

THE STRUCTURE AND OPTICAL PROPERTIES OF COPOLYMER OF CHOLESTERIC ESTER*

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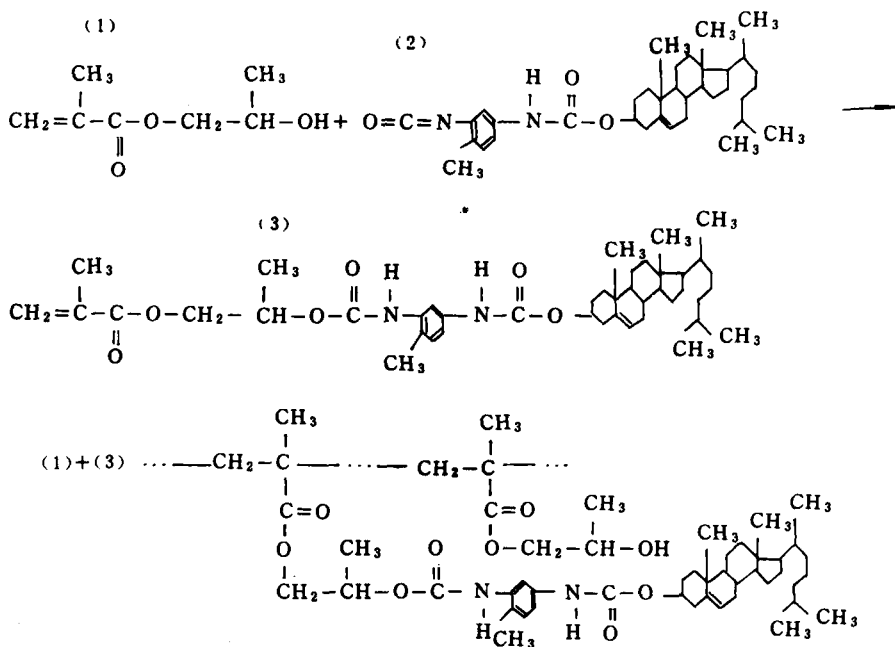
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ABSTRACT

The structure and switching properties of liquid crystalline side chain copolymers of cholesteric ester of 1,2-hydroxypropyl 2,4-di-isocyanatoluene methylmethacrylate (PHCPM) have been studied in detail. The cholesteric mesophase of PHCPM is shown by polarizing microscopy, X-ray diffraction and selective light reflection. Solution of PHCPM in CHCl_3 is optically anisotropic; its optical properties were determined by specific rotation $[\alpha]$, circular dichroism (CD) and wide-angle light scattering (WALS) methods.

Recently, much attention has been paid to the study of polymeric liquid crystals. Owing to the specific helical structure, the cholesteric liquid crystal has special optical properties^[1-3]. This paper presents a detailed study on the structure and switching properties of liquid crystalline side chain copolymers of cholesteric ester of 1,2-hydroxypropyl 2,4-di-isocyanatoluene methylmethacrylate (PHCPM), in which the liquid crystalline moieties (the mesogenic groups) are connected to the main polymer chain by flexible spacer groups^[4].



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The monomer containing cholesteric group was prepared by reacting 2,4-di-isocyanatoluene with cholesterol and hydroxypropyl methacrylate. The monomer was then copolymerized with hydroxypropyl methacrylate in various proportions (*m*). The formation of both the monomer and copolymer has been confirmed by IR and ^1H NMR techniques.

The IR absorption spectra were obtained with a 580 B spectrophotometer; and the specimens were made in the form of film with KBr. The ^1H NMR analysis was done by FX-100 FT with their chloroform solutions. Fig.1 is the IR spectra of monomer and copolymer of PHCPM. The presence of 1640 cm^{-1} (vibration $\text{C}=\text{C}$ in MMA) showed that copolymerization was realized. Fig.2 is the ^1H NMR spectra of monomer and copolymer of PHCPM. The copolymerization was indicated by the absence of 5.58 and 6.11 ppm peaks.

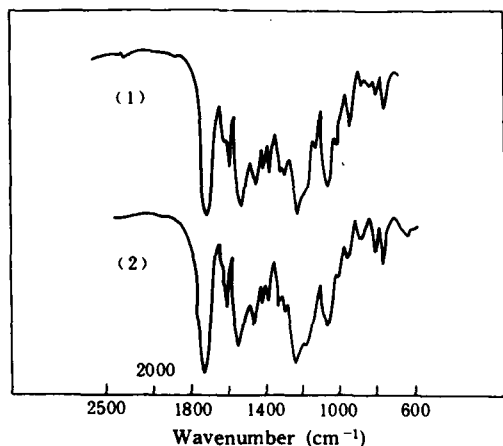


Fig.1 IR spectra of (1) monomer of PHCPM; (2) copolymer of PHCPM.

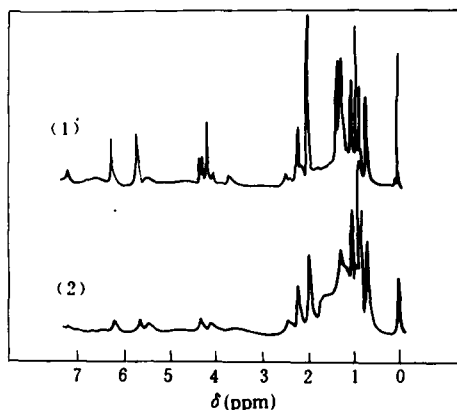


Fig.2 ^1H NMR spectra of (1) monomer of PHCPM; (2) copolymer of PHCPM.

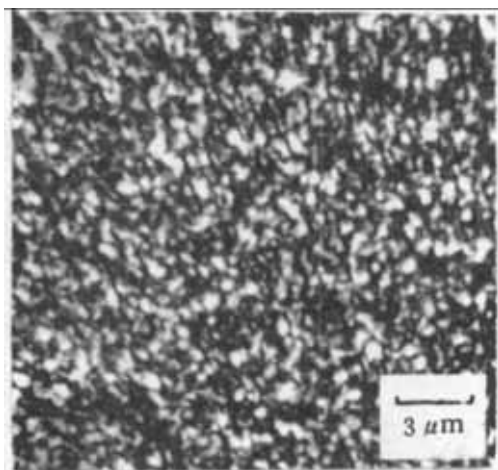


Fig.3 Optical micrograph of cholesteric phase of copolymer PHCPM under crossed polarizers

Under certain definite condition, turning of PHCPM into liquid crystalline state was observed under crossed polarizers of a Carl Zeiss Jena polarizing microscope with a hot stage (TRL-01), the temperature of which was adjusted by a control unit.

Film specimens were formed by casting solution on the surface of glass. Cooling of the copolymer melt from 110°C leads to the formation of a liquid crystalline phase (at 89°C), which can be frozen to the glassy state, and the pictures were taken at room temperature. Fig.3 is the optical microphotograph of cholesteric phase of copolymer PHCPM-2 under crossed polarizers. It indicates that this copolymer displays a cholesteric fingerprint pattern.

On X-ray diagram of the optically anisotropic copolymer PHCPM there exists only one diffuse broad diffraction maximum at wide angles. Those X-ray patterns of PHCPM in the liquid crystalline state demonstrate that no three dimensional order structure exists.

A specific feature of cholesteric liquid crystals is selective light reflection. The wavelength of selective light reflection from copolymers is determined by measuring the transmittance with a "Specorol UV-Vis" spectrophotometer (Karl Zeiss, Jena). Spectrophotometric study of the films of copolymers has shown the existence of a broad reflection maximum in the 310—340 nm region. Fig.4 is the optical extinction versus free space wavelength for PHCPM.

For cholesteric liquid crystals, the wavelength of selective light reflection λ_R is related to the pitch of the cholesteric helix P in the following manner: $\lambda_R = \bar{n}P$, where $\bar{n}$ is the refractive index. It is evident that the selective reflection for a cholesteric mesophase is in the UV-light regions.

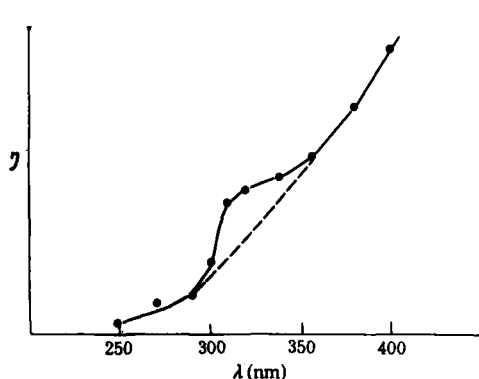


Fig.4 Selective light reflection curve for PHCPM at room temperature

These results demonstrate that copolymers with cholesteric side groups PHCPM exhibit the thermotropic liquid crystalline properties. The solution of copolymers PHCPM in CHCl_3 becomes optically anisotropic, due to the existence of hydroxyl group on its side chains. The optical properties of copolymers were determined by specific rotation $[\alpha]$, circular dichroism (CD) and wide-angle light scattering (WALS) methods.

The specific rotation $[\alpha]$ was measured by using a polarimeter Perkin-Elmer 241 at a range of

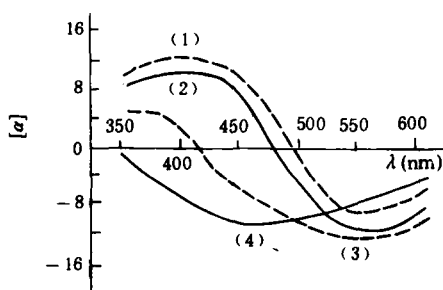


Fig.5 Specific rotation $[\alpha]$ versus wavelength for PHCPM/ CHCl_3 liquid crystalline solution.

wavelength 300—600 nm, using sodium Na(589nm) and maercury Hg(578, 546, 436 and 365 nm) lamp as light source to mesure the rotation angle θ . The specific rotation $[\alpha]$ under defined temperature and wavelength is:

$$[\alpha]_{\lambda}^t = \frac{10 \theta}{c \cdot l},$$

where: α — specific rotation ($\text{deg} \cdot \text{cm}^{-1} \cdot \text{g}^{-1} \cdot \text{ml}$); t — temperature ($^{\circ}\text{C}$); θ — rotation angle (degrees); λ — wavelength (nm); c — concentration (g/ml); l — cell length (cm).

Fig.5 is the specific rotation $[\alpha]$ versus wavelength for PHCPM/ CHCl_3 liquid crystalline solution. λ_0 is the wavelength at the point where $\alpha_{(\lambda)}$ changes signs. $\Delta \bar{n}$ is the birefringence of the layers which is rotated about the N axis to form the cholesteric phase. It is calculated by the following equation:

$$\alpha_{(\lambda)} = \frac{-\pi \Delta \bar{n}^2 \lambda_0}{4n \lambda^2 [1 - (\frac{\lambda}{\lambda_0})^2]}$$

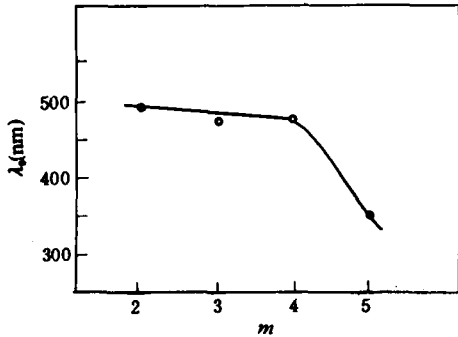


Fig.6 The wavelength versus m for PHCPM.

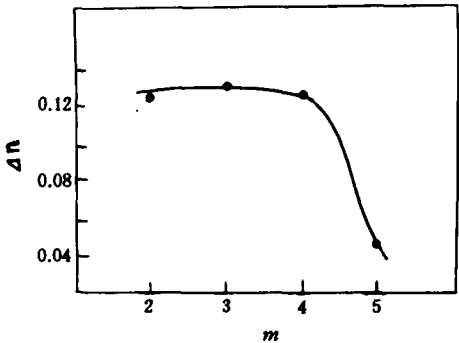


Fig.7 The birefringence of the layers $\Delta \bar{n}$ versus m for PHCPM.

As is seen from Table 1, $\Delta \bar{n}$ for PHCPM is in the range of $0.13 > \Delta \bar{n} > 0.04$, which decreases with the increase in the ratio of methylmethacrylate to cholesteryl group m . $\Delta \bar{n}$ of the copolymers decreases rapidly when $m > 4$. For instance, copolymer PHCPM-4 ($m=5$) is only slightly birefringent, exhibiting no optical anisotropy. When $m > 5$, the copolymer becomes totally

Table 1 The optical properties of PHCPMs

Sample	m	$\bar{n}_{589}^{20}$	$[\alpha]_{589}^{20}$	$\lambda_0(\text{nm})$	$\lambda^0(\text{nm})$	$P(\text{nm})$	$\Delta \bar{n}$
PHCPM-1	2	1.451	-8.19	494	310	213.69	0.1225
PHCPM-2	3	1.455	-11.36	440	340	233.41	0.1249
PHCPM-3	4	1.452	-11.03	477	320	220.42	0.1249
PHCPM-4	5	1.451	-7.67	350	330	227.45	0.0480

amorphous (Fig.6 and Fig.7). Fig.6 is the plot of wavelength λ_0 versus m for PHCPM, while Fig.7 is the plot of the birefringence of the layers Δn versus m for PHCPM.

Circular dichroism (CD) measurements were carried out on a Jobin Yvon dichrograph 5, using 10 mm path length cell. A strong CD peak of ~ 10 g/100ml PHCPM/CHCl₃ anisotropic solution was found at the wavelength λ^0 of 310–340 nm. The selective light reflection is observed in the same wavelength region. Thus copolymers produce a cholesteric mesophase with intrinsic selective UV-light reflection. Fig.8 is the circular dichroism spectra for PHCPM/CHCl₃ liquid crystalline solution. The absorption of circular dichroism can be calculated by the following equation:

$$\Delta\varepsilon = \varepsilon_L - \varepsilon_R = \frac{1}{[M] \cdot l} \cdot \log_{10} \left(\frac{I_R}{I_L} \right)$$

where: $\Delta\varepsilon$ —the difference in molecular extinction coefficient; $\varepsilon_L - \varepsilon_R$ —the molecular extinction coefficient for left and right hand rotation; $[M]$ —molar concentration (mole); l —cell pathlength; I_R, I_L —intensity of transmission light of right handed and left handed circularly polarized vibration.

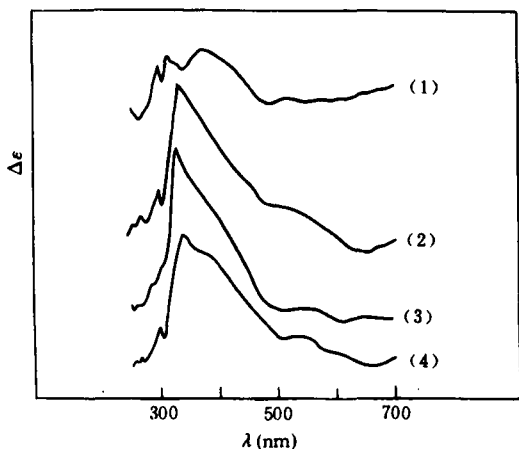


Fig.8 Circular dichroism spectra for PHCPM/CHCl₃ liquid crystalline solution

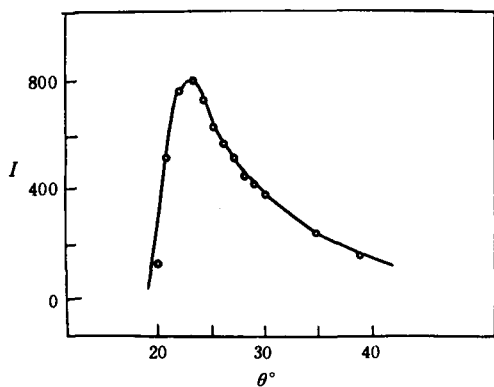


Fig.9 The wide-angle light scattering curve of PHCPM/CHCl₃ liquid crystalline solution

The theory of CD about cholesteric phase shows that $\Delta\varepsilon$ is maximum when the wavelength λ^0 in the sample is equal to the length of the cholesteric helical pitch $\lambda^0 = \bar{n}P$ (the coefficient $\bar{n}$ is a mean refractive index). λ^0 is a direct measure of the helical twisting P and is a linear function of ratio m . The helical pitch of PHCPM increases with the decrease in the content of the cholesteric monomer units (Table 1). It should be pointed out that the more the content of cholesteric units in PHCPM, the tighter the twisting of cholesteric liquid crystals. It is seen from Table 1 that for all the copolymers the wavelength of selective light reflection λ^0 decreases when the fraction of chiral units increases.

The wide-angle light scattering (WALS) results of PHCPM/CHCl₃ at a wavelength of 436 nm, are shown in Fig.9. The wide angle light scattering curve of PHCPM/CHCl₃ liquid crystalline solution gives a peak at 22.5°, from which and the results of CD could be calculated the number of twisting of the cholesteric helix, which persists over 10 turns from this particular copolymers.

The results of this work demonstrate that copolymers with mesogenic side groups PHCPM

exhibit the cholesteric mesophase, shown by polarizing microscopy, X-ray diffraction and selective light reflection. Solution of PHCPM in CHCl_3 becomes liquid crystalline above a certain critical concentration. By using the techniques of spectrophotometry, wide-angle light scattering and circular dichroism it is shown that the mesophase formed is cholesteric. We have measured its pitch, which depends on polymer concentration and the ratio of methylmethacrylate to cholesteryl group (m). Copolymers PHCPM showing the thermotropic and lyotropic liquid crystalline properties, can be explained by the existence of cholesteric and hydroxyl group on the side chains.

Keywords:

Structure of polymers; Liquid crystals; Cholesteric mesophase; Optical properties.

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