Photochemical Modification of a Side Chain Copolysiloxane with a Cholesteric Phase

Sandi Campbell, Yuhui Lin, Uwe Müller, and L.-C. Chien*

Liquid Crystal Institute and NSF ALCOM Center, Kent State University, Kent, Ohio 44242

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Using a nematic monomer and a chiral monomer, we have synthesized several cholesteric side chain copolysiloxanes. The chiral monomer contains a photosensitive group which can be racemized or have its chirality removed by a photochemical reaction. The racemization of the chiral monomer proceeds by abstraction of a hydrogen atom from the 2-hydroxyl group of binaphthol. The reduction in chirality of a cholesteric copolysiloxane is proportional to the dosage of ultraviolet (UV) irradiation. The resultant polymer showed an increase in glass transition temperature and a decrease in cholesteric to isotropic transition temperature.

Introduction

Cholesteric liquid crystals have long-range orientation order, and their elongated molecules are locally oriented in layers along a common direction similar to that of nematic liquid crystals.[1−3] The director of the molecules rotates around a helical axis. The distance over which the director rotates 360° is called the pitch. The pitch of a cholesteric liquid crystal depends on the chirality of the molecule. In an induced cholesteric phase, a nematic liquid crystal doped with a chiral additive, the pitch of the cholesteric phase is inversely proportional to the content of the chiral additive. One could imagine that a copolymer consisting of a nematic monomer and a chiral monomer would exhibit a cholesteric phase. Extensive synthesis of cholesteric polymers have been reported by several groups.[4−6]

Photochemically induced modification of helical pitch using a cholesteric liquid crystal was first reported by Haas et al.[7] In addition, similar studies were reported on doping a nematic liquid crystal with photosensitive dis-symmetric chiral compounds. Upon UV irradiation, these compounds undergo photochemical reactions, resulting in a change in helical pitch.[8−13]

In our previous work,[14−19] we have described the use of a tunable chiral material (TCM) in preparing a multicolor reflective cholesteric display (MRCD), in which the color of a cholesteric display is determined by the pitch of the liquid crystal. If a multicolor is desired, the pitch of the liquid crystal in different pixels has to be different. In the case of a TCM, the pitch of the cholesteric liquid crystal is adjusted by the dose of UV irradiation. However, there is a diffusion of liquid crystal between pixels due to the low molecular weight TCM used. We are interested in exploring TCM-containing polymers as the chiral additive to prevent the diffusion problem in a MRCD because of the high viscosity of the polymer. We expect that a liquid-crystalline copolymer containing the TCM will have a higher solubility than a synthesized homopolymer.[19] In this study, the synthesis of cholesteric polymers containing a TCM is described. The mesomorphic behavior and photochemical modification of a cholesteric side-chain polymer were investigated.

Experimental Section

Materials. All starting materials were obtained from Aldrich Chemical Co. and were used as received. Reagent grade solvents were used without purification, unless otherwise stated. Free radical photoinitiators, Irgacure 369 and 907, were gifts from Ciba Additives, Inc. The nematic liquid crystal E48 (a mixture of 4-alkyl-4′-cyanobiphenyl, 4-alkyl-4′-cyanoterphenyl, and 4-alkoxy-4′cyanobiphenyl; nematic range, −30 to ~70 °C) was obtained from the Merck Industry (New York, NY). Infrared spectra were obtained using a Nicolet

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Scheme 1
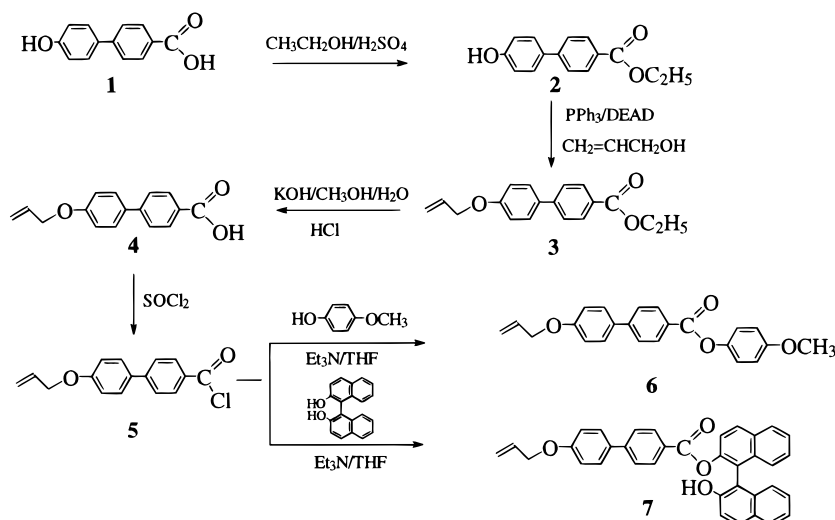
Magna-IR spectrometer 550. All samples were prepared in KBr, unless otherwise stated. Melting points are uncorrected and measured on a Thomas-Hoover capillary melting point apparatus. Transition temperatures were measured on a Perkin-Elmer DSC-7. Thermogravimetric analyses were obtained using a TA Instruments High-Resolution TGA 2950. Transition temperatures and optical textures were observed using a Leitz-Laborlux S optically polarized microscope fitted with a Mettler FP-heating stage. An Optical Activity AA-10 automatic polarimeter, from Optical Activity, Ltd., was employed for optical activity measurements. Elemental analyses were determined by Oneida Research Services (Whitesboro, NY). Proton nuclear magnetic resonance spectra were obtained on a Varian FT-200 spectrometer (200 MHz) in CDCl$_3$ and using tetramethylsilane as an internal standard, unless otherwise stated. Chemical shifts are reported in parts per million and coupling constants are reported in hertz.

Synthesis of Monomers. The procedures for the synthesis of the nematogenic and chiral monomers are outlined in Scheme 1.

Synthesis of 4-Methoxyphenyl 4-(4′-Allyloxyphenyl)-benzoate (6). In an addition funnel, *p*-methoxyphenol (1.37 g) and triethylamine (1.53 mL) were dissolved in 30 mL of anhydrous THF. In a round-bottomed flask, compound **5** (3.00 g) was dissolved in 30 mL of anhydrous THF. The contents of the addition funnel were added slowly to the round-bottomed flask, and the mixture was stirred overnight at room temperature. The THF was evaporated from the flask and the solid was washed with a mixture of ethyl acetate and 5% hydrochloric acid. The organic layer was separated and the product was extracted from the water layer with three portions of ethyl acetate. The organic layers were combined and dried over sodium sulfate. The solvent was then evaporated and the monomer was recrystallized from ethanol (2.61 g 69%). ^{1}H NMR (CDCl$_3$, δ pm): 3.82 (s, 3H, $-$OCH_3), 4.60 (dt, 2H, CH$_2$=CHCH_2, J_d = 5.2, J_t = 1.5), 5.31 (dq, 2H, CH_2=CHCH$_2$, J_d = 10.0, J_q = 1.6), 5.46 (dq, 2H, CH_2=CHCH$_2$, J_d = 17.4, J_q = 1.6), 5.98$-$6.19 (m, 1H, CH$_2$=CHCH$_2$), 6.91$-$7.19 (m, 8H, Hs ortho to C=O and $-$OCH$_3$, Hs meta to $-$OCH$_3$), 7.58$-$7.69 (m, 4H, Hs meta to C=O and OCH$_2$), 8.21 (d, 2H, Hs ortho to OCH$_2$, J = 8.2). FTIR (KBr, cm^{-1}): 3074 (aromatic, C$-$H), 1725 (C=O), 1604, 1509 (aromatic, C=C), 1251, 1193 (C$-$O). Elemental analysis for C$_{23}$H$_{20}$O$_4$: calculated, C 76.64, H 5.60; found, C 75.54, H 5.60.

Synthesis of (S)-1,1′-Bis-2-naphthyl 4-(4′-Allyloxy-phenyl)benzoate (7). In an addition funnel, compound **5** (3.62 g) and triethylamine (1.85 mL) were dissolved in 30 mL of anhydrous THF. In a round-bottomed flask, (*S*)-Bi-2-naphthol (3.80 g) was dissolved in 30 mL of anhydrous THF. The contents of the addition funnel were added dropwise to the round-bottomed flask, and the mixture was stirred over-

night at room temperature. The THF was evaporated from the flask and the solid was washed with both ethyl acetate and 5% hydrochloric acid. The organic layer was separated and the product was extracted from the water layer with three portions of ethyl acetate. The organic layers were combined and dried over sodium sulfate. The solvent was evaporated and the monomer was recrystallized from ethanol (7.58 g 92%). ^{1}H NMR (CDCl$_3$, δ ppm): 4.56 (dt, 2H, CH$_2$=CHCH_2, J_d = 5.3, J_t = 1.5), 5.30 (dq, 2H, CH_2=CHCH$_2$, J_d = 10.1, J_q = 1.6), 5.45 (dq, 2H, CH_2=CHCH$_2$, J_d = 17.4, J_q = 1.6), 5.95$-$6.14 (m, 1H, CH$_2$=CHCH$_2$), 6.95 (d, 2H, Hs ortho to C=O, J = 2), 7.11$-$8.06 (m, 17H aromatic), 8.23 (d, 2H, Hs ortho to CH$_2$O$-$, J = 3.6). FTIR (KBr, cm^{-1}): 3430 (O$-$H), 3059 (aromatic, C$-$H), 1725 (C=O), 1603 (aromatic, C=C), 1271, 1185 (C$-$O). [α]$^{20}_D$ = $-$104.76. Elemental analysis (C$_{36}$H$_6$O$_4$): calculated, C 82.73, H 5.01; found, C 82.42, H 5.23.

Synthesis of Polymers. The syntheses of side chain copolysiloxanes with varying chiral to nematic molar ratios follow the method outlined in Scheme 2. The experimental procedure for the synthesis of **P82** is outlined below.

Synthesis of Copolysiloxane P82. This polymer was prepared by combining monomers **7** and **6**, in the molar ratio of 80:20. The experiment was carried out by combining both monomers with polymethylhydrosiloxane (1:1 mole ratio) in a dry round-bottomed flask. The mixture was dissolved in freshly distilled toluene and a 5% solution of H$_2$PtCl$_6$ in 2-propanol (3 drops) was added to the flask. The solution was refluxed overnight under nitrogen atmosphere. The toluene was evaporated and the polymer was dissolved in dichloromethane. The CH$_2$Cl$_2$ solution was added slowly to the methanol to precipitate the polymer. The precipitation step was repeated until no monomer was found in TLC.

The polymer was decolorized by dissolving it in 200 mL of dichloromethane, adding approximately 0.3 g of activated charcoal, and stirring overnight. The NMR and FTIR data of the five polymers are very similar. ^{1}H NMR (CDCl$_3$, ppm): 0.1 (8H, b), 0.7 (2H, b), 1.1 (2H, b), 1.8 (5H, b), 3.7 (9H, b), 5.5 (1H, b), 5.9$-$7.5 (26H, m), 7.9 (3H, b). FTIR (neat film, cm^{-1}): 3435 ($-$OH), 3064 (aromatic), 1732 (C=O), 1605, 1507 (aromatic), 1274, 1193 (str C$-$O$-$C).

Photochemical Modification of a Copolysiloxane P73. In a quartz cell, the **P73** (15 mg) was dissolved in deuterated chloroform (3.5 mL). A small amount of photoinitiator, Irgacure 369, was added and the solution was purged with nitrogen for 20 min. The cell was capped, cooled on ice, and exposed to 35.6 J/cm^2 of UV radiation using a metal halide lamp with neutral density filter. The sample was analyzed by IR and ^{1}H NMR. This procedure was repeated except that the UV irradiation was increased to 71.3 J/cm^2. The same procedure was followed using Irgacure 907 as the photoinitiator and an UV irradiation of 35.6 J/cm^2.
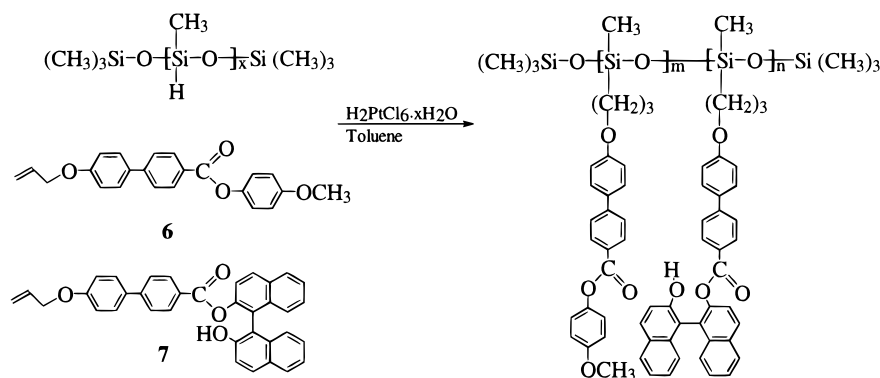
Scheme 2

Table 1. Elemental Analyses and Molecular Weights of Copolysiloxanes

polymer	mol %		%C		%H		$M_n{}^a$	γ^b
	m (**6**)	n (**7**)	calcd	obsd	calcd	obsd		
P91	90	10	71.50	66.33	5.59	5.44	c	c
P82	80	20	72.44	67.88	5.50	5.43	46 500	2.44
P73	70	30	73.29	69.19	5.41	5.33	65 600	2.88
P55	50	50	74.81	70.78	5.26	5.40	62 500	2.77
P010	0	100	76.25	74.26	4.51	5.35	75 600	2.78

[a] M_n: number average of molecular weight (using polystyrene as the standard). [b] γ: polydispersity. [c] Very poor solubility in THF.

Optical Activity Measurement. In a quartz cell, the **P73** (10 mg) and a small amount of photoinitiator (Irgacure 907) were dissolved in chloroform (3.5 mL). A small mark was made on the cell so that the volume could be kept constant at 3.5 mL. The optical activity of the sample was measured. After the measurement, the sample was transferred to a quartz cell. The solution was purged with nitrogen for 20 min, and the cell was capped, cooled on ice, and irradiated with 8.9 J/cm² of UV radiation ($\lambda \geq 330$ nm). Chloroform was added to the 3.5 mL mark to replace what had evaporated and the optical activity was measured. The procedure was repeated four times, increasing the irradiation time until the sample was exposed to 62.4 J/cm² of radiation.

Induced Cholesteric Phase in a Nematic Liquid Crystal. A cholesteric material consisting of 3% of **P73** and 97% of a nematic mixture E48 (from Merck) was weighed into a vial and mixed with the addition of a few drops of dichloromethane. After evaporation of the solvent under reduced pressure, the mixture was loaded in the isotropic phase into a commercial display cell (two glass plates separated by 5 μm spacers). The inner surfaces of the cell were coated a thin layer of polyimide film (~200 Å). The cell was exposed to UV irradiation ($\lambda \geq 330$ nm) of 23.4 J/cm².

Results and Discussion

Physical and Mesomorphic Properties. The elemental analyses of copolysiloxanes show that the percentage of carbon calculated theoretically is consistently higher than the percentage found, by 4.0% to 4.5%. This difference is due to the amount of methylhydrosiloxane reactive groups that did not react, indicating that the yields of platinum-catalyzed hydrosilation were around 95%. The elemental analyses, molecular weight, and molecular weight distribution of the polymers are summarized in Table 1. Since the chiral monomer has a higher molecular weight than the nematic monomer, we expect the percentage of carbon to increase with increasing concentration of this monomer. The molecular weights of copolymers were determined by gel permeation chromatography, with the

Table 2. Thermal Properties of Copolysiloxanes

polymer	temp at 5% weight loss (°C)	transition temp (°C)^a
P91	410.1	g 81.4 Ch 204.5 I
P82	390.9	g 78.7 Ch 208.6 I
P73	393.9	g 81.2 Ch 205.4 I
P55	396.8	g 95.9 Ch 211.1 I
P010	363.1	g 132.0 I

[a] g, glass transition; Ch, cholesteric; I, isotropic.

exception of the **P91**, because it is insoluble. Of the two monomers, the chiral monomer has the higher molecular weight; therefore, we would expect the molecular weight of the polymers to increase with increasing concentration of the chiral unit.

The transition temperatures, determined by a second heating scan of DSC, are summarized in Table 2. In the monomer analyses, the DSC heating and cooling rate was 10 °C/min. For polymers **P91**–**P010**, the DSC analyses were accomplished by heating and cooling scans at a rate of 20 °C/min. All the copolysiloxanes exhibit a cholesteric phase except polymer **P010**, because it was synthesized from the nonmesogenic chiral monomer **7**. A DSC thermogram of **P73** is shown in Figure 1a. Figure 1b shows a plot of the transition versus the molar ratio of the chiral monomer. There is a progressive increase in transition temperatures parallel with the increase in chiral monomer content, which may be due to the increase in rigidity of the polymer. Copolymers **P55** and **P010**, containing a larger amount of the chiral side chain, are more brittle and crystalline. Examination of the texture of the phases by polarizing optical microscopy required annealing the polymer samples for several hours. A photomicrograph of the cholesteric texture of **P73** is shown in Figure 1c. These copolysiloxanes are quite thermally stable, as shown in the data of Table 2.

Photochemical Modification of a Copolysiloxane P73. The photochemical modification of a cholesteric polymer was meant to demonstrate the capability of reducing the chirality of the cholesteric polymer. This is accomplished by a free radical reaction where the phenolic proton of the chiral monomer is removed.[20] The decrease in the intensity of the hydroxyl group was monitored at 3440 cm⁻¹ by IR and at 5.6 ppm by ¹H NMR spectroscopy. The intensity of the signals corresponding to the hydroxyl group were compared in each spectrum before and after UV irradiation. There is a
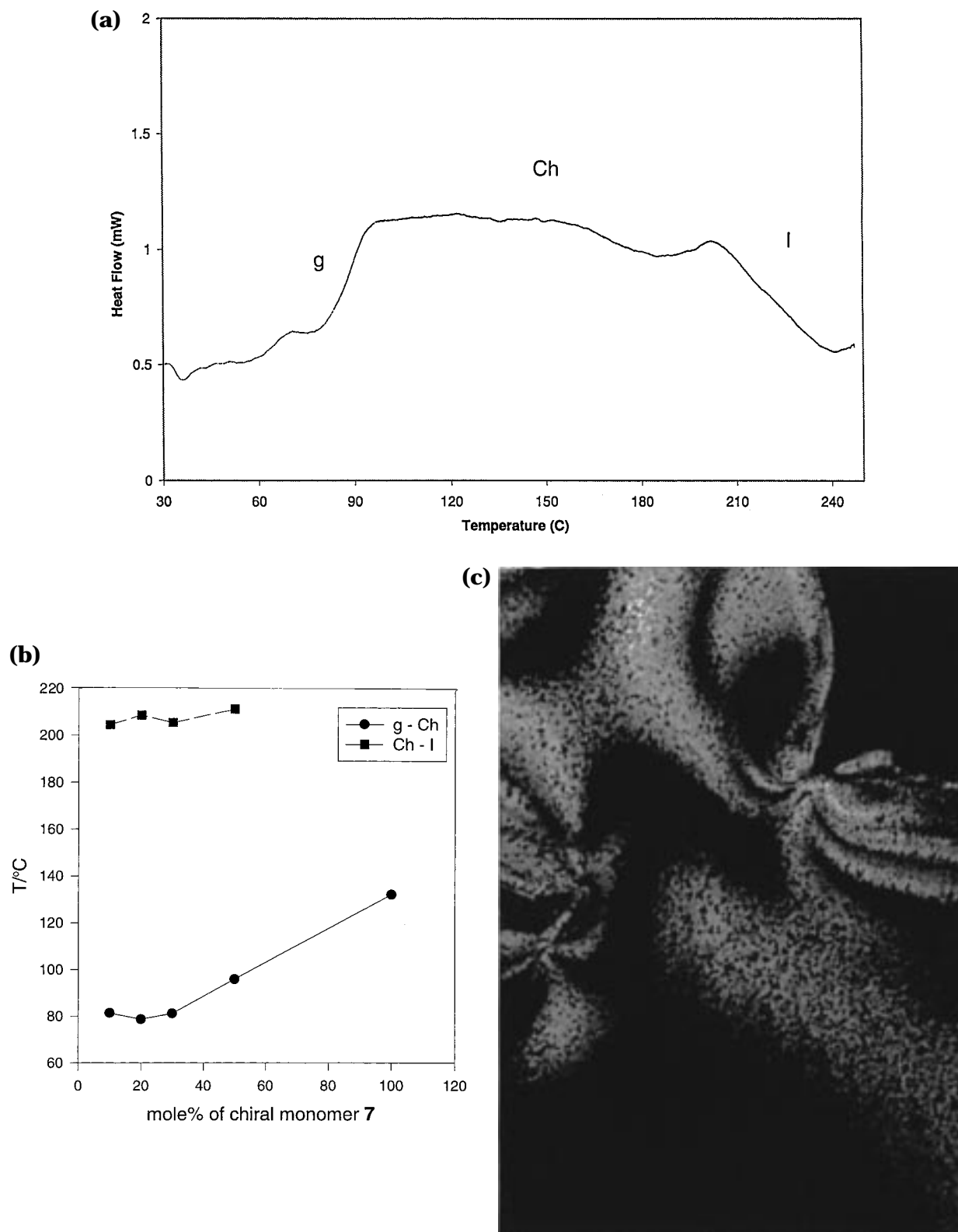
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Figure 1. (a) The DSC thermogram for **P73**, (b) a plot of the transition temperature versus mole% of the chiral monomer **7**, and (c) the photomicrograph of a cholesteric polymer **P73**.

decrease in the intensity of the peak in NMR spectra, as illustrated in Figure 2. The ratio $A_{5.6}/A_{3.8}$ of **P73** is 0.08 and 0.03 before (Figure 2a) and after (Figure 2b) UV irradiation, respectively.

    In a polymer, it is much harder to reduce the chirality of the compound by a photochemical reaction than for its low molecular weight analogue. Therefore, we investigated the effect of photochemical modification of

a (*S*)-bi-2-naphthol using a ^{1}H NMR spectrometer. The results were similar to those obtained from the polymeric studies. The difference is that the decrease in the intensity of the hydroxy peak is much more noticeable, as illustrated in Figure 3. This loss of chirality was also monitored by optical activity measurements. Figure 4 illustrates the loss of optical activity with an increase in UV dosage. The calculated photochemical
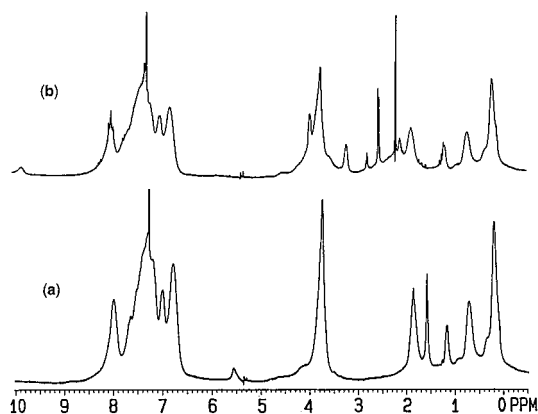
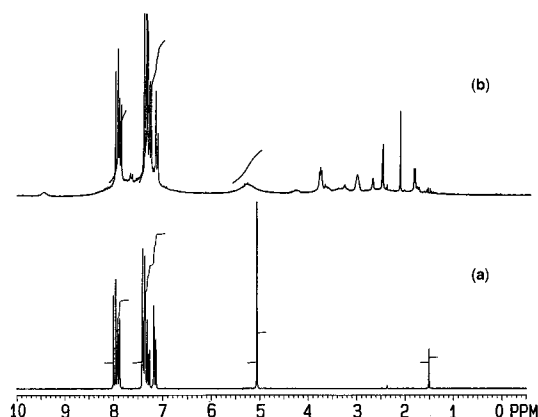**Figure 2.** The ¹H NMR spectra of **P73**: (a) before and (b) after irradiation.

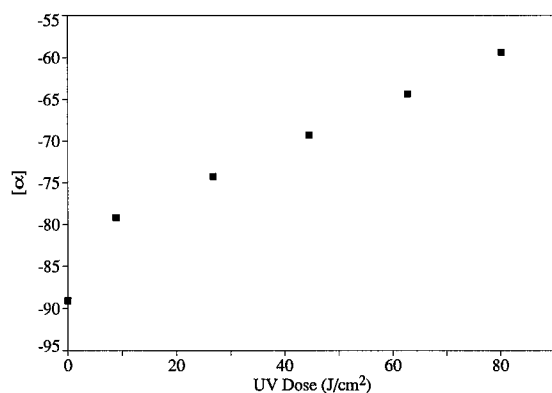**Figure 3.** The ¹H NMR spectra of (*S*)-bi-2-naphthol: (a) before and (b) after irradiation.

Figure 4. A plot of the optical activity of **P73** versus UV dosage.
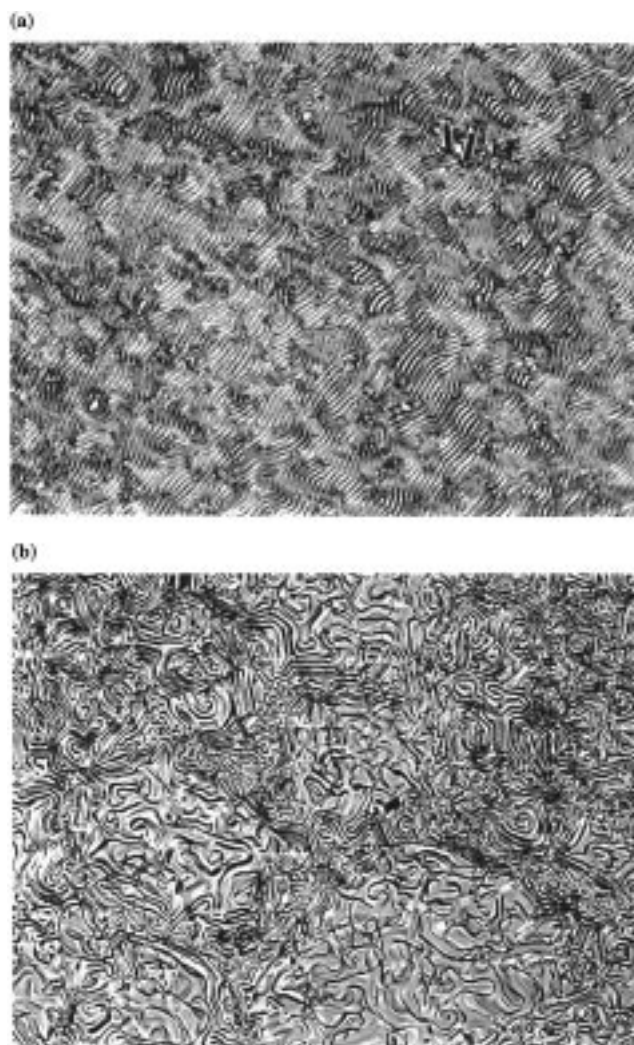

Figure 5. (a) The fingerprint texture of induced chiral phase in a low molecular weight nematic liquid crystal E48 in a test cell. (b) The distorted fingerprint texture after exposing to a 23.4 J/cm² UV radiation.

conversion for polymer **P73** is 34% with the UV dose of 80 J/cm², with accompanying changes in transition temperatures of the resultant polymer: glass, 98 °C; cholesteric phase, 120 °C; isotropic phase.

Induced Cholesteric Phase in a Nematic Liquid Crystal. The ability of the polymers to induce a chiral phase in low molecular weight nematic liquid crystal is studied with a cholesteric material which contains 3% of **P73** and 97% of E48 nematic liquid crystal by weight. The mixture was loaded in a test cell. Figure 5a shows the fingerprint texture of the induced chiral phase with 7.5 μm pitch length. After irradiating the cell with a dosage of 23.4 J/cm² of UV at 330 nm, the pitch of the chiral phase is elongated and exhibits a distorted fingerprint texture (Figure 5b). This indicates that the cholesteric polymer loses its chirality (helical twisting power) due to the removal of its chirality by photoinduced racemization or chemical reaction.

Conclusion

We have synthesized a series of photosensitive cholesteric side chain copolysiloxanes. The chirality of the chiral side chain can be photochemically removed. The photochemical reaction proceeds by the abstraction of a hydrogen atom from the 2′-hydroxyl group of a monosubstituted binaphthol. The reduction in chirality of a cholesteric copolysiloxane is proportional to the dosage of UV irradiation. Complete removal of the chirality of such a cholesteric polymer would require a lengthened UV irradiation due to the complex arrangement of the polymer structure. The chiral polymer is able to induce a cholesteric phase in a low molecular weight nematic liquid crystal.