Facilitating the Formation of the Grandjean Texture in Thermotropic Chiral Nematic Side-Chain Copolymers via Modulation of Backbone Flexibility

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I. Introduction

Thermotropic chiral nematic copolymers, comprising chiral and nematogenic comonomers, have found potential applications in the fabrication of optical devices[1,2] and in information storage.[3,4] All these applications rely on the formation of the cholesteric mesophase, resulting in the property of selective wavelength reflection as well as changes in the index of refraction and optical birefrigence accompanying the mesomorphic transition. As defined by the sense of the reflected circularly polarized light,[5] the cholesteric mesophase poses either a right- or left-handed helical structure on the supramolecular scale.

Because of its apparent high helical twisting power (HTP), naturally occurring cholesterol [i.e, (-)-5-cholesten-3β-ol] has been the most widely used chiral building block in the synthesis of thermotropic chiral nematic copolymers.[6,7] However, cholesterol is known to give rise to left-handed structures[8] presumably because of the given set of absolute configurations at several asymmetric centers within the molecule.[9] To make possible both right- and left-handed helical structures, we have conducted a series of studies involving the issues of helical sense and HTP by using enantiomers as chiral building blocks coupled with nematogens with varying mesomorphic stability.

As indicated in a recent series of papers,[8,10,11] helical sense is a consequence of chiral/nematic molecular interactions, while the HTP is favored by the structural similarity between the two comonomers. As the HTP is optimized with a chosen set of chiral and nematic comonomers, the ease with which the cholesteric mesophase with a high degree of supramolecular arrangement could be obtained depends on the nominal mesophase temperature range, ΔT, defined as $T_{\mathrm{Ch}\to\mathrm{I}} - T_g$, where $T_{\mathrm{Ch}\to\mathrm{I}}$ is the clearing temperature and T_g is the glass transition temperature of a given copolymer. The objective of the present work is to investigate the extent to which the Grandjean texture formation could be facilitated by introducing the more flexible acrylate units[12] into the relatively stiff methacrylate backbone structure. The effect of the backbone structure on the HTP of copolymers containing (*S*)-(-)-1-phenylethylamine and cholesterol is also examined.

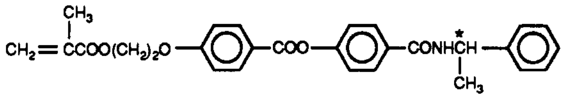
II. Experimental Section

All the reagents necessary for the synthesis of monomers and copolymers are the same as used previously.[8,10] The experimental procedure and the instrumentation for characterization are all as described elsewhere[8,10] with the exception that the optical elements are consistently annealed at 95% of the clearing temperature prior to the measurement of λ_R, the selective reflection wavelength.

III. Results and Discussion

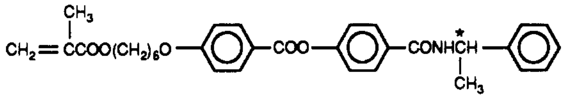
Table I
Chemical Structures and Thermal Properties of the Monomers Used in the Present Study

Chiral Monomer (i) Based on (*S*)-(-)-1-Phenylethylamine



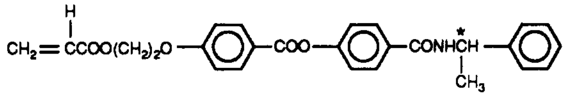
K 437 I, ref 8

Chiral Monomer (ii) Based on (*S*)-(-)-1-Phenylethylamine



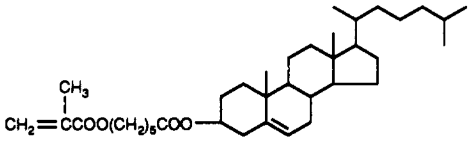
K 382 I, present work

Chiral Monomer (iii) Based on (*S*)-(-)-1-Phenylethylamine



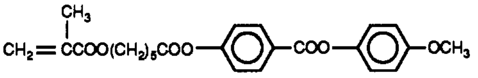
K 449 I, present work

Chiral Monomer (iv) Based on Cholesterol



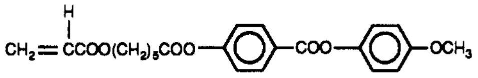
K 320 Ch 331 I (I 299 S), ref 10

Nematogenic Monomer (v)



K 327 I (I 309 N), ref 10

Nematogenic Monomer (vi)



K 338 I (I 323 N), ref 18
K 346 I (I 316 N), present work

The chemical structures of the monomers and chiral nematic copolymers are summarized in Tables I and II, respectively. The choices of (*S*)-(-)-1-phenylethylamine as the chiral moiety and *p*-methoxyphenyl benzoate as the nematic core are based on the considerations of the monotropic nature (i.e., isotropic to nematic transition upon cooling) of the latter and a reasonable degree of structural similarity between the two comonomers that might give rise to a relatively high HTP value.[10,11] Note that HTP $\equiv \bar{n}(\mathrm{d}\lambda_R^{-1}/\mathrm{d}x)$, $x \ll 1$, in which $\bar{n}$ is the average index of refraction, λ_R is the selective reflection wavelength, and x is the mole fraction of the chiral monomer in a given copolymer system. Table III presents the structural characteristics, thermotropic transition temperatures, and the selective reflection wavelengths for the copolymers synthesized and characterized for the present study.

In copolymers 1-3, the close proximity of $T_{\mathrm{Ch}\to\mathrm{I}}$ to T_g is found to prevent adequate supramolecular arrangement from being achieved through thermal annealing, as evidenced by the inability to obtain a reasonably strong selective reflection peak intended for the λ_R determination. However, it is possible to identify the cholesteric texture (i.e., oily streaks) with hot-stage polarized optical microscopy in most cases by adding a small amount of *p*-methoxybenzylidene-*p*′-butylaniline, as accomplished by Finkelmann and Rehage[12] for a polysiloxane series. Note that with a longer spacer or an acrylate chiral comono-

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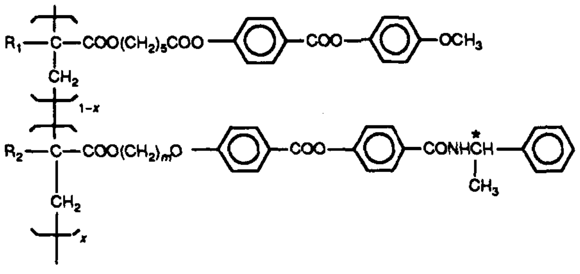
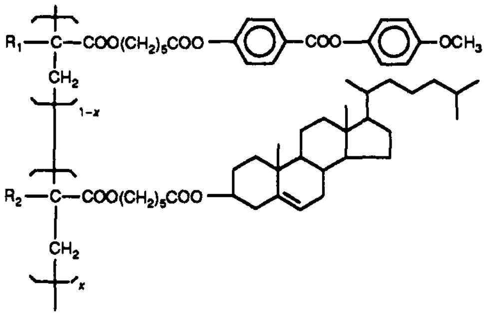
Table II
Chemical Structures of Thermotropic Chiral Nematic Copolymers Investigated in the Present Study



copolymer 1: $R_1 = CH_3$, $R_2 = CH_3$, $m = 2$
copolymer 2: $R_1 = CH_3$, $R_2 = CH_3$, $m = 6$
copolymer 3: $R_1 = CH_3$, $R_2 = H$, $m = 2$
copolymer 4: $R_1 = H$, $R_2 = CH_3$, $m = 2$
copolymer 5: $R_1 = H$, $R_2 = H$, $m = 2$



copolymer 6: $R_1 = H$, $R_2 = CH_3$
copolymer 7: $R_1 = CH_3$, $R_2 = CH_3$
copolymer 8: $R_1 = H$, $R_2 = H$, ref 19

mer, as copolymers 2 and 3 are compared to copolymer 1, the difficulty with alignment is not alleviated to an appreciable extent. Lowering the melt viscosity by reducing $\bar{M}_w$ by a factor of 3 for copolymer 1 does not seem to enhance the extent of supramolecular arrangement. In fact, the reduction in $\bar{M}_w$ is found to have no effect on T_g (see Table III) while $T_{Ch\to I}$ is expected to decrease as suggested by experimental observations[13,14] on polysiloxane and by a thermodynamic argument.[15] As $T_{Ch\to I}$ approaches T_g, it becomes increasingly difficult to achieve cholesteric mesophase formation under the dynamic conditions of the DSC measurements of mesomorphic transitions. Thus, the combined effects of $\bar{M}_w$ on T_g and $T_{Ch\to I}$ explain the disappearance of the endothermic peak associated with the cholesteric to isotropic transition from the DSC thermogram of copolymer 1 with $\bar{M}_w$ less than 10 000. However, as the acrylate units constitute the major portion of the polymer backbone, as in copolymers 4 and 5, the observed optical density, ΔOD, is found to approach the theoretical limit of 0.30. In contrast, the spectrophotometric peaks gathered for the determination of λ_R for copolymers 1–3 are either barely identifiable or extremely weak. Referring to Table III again, one finds that the T_g's of copolymers 4 and 5 are about 20 K lower than those of copolymers 1–3 as expected,[16] whereas the $T_{Ch\to I}$'s are roughly the same for copolymers 1–5. Hence, it appears that the extent of supramolecular arrangement into the cholesteric mesophase could be enhanced by modulating the backbone flexibility. The ability to accomplish this has a significant technological impact in that materials processability can be fine-tuned as an optimal set of chiral and nematic copolymers is selected based on considerations of both helical sense and twisting power for an intended application.

Copolymers 6–8 containing cholesterol are included here for further assessments of the issues involving suppressing T_g with an acrylate nematogen and the HTP in comparison to that based on (*S*)-(–)-1-phenylethylamine. Note that $\bar{n}$ needed for the calculation of the HTP value does not vary by more than ±3% for copolymers 1–8 based on a group-contribution method.[17] With an experimental uncertainty of ±5% associated with the λ_R measurement, the slope of the linear relationship between λ_R^{-1} and x, as plotted in Figure 1, is directly proportional to HTP. The fact that a single straight line emerges within experimental uncertainties suggests that (*S*)-(–)-1-phenylethylamine is as effective a twisting agent as cholesterol with an appropriate nematogenic comonomer. Furthermore, the backbone flexibility within the acrylate/methacrylate series does not seem to affect HTP to an appreciable extent. It is also noted that optical device fabrication involving copolymer 6 should be facilitated by a ΔT value about 20 K greater than of copolymer 7, as demonstrated above for copolymer 4 in comparison to copolymer 1.

Table III
Structural, Thermal, and Optical Properties of Copolymers 1–7

x^a	T_g,[b] K	$T_{Ch\to I}$,[c] K	λ_R, nm	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
		Copolymer 1			
0.12	323	356	*d*	24.9	2.5
0.14	325	352	*d*	25.1	2.6
0.10	320		*e*	6.9	1.6
0.20	333		*e*	9.9	1.8
0.28	337		*e*	9.9	1.7
		Copolymer 2			
0.12	317	358	*d*	23.1	2.5
0.20	324	350	*d*	43.9	2.5
0.30	324	342	*d*	35.1	2.5
		Copolymer 3			
0.12	320	360	*d*	21.6	2.3
0.16	323	354	*d*	23.8	2.5
		Copolymer 4			
0.11	296	360	1031	11.8	2.0
0.13	303	363	920	15.5	2.1
0.14	300	354	768	14.0	2.1
		Copolymer 5			
0.12	303	370	983	11.4	1.8
0.14	304	366	873	12.2	1.9
0.17	306	357	650	11.7	1.8
0.22	313	360	538	34.2	2.5
		Copolymer 6			
0.12	296	387	942	13.9	2.3
0.15	294	385	745	13.7	2.3
0.28	302	380	437	11.2	1.8
		Copolymer 7[f]			
0.08	313	379	1244	16.7	*g*
0.17	323	393	642	33.6	*g*
0.21	314	386	534	17.7	*g*

[a] Mole fraction of the chiral moiety. [b] Glass transition temperature. [c] Mesomorphic transition temperature. Symbols: Ch, cholesteric; I, isotropic. [d] Unable to obtain adequate mesophase arrangement for λ_R measurement as $T_{Ch\to I}$ approaches T_g. [e] No Ch → I transition observed on DSC thermogram as $T_{Ch\to I}$ decreases because of a low polymer molecular weight. [f] Tsai, M. L. Ph.D. Thesis, University of Rochester, NY, 1990. [g] $\bar{M}_w/\bar{M}_n$ in the range 1.5–2.0 as reported in footnote *f*.

IV. Summary

Several series of thermotropic chiral nematic copolymers containing (*S*)-(–)-1-phenylethylamine and cholesterol with methacrylate, acrylate, and acrylate/methacrylate mixed backbone structures have been synthesized and characterized. It is found that, by regulating the backbone flexibility, the nominal temperature range for the existence of the cholesteric mesophase can be increased by about 20

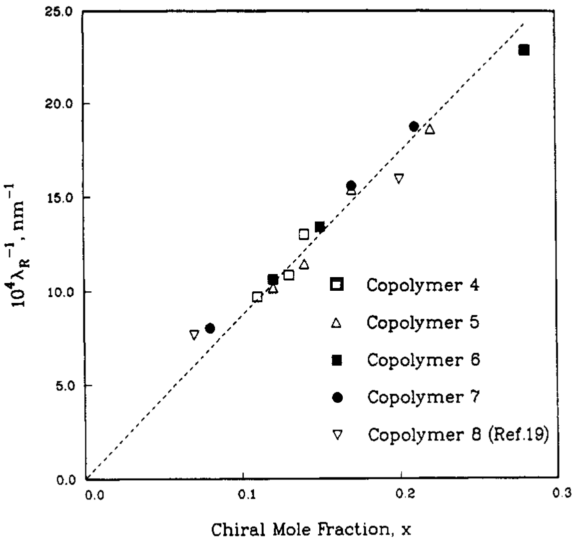


Figure 1. Linear relationship between λ_R^{-1} and x for copolymers 4–8.

K, which has been demonstrated to be adequate to facilitate the formation of uniform Grandjean texture. Furthermore, the helical twisting power does not seem to be affected by the backbone structure within the acrylate/methacrylate series. It is also noted that the helical twisting power of (*S*)-(−)-1-phenylethylamine with a nematogenic comonomer containing *p*-methoxyphenyl benzoate core structure is essentially identical with that of cholesterol, suggesting that helical twisting power is not intrinsic to the chiral moiety.

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