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Notes

Photopolymerization in Cholesteric Mesophases

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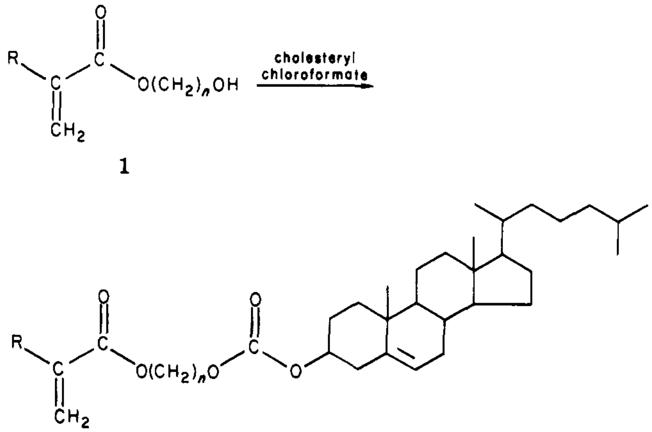
We have been interested in the synthesis of polymeric liquid crystals that exhibit the optical properties of low molar mass cholesteric liquid crystals.[1] The early work of Liebert and Strzelecki[2] indicated that the cholesteric structure of twisted nematic phase could be "frozen-in" by rapid polymerization in the presence of high amounts of cross-linkers. Similarly, lyotropic cholesteric mesophases consisting of poly(γ-butyl L-glutamate) and triethylene glycol dimethacrylate have been photopolymerized without destruction of the cholesteric optical properties.[3] Ringsdorf et al.[4] demonstrated that cross-linking was not necessary in order to maintain cholesteric propertes in a polymer. Through use of the concept of flexible spacer groups to decouple the meseogenic units from the restrictions of the main polymer chain, they found a 1:1 methacrylate copolymer consisting of cholesteryl esters with spacer groups of different lengths that exhibited cholesteric properties. Polymers exhibiting cholesteric properties also were obtained by copolymerization of nematic monomers with small amounts of chiral mesogenic monomers.[5] Extending the idea of flexible spacer groups, Finkelmann and Rehage[6-8] prepared several cholesteric polysiloxanes by using cholesteric esters as the chiral component in formation of twisted nematic phases. The same group also demonstrated that polymerization of chiral monomers that normally do not exhibit a liquid crystalline state can give homopolymers that exhibit cholesteric properties.[9] Recently, thermotropic polymers based on derivatives of (2-hydroxypropyl)cellulose also have been shown to exhibit cholesteric optical properties.[10-13]

With one notable exception,[4] monomers consisting of only cholesteryl ester mesogens, with or without flexible spacer groups, have failed to give polymers that exhibit cholesteric properties. In all cases the smectic structures have dominated the liquid crystalline phase of the polymers.[14-18] Polymerization of mesogenic monomers stabilizes the liquid crystalline state, and the polymers exhibit a higher degree of order than the monomers.[9] To circumvent the preference for smectic structures in polymers containing cholesteryl esters mesogens, polymerizations have been initiated in the cholesteric mesophases of the monomers. However, in all cases that do not involve extensive cross-linking, phase separation has resulted in amorphous or smectic polymers.[19]

We report here that cholesteric liquid crystalline monomers of structure **2** and **3**, in combination with suitable photoinitiators, undergo efficient photopolymerization to "freeze-in" the planar texture characteristic of low molar mass cholesteric liquid crystals.

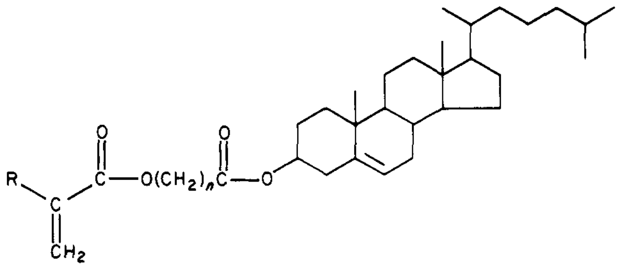
Results and Discussion

The synthesis and phase transitions of the cholesteryl esters **3** have been described.[20] Monomers with cholesteryl carbonate moieties (**2**) were prepared by acylation of hydroxyalkyl acrylates or hydroxyalkyl methacrylates with cholesteryl chloroformate (eq 1). The phase transitions and spectral data for monomers **2** are listed in the Experimental Section.



2a, $n = 6$, R = CH_3
b, $n = 2$, R = CH_3
c, $n = 6$, R = H
d, $n = 2$, R = H

(1)



3a, $n = 10$, R = CH_3
b, $n = 5$, R = CH_3
c, $n = 3$, R = CH_3
d, $n = 10$, R = H
e, $n = 5$, R = H
f, $n = 3$, R = H

Cholesteric mesophases typically are characterized by their ability to reflect light selectively in the infrared, visible, and ultraviolet regions. The wavelength of maximum 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 may be quite sensitive

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Table I
Temperature Ranges for the Cholesteric Color Responses of Monomers 2 and 3

monomer[a]	n	R	temp range,[b] °C	color response[c]
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
3d:3f	10, 3	H	+68 to −15	v–o
3d:3f[d]	10, 3	H	+65.5 to −15	v–or
2a	6	CH_3	51–0	v
2b	2	CH_3		colorless
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.

Table II
Cholesteric Reflection Bands for Monomer Compositions before and after Photopolymerization

		monomer film			polymeric film		
comp[a]	film temp, °C	λ_{max}, nm	% T	W-90,[b] nm	λ_{max}, nm	% T	W-90,[b] nm
2a	27	430	45	23	430	46	22
2c	26	428	49	23	426	48	24
3b	35		*c*		475	42	57
3e	35		*c*		482	47	50
3a:3c (1:1)	27	558	42	33	570	48	43
3d:3f (1:1)	27	516	44	31	517	46	35
3a:2b (1:1)	25	612	48	39	612	48	43
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.

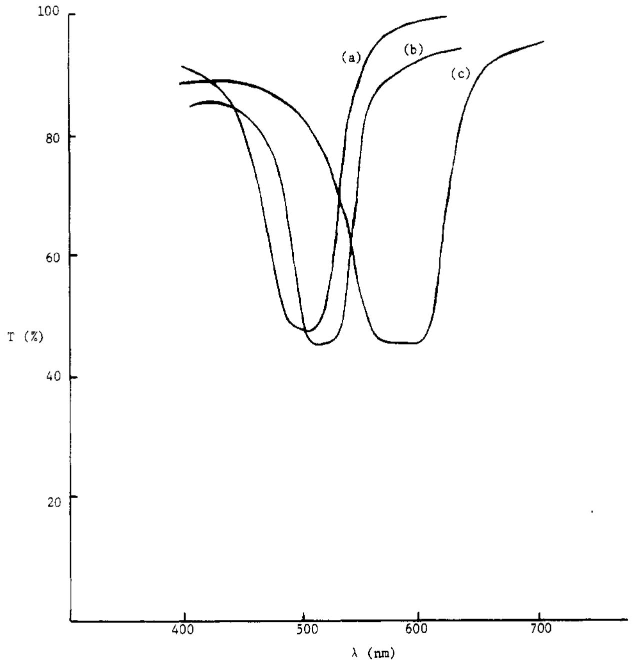

Figure 1. Transmission spectra of films prepared from a composition of **3d:3f** (1:1) photolyzed at various temperatures: (a) 40 °C; (b) 27 °C; (c) 18 °C.

to changes in temperature or composition of the mesophase and, as a result, the wavelength of maximum reflection can change significantly with changes in temperature or composition. The width of the reflection band ($\Delta\lambda$) is given by $\Delta\lambda = (\Delta n/\bar{n})\lambda_R$, where Δn is the birefringence ($n_0 - n_e$) of the sample.[1] Thus, the width of the reflection band also is dependent on the temperature and composition of the cholesteric mesophase. Mesophases of cholesteryl alkanoates typically show a decrease in λ_R with increasing temperature; a cholesteric mesophase reflecting red light will shift the reflection band toward the violet with increasing temperature.

The cholesteric color response ranges of the monomers 2 and 3 and selected mixtures of these monomers are listed in Table I. Two items are noteworthy. A mixture of monomers having different alkyl chain lengths exhibits color responses over broader temperature ranges than individual components. And, addition of Irgacure 651 (1% by weight) to a monomer mixture decreases the temperature range of the cholesteric color response, but this is of little consequence in composition exhibiting broad color response ranges. Although some cholesteric mesophases derived from single monomers could be photopolymerized, many mesophases underwent crystallization or exhibited only narrow cholesteric color ranges. Mixtures of two monomers, with broad cholesteric mesophases, were most convenient to study.

Samples of the monomers in their cholesteric mesophases were prepared by heating a mixture of the monomer components and photoinitiator (1% by weight) to a melt and aligning the resulting viscous fluid between glass plates separated by a 0.6-mm spacer. The monomer films were placed in a thermostated water bath and irradiated with a 450-W Hg arc lamp. In all cases the polymerization was rapid; 30-s irradiation gave 70–80% conversion to polymer as determined by gravimetric techniques. Most of the polymers are soluble in tetrahydrofuran, and $\bar{M}_w$, as determined with GPC (based on a narrow-distribution polystyrene standard), is about 150 000 for the polyacrylates and higher for the polymethacrylates.

Table II lists the monomer compositions of several cholesteric mesophases and the dimensions of their cholesteric reflection band before and after photopolymerization. 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. 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).

Because cholesteric mesophases are circularly dichroic, unpolarized 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 cholesteric mesophase at λ_R.[1] Thus, a well-aligned cholesteric mesophase at λ_R should exhibit 50% transmittance. In practice, most cholesteric mesophases are found to exhibit somewhat less than 50% transmittance at λ_R because outside the relection band the mesophase exhibit less than 100% transmittance. If the transmittance outside the reflection band is considered, then the percent transmittance at λ_R is found to be very close to half the value.

Table III lists the glass transitions and cholesteric–isotropic transitions of the cholesteric polymer films. The isotropic transitions of most of the polymers are between 120 and 150 °C, with the acrylate polymers generally exhibiting higher isotropic points than the methacrylates. The isotropic transition measured by optical microscopy is 5–10 °C higher than the minimum of the endothermal curve as determined by DSC. It should be noted that the polymer films are actually mixtures consisting of polymer and unreacted monomer. Since the monomer may act as

Table III
Glass Transitions and Cholesteric-Isotropic Transitions of Cholesteric Polymers

		DSC		
comp[a]	conv,[b] %	T_g, °C	C-I transition,[c] °C	opt microscope C-I transition, °C
2a	72	21	131	139
2c	70	25	144[d]	152
3b	85	39	168	183
3e	77	28	180	188
3a:**3c** (1:1)	77	43	132	143
3d:**3f** (1:1)	69	33	142	150
3a:**2b** (1:1)	71	48	130[d]	135
3d:**2d** (1:1)	67	23	118	120

[a] Monomer compositions contain 1% Irgacure 651. [b] Determined by isolation of unreacted monomer after 30-s 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.

Table IV
Effect of Extended Irradiation on the Percent Conversion and Cholesteric-Isotropic Transitions of Polymer Films

comp[a]	irrad time, s	conv,[b] %	C-I transition,[c] °C
2c	30	70	152
	300	85	155
3d:**3f** (1:1)	30	69	150
	120	83	149
	300	86	151
3d:**2d** (1:1)	30	67	120
	120	77	130
	300	81	134

[a] Monomer compositions contain 1% Irgacure 651. [b] Determined by isolation of unreacted monomer. [c] Determined with optical microscope.

a plasticizer, the glass transitions and isotropic points may vary with the degree of polymerization. As Table IV indicates, longer irradiation time increases the degree of polymerization in the films to some extent. The isotropic transitions also increase but the effect is not always a large one. DSC and optical microscopy indicate that the remaining monomer probably undergoes further polymerization at elevated temperatures. The isotropic transition is always 5–10 °C higher in the reheat cycle than in the initial heating cycle.

The cholesteric optical properties of the polymers have remained unchanged for 1 year under ambient conditions. The polymer films can be heated to 100 °C with little change in λ_R over short periods of time.[21] About 10 °C below the isotropic transition (optical microscopy) 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.[22] There are exceptions to this; the polymer derived from **3b** exhibits a well-defined focalconic texture when cooled from the isotropic melt, and the polymer derived from **3d**:**3f** (1:1) after 5-min irradiation still exhibits a planar texture and reflects visible light when cooled from the isotropic melt. However, the latter polymer film also is insoluble in organic solvents, suggesting that, in this case, the retention of the cholesteric planar texture upon cooling from the isotropic melt may be a function of the degree of cross-linking in the film.[23]

To summarize, cholesteric mesophases have been photopolymerized to "freeze-in" the cholesteric planar texture typical of low molar mass cholesteric liquid crystals. The resulting films are mixtures of polymer and monomers that maintain stable cholesteric optical properties for up to 1 year under ambient conditions. The photopolymerization of mesophases demonstrated here may be an attractive method to fix structure in other polymer systems.

Experimental Section

Materials. Commercial samples of 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, and cholesteryl chloroformate were used without purification. The monoacrylate and monomethacrylate of 1,6-hexanediol were prepared by heating 6-bromohexanol with potassium acrylate or potassium methacrylate in dimethylformamide. The monoacrylate was isolated from the solvent by distillation in a Kugelrohr apparatus at 0.5 mmHg. The cholesteryl esters **3** were prepared as described earlier.[20] Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone) was the photoinitiator.

Cholesteryl 2-(Methacryloyloxy)ethyl Carbonate (2b). Typical Procedure. To a solution of 2-hydroxyethyl methacrylate (7.80 g, 60 mmol) and pyridine (3.5 g, 44 mol) in dichloromethane (40 mL) was added dropwise a solution of cholesteryl chloroformate (18.0 g, 40 mmol) in dichloromethane (40 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred 6 h. The mixture was diluted with dichloromethane (250 mL), washed with 1 N hydrochloric acid (60 mL), washed with water, and dried over magnesium sulfate. Concentration gave a solid, which was recrystallized from acetone–ethanol (1:1) to give **2b**: 17.8 (82%); mp 80–81 °C.

Table V
Physical and Spectroscopic Data of Carbonates 2

product no.	*n*	R	yield, %	phase transitions,[a,b] °C	IR ($CHCl_3$) ν, cm^{-1}	^1H NMR ($CDCl_3/Me_4Si$) δ, ppm
2a	6	CH_3	68	k 58.5–60 i (51.0 c)	1740 1715 1640	2.15–0.65 (m, 52 H), 2.40 (m, 2 H), 4.10 (d, of t, 4 H), 4.45 (m, 1 H), 5.4 (m, 1 H), 5.53 (m, 1 H), 6.1 (m, 1 H)
2b	2	CH_3	82	k 80–81 i (40.1 c)	1740 1715 1635	2.15–0.65 (m, 44 H), 2.40 (m, 2 H), 4.36 (m and s, 5 H), 5.4 (m, 1 H), 5.6 (m, 1 H), 6.15 (m, 1 H)
2c	6	H	62	k 52 c 62 i	1740 1720 1635 1615	2.15–0.65 (m, 49 H), 2.4 (m, 2 H), 4.10 (m, 4 H), 4.45 (m, 1 H), 5.4 (m, 1 H), 6.55–5.70 (m, 3 H)
2d	2	H	81	k 85.8–87 i (56.0 c)	1735 1635 1615	2.15–0.65 (m, 41 H), 2.4 (m, 2 H), 4.35 (m and s, 5 H), 5.38 (m, 1 H), 6.6–5.70 (m, 3 H)

[a] All compounds gave satisfactory C and H analysis. [b] Transition temperatures: k = crystal; c = cholesteric; i = isotropic; transitions in parentheses are monotropic.

Photopolymerizations. The monomer compositions were mixed with Irgacure 651 (1% by weight), melted, and aligned between rubbed glass plates separated by a 0.6-mm spacer. The films were submerged 0.5 in. in a thermostated water bath and positioned 9 in. from a 450-W Hg arc lamp for 30 s.

Optical and Thermal Measurements. A Perkin-Elmer 552 UV/vis spectrophotometer was used to measure the reflectance spectra of the materials as "apparent absorbance". Spectra were measured in the transmittance mode with Nujol in the reference cell. The DSC measurements were recorded with a Du Pont Model 900 thermal analyzer. Mesophase ranges were measured with a Leitz optical microscope using a Mettler FP5 and FP52 temperature control.

Acknowledgment. The author thanks A. G. Geigley for NMR measurements, C. R. Foltz and B. J. Roye for DSC measurements, S. M. Kolibab for GPC measurements, and J. L. Edwards for technical assistance.

Registry No. 2a, 89734-62-3; **2a** (homopolymer), 91210-48-9; **2b**, 68091-11-2; **(2b)·(3a)** (copolymer), 91210-49-0; **2c**, 89734-64-5; **2c** (homopolymer), 91210-50-3; **2d**, 89734-63-4; **(2d)·(3d)** (copolymer), 91210-51-4; **3a**, 53816-29-8; **(3a)·(3c)** (copolymer), 91228-85-2; **3b**, 77225-90-2; **3b** (homopolymer), 77222-09-4; **3c**, 86689-87-4; **3d**, 79679-30-4; **(3d)·(3f)** (copolymer), 91228-86-3; **3e**, 79679-29-1; **3e** (homopolymer), 79702-51-5; **3f**, 86689-89-6; 2-hydroxyethyl methacrylate, 868-77-9; cholesteryl chloroformate, 7144-08-3.

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(21) Finkelmann and Rehage found that the optical properties of cholesteric poly(siloxanes) were also insensitive to changes in temperature below the isotropic transition.[7]
(22) The fine-grained textures are reminiscent of Shibaev's smectic polymer textures.[18] **Note Added in Proof**: X-ray diffraction data on the polymer film derived from **2c**, obtained after cooling from the isotropic melt, corresponds well with a smectic structure. This suggests that the cholesteric structure is metastable and heating to the isotropic transition allows the polymer to reorganize to a more stable smectic structure upon cooling.
(23) Addition of cross-linking agents to the monomer compositions also produces polymers that regenerate the cholesteric planar texture upon cooling from the isotropic melt.

"Zipper" Crystallization of Polymers with Spiropyran Side Groups

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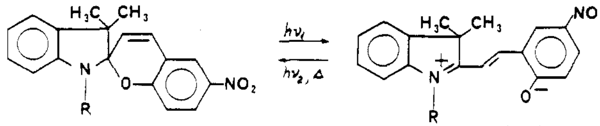
The transformation of spiropyrans into merocyanine dyes



A (spiropyran) B (merocyanine)

leads to substantial structural changes of macromolecules containing spiropyran groups (see references in previous papers[1,2] and ref 3). In particular, the capability of the merocyanine dyes to aggregate into giant molecular stacks[4] is a driving force for a new type of crystallization of atactic polymethacrylate bearing spiropyran side groups which was reported in a previous work.[1] A polymer of up to 40% crystallinity was obtained by slow evaporation of solvent from methyltetrahydrofuran (MTHF) solution of the polymer or by swelling of the amorphous polymer in this solvent. The crystallization of the polymer occurs cooperatively with the spiropyran–merocyanine conversion. The following crystallization mechanisms has been proposed: Slow precipitation of the polymer in MTHF leads to partial spiropyran–merocyanine conversion. This in turn results in incorporation of the merocyanine side groups into *inter*molecular stacks, with alternate antiparallel alignment of their molecular dipoles. Further development of this process brings about formation of crystalline domains, and the spiropyran side groups attached to the segments of the polymer chain adjacent to a domain are brought closer together. This and the increase of the polarity in the surroundings of the domains promote further solvatochromic spiropyran–merocyanine conversion followed by stacking of merocyanines and hence further ordering of the macromolecules. Evidently the ordering can proceed in the polymer only in the presence of solvent which enables segmental movement.

The important feature of this process is the mutual stimulation of the chemical reaction and crystallization. Apparently a high degree of crystallinity is achieved if the cooperative spiropyran–merocyanine conversion occurs step-by-step along the polymer chains. We called this process "zipper crystallization".

While the above process was interpreted in terms of intermolecular stacks, the concept of *intra*molecular stack formation was proposed to explain our results from flash photolysis studies of different vinyl polymers with photochromic spiropyran side groups.[2] The merocyanine side groups organized in these stacks fade much more slowly than do isolated groups. These two types of merocyanines are differentiated also by other kinetic and spectroscopic prroperties. For instance, polar and nonpolar solvents affect oppositely the rates of the thermal merocyanine–spiropyran conversion of isolated merocyanines and those organized in the stacks. The effects of the polymer chain structure and of the length of the spacer connecting the photochromic side group to the main chain on the thermal fading and ability to form the intramolecular merocyanine stacks were also investigated. It is noteworthy that the polymers with the long, C-6 spacers did not reveal any tendency to stack formation.

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