Mesomorphic Behavior of Side-Chain Copolymers Containing Chiral as Well as Nematogenic Moieties Comprising p-Phenylene and trans-Cyclohexylene Rings

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ABSTRACT: The effect of different ring systems on liquid crystalline (LC) mesomorphism has been addressed in terms of thermotropic side-chain polymers incorporating p-phenylene and trans-cyclohexylene units. It was found that the nematogenic monomer based on a p-n-butylbenzoyl p'-phenyl ester core copolymerized with chiral comonomers containing (S)-(-)-1-phenylethanol and (-)-5-cholesten-3β-ol (i.e., cholesterol) gives rise to the cholesteric mesophase with selective reflection wavelengths in the visible region. However, partial or complete replacement of the p-phenylene moiety with the trans-cyclohexylene ring results in smectic mesophase formation. The LC mesophases were identified with polarized optical microscopy and wide-angle X-ray diffraction, the latter technique being particularly useful in cases where thermal annealing fails to yield mesophases identifiable with optical microscopy.
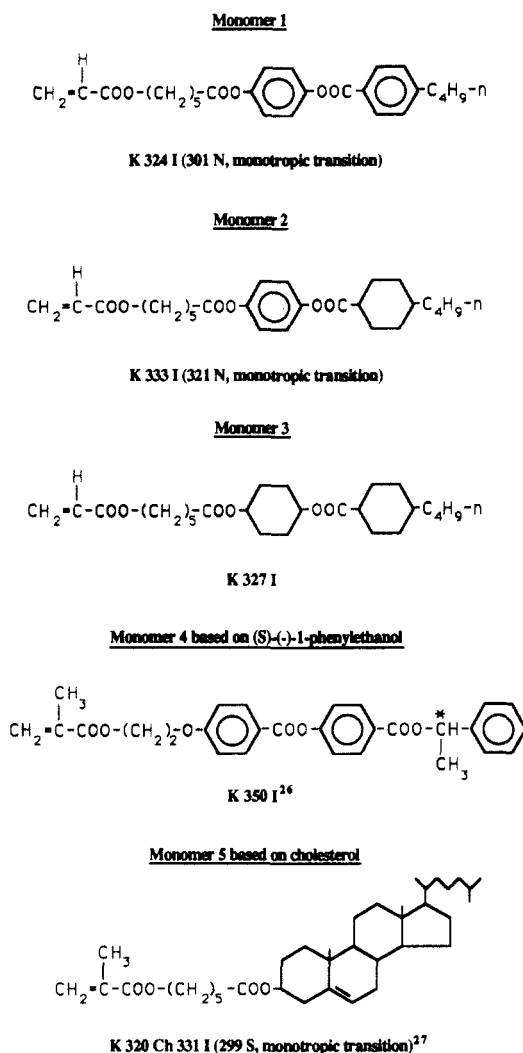
I. Introduction

Liquid crystalline mesomorphism has often been observed in compounds possessing a rigid rodlike shape.[1,2] Among the various building blocks reported in the literature, the p-phenylene unit has been the most widely used not only because of its rigid and perfectly linear molecular structure but also because of the availability and/or ease in the synthesis of a variety of 1,4-disubstituted benzene rings.[3] Further justification for an extensive use of the p-phenylene unit lies in the high polarizability of its π-electrons, which has been suggested to contribute to mesophase stability by intermolecular van der Waals forces and via intermolecular dipole–dipole interactions in the presence of adjacent electromeric groups.[4,5] Since aromatic rings are known to strongly absorb light in the ultraviolet region, alternative saturated ring systems have been considered as an option in numerous studies. In one of the earlier studies of liquid crystals involving three-ring systems,[5] the decreasing nematic to isotropic transition temperature ($T_{N \to I}$) was observed in the order p-phenylene (PH) > 1,4-bicyclo[2.2.2]octylene (BCO) > trans-1,4-cyclohexylene (CH), suggesting that the geometric factor predominates over polarity in affecting mesophase stability.

From a practical standpoint, some applications involving the electrooptic effect in liquid crystals (e.g., twisted nematic and guest–host displays) require nematic mesophases with low birefringence and low viscosity.[6,7] Systematic studies over the years have shown that this can be achieved by replacement of aromatic moieties in liquid crystals with saturated cyclohexane rings.[6-9] Furthermore, in liquid crystals involving two rings connected directly or via a bridging group, enhanced mesophase stability was observed with an increasing degree of saturation of the ring system. The decreasing trend of $T_{N \to I}$ in the order BCO > CH > PH in these liquid crystals[10] is different from that observed in three-ring systems.[5] The only exception to this trend was found in systems where an alkoxy group was linked to the ring with a p-phenylene-based system, which shows the highest $T_{N \to I}$ followed by 1,4-bicyclo[2.2.2]octylene; liquid crystalline mesomorphism is absent in the case of trans-1,4-cyclohexylene.[10,11]

The role of saturated rings in liquid crystal polymers has been receiving increasing attention in recent years. A number of main-chain liquid crystal polymers containing the trans-cyclohexylene[12-16] as well as bicyclo[2.2.2]octylene[17,18] rings have been reported in the literature. In the area of side-chain liquid crystal polymers, saturated cyclohexane rings have been used as part of the pendant group in both the end-on[19-21] and side-on[22] orientations as well as in paired mesogens.[23] In the present work, new monomers containing p-phenylene and trans-cyclohexy-

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Monomer 1

$CH_2=C-COO-(CH_2)_5-COO-\langle\bigcirc\rangle-OOC-\langle\bigcirc\rangle-C_4H_9-n$

K 324 I (301 N, monotropic transition)

Monomer 2

$CH_2=C-COO-(CH_2)_5-COO-\langle\bigcirc\rangle-OOC-\langle\bigcirc\rangle-C_4H_9-n$

K 333 I (321 N, monotropic transition)

Monomer 3

$CH_2=C-COO-(CH_2)_5-COO-\langle\bigcirc\rangle-OOC-\langle\bigcirc\rangle-C_4H_9-n$

K 327 I

Monomer 4 based on (S)-(-)-1-phenylethanol

$CH_2=C-COO-(CH_2)_2-O-\langle\bigcirc\rangle-COO-\langle\bigcirc\rangle-COO-CH-\langle\bigcirc\rangle$
with CH_3 groups

K 350 I[26]

Monomer 5 based on cholesterol

$CH_2=C-COO-(CH_2)_5-COO-$ (cholesteryl)
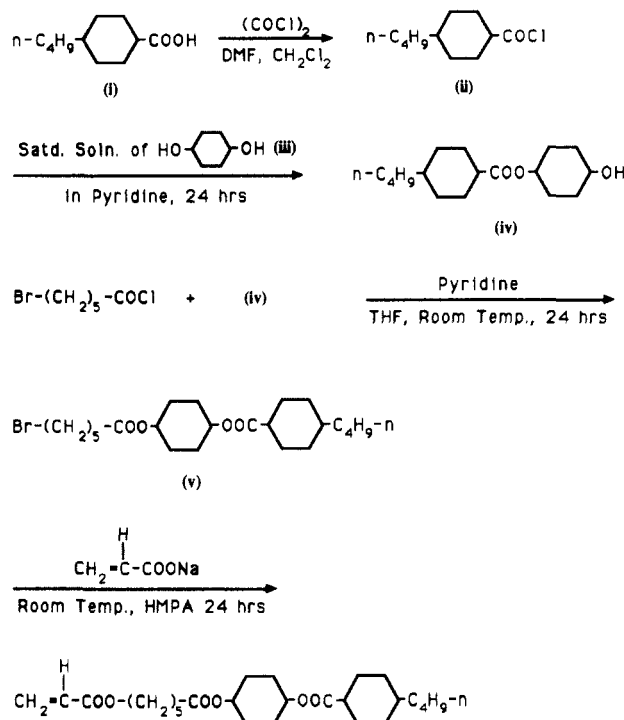
K 320 Ch 331 I (299 S, monotropic transition)[27]

Symbols : K, crystalline; N, nematic; S, smectic; Ch, cholesteric; I, isotropic.

Figure 1. Chemical structures and thermal properties of monomers used in the present study.

$n-C_4H_9-\langle\bigcirc\rangle-COOH \xrightarrow[DMF, CH_2Cl_2]{(COCl)_2} n-C_4H_9-\langle\bigcirc\rangle-COCl$

(i) → (ii)

$\xrightarrow[\text{In Pyridine, 24 hrs}]{\text{Satd. Soln. of } HO-\langle\bigcirc\rangle-OH \text{ (iii)}}$

$n-C_4H_9-\langle\bigcirc\rangle-COO-\langle\bigcirc\rangle-OH$

(iv)

$Br-(CH_2)_5-COCl \quad + \quad (iv) \xrightarrow[\text{THF, Room Temp., 24 hrs}]{\text{Pyridine}}$

$Br-(CH_2)_5-COO-\langle\bigcirc\rangle-OOC-\langle\bigcirc\rangle-C_4H_9-n$

(v)

$\xrightarrow[\text{Room Temp., HMPA 24 hrs}]{CH_2=C-COONa}$

$CH_2=C-COO-(CH_2)_5-COO-\langle\bigcirc\rangle-OOC-\langle\bigcirc\rangle-C_4H_9-n$

Figure 2. Synthesis scheme for monomer 3.

II. Experimental Section

The chemical structures and phase transition temperatures of the acrylate monomers employed in the present work are included in Figure 1. All the reagents for the synthesis of monomers and polymers are the same as used previously[28,29] except for 4-n-butylbenzoyl chloride (97%; Aldrich Chemical Co.), 1,4-cyclohexanediol (99%, mixture of cis and trans; Aldrich Chemical Co.), and trans-4-n-butylcyclohexanecarboxylic acid (99+%; American Tokyo Kasei), which were all used as received. For monomer 3, the trans-1,4-cyclohexanediol (iii) was isolated from a mixture of cis and trans isomers according to reported procedures.[30] The synthetic route of Haut and co-workers[31] was followed for the preparation of iv for monomers 1-3. The diester side product in this reaction was removed by column chroma-

lene rings have been synthesized and characterized. These monomers incorporate core structures which have shown either a monotropic or an enantiotropic nematic mesophase in low molar mass liquid crystals.[24,25] New side-chain homopolymer and copolymers based on previously reported chiral monomers containing (S)-(-)-1-phenylethanol[26] and (-)-5-cholesten-3β-ol[27] have also been included in the present study. The liquid crystalline mesophases in the polymeric systems have been studied with wide-angle X-ray diffraction (WAXD) in addition to polarized optical microscopy. The ability of the p-phenylene and trans-1,4-cyclohexylene rings to generate different liquid crystalline mesophases is discussed.

tography over silica gel using methylene chloride as the eluant. The overall scheme for the synthesis of monomer 3 is given in Figure 2; monomers 1 and 2 were prepared in a similar way. The purification of all three monomers was accomplished by column chromatography with 2 vol % ethyl acetate in methylene chloride as the eluant followed by recrystallization from ethanol. The structures of the monomers and those of the intermediate compounds were verified with ^1H NMR (QE-300; GE) and IR (710B; Perkin-Elmer) spectroscopy. Elemental analysis (Oneida Research Services, Inc.) of monomers 1-3 showed C = 71.32% and H = 6.84%; C = 70.69% and H = 8.22%, and C = 69.62% and H = 9.39%, respectively. These values compare favorably to the theoretical values of C = 71.21% and H = 6.90%, C = 70.24% and H = 8.16%, and C = 69.30% and H = 9.40%, respectively. Other experimental procedures and the instrumentation for characterization were all as described elsewhere.[26,27] All optical elements fabricated from copolymers were annealed at 98% of their respective clearing temperatures followed by quenching prior to the measurement of the selective reflection wavelength.

The WAXD patterns at room temperature were obtained in the reflection mode using a Rigaku RU-300 Bragg-Bretano diffractometer equipped with a rotating copper anode, a diffracted beam graphite monochromator tuned to Cu Kα, and a scintillation detector. Samples were prepared by placing powdered material on a zero background quartz plate, which was heated to the isotropic temperature and then quenched in air.

In situ high-temperature diffraction data were collected in the reflection mode using a Siemens D500TT diffractometer equipped with an Anton-Paar TTK temperature stage, a Buehler temperature controller, and a Braun position-sensitive detector. The source was a sealed copper X-ray tube filtered with a nickel foil. Samples were prepared as powders on a platinum heating strip, which were heated to isotropic temperature and then quenched in air. Subsequent processing involved heating the sample to a desired temperature and holding for 5 or 30 min prior to collecting the diffraction data.
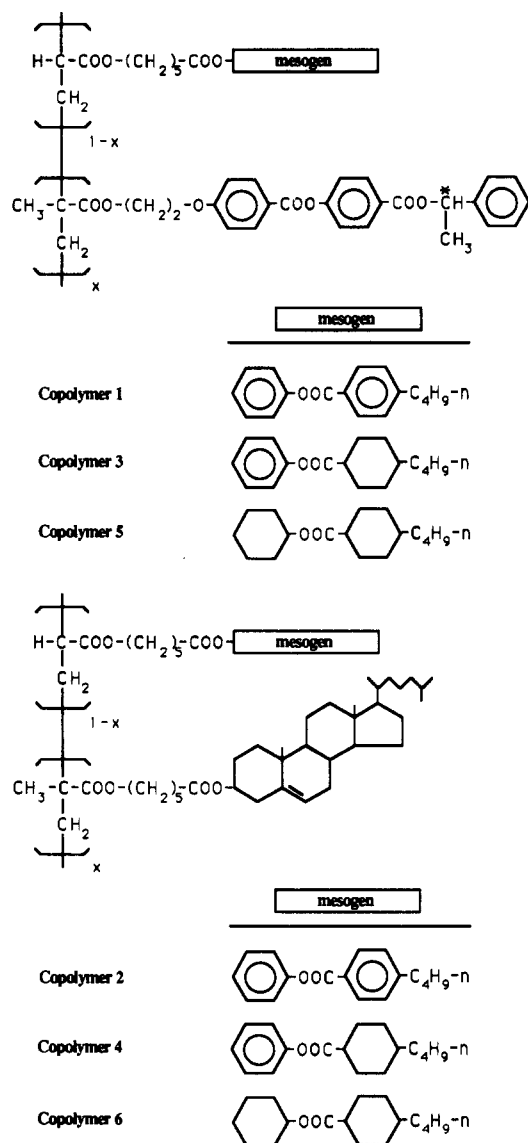
III. Results and Discussion

Of the three new monomers investigated in the present study, monomers 1 and 2 show a monotropic nematic mesophase, while monomer 3 is nonmesomorphic. These monomers were copolymerized with the previously reported[26,27] chiral monomers 4 and 5 to give copolymers

Table I
Structural, Thermal, and Optical Properties of Copolymers 1 and 2

mole fraction chiral moiety x^a	glass transition temperature T_g (K)	mesomorphic transition $T_{S \rightarrow Ch}$ (K)	mesomorphic transition $T_{Ch \rightarrow I}$ (K)	λ_R (nm)	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
		Copolymer 1 Based on (S)-(−)-1-Phenylethanol				
0.07	293	329	354	1517	9.85	1.5
0.11	290	321	343	769	8.08	1.4
0.17	289		332	519	8.03	1.5
0.21	293		324	b	10.40	1.6
		Copolymer 2 Based on (−)-5-Cholesten-3β-ol				
0.10		328	362	1030	8.15	1.4
0.16		322	365	700	10.40	1.6
0.22		321	371	586	11.58	1.6

^{a} x determined with integration of appropriate NMR signals. ^{b} Unable to obtain adequate cholesteric mesophase arrangement for λ_R measurement as $T_{Ch \rightarrow I}$ approaches T_g, as also reported in ref 29.

Figure 3. Chemical structures of copolymers 1–6 used in the present study.

Table II
Structural, Thermal, and Optical Properties of Copolymers 3–6

mole fraction chiral moiety x^a	glass transition temperature T_g (K)	mesomorphic transition $T_{S' \rightarrow S}$ (K)	mesomorphic transition $T_{S \rightarrow I}$ (K)	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
		Copolymer 3 Based on (S)-(−)-1-Phenylethanol			
0.12		338	389	11.73	1.3
0.23		327	369	16.98	1.6
		Copolymer 4 based on (−)-5-Cholesten-3β-ol			
0.25	290		417	11.78	1.4
0.30	290		426	15.65	1.8
		Copolymer 5 Based on (S)-(−)-1-Phenylethanol			
0.10		360	392	25.05	1.7
0.20	287		325	8.35	1.5
		Copolymer 6 Based on (−)-5-Cholesten-3β-ol			
0.18	291		374	6.36	1.3
0.20	290		388	14.64	1.6

^{a} x determined with integration of appropriate NMR signals.

the nature of these endotherms, homopolymer 1 was synthesized from monomer 1 ($\bar{M}_w$ = 8880; $\bar{M}_w/\bar{M}_n$ = 1.22). The DSC thermogram of homopolymer 1 shows two endotherms at 341 and 365 K, suggesting that the low-temperature endotherms in the copolymers might have resulted from the nematogenic component. Under polarized optical microscopy, the transitions from the liquid crystalline to isotropic state in homopolymer 1 and copolymers 1 and 2 revealed a nematic to isotropic and cholesteric to isotropic transition, respectively. However, no positive mesophase identification could be accomplished below the low-temperature endotherms in spite of thermal annealing over extended periods of time. The inability to obtain a characteristic texture of a mesophase close to the glass transition temperature has also been reported in the past.[29,32]

To further elucidate the mesophase behavior in these polymeric systems, room-temperature WAXD experiments were performed on samples of homopolymer 1 and copolymer 2 with a chiral content of 10 mol %. Figure 4 shows that both samples are characterized by the presence of a relatively broad peak around $2\theta = 20°$ and three peaks at $2\theta < 6°$ corresponding to 3 orders of reflection with a periodicity of 4.6 and 5.2 nm for homopolymer 1 and copolymer 2, respectively. Nematogenic homopolymers with molecular structures similar to that of homopolymer 1 were found to possess smectic mesophase(s) in addition to the nematic mesophase.[33] Moreover, the X-ray diffraction pattern of one of these homopolymers in the smectic state[34] resembles that of homopolymer 1. Thus, for the polymers under present investigation, while the wide-angle peak is indicative of the lateral packing of mesogenic groups, the three low-angle peaks correspond to 3 orders of reflection from a smectic plane. These

1–6, the chemical structures of which are given in Figure 3. The composition, thermal, and optical properties of copolymers 1 and 2 are included in Table I and those of copolymers 3–6 in Table II. It was found that for low contents of the chiral moiety, both copolymers 1 and 2 show two endothermic peaks in their DSC thermograms and that the low-temperature endotherms in copolymers 1 and 2 diminish in intensity as well as in area with increasing content of the chiral comonomer. At a chiral content of 17 mol % and higher, the lower temperature endotherm of copolymer 1 was found to vanish. To unravel
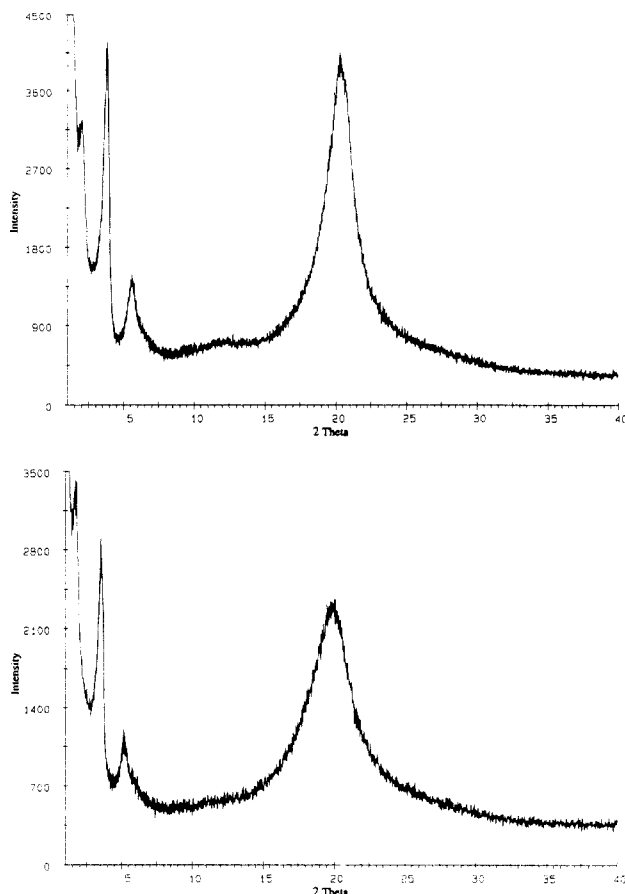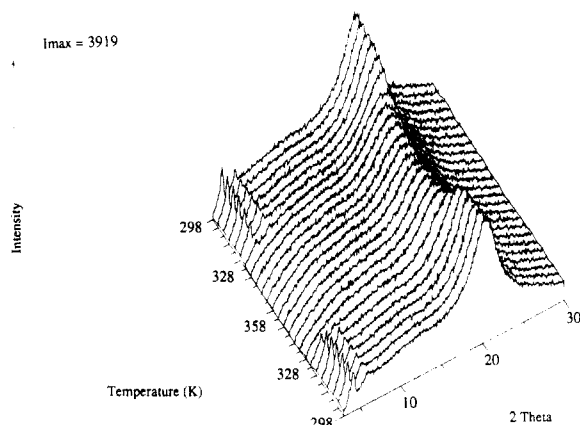
Figure 4. Room temperature WAXD pattern of (a) homopolymer 1 and (b) copolymer 2 with a chiral content of 10 mol %.

Figure 5. In situ high-temperature WAXD pattern of copolymer 2 with a chiral content of 10 mol %.

observations seem to suggest that the low-temperature endotherms in homopolymer 1 and copolymers 1 and 2 represent a smectic to nematic and smectic to cholesteric transition, respectively. Furthermore, based on molecular modeling (Alchemy II, Tripos Associates, Inc.), the length of the side chain in homopolymer 1 was found to be 2.35 nm. As a result, a bilayer structure appears to exist in the homopolymer in view of the smectic layer thickness of 4.6 nm as revealed by the WAXD pattern.

The effect of temperature on the mesophase behavior of copolymer 2 with a chiral content of 10 mol % was further studied by WAXD. It is clearly seen from Figure 5 that the peaks at $2\theta < 6°$ persist below 328 K in both heating and cooling scans, which is consistent with the earlier assignment of the low-temperature endotherm to a smectic to cholesteric transition. Furthermore, the cholesteric mesophase existing in the 328–362 K temper-
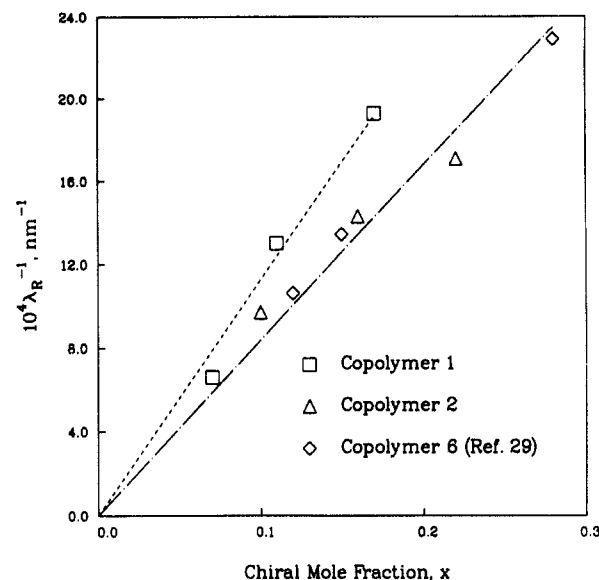

Figure 6. Linear relationship between λ_R^{-1} and x for the evaluation of HTP of copolymers 1 and 2.

ature range (Table I) and the isotropic state beyond 362 K are both characterized by an absence of peaks at low angles in the diffraction pattern. The absence of low-angle peaks in the cholesteric mesophase has also been observed in other cholesterol-containing copolymers.[35] In addition, a broadening of the wide-angle peak is observed with increasing temperature, suggesting a reduced intralayer ordering due to increased thermal motions of the mesogenic moieties.[34]

Next, we turn to the evaluation of the helical twisting power (HTP) in copolymers 1 and 2. The HTP is defined[36] as $(\bar{n} \, d\lambda_R^{-1}/dx)$ for $x \ll 1$, where $\bar{n}$ is the average index of refraction, λ_R is the selective reflection wavelength, and x is the mole fraction of the chiral comonomer. A group contribution method[37] for the calculation of refractive indices in these systems results in values not differing from each other by more than ±3%. Hence, the slope of the λ_R^{-1} vs x plot at $x \to 0$, as shown in Figure 6, is a reasonable measure of HTP. The copolymer containing (S)-(−)-1-phenylethanol clearly shows a much higher HTP than that based on cholesterol, which is consistent with the trend observed for a different nematognic comonomer.[26] Figure 6 also includes earlier data[29] for cholesterol-containing copolymers with a nematogenic comonomer based on a p-methoxyphenyl benzoate core structure.

We now address the other relevant issue, namely, the effect of substitution of aromatic rings with saturated ones on the mesomorphic behavior of the resultant side-chain copolymers. As presented in Table II, in addition to the liquid crystalline to isotropic transition, the DSC thermograms show a glass transition temperature for copolymers 4 and 6, while a glass transition temperature or a low-temperature endotherm is observed in copolymers 3 and 5. Furthermore, the liquid crystal to isotropic transitions in copolymers 3, 4, and 6 were confirmed to be smectic to isotropic transitions, as revealed by the fan-shaped textures characteristic of a smectic mesophase[38] under polarized optical microscopy. However, in spite of annealing at 98% of the clearing temperature for 5–7 days, copolymer 5 shows only a fine grain texture which has often been assigned to a smectic state.[39] Indeed, the WAXD pattern verifies the existence of a smectic mesophase as discussed below.

The mesophase behavior in some of the polymeric systems was further examined by WAXD. Figure 7 summarizes the room-temperature WAXD curves for
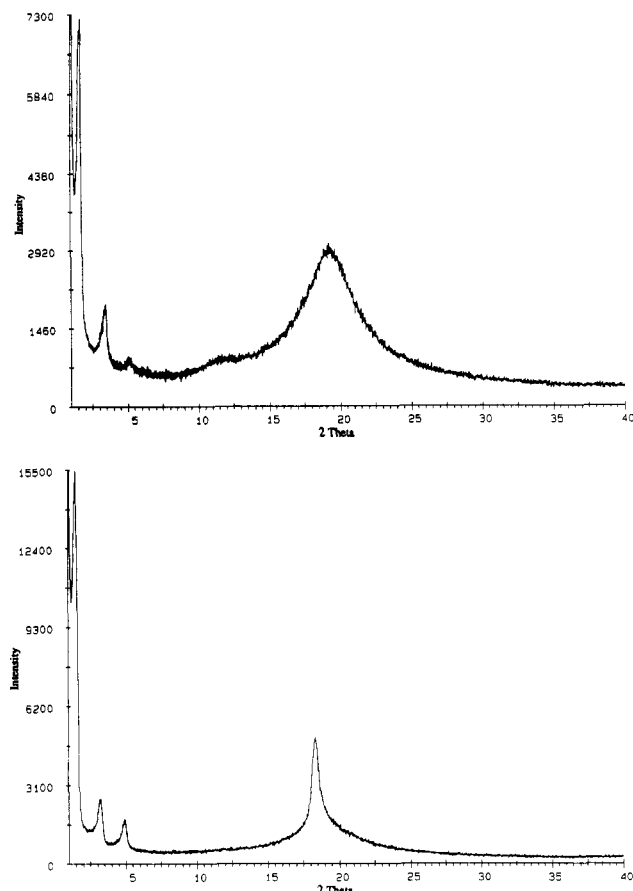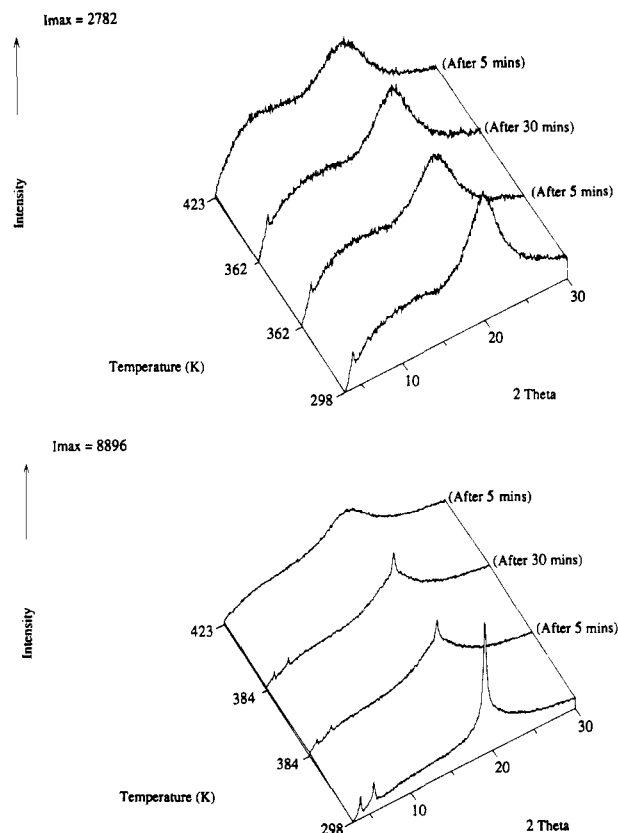
Figure 7. Room-temperature WAXD pattern of (a) copolymer 3 with 23 mol % and (b) copolymer 5 with 10 mol % chiral content.

Figure 8. In situ high-temperature WAXD pattern of (a) copolymer 3 with 23 mol % and (b) copolymer 5 with 10 mol % chiral content.

copolymer 3 (chiral content 23 mol %) and 5 (chiral content 10 mol %). Both samples show a wide-angle peak and three low-angle peaks with a periodicity of 5.3 and 5.6 nm, respectively. The relatively sharp wide-angle peak observed in copolymer 5 indicates that the mesogenic units are highly ordered in the smectic mesophase.[34] In situ high-temperature WAXD experiments were also performed on the two samples, and the diffraction traces are given in Figure 8. The presence of peaks at low angles in the diffraction traces up to isotropization confirms the presence of a smectic mesophase. For copolymer 3 (chiral content 23 mol %), this observation further corroborates the smectic texture observed by polarized optical microscopy. Furthermore, in both cases, the presence of low-angle peaks above and below the low-temperature endotherm suggests that this endotherm is a S' → S (smectic to smectic) transition on heating. Moreover, a decreasing order in the packing of mesogenic groups with increasing temperature is observed in both the systems, as suggested by a broadening of the wide-angle peak. Thus, for the polymeric systems investigated in this study, an increasing degree of saturation for the ring systems seems to result in the formation of higher order smectic mesophases, which is consistent with the trend observed in low molar mass liquid crystals.[11,40]

IV. Summary

Several thermotropic side-chain polymers with mesogenic moieties comprising *p*-phenylene and *trans*-cyclohexylene rings have been synthesized and characterized. While the *p*-*n*-butylbenzoyl *p*′-phenyl ester core was found to contribute to nematic mesophase formation in the homopolymer, it does lead to the formation of the cholesteric mesophase when copolymerized with chiral monomers containing (*S*)-(−)-1-phenylethanol and (−)-5-

cholesten-3β-ol. However, substitution of *p*-phenylene with *trans*-cyclohexylene rings in the mesogenic core yields a higher order smectic mesophase. A number of systems failed to show characteristic textures for certain mesophase transitions for interpretation by polarized optical microscopy. In situations where thermal annealing fails to reveal characteristic textures for mesophase identification with polarized optical microscopy, both room-temperature and in situ high-temperature WAXD measurements were shown to be instrumental to the investigation of structure–property relationships involving thermotropic polymers.

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