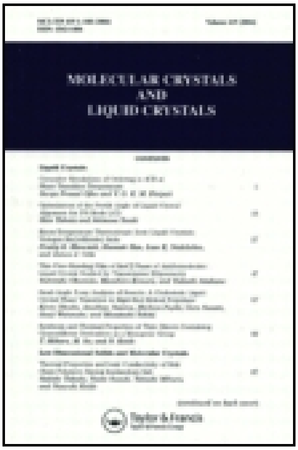

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PHOTOPOLYMERIZATION IN CHOLESTERIC MESOPHASES

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Cholesteric liquid crystalline monomers undergo efficient photopolymerization to "freeze in" the planar texture characteristic of low molar mass cholesteric liquid crystals. The monomers consist of polymerizable moieties separated from the cholesteryl mesogens by flexible spacer groups. Individual monomers and mixtures give homopolymers and copolymers, respectively, that exhibit cholesteric textures to within 10 to 15°C of the isotropic transition.

1. INTRODUCTION

The helicoidal structure of cholesteric mesophases results in unusual optical properties, including the selective reflection of visible light and circular dichroism[1]. Polymers exhibiting cholesteric optical properties have been prepared and elegantly characterized by Finkelmann in collaboration with Ringsdorf and Rehage[2-7]. The general approach was to prepare the polymers in solution (by radical polymerization or addition of mesogens to a polymer backbone), and then to align the polymers to obtain the desired planar cholesteric textures. This works well for polymers with twisted nematic structures but, with one exception[2], monomers consisting of only cholesteryl ester mesogens have failed to give polymers with cholesteric optical properties[8-12]. In all cases smectic structures have dominated the mesophases of these polymers.

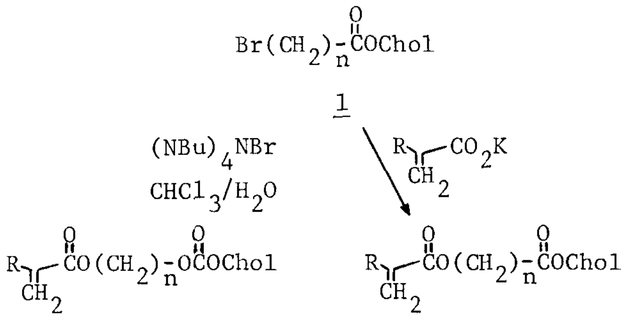
An alternative approach to polymers with cholesteric properties is to align mesogenic material in a desired orientation and then perform the polymerization, hoping that the process does not alter the order in the mesophase. Liebert and Strzelecki[13,14] showed that the cholesteric structure of twisted nematic phases could be "frozen in" by rapid polymerization in the presence of crosslinkers, and lyotropic mesophases consisting of poly(γ-butyl-L-glutamate) have been photopolymerized without destruction of the cholesteric optical properties[15]. However, polymerizations initiated in the mesophases of cholesteryl ester mesogens have more frequently led to phase separation and the formation of amorphous or smectic polymers[16].

We show here that cholesteryl carbonates 2 and esters 3 undergo efficient photopolymerization to "freeze in" the planar texture characteristic of low molar mass cholesteric liquid crystals.

2. RESULTS AND DISCUSSION

The synthesis and phase transitions of cholesteryl carbonates 2 and esters 3 have been described[17-19]. The phase transfer conditions we used to incorporate the acrylate moiety into esters 3 make a wide variety of these materials readily available.

Cholesteric mesophases are characterized by their ability to reflect light selectively in the infrared, visible, and ultraviolet region. The wavelength of maximum



Chol = cholesteryl

	n	R		n	R
2a	6	CH_3	3a	10	CH_3
2b	2	CH_2	3b	5	CH_3
2c	6	H	3c	3	CH_3
2d	2	H	3d	10	H
			3e	5	H
			3f	3	H

reflection (λ_R) is related directly to the helical pitch (p) and the mean index of refraction ($\bar{n}$) of the cholesteric mesophase by $\lambda_R = \bar{n}p$[1]. The pitch is sensitive to changes in temperature or composition of the mesophases so λ_R can be controlled with these functions. The mesophases also are circularly dichroic at λ_R[1]. Light impinging on a cholesteric mesophase is split into two circularly polarized components; one is totally transmitted and the other is totally reflected by the mesophase at λ_R.

The cholesteric color response of monomers 2 and 3 and selected mixtures of the monomers are listed in Tables I and II. All monomers exhibit at least monotropic cholesteric phases and general trends in the color response of

TABLE I Temperature ranges for the cholesteric color responses of monomers 2 and 3.

Monomer	n	R	Temp. Range (°C)[a]	Color Response[b]
3a	10	CH_3	55.8 - 55.3	v - r
3d	10	H	59.2 - 57.8	v - r
3e	5	H	48.5 - 33.0	v - o
3f	3	H		colorless
2a	6	CH_3	51 - 0	v
2b	2	CH_3		colorless

[a] Measured in a cooling cycle

[b] v = violet; o = orange; r = red

TABLE II Temperature ranges for cholesteric color responses of mixtures of monomers 2 and 3.

Monomers[a]	n	R	Temp. Range (°C)[b]	Color Response[c]
3a:3d	10,10	CH_3,H	56.5 - 55.9	v - r
3d:3f	10,3	H	68 - -15	v - o
3d:3f[d]	10,3	H	65.5 - -15	v - or
3a:2b[d]	10,2	CH_3	37 - 0	g - r

[a] Mixtures are 1:1 by weight

[b] Measured in a cooling cycle

[c] v = violet; o = orange; g = green; r = red

[d] 1% Irgacure 651 added

the monomers are observed. Monomers with long alkyl chains reflect light of the entire visible spectrum over narrow temperature ranges. Monomers of intermediate alkyl chain length exhibit nearly full color responses in relatively broad temperature ranges, and monomers with short alkyl chains reflect only infrared light. Exceptions are carbonates 2a and 2c, which exhibit only violet color responses.

Mixtures of two monomers with the same alkyl chain length have cholesteric color ranges similar to the individual monomers. However, a mixture of monomers having different alkyl chain lengths exhibits color responses over significantly broader temperature ranges (Table II). Addition of Irgacure 651 (1% by wt.) to a monomer mixture decreases the temperature range of the color response as expected, but this is of little consequence for compositions with broad color response ranges.

The photopolymerization was most convenient to study with mixtures of two monomers having broad cholesteric mesophases. Some mesophases derived from single monomers could be photopolymerized but others underwent crystallization or exhibited narrow color responses. Samples of the monomers were prepared by heating the monomer components and photoinitiator (1% by wt.) to a melt and aligning the resulting viscous fluid between glass plates separated by a 0.6 mm spacer. The films were placed in a thermostatted water bath and irradiated with a 450 W Hg arc lamp. In all cases the polymerization was rapid; 30 seconds irradiation gave 70 to 80% conversion to polymer as determined by monomer recovery. Most of the polymers are soluble in tetrahydrofuran; and $\overline{M}_w$, as determined by GPC (based on a narrow distribution polystyrene standard), is about 1.5 x

10^5 for the poly(acrylates) and 7.0 x 10^5 for the poly(methacrylates).

The compositions of several cholesteric mesophases and the dimensions of their cholesteric reflection bands before and after photopolymerization are listed in Table III. Although only acrylate monomers are listed, methacrylate monomers have been shown to perform in a similar manner. Polymers with λ_R ranging throughout the visible region were prepared by photopolymerization of various compositions. Optical microscopy showed virtually no change in the planar cholesteric texture, and most compositions exhibited no change in λ_R upon polymerization of well-aligned cholesteric mesophases. In some cases, the percent transmittance (% T) and the width of the reflection band increased slightly. Most mesophases are found to exhibit somewhat less than the expected 50% transmittance at λ_R (circular dichroism) because outside the reflection band the mesophases exhibit less than 100% transmittance. Changing the temperature of the cholesteric mesophase before polymerization gave a concomitant shift of λ_R in the polymer. A composition of 3d:3f (1:1) was photopolymerized at 18, 27, and 40°C to give polymers exhibiting λ_R at 580, 517, and 500 nm, respectively. Figure 1 shows a cholesteric reflection band of 2c before and after photopolymerization of the mesophase.

Table IV lists the percent conversions, glass transitions and cholesteric-isotropic transitions of acrylate polymer films. It should be noted that the polymer films are actually mixtures of polymer and unreacted monomer. Since the monomer may act as a plasticizer, the glass transitions and isotropic points may vary with the degree of polymerization. Extending the irradiation time to five

TABLE III Cholesteric reflection bands for monomer compositions before and after photopolymerization.

		Monomer Film			Polymeric Film		
Composition[a]	Temp. (°C)	λ_{max} (nm)	% T	W-90[b] (nm)	λ_{max} (nm)	% T	W-90 (nm)
2c	26	428	49	23	426	48	24
3e	35		c		482	47	50
3d:3f (1:1)	27	516	44	31	517	46	35
3d:2d (1:1)	24	648	49	52	648	50	52

[a] All compositions contain 1% Irgacure

[b] Width of reflection band at 90% of band height

[c] Not measured

TABLE IV Glass transitions and cholesteric-isotropic transitions of cholesteric polymers.

		DSC		Microscopy
Composition[a]	Conversion[b] (%)	Tg (°C)	C-I[c] (°C)	C-I (°C)
2c	70	25	144[d]	152
3e	77	28	180	188
3d:3f (1:1)	69	33	142	150
3d:2d (1:1)	67	23	118	120

[a] Monomer compositions contain 1% Irgacure 651

[b] Determined by isolation of unreacted monomer after 30 seconds irradiation

[c] Temperature given corresponds to the minimum of the endothermal curve in the initial heating cycle

[d] A weak endotherm at 80-120°C also was observed

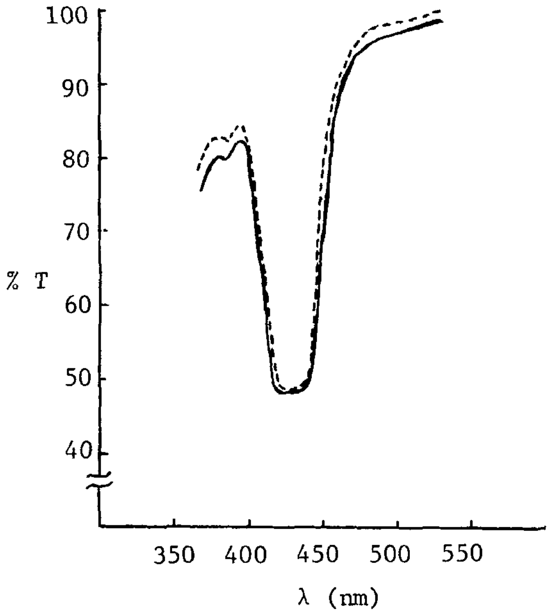


FIGURE 1 Cholesteric reflection band of 2c before (——) and after (---) photopolymerization.

minutes increases the percent conversion, but the polymerization levels off at about 85% conversion. The isotropic transitions increase, but the effect is not always large. For example, irradiation of acrylate 2c for 30 and 300 seconds gives 70 and 85% conversion to polymer and C-I transitions of 152 and 155°C, respectively. DSC and optical microscopy indicate that the remaining monomer probably undergoes further polymerization at elevated temperatures. The isotropic transition is always 5 to 10 degrees higher in the reheat cycle than in the initial heating cycle.

The cholesteric optical properties of the polymers have remained unchanged for a year under ambient conditions. The polymer films can be heated to 100°C with little change in λ_R over short periods of time. About 10°C below the isotropic transition, the polymers rapidly lose their color.

When the clear isotropic liquid, obtained on heating the polymers above the cholesteric-isotropic transition, is cooled, a nondescript texture usually forms that does not selectively reflect visible light. The textures are reminiscent of those of Shibaev's smectic polymers that were prepared by solution polymerization[11,12]. This suggests that the cholesteric structure is metastable, and heating to the isotropic transition allows the polymer to reorganize to a more ordered smectic structure upon cooling. This is supported by X-ray diffraction data. The initial polymer film derived from acrylate 2c shows no reflections other than a broad peak at 5.5 Å. After cooling from the isotropic melt, the diffraction pattern of the polymer film shows two new peaks: a sharp, intense peak at 30 Å and a weaker one at 19 Å. These reflections correspond well with those observed by Shibaev in his smectic polymers[11,12]. There are exceptions to this behavior. The polymer derived from 3d:3f (1:1) after five minutes' irradiation, when cooled from the isotropic melt, still exhibits a planar texture and reflects visible light. However, the polymer also is insoluble in organic solvents, suggesting that the retention of the cholesteric planar texture upon cooling may be a function of the degree of crosslinking in the film.

To summarize, cholesteric mesophases have been photopolymerized to "freeze in" the cholesteric planar texture. The resulting films are mixtures of polymer and monomers that have maintained stable optical properties for a year under ambient conditions. In the absence of crosslinking the planar texture dissipates irreversibly when the films are heated past the C-I transition. The photopolymerization of mesophases may be an attractive method to fix order in other polymer systems.

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REFERENCES

1. J. L. Fergason, Mol. Cryst., 1, 293 (1966).
2. H. Finkelmann, H. Ringsdorf, W. Siol, and J. H. Wendorff, Makromol. Chem., 179, 829 (1978).
3. H. Finkelmann, J. Koldehoff, and H. Ringsdorf, Angew. Chem. Int. Ed. Engl., 17, #12 935 (1978).
4. H. Finkelmann and G. Rehage, Makromol. Chem., Rapid Commun., 1, 31 (1980).
5. H. Finkelmann and G. Rehage, Makromol. Chem., Rapid Commun., 1, 733 (1980).
6. H. Finkelmann, H. J. Kock and G. Rehage, Makromol. Chem., Rapid Commun., 2, 317 (1981).
7. H. Finkelmann and G. Rehage, Makromol. Chem., Rapid Commun., 3, 859 (1982).
8. A. Blumstein, S. B. Clough, and E. C. Hsu, J. Polym. Sci., Polym. Lett. Ed., 15, 545 (1977).
9. A. Blumstein and Y. Osada, J. Polym. Sci., Polym. Lett. Ed., 15, 761 (1977).
10. V. P. Shibaev, N. A. Plate, and Ya. S. Freidzon, J. Polym. Sci., Polym. Chem. Ed., 17, 1655 (1979).
11. V. P. Shibaev, A. V. Kharitonov, Ya. S. Freidzon, and N. A. Plate, Polymer Sci. USSR, 21, 2044 (1980).
12. Ya. S. Freidzon, V. P. Shibaev, A. V. Kharitonov, and N. A. Plate, Advances in Liquid Crystal Research and Applications, L. Bata, Ed., (Pergamon Press, Oxford, 1980).
13. L. Liebert and L. Strzelecki, Bull. Soc. Chim. Fr., 597, 603 (1973).
14. L. Liebert and L. Strzelecki, and D. Vacogne, Bull. Soc. Chim. Fr., 2073 (1975).
15. T. Tsutsui and R. Tanaka, Polymer, 21, 1351 (1981).
16. F. Cser, K. Nyitrai, and G. Hardy, Mesomorphic Order in Polymers, A. Blumstein, Ed., (ACS Sym. Ser., 74, Washington, 1978) p. 95.
17. P. J. Shannon, Macromolecules, 16, 1677 (1983).
18. P. J. Shannon, Macromolecules, in press (1984).
19. Ya. S. Freidzon, A. V. Kharitonov, V. P. Shibaev, and N. A. Plate, Mol. Cryst. Liq. Cryst., 88, 87 (1982).