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Thermotropic and Optical Properties of Chiral Nematic Polymers[1]

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The thermotropic and optical properties of methacrylate copolymers and chemically modified poly(γ-benzyl *L*-glutamate) were investigated as part of our effort to explore the optical applications of these materials. It was found that besides the commonly cited comonomer ratio, physical blending and annealing followed by quenching represent a new and more flexible means to tune the selective reflection wavelength. In the chemically modified poly(γ-benzyl *L*-glutamate) system with Tg as low as −25°C, it appears that the relatively high-melt viscosity is capable of sustaining the cholesteric mesophase, generated by annealing and quenching, while subjected to heating up to 100°C.

KEY WORDS: chiral nematic polymers; optical properties; polymers; thermotropic properties.

1. INTRODUCTION

Although thermotropic liquid crystalline behavior was first observed for cholesteryl benzoate a century ago [1], major advances in practical applications have been made only during the past two decades, notably in medical diagnostics [2, 3] and optics [4, 5]. Applications of liquid crystals as active or passive elements in laser systems have recently been reviewed by Jacobs [6, 7]. Because of the fluid nature of the low molar mass liquid crystals (LCs), high-quality glass substrates are required to support a thin film in optical applications. Lack of environmental durability (e.g., sensitivity to temperature changes and humidity) is another problem with

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LCs. In view of these limitations, liquid crystalline polymers (LCPs) have been introduced in recent years. Compared to LCs, LCPs are unique in that the particular mesophase desired for an intended application can be frozen in the polymer matrix by first heating the sample up to the corresponding liquid crystalline phase transition temperature and then quenching it to below the polymer glass transition temperature. Thus, it is conceivable that LCPs can be used as freestanding films, thereby obviating the requirement of optical substrates. Moreover, since the mesophase has been frozen in the polymer glass, better environmental stability/durability is anticipated.

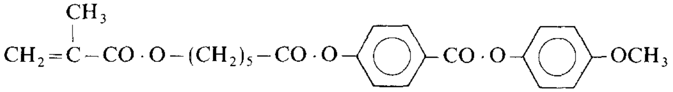
Thermotropic LCPs have been the object of extremely active research for the past 15 years or so due to the pioneering studies of Ringsdorf and Finkelmann in Germany, Platè and Shibaev in the USSR, and Blumstein in the United States [8]. Recent advances in the synthesis, characterization, and applications are the subjects of three monographs [9–11] and several review articles [12–15]. From the structural point of view, thermotropic LCPs can be categorized into either main-chain or side-chain polymers. Main-chain LCPs are useful for the formation of high-strength fibers and other shaped articles due to the unusual rheological behavior [16]. Side-chain LCPs are better suited for applications as optical elements because of the lower glass transition and mesomorphic transition temperatures which facilitate materials processing.

The main theme of the present work is on the side-chain polymers that are potentially useful for applications in the fields of optical and laser systems engineering. Emphasis is placed on the cholesteric mesophase of LCPs which exhibits the property of selective wavelength reflection. The cholesteric mesophase can be described as being composed of a helical arrangement of molecules. The right (left)-handed helix will reflect the right (left)-handed circularly polarized component of incident light at a wavelength determined by the pitch length of the helix and the refractive index of the material. Applications of the selective reflection property include optical isolators, circular polarizers, and notch filters [6, 7]. Both right- and left-handed materials are needed for these applications. There exist several polymeric systems in the literature that appear to be suitable for the intended applications. For example, left-handed acrylate copolymers [17] and polysiloxane [18], as well as right-handed polyglutamate [19] and (hydroxylpropyl) cellulose [20], have been reported. One of the objectives of this paper is to examine the thermotropic and optical properties of a series of methacrylate copolymers and chemically modified poly(γ-benzyl *L*-glutamate) that are perceived to be suitable for applications as left-handed and right-handed materials, respectively. Methods to tune the selective reflection wavelength and the thermal stability of the annealed and quenched cholesteric mesophase are also be addressed. A particularly new feature of the present study is to examine the feasibility of sustaining an annealed cholesteric mesophase in a polymeric matrix above its glass transition temperature.

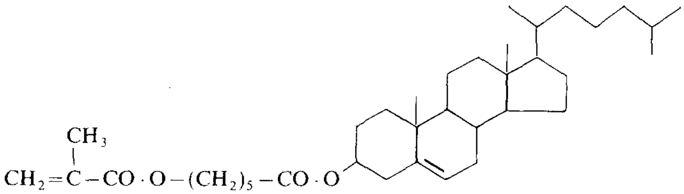
2. EXPERIMENTAL

2.1. Material Synthesis

Two methacrylate monomers (**I** and **II**) were synthesized according to the procedures reported by Mousa et al. [21].

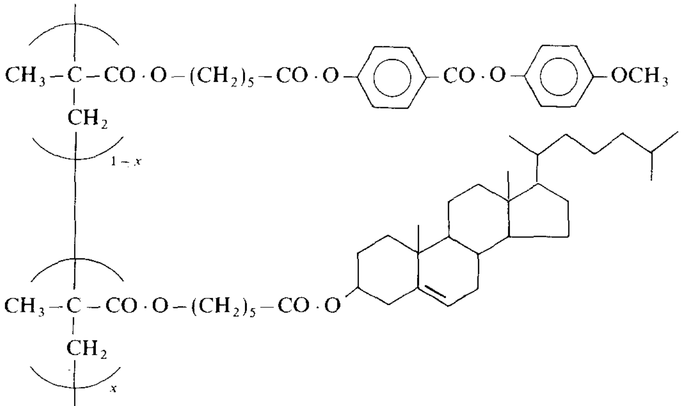


I



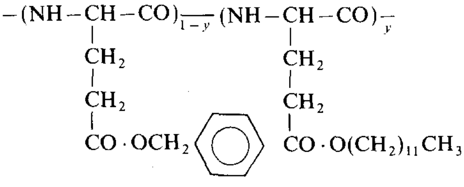
II

These monomers were copolymerized in benzene using azobisisobytyronitrile as the initiator. The mole fraction x of the chiral component (**II**) in the copolymer (**III**)



III

was verified with proton NMR spectroscopy. The other copolymer under present investigation is derived from poly(γ-benzyl *L*-glutamate) (Sigma Chemical Company, $\bar{M}_v = 75{,}000$ and 120,000) by partial transesterification with *n*-dodecanol [19]. The structure of the product, poly[(γ-benzyl *L*-glutamate)-co-(y-dodecyl *L*-glutamate)], is depicted as



IV

The extent of transesterification y, depends on the reaction time and the concentration of the acid catalyst, *p*-toluene sulfonic acid. The comonomer ratio was determined with proton NMR; for the two samples of copolymer **IV**, y was found to be 0.432 and 0.493 for $\bar{M}_v$ = 120,000 and 75,000, respectively.

2.2. Characterization of Thermal and Optical Properties

Mesomorphic properties of copolymers (**III** and **IV**) were determined with a differential scanning calorimeter (DSC-4, Perkin–Elmer) and a polarizing optical microscope (Leitz Orthoplan-Pol) equipped with a hot stage (FP52, Mettler). The DSC was constantly purged with helium at $20\,\mathrm{ml\cdot min^{-1}}$ and the scan rate was consistently set at $40°\mathrm{C\cdot min^{-1}}$.

Prior to the measurement of selective reflection wavelength, λ_R, the polymeric materials were sandwiched between a pair of glass substrates. Mechanical shearing was applied to prepare a thin film to help induce molecular alignment as the sample was heated beyond its clearing temperature. Annealing at a temperature between the glass transition and clearing temperatures then followed for a minimum of 24h. The annealed cholesteric mesophase was finally locked in by quenching, and the selective reflection spectrum was obtained on a UV-VIS-NIR spectrophotometer (Lambda 9, Perkin–Elmer). The wavelength corresponding to maximum optical density was determined to be λ_R.

3. RESULTS AND DISCUSSION

Summarized in Table I are the T_g (°C, midpoint), clearing temperature $T_{C\rightarrow I}$ (°C), selective reflection wavelength λ_R, and weight-average

Table I. Thermal and Optical Properties of Copolymer **III**

x (mole fraction)	T_g (midpoint; °C)	$T_{C\rightarrow I}$ (max.; °C)	λ_R (nm)	$\bar{M}_w$
0.10	40	106	1244	16,750
0.20	45	120	642	33,590
0.28	41	113	534	17,730

molecular weight $\bar{M}_w$ (determined with GPC) of a series of copolymer **III** at x values ranging from 0.10 to 0.28. Figure 1 shows a typical DSC thermogram that was used to determine T_g and $T_{C\rightarrow I}$. The cholesteric texture of the copolymer (**III**) with $x = 0.28$ is shown in Fig. 2 taken under a polarizing optical microscope: Optical density, as a function of wavelength, is shown in Fig. 3 for $x = 0.20$, in which the wavelength of maximum attenuation is taken as λ_R. Note that the attenuation around 650 nm is due to selective reflection. The left-handed cholesteric sense was verified by comparing to a low molar mass liquid crystal with known handedness. It is demonstrated in Table I that λ_R is a relatively strong function of x, while $\bar{M}_w$ plays a rather insignificant role. In an effort to find an alternative way of tuning the selective reflection wavelength, copolymer **III** with $x = 0.28$ was blended with that of $x = 0.10$ by coprecipitation from benzene solution with methanol. Figure 4 shows the characteristic texture of the cholesteric mesophase for the blend that is composed of 75 wt% of $x = 0.28$ and

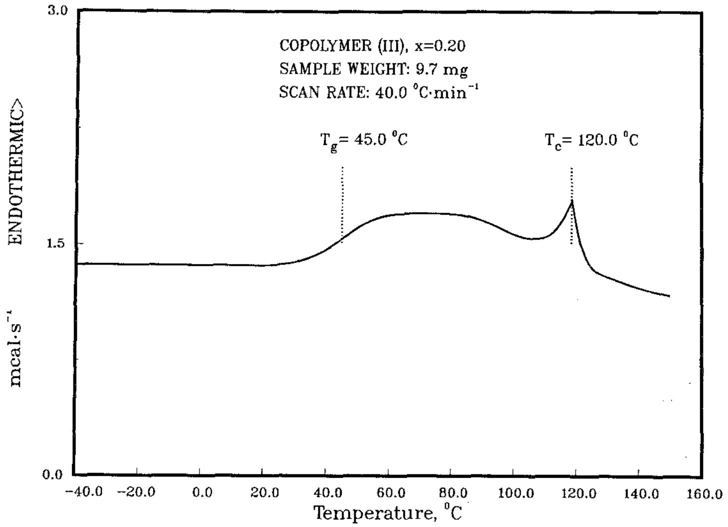


Fig. 1. DSC thermogram of copolymer **III** with $x = 0.20$; second heating scan.

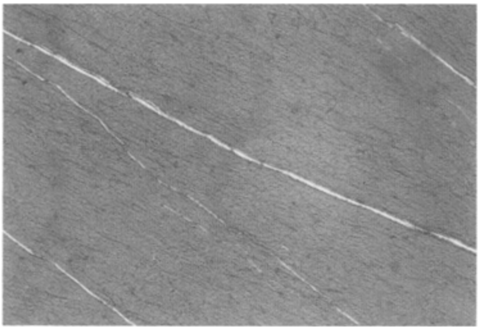


Fig. 2. Typical cholesteric texture of copolymer **III** with $x = 0.28$. 100 ×; reduced 50% for reproduction.

25 wt% of $x = 0.10$. As shown in Fig. 5, physical blending furnishes a more flexible means to vary the λ_R value. Because of the close similarity in chemical structure of the copolymer with $x = 0.28$ to that with $x = 0.10$, phase separation problems are anticipated to be minimal; however, this is an interesting point that deserves further investigation.

As an example of the right-handed polymeric material, we have synthesized copolymer **IV** with $y = 0.493$ and 0.432 using poly(γ-benzyl *L*-glutamate) with viscosity average molecular weights of 75,000 and 120,000, respectively, following the procedures reported by Watanabe et al. [22]. While T_g of copolymer **III** is above room temperature, suggesting the

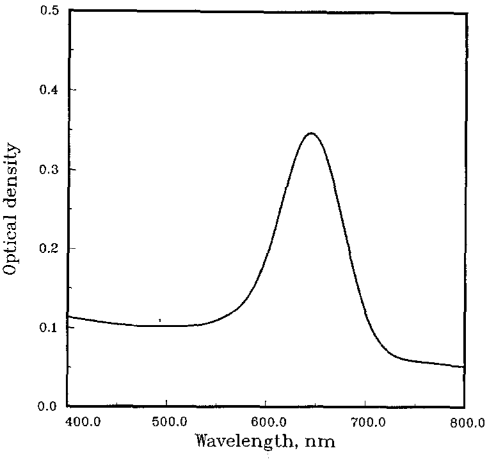


Fig. 3. Selective reflection spectrum of copolymer **III** with $x = 0.20$ as a function of wavelength.

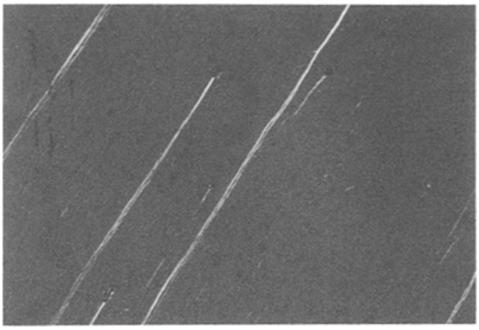


Fig. 4. Typical cholesteric texture of a binary blend of copolymer **III** with $x = 0.28/(x = 0.10) \cong 3/1$. 100 ×; reduced 50% for reproduction.

feasibility of locking the cholesteric mesophase in a glassy matrix by sample annealing and subsequent quenching below T_g, copolymer **IV** shows T_g around −25°C. The question, then, is whether or not it is possible for the high-melt viscosity to sustain the cholesteric mesophase aligned by annealing at elevated temperatures followed by quenching. It is noted that the clearing temperature is above 200°C, thereby offering a wide temperature range over which cholesteric mesophase exists for practical applications.

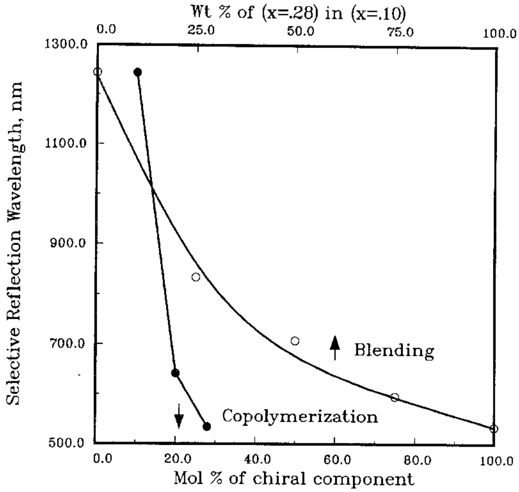


Fig. 5. Selective reflection wavelength as a function of composition in copolymer **III** and in binary blends of copolymers: (●), copolymerization; (○) blending.

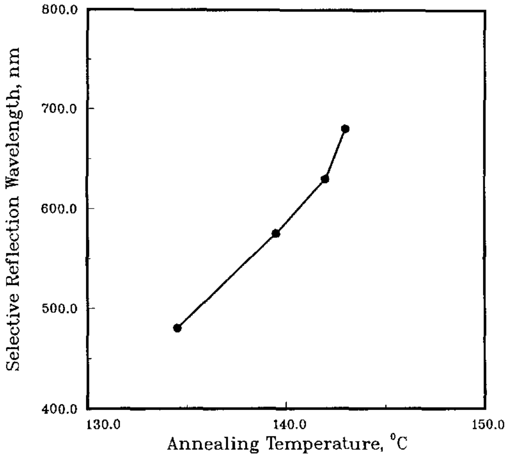


Fig. 6. Selective reflection wavelength of copolymer **IV** with $y = 0.432$ and $\bar{M}_v = 138{,}500$ annealed at 134.5°C and then quenched to room temperature as a function of annealing temperature.

Moreover, the selective reflection wavelength is a much stronger function of temperature for copolymer **IV** than for **III**, in agreement with the behavior observed for acrylate copolymers [17]. These observations suggest that one might be able to vary λ_R by annealing at different temperatures over an extended period of time and then quenching to room

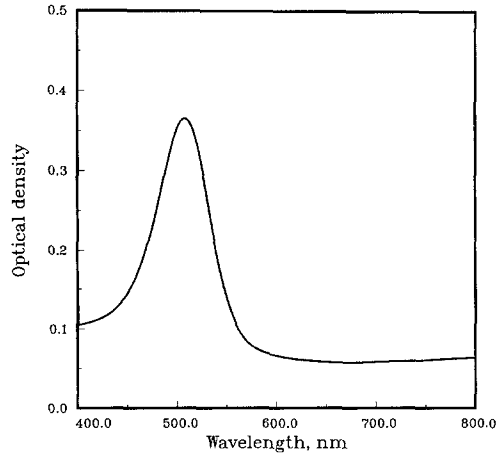


Fig. 7. Selective reflection spectrum of copolymer **IV** with $y = 0.432$ and $\bar{M}_v = 138{,}500$ as a function of wavelength.

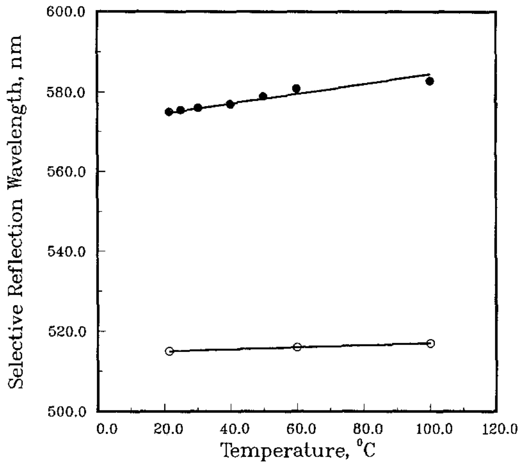


Fig. 8. Selective reflection wavelength of copolymer **IV** as a function of temperature at different molecular weights: (●) $\bar{M}_v = 138{,}500$ ($y = 0.432$); (○) $\bar{M}_v = 88{,}200$ ($y = 0.493$).

temperature in the hope of maintaining the desired pitch length of the helical structure (hence, λ_R) with presumably relatively high-melt viscosity. In addition, in view of the fact that copolymer **IV** possesses T_g considerably below room temperature, one should also examine the mesophase stability without the glassy matrix as encountered with copolymer **III**.

To test the idea of freezing-in the cholesteric mesophase with varying pitch length by annealing copolymer **IV** at several temperatures below the clearing temperature, we show in Fig. 6 the selective reflection wavelength (after the sample was annealed and quenched) as a function of the annealing temperature. The quality of molecular alignment can be inferred from Fig. 7, in which the observed attenuation 0.29 is close to the theoretical limit of 0.30 optical density unit (or 50% transmittance). To address the issue of the stability of the mesophase after annealing and quenching, we placed the sample in an oven set at temperatures up to 100°C for a minimum of 1h. The results plotted in Fig. 8 indicate that the change in λ_R value falls within 10nm across a range of 80°C. The combination of our data plotted in Figs. 7 and 8 forms the basis for a new and versatile approach to the optical applications of polymer liquid crystals.

4. CONCLUSIONS

We have explored the feasibility of a left-handed methacrylate copolymer and a right-handed chemically modified poly(γ-benzyl L-glutamate) for applications in optics and laser systems engineering. Materials issues addressed include thermotropic behavior and selective wavelength reflection. In addition to the comonomer ratio, physical blending and annealing at different temperatures followed by quenching were established to be effective methods for locking in a well-ordered cholesteric mesophase that can be sustained over an extended period of time. The mesophase created in chemically modified poly(γ-benzyl *L*-glutamate) was shown to be stable up to 100°C even though the glass transition temperature was found to be about -25°C, in contrast to the conventional thought that a glassy matrix is required for achieving mesophase stability.

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