Synthesis and Properties of Side Chain Cholesteric Liquid-Crystalline Polyacrylates Containing Two Mesogenic Groups

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ABSTRACT: The synthesis of side chain cholesteric liquid-crystalline polymers containing both 4-cholesteryl-4'-acryloyloxybenzoate (M_I) and 4-methoxyphenyl-4'-acryloyloxybenzoate (M_{II}) mesogenic side groups is described. The chemical structures of the obtained monomers and polymers are confirmed by Fourier transform infrared (FTIR) spectroscopy. The phase behavior and optical properties of the synthesized monomers and polymers were investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and thermogravimetric analyses (TGA). The homopolymer IP reveals a cholesteric phase and VIIP displays a nematic phase. The copolymers IIP–VIP exhibit, respectively, cholesteric oily-streak texture and focal-conic texture. The fixation of the helical pitch and oily-streak texture of the cholesteric phase is achieved by quenching, and polymer films with different reflection colors are obtained. The experimental results demonstrate that the glass transition temperature (T_g) and the melting temperature (T_m) of the copolymers IIP–VIP decrease, whereas the isotropization temperature (T_i) and the mesomorphic temperature range (ΔT) increase with increasing content of mesogenic M_{II} units. TGA results indicate that the temperatures at which 5% mass loss occurred ($T_{5wt\%}$) of all copolymers are >245°C. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1936–1941, 2003

Key words: phase behavior; liquid-crystalline polymers; cholesteric phase; oily-streak texture

INTRODUCTION

In recent years, thermotropic cholesteric liquid-crystalline polymers (ChLCPs) have attracted considerable attention and interest, mainly because of their unique optical properties, including selective reflection and transmission of light, thermochromism, and circular dichroism, and potential applications in numerous areas, especially in the field of flat-panel displays, full-color thermal imaging, switchable optical devices, and organic pigment.[1–11] The cholesteric mesophase is formed by a rod-like, chiral molecule, which is responsible for its helical aspect. The unique optical properties of ChLCPs are related to the helix supermolecular structure of the mesophase, the pitch of which controls the wavelength of the light reflected. From a technological point of view, two important questions about ChLCPs are (1) how to adjust the pitch and (2) how to keep the pitch constant once it has been adjusted. In general, the helical pitch of cholesteric phase depends on the chemical structure of ChLCPs, the concentration of the chiral constituents, the temperature, and the outer field. In the case of ChLCPs, any potential application requires a fixation of the helical pitch and texture of the cholesteric phase, which can in principle be achieved by three different methods: (a) by quenching to freeze the cholesteric texture and colors; (b) by photocrosslinking, when suitable photocure reactive groups are present; and (c) by thermal crosslinking. Therefore, it would be both necessary and useful to synthesize various kinds of side chain ChLCPs to explore their potential applications.

For side chain liquid-crystalline polymers, the mesogenic units are usually attached to the polymeric backbone via a flexible spacer. The flexible spacer decouples the mesogenic side groups from the polymeric backbone and renders the mesogenic units to order anisotropically. However, when a rigid mesogenic unit is directly attached to the polymeric backbone, the liquid-crystalline polymers can be obtained too. Poly(4-cyclohexylphenyl acrylate),[12] poly(4-biphenyl acrylate),[13] poly(4-biphenyloxycarbonylphenyl methacrylate),[14] and so on, are the side chain liquid-crystalline polymers that exhibit mesomorphic properties without the presence of any flexible spacer.

In the previous studies, we reported the synthesis and characterization of chiral and cholesteric side chain liquid-crystalline polysiloxanes.[15–17] In this study, the synthesis of side chain cholesteric liquid-crystalline polyacrylates containing both 4-cholesteryl-4'-acryloyloxybenzoate (M_I) and 4-methoxyphenyl-4'-acryloyloxybenzoate (M_{II}) mesogenic side groups is

presented. The phase behavior and optical properties of these compounds are studied by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and thermogravimetric analyses (TGA). By quenching, the oily-streak texture and reflection colors of the polymers IP–VIP are fixed and the cholesteric polymer films are obtained. Moreover, the methods of the fixation of cholesteric phase and reflection colors by photocrosslinking and by thermal crosslinking are also studied.

Scheme 1 Synthetic routes of monomers.

EXPERIMENTAL

Materials

Acrylic acid was purchased from Shenyang Xinxi Chemical Reagent Company (China). 4-Hydroxybenzoic acid was purchased from Beijing Fuxing Chemical Industry Company (China). 4-Methoxyphenol was purchased from Shanghai Chemical Reagent Company (China). Cholesterol was purchased from Henan Xiayi Medical Company (China). Toluene used in the hydroxylation reaction was first refluxed over sodium and then distilled. All other solvents and reagents were purified by standard methods.

Experimental techniques

Fourier transform infrared (FTIR) spectra were measured on a Nicolet 510 FTIR spectrometer (Nicolet Instruments, Madison, WI). Polymer sample films used for measurements were obtained by casting on a KBr table. Phase transitions and thermodynamic parameters were determined with a Perkin-Elmer DSC-7 (Perkin–Elmer, Foster City, CA) equipped with a liquid nitrogen cooling system. Heating and cooling rates were 20°C/min. Phase transitions reported were collected during the second heating and cooling scans. The thermal stability of the polymers under nitrogen atmosphere was measured with a Perkin-Elmer TGA-7 thermogravimetric analyzer at a 20°C/min heating rate. A Leitz Microphot-FX (Leitz, Wetzlar, Germany) polarizing optical microscope equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe the phase transitions and to analyze mesophase for the liquid-crystalline pure compounds and polymers by observations of the optical textures. The inherent viscosities were measured with a Ubbelohde viscometer (No. 3-0.48), the flow times were sufficiently long (i.e., >100 s) so that kinetic energy corrections were neglected.

Synthesis of the monomers

The synthesis of vinyl monomers is carried out as shown in Scheme 1.
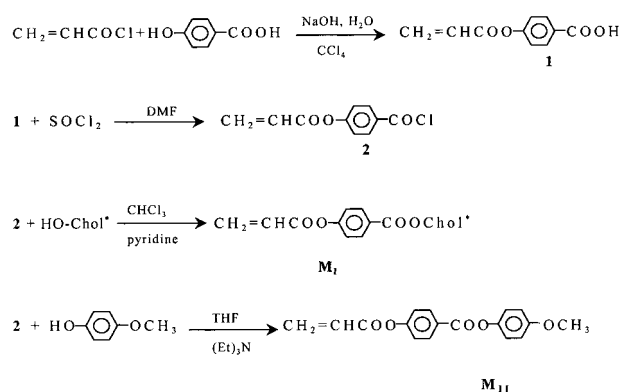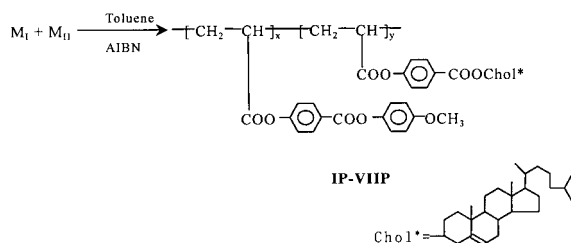
4-Acryloyloxybenzoic acid

First, 13.8 g (0.1 mol) of 4-hydroxybenzoic acid was dissolved in a mixture of 25 mL of carbon tetrachloride and 9.2 g of sodium hydroxide in 55 mL of water. Next, 0.12 mol of acryloyl chloride (laboratory synthesized) was added in a dropwise manner to the cold mixture. After stirring for 6 h at room temperature, the reaction mixture was neutralized with dilute hydrochloric acid. The resulting precipitate was filtered and washed with warm water, dilute hydrochloric acid, and water, successively. The crude product was recrystallized from ethanol. The white solid powders were obtained: mp 175°C; yield, 73%. IR (KBr) $\mu\sim$ (cm^{-1}): 2665, 2562 (COOH), 1732, 1691 (COO), 1635 (C$=$C), 1608, 1512 (Ar).

4-Acryloyloxybenzoyl chloride

First, 9.6 g (0.05 mol) of 4-acryloyloxybenzoic acid was reacted at 45–50°C with 30 mL of thionyl chloride containing a few drops of N,N-dimethylformamide for 10 h, and then the excess thionyl chloride was removed under reduced pressure to give the corresponding acid chloride. Yield, 98%.

4-Cholesteryl-4'-acryloyloxybenzoate (M$_I$)

First, 0.05 mol of 4-acryloyloxybenzoyl chloride was dissolved in 15 mL of dry chloroform, and then the mixture was added in a dropwise manner to a solution containing 19.4 g (0.05 mol) of cholesterol and 4 mL of pyridine in 100 mL of chloroform. The reaction mixture was stirred for 10 h at room temperature. The precipitate was removed by filtration, and the crude product was precipitated by adding ethanol to the filtrate and recrystallized from ethanol. A white solid powder was obtained: mp 120°C; yield, 48%. IR (KBr) $\mu\sim$ (cm^{-1}): 3065, 3034 ($=$C-H), 2943, 2863 (CH$_3$, CH$_2$), 1745, 1714 (COO), 1634 (C$=$C), 1605, 1510 (Ar).

Scheme 2 Synthetic routes of polyacrylates.

4-Methoxyphenyl-4'-acryloyloxybenzoate (M_{II})

First, 0.05 mol of 4-acryloyloxybenzoyl chloride was dissolved in 25 mL of dry tetrahydrofuran, and then the mixture was added in a dropwise manner to a solution containing 7.5 g (0.06 mol) of 4-methoxyphenol and 9 mL of triethylamine in 100 mL of dry tetrahydrofuran at 0–5°C. The solution was stirred for 5 h at room temperature, poured into a 3- to 4-fold excess of water, precipitated, filtered, and washed several times with dilute hydrochloric acid and warm water, successively. The crude product was recrystallized from ethanol. A white solid powder was obtained: mp 68°C; yield, 51%. IR (KBr) $\mu\sim$ (cm^{-1}): 3045, 3012 ($=$C-H), 2932, 2868 (CH$_3$, CH$_2$), 1742, 1712 (COO), 1632 (C$=$C), 1605, 1508 (Ar).

Synthesis of the polymers

The synthetic routes of the polymers are outlined in Scheme 2. All synthesized polymers are listed in Table I. The same method was adopted for the synthesis of polymers IP–VIIP. The synthesis of polymer IIIP is given as an example.

The polymer IIIP was synthesized by radical polymerization of the monomers M_I and M_{II} in dry, freshly distilled toluene using recrystallized α,α'-azobisisobutyronitrile (AIBN, 2 mol% to the monomers) as an initiator at 65°C for 48 h under nitrogen and anhydrous conditions. The polymer was obtained by precipitation with methanol. The crude polymer was dis-

solved in tetrahydrofuran, precipitated twice with methanol, and then dried at 40°C under vacuum. The yield and FTIR spectra were obtained.

IR (KBr) $\mu\sim$; (cm^{-1}): 2980, 2870 (CH$_3$, CH$_2$), 1743, 1715 (C$=$O), 1612, 1509(Ar), 1210 (COC).

RESULTS AND DISCUSSION

Texture analysis

In general, cholesteric liquid-crystalline at zero field exhibits two optically contrasting stable states: planar (including oily-streak and grandjean) texture and focal-conic texture. When a cholesteric liquid-crystalline is in the planar texture, the helical axis is perpendicular to the cell surface and the material Bragg-reflects colored light. When the liquid-crystalline is in the focal-conic texture, the helical axis is more or less parallel to the cell surface, and the material is forward-scattering and does not appear selective light reflection. If a cholesteric phase has a shorter helical pitch length than the wavelength of visible light, focal-conic texture is usually observed.

The optical textures of the polymers observed by POM with hot stage under nitrogen atmosphere are given in Table II. The visual observations under POM revealed that the monomer M_I exhibits cholesteric oily-streak texture and focal-conic texture during both its heating and cooling cycles. When M_I was heated to ~120°C, the sample started to melt and the mesomorphic phase appeared. As heating continued to 126°C, the obvious oily-streak texture and selective light reflection of the cholesteric phase appeared, and the texture and color of cholesteric phase disappeared at 225°C. When the isotropic state was cooled to 223°C, the focal-conic texture was formed and did not change until crystallization occurred at 106°C. However, during cooling from the isotropic melt, if a mechanical field was superimposed on the sample M_I, for example, slight shearing the melt caused macroscopic orientation of the cholesteric domains and the oily-streak texture and the property of selective light reflection

TABLE I
Polymerization, DSC, and TGA Data of the Polymers

| Sample | Feed | | | | DSC | | TGA |
	M_I (mol%)	M_{II} (mol%)	Yield (%)	η_{inh}[a] (dL/g)	T_g (°C)	T_m (°C)	$T_{5\,wt\%}$[b] (°C)
IP	100	0	94	0.08	—	156.6	264.7
IIP	95	5	92	0.09	129.1	157.8	257.6
IIIP	90	10	90	0.12	127.3	159.3	254.3
IVP	85	15	93	0.10	121.2	150.9	245.8
VP	80	20	91	0.14	117.4	147.9	253.9
VIP	75	25	92	0.15	116.6	144.2	250.4
VIIP	0	100	87	0.20	—	150.2	222.3

[a] Measured at 25°C in toluene.
[b] The temperature at which 5% mass loss occurred.

TABLE II
POM Data of the Polymers

Polymer	T_m (°C)	$T_r{}^a$ (°C)	$T_i{}^b$ (°C)	$T_{ai}{}^c$ (°C)	ΔT^d (°C)	LC Phase
IP	158	160	273	271	115	Ch
IIP	148	164	255	244	107	Ch
IIIP	150	167	260	257	110	Ch
IVP	143	168	269	268	126	Ch
VP	139	173	274	262	135	Ch
VIP	135	180	280	272	145	Ch
VIIP	147	—	>300	—	—	N

^a The temperature at which the reflection color occurred.
^b The temperature at which the birefringence disappeared completely.
^c The temperature at which the mesomorphic phase occurred.
^d The liquid crystalline range ($T_i - T_m$)

were exhibited. The monomer M_{II} displays characteristic nematic thread and schlieren textures. When M_{II} was heated to 68°C, thread texture appeared. As heating was continued to 84°C, the thread texture changed gradually to schlieren texture. The birefringence totally disappeared at 108°C. The schlieren and thread textures appeared again during cooling. The homopolymer IP displays cholesteric oily-streak texture and VIIP exhibits a normal nematic schlieren texture with its characteristic black threads. The copolymers IIP–VIP exhibit oily-streak texture during heating and focal-conic texture during cooling, whereas, focal-conic texture can change to oily-streak texture by shearing. The photomicrographs of IVP are shown in Figure 1 as an example. The type and texture of mesomorphic phase of the copolymers IIP–VIP do not change with a change in the concentration of M_{II} unit. However, the properties of selective light reflection are influenced not only by the structure of the mesogenic groups, but also by the copolymer composition, which is discussed in more detail in the next section.

Thermal analysis

The data of the phase transitions of the obtained monomers and polymers derived from DSC measurements and POM are summarized in Tables I–III. Representative DSC curves of the polymers, obtained on the second heating scan, are presented in Figure 2. From the data in Table III and the DSC thermogram, it is evident that the monomer M_I shows an endotherm peak at 122.7°C due to crystal–liquid crystal phase transition (T_m), and a second endotherm peak at 220.8°C corresponding to liquid crystal–isotropic transition (T_i). The monomer M_{II} shows two endotherm peaks corresponding to T_m at 71.0°C and T_i at 110.3°C. All phase transitions are reversible and do not change on repeated heating and cooling cycles. The phase transition temperatures noted in the DSC thermo-
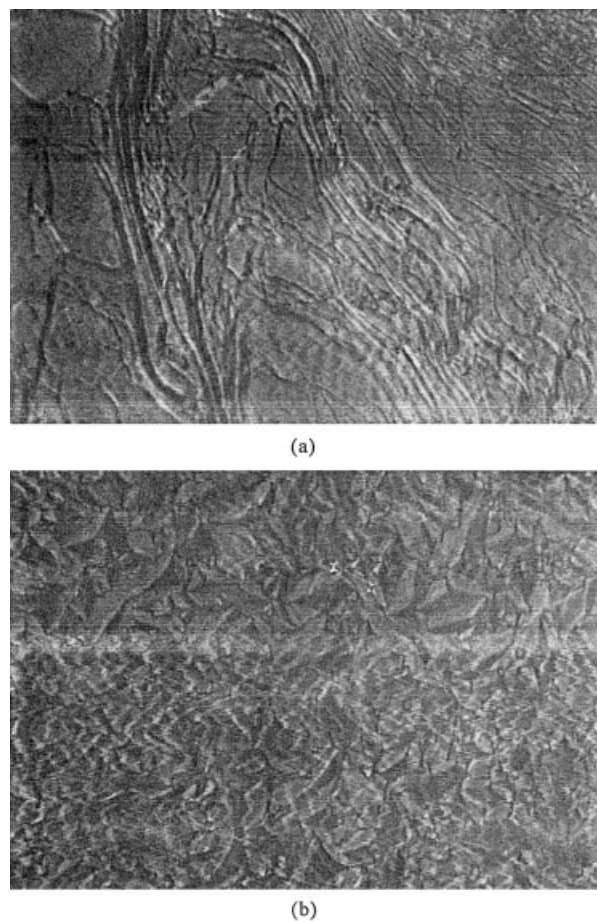

(a)

(b)

Figure 1 Optical polarizing micrographs of copolymers IVP (×320): (a) heating to 230°C; (b) cooling to 235°C.

grams are consistent with the mesomorphic transition temperatures observed by POM.

On the second heating scan of the copolymers IIP–VIP, common T_g and T_m values are observed. The sample becomes fluid at the latter temperatures. In contrast, on the second heating scan of the homopolymers IP and VIIP, only T_m is observed and an obvious T_g is not detected. Because of thermal degradation, the isotropization process of the cholesteric melt is not shown. Therefore, the isotropization temperatures are detected by POM.

TABLE III
Phase Transitions of the Monomers^a

Monomer	Phase Transitions, °C (Corresponding Enthalpy Changes in J/g) Heating / Cooling
M_I	K122.7(18.42)Ch220.8(1.14)I I213.8(0.49)Ch98.8(11.72)K
M_{II}	K71.0(45.76)N110.3(1.32)I I104.1(0.90)N

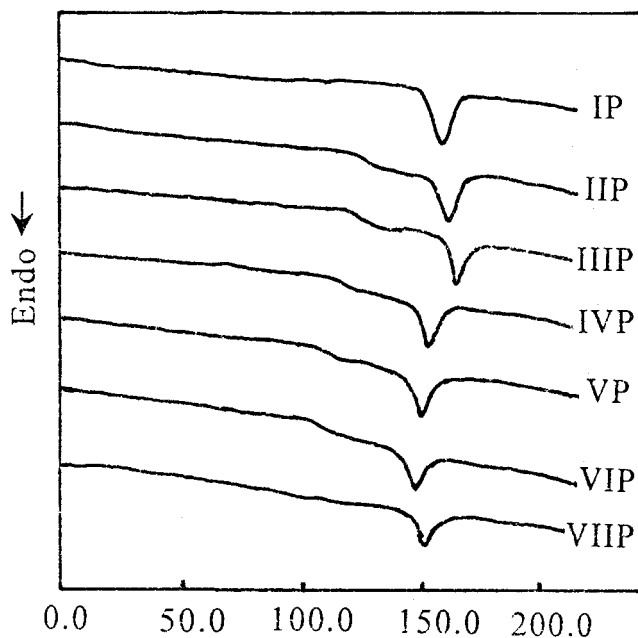^a K, solid; Ch, cholesteric; N, nematic; I, isotropic.

Figure 2 DSC thermograms of IP–IVP (second heating).

The T_g is an important parameter in connection with the structures and properties of the polymers. In general, the T_g value of the side chain liquid-crystalline polymers is strongly influenced by the polymeric chain flexibility, molecular weight, the mesogenic group, and the length of the spacer group. The results in Figure 3 show that the T_g values of IIP–VIP decrease with an increase in the concentration of mesogenic M_{II} units in the copolymers. As we know, T_g involves the mobility of chain segments, and the T_g value decreases with an increase in the mobility of chain segments. In the copolymers IIP–VIP, with an increase in the concentration of M_{II} units, the space steric hindrance decreases, which makes the chain flexibility increase. The increase in chain flexibility thus increases the mobility of chain segments and decreases the T_g value. From the data in Table I and the DSC curves, it is seen that the T_g values of IIP–VIP are 129.1–116.6°C. The reason for the higher T_g value is the bigger space steric hindrance and shorter spacer length of the mesogenic units. Compared with the T_g value of IIP–VIP, with an increase in the concentration of M_{II} units in the copolymers, the melting temperature (T_m) decreases, whereas, the isotropization temperature (T_i) increases and, consequently, the mesomorphic temperature range (ΔT) widens.

The TGA results show that the temperatures at which 5% mass loss occurred ($T_{5wt\%}$) of all the copolymers are >245°C, which shows that the synthesized side chain cholesteric liquid-crystalline copolyacrylates have better thermal stability.

Selective reflective of light

In the cholesteric phase, rod-like molecules are orientated, on the average, parallel to one another in a given plane. The direction of this orientation varies linearly with position in the direction normal to the plane, which results in a spatially periodic twisted helical structure that is responsible for the rod-like molecules to selectively reflect visible light and exhibit brilliant colors if the pitch of the cholesteric helix coincides with the wavelength of visible light. Because of the angular dependence of the reflection conditions, different observation angles lead to the observance of different colors. The wavelength of selective light reflection obeys the Bragg condition:

$$\lambda_m = 2nd \cos \phi = np \cos \phi \quad (1)$$

where n is the average refractive index of cholesteric phase, d is the lattice constant equal to $p/2$, p is the pitch of the cholesteric helix, and ϕ is the angle of incidence. When $\phi = 0°$ (normal incidence), then $\lambda_m = \lambda_0 = np$. The intensity of reflected light is a maximum at $\lambda_m = \lambda_0$, and it falls off very rapidly on either side of λ_0.[18] In reality, the orientation of the helices is not exactly perpendicular to the cell surface. Taking this orientation into account, eq. 1 changes to

$$\lambda_m = np \cos\left\{\frac{1}{2}\left[\sin^{-1}\left(\frac{\sin \alpha}{n}\right) + \sin^{-1}\left(\frac{\sin \beta}{n}\right)\right]\right\} \quad (2)$$

where α and β are the angle of incidence and observation angle, respectively.[19]

Although the microscopic origins of pitch are still a subject of study,[20] it is known that the helical pitch of
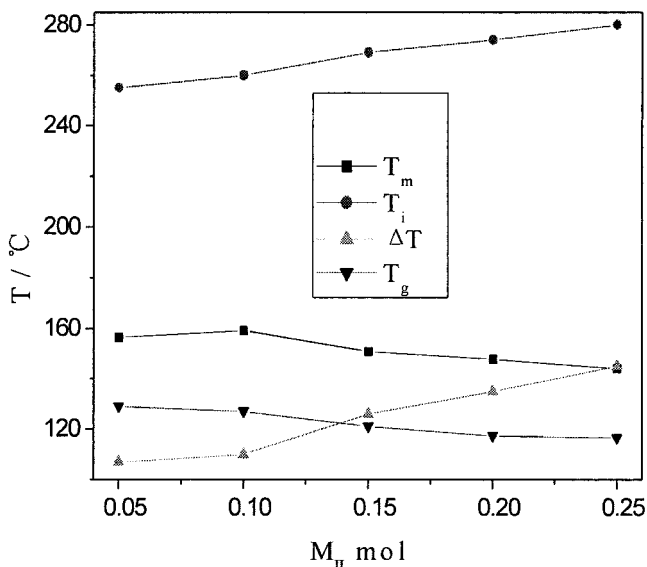

Figure 3 The phase transition temperature depending on M_{II} content of IIP—VIP.

cholesteric phase and the reflected colors mainly depend on the polymer structure, the temperature, and the copolymer composition. In the polymers IP–VIP, the helical pitch length decreases with increasing temperature, so the reflection wavelength of cholesteric phase is also temperature dependent. On heating, a blue shift of the reflection wavelength is observed. The temperature dependence of the pitch cannot be calculated because the controlling factors are currently unknown. The pitch length and the reflection wavelength for the copolymers increase with increasing composition of M_{II} units. Moreover, the observation angle, the outer field, and the thick of cholesteric film can also affect the reflection colors of the cholesteric phase.

The polymers IP–VIP change color from red to blue between T_r and T_i, but the main reflection color of IP is green and that of IIP–VIP is red. Cholesteric polymer films with different reflection and transmission colors were obtained by bringing the molten polymers to the temperature just below T_i, which was accomplished by uniaxially shearing of the polymer that was covered with a glass slide and in a uniform orientation. The "locked" color and texture do not change before reaching T_m. At present, the obtained cholesteric films with different colors are being studied as dye pigments or "copy safe" color for documents.

CONCLUSIONS

In this study, a series of side chain cholesteric liquid-crystalline polyacrylates containing both 4-cholesteryl-4'-acryloyloxybenzoate (M_I) and 4-methoxyphenyl-4'-acryloyloxybenzoate (M_{II}) mesogenic side groups were prepared successfully. The synthesized copolymers IIP–IVP exhibit cholesteric oily-streak texture and focal-conic texture, and all optical textures are reversible and do not change on repeated heating and cooling cycles. The obtained cholesteric polymer films have selective light reflection in the visible spectral ranges.

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