized the polyester of azoxyphenol (DDA-8, polymer a, Table 1). This polymer in analogy with the diacetate ester of pp'-azoxyphenol displayed nematic "schlieren" textures when heated above 210°C (see Figure 1a). In the second step an asymmetric center was introduced into the flexible spacer using the d- optical isomer of the 3-methyladipic acid (MAA*). This polymer (MAA*-8; polymer b) is cholesteric and shows at 260°C between slide and coverslip a typical cholesteric texture with "oily streaks" (see Figure 1b). This polyester does not show any iridescence in the visible spectrum. In analogy to a number of low-molecular cholesteric systems it is probable that the pitch of the helical structure is too small for the selectively reflected radiation to be visible. The pitch of the helical structure can be increased by decreasing the population of chiral centers (6). In order to do this a copolymer of pp'-azoxyphenol and a 50/50 (mole %) mixture of MAA* and DDA was synthesized (polymer c). This co-polyester when heated to 175°C flows and displays yellow-green iridescence ($\lambda_R \sim 5000\text{-}5600\mathring{A}$) (see Figure 1c).

TABLE 1 PROPERTIES OF THERMOTROPIC CHOLESTERIC POLYESTERS

Polymer	$[\eta]$ dl/g*	Transition T_m °C**	Mesophase***
(a) DDA-8	0.76	K216N265I	Nematic
(b) MAA*-8	0.38	K221CH294.5I	Cholesteric
(c) MAA*/DAA-8	0.50	K162CH278.5I	Cholesteric

(*) Intrinsic viscosity in 1:1 m-cresol:chloroform at 30°C

(**) Transition temperature as determined from polarizing microscopy K-crystal, N-nematic, CH-cholesteric

(***) The nature of mesophase as determined from microscopy and X-ray patterns

All three polymers are characterized by an intrinsic viscosity which for this type of poly(esters) corresponds to molecular weights in the 10,000 range. The polymers are crystalline at room temperature. The co-polyester (polymer gives 3 strong WAX reflections at 3.89Å, 4.35Å and 5.18Å at 25°C which disappear and merge into a broad halo centered about 6-7Å at 180°C (above T_m). It is apparent from Table 1 that the copolyester (polymer c) in addition to having a larger helical pitch than the polyester b displays a significantly lower transition temperature T_m than both polymers a and b.

Further study of this group of chiral polyesters is in progress.

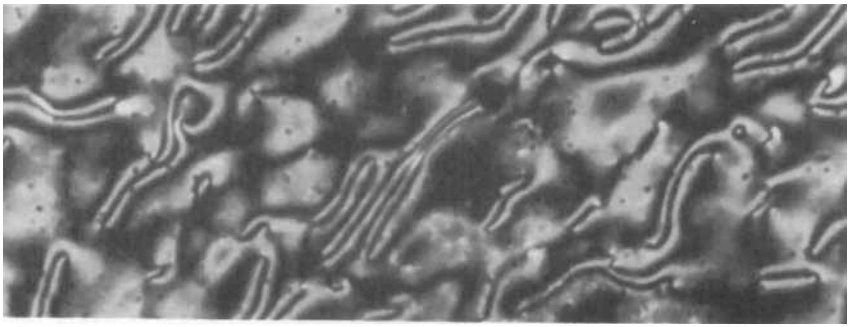


FIGURE 1a Polymer a, Nematic Mesophase at 235°C, Crossed Polars. Magn. 320X

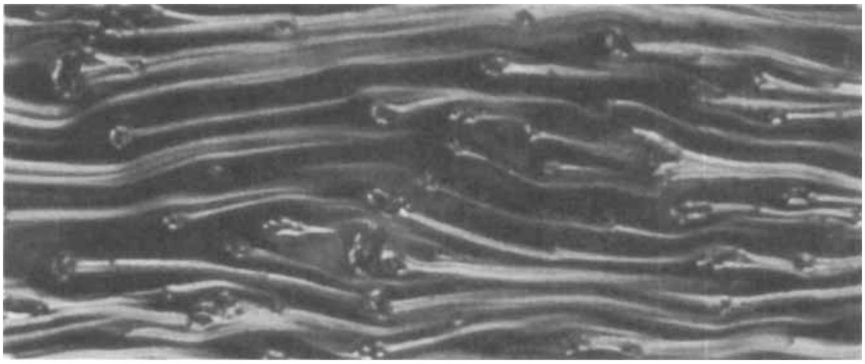


FIGURE 1b Polymer b, Cholesteric Mesophase, Grandjean Texture With "oily streaks", at 260^{o}C, Crossed Polars. Magn. 320X

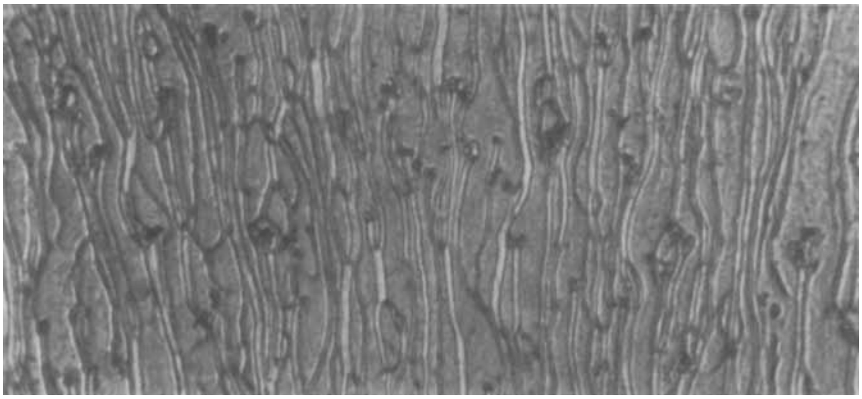


FIGURE 1c Polymer c, Cholesteric Mesophase, Grandjean Texture With "oily streaks" at 240oC, Crossed Polars. Magn. 320X

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