Photo-Cross-Linkable and Optically Active Side-Chain Liquid-Crystalline Copolymers

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ABSTRACT: A series of new photo-cross-linkable and optically active side-chain liquid-crystalline copolymers, **1a–e**, were prepared from the hydrosilylation reactions of poly(methylhydrosiloxanes) with (*S*)-3-[2-((4-cyano-4′-biphenyloxy)-2-methylethoxy]propene (**2**) and the nematogenic monomer 4-methoxyphenyl 4-(6-hexenyloxy)cinnamate (**3**) in the presence of Speier's catalyst ($H_2PtCl_6·6H_2O$ in propan-2-ol). The copolymers were found to exhibit chiral smectic C phases. Photo-cross-linking these copolymers at their mesomorphic state enhances the thermal stability of the mesophase.

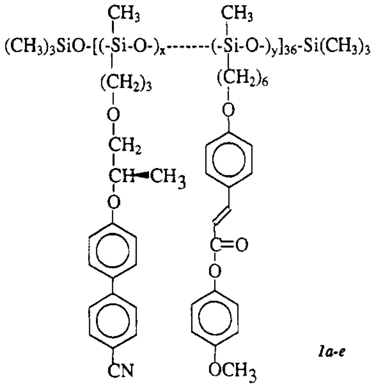
Introduction

Liquid-crystal polymers (LCPs) have become an interesting research topic in the past decade because of the potential applications of LCPs[1–6] or their composites with low molecular mass liquid crystals in electro-optic devices.[7–10] This has led to a fairly large number of side-chain LCPs synthesized in the past two decades to improve their applicability as electro-optic materials. The field of side-chain liquid-crystalline polymers was recently reviewed.[11] Liquid-crystalline polymers have the capability of self-organizing the mesogenic groups into the ordered structure of mesophases and have unique physical polymer characteristics such as freezing the order at the glass transition temperature. In some cases, the induced orientation of the LCPs can be frozen-in by *in-situ* polymerization or cross-linking the monomers in their ordered state.[12–15]

In the smectic mesophase, the molecules are organized in two or three dimensions. Smectic liquid crystals, when consisting of optically active molecules, give rise to a stacking of layers with a preferential twist of the tilt director.[16] Chirality and optical activity can be generated in the LCPs inherently established through the rational design and synthesis of LCPs. In the case of the chiral smectic C phase, the phase composed of optically active molecules, there is a helical superstructure.[17] If the helix is unwound, the layer polarizations point in the same direction and hence the phase will exhibit ferroelectric properties. The subsequent invention of a fast switching light shutter, based on the properties of a ferroelectric liquid crystal, by Clark and Lagerwall[18] led to an explosion of interest in ferroelectric liquid crystals for the display applications.

The study of side-chain liquid-crystalline polysiloxanes with the phenyl cinnamate functional group is of interest primarily because of the ability of the cinnamate group to undergo photo-cross-linking reaction and its effectiveness to form smectic C side-chain polysiloxanes.[19] Photo-cross-linking of this type of linear polymer provides a method of creating liquid-crystalline side-chain polysiloxane networks which may be utilized in the preparation of macroscopically oriented organic ferroelectric polymers for electro-optic devices. Most of the reported optically active side-chain liquid-crystalline polymers have focused on the chiral smectic C phase with the chiral center placed at the tail. Recently, some works on copolymers with the chiral center being part of the flexible spacer have been reported.[20,21] These materials were found to form chiral nematic phases.

The objective of this work was to investigate the locked-in mesomorphic phase or alignment of a side-chain liquid-crystalline polymer through the *in-situ* photo-cross-linking reaction. Mesomorphic monomers (*S*)-3-[2-((4-cyano-4′-biphenylyloxy)-2-methylethoxy]propene (**2**) and 4-methoxyphenyl 4-(6-hexenyloxy)cinnamate (**3**) were selected for this study because they offer the distinct advantage of locking in the liquid-crystal structure of the resulting polymers.



1a-e

	1a	*1b*	*1c*	*1d*	*1e*
x	0.10	0.20	0.40	0.60	0.95
y	0.90	0.80	0.60	0.40	0.05

Experimental Section

Materials. Poly(methylhydrosiloxane) (PMHS) (MW = 2270; DP = 36), (*S*)-(–)-ethyl lactate (98%, $[\alpha]_D^{24} = -8.70$), 3,4-dihydro-2*H*-pyran (DHP), 6-bromo-1-hexene, allyl bromide, $LiAlH_4$, and the other reagents from Aldrich were used as received. Amberlyst 15 was obtained from Aldrich, and hexachloroplatinic hexahydrate, from Strem Chemicals. NaH (80% dispersed in mineral oil, Aldrich) was washed with dry hexane prior to use. 4-Hydroxy-4′-cyanobiphenyl (95%) was purchased from Americal Tokyo Kasei Chemical Co. and used as received.

Anhydrous sodium sulfate was used to dry all organic extracts. Diethyl ether was dried by distilling over Na metal and storing it with Linde molecular sieves. DMF was dried by distilling over P_2O_5 and storing it with Linde molecular sieves.

Techniques. The infrared spectra of the vinylic monomers and their intermediates were obtained from a Pye-Unican 3-200 instrument. For the copolymers, a Nicolet Magna-IR spectrometer 550 was used. The NMR spectra were obtained from a Varian FT-200 spectrometer. For the optical rotation measurement, a Polyscience SR6 polarimeter was used. Transition temperatures were determined from the maxima of the endotherms obtained

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from thermal scans using a Perkin-Elmer DSC-7 equipped with a TAC-7 analyzer. A heating and cooling scan rate of 5 °C/min was used for the vinylic precursors, and a rate of 10 °C/min for the copolymers. Glass transition temperatures (T_g) were read from the endothermic DSC traces, approximated to be midpoints between extrapolated tangents to the baselines above and below the glass transition regions. Photoirradiations of copolymer films were performed using a Perkin-Elmer DPA-7 450-W Xe lamp or a TLC 4-W Hg lamp with the UV intensity of 40 or 2 mW/cm^2 (365 nm), respectively. The textures of the copolymers were studied using a Leitz Laborlux S polarized microscope (magnification 400×) equipped with a Mettler FP52 hot stage, a Mettler FP5 control unit, and a Wild Leitz MP552 camera. X-ray diffraction measurements were made using a Siemens X-1000 WAXS.

Synthesis of 3-[2-((4-Cyano-4′-biphenylyloxy)-2-methylethoxy]propene (2). Ethyl (*S*)-2-(Tetrahydro-2-pyranoxy)propanoate. DHP (140 g, 1.67 mol) was added to (*S*)-(−)-ethyl lactate (118 g, 1.00 mol), followed by concentrated HCl (10 drops). The solution was stirred for 16 h at room temperature. $\mathrm{Na_2CO_3}$ (10 g) was added and the resulting mixture stirred for an additional 2 h. The reaction mixture was filtered and the filtrate rotovaped to give the crude product. The material was distilled at reduced pressure and the desired compound collected at 70–72.5 °C (0.30 mmHg). Yield: 175.6 g (86.4%). IR (film, cm^{-1}): 1740 (str, $\mathrm{CO_2CH_2CH_3}$) and no OH at 3400. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 1.26–1.92 (m, 3$\mathrm{CH_2}$ of THP, 2$\mathrm{CH_3}$, 12H), 3.44–4.26 (m, $\mathrm{OCHOC}\mathit{H}_2$ of THP, $\mathrm{CO_2CH_2}$, 4H), 4.43 (q, $\mathrm{C^*HCO_2}$, 1H), 4.73 (broad t, $\mathrm{OC}\mathit{H}\mathrm{O}$ of THP, 1H).

(*S*)-2-(Tetrahydro-2-pyranoxy)-1-propanol. $\mathrm{LiAlH_4}$ (12 g, 0.32 mol) in 400 mL of dry diethyl ether was contained in an 1-L 2-necked flask equipped with a condenser, drying tube, and dropping funnel. The solution was cooled in an ice bath as ethyl (*S*)-2-(tetrahydro-2-pyranoxy)propanoate (100 g, 0.50 mol) in 150 mL of dry ether was added gradually over 2 h. After addition, the reaction mixture was refluxed for 48 h and then cooled, after which the following were added successively: 12 mL of $\mathrm{H_2O}$, 9 mL of 20% NaOH solution, and 20 mL of $\mathrm{H_2O}$, shaking the flask after each addition. The material was filtered and the filtrate concentrated on a rotovapor and then distilled through a short Vigreux column at reduced pressure. The fraction distilling at 72–75 °C (1.2 mmHg) was collected. Yield: 52.7 g (66.7%). IR (film, cm^{-1}): 3400 (br, str, OH) and no ester absorption. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 1.12–1.24 (2d, $\mathrm{CH_3}$, 3H), 1.53–1.84 (m, 3$\mathrm{CH_2}$ of THP, 6H), 2.51 (t, OH, 1H), 3.41–3.81 (m, OC*H, $\mathrm{OCH_2}$ of THP, 3H), 3.84–4.03 (m, $\mathrm{CH_2OH}$, 2H), 4.56–4.75 (2d, OCHO, 1H).

3-[(*S*)-2-(Tetrahydro-2-pyranoxy)propoxy]propene. To an ice-cooled slurry of NaH (8.4 g, 0.28 mol) in dry DMF under $\mathrm{N_2}$ was added (*S*)-2-(tetrahydro-2-pyranoxy)-1-propanol (22 g, 0.14 mol). The resulting mixture was stirred for 1 h. Allyl bromide (17 g, 0.14 mol) in 10 mL of DMF was then added slowly and the solution stirred at 50 °C for 24 h. To the residue was added 50 mL of $\mathrm{H_2O}$ and the material extracted with diethyl ether twice. The organic extract was dried, concentrated, and distilled through a short Vigreux column. The product was collected as distillate boiling at 80 °C (1 mmHg). Yield: 23.3 g (84.1%). IR (film, cm^{-1}): no OH absorption. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 1.12–1.24 (2d, $\mathrm{CH_3}$, 3H), 1.54–1.86 (m, 3$\mathrm{CH_2}$ of THP, 6H), 3.36–3.87 (m, OC*H, $\mathrm{OCH_2}$ of THP, 3H), 3.90–4.06 (m, $\mathrm{CH_2OCH_2}$, 4H), 4.71–4.82 (m, OCHO, 1H), 5.13–5.33 (m, $\mathrm{CH{=}C}\mathit{H}_2$, 2H), 5.83–5.99 (m, $\mathrm{C}\mathit{H}\mathrm{{=}CH_2}$, 1H).

3-[(*S*)-2-Hydroxypropoxy]propene. To a stirred suspension of Amberlyst 15 (5.0 g) in dry methanol was added 3-[(*S*)-2-(tetrahydro-2-pyranoxy)propoxy]propene (23.3 g, 0.12 mol) in dry methanol. Stirring was continued for 4 h at 40 °C. The resulting mixture was filtered, and the filtrate was concentrated in the rotovapor at room temperature. The concentrate was washed with saturated $\mathrm{NaHCO_3}$ and then water. The solution was extracted twice with diethyl ether. The organic layer was dried, and the solvent was removed by rotovapor to give a clear liquid. Yield: 16.3 g (crude). IR (film, cm^{-1}): 3600–3200 (br, str, OH); 3100, 1650 ($\mathrm{C{=}C}$). ^{1}H NMR ($\mathrm{CDCl_3}$, δ, ppm): 1.15 (d, $\mathrm{CH_3}$, 2H), 2.55 (s, OH, 1H), 3.20–3.29 (m, C*H, 1H), 2.55 (m, $\mathrm{C^*{-}CH_2}$, 2H), 4.01–4.05 (broad d, $\mathrm{OCH_2}$), 5.16–5.34 (m, $\mathrm{C{=}CH_2}$, 2H), 5.85–5.99 (m, $\mathrm{CH{=}C}$, 1H).

3-[(*S*)-2-(4-Tolylsulfonoxy)propoxy]propene. To a cold solution of the 3-[(*S*)-2-hydroxypropoxy]propene (16.31 g) in 15 mL of dry pyridine was added in small portions *p*-toluenesulfonyl chloride (19.6 g, 0.14 mol) dissolved in pyridine. The cold reaction mixture was stirred for an additional 1.5 h and was stored in the refrigerator overnight. The precipitated pyridine hydrochloride was filtered off and rinsed with ether. The combined filtrate and washings were concentrated on a rotovapor at room temperature. The concentrate was poured into a 160-mL slurry of ice and water, and the layers were separated. The dark red aqueous phase was acidified slowly with 3 N HCl and extracted twice with 40-mL portions of ether. The combined organic fractions were washed with equal volumes of cold 3 N HCl divided in three portions and twice with water. The organic extract was dried over $\mathrm{K_2CO_3}$ and $\mathrm{Na_2SO_4}$. The solvent was removed at room temperature to give a crude viscous yellow oil. This material was used in the next reaction without further purification. IR (film, cm^{-1}): no OH absorption; 1360, 1180 ($\mathrm{SO_2}$). ^{1}H NMR ($\mathrm{CDCl_3}$, δ, ppm): 1.30 (d, $\mathrm{C^*{-}CH_3}$, 3H), 2.44 (s, $\mathrm{C_{Ar}{-}CH_3}$, 3H), 3.38–3.50 (m, $\mathrm{C^*{-}CH_2}$, 2H), 3.85–3.90 (d, $\mathrm{OCH_2C{-}C}$, 2H), 4.69–4.72 (m, C*H, 1H), 5.11–5.30 (m, $\mathrm{C{=}CH_2}$, 2H), 5.70–5.78 (m, $\mathrm{CH{=}C}$, 1H), 7.31 (d, aromatic H's ortho to $\mathrm{CH_3}$, 2H), 7.81 (d, aromatic H's ortho to H's to $\mathrm{SO_2}$, 2H).

3-[2-((4-Cyano-4′-biphenylyloxy)-2-methylethoxy]propene (2). To a slurry of NaH (5.2 g, 0.17 mol) and dry DMF stirred under a stream of $\mathrm{N_2}$ was added dropwise a solution of 4-hydroxy-4′-cyanobiphenyl (27.3 g, 0.14 mmol) in DMF. The resulting mixture was stirred for an additional 1.5 h. To this was gradually added a solution of 3-[(*S*)-2-(4-tolylsulfonoxy)propoxy]propene in DMF. The reaction mixture was stirred at 70 °C for 17 h; afterward the temperature was raised to 100 °C and the stirring was continued for 4–6 h. The mixture was concentrated at reduced pressure. Water was added to the concentrate, and the material was extracted twice with ether. The organic extract was washed with 5% aqueous NaOH and then with water and was dried. The ether was rotovaped to yield the crude yellow viscous material which was purified by flash column chromatography using a 2:3 mixture of $\mathrm{CH_2Cl_2}$:hexane as the eluent. The product was further purified by distillation using a Kugelrohr distilling apparatus and was collected at 180 °C (0.45 mmHg). Yield: 17.4 g (59.4%). $[\alpha]_D{}^{24}$ = (+)17.28 ($\mathrm{CH_2Cl_2}$). IR (film, cm^{-1}): 3050 ($\mathrm{C{=}C}$), 2225 (CN); 1600, 1490 (aromatic $\mathrm{C{-}C}$); 1250 ($\mathrm{c{-}O{-}Ph}$). ^{1}H NMR ($\mathrm{CDCl_3}$, δ, ppm): 1.36 (d, $\mathrm{CH_3}$, 3H), 3.52–3.71 (m, $\mathrm{C^*{-}CH_2}$, 2H), 4.07 (d, $\mathrm{OCH_2}$, 2H), 4.58–4.67 (m, C*H, 1H), 5.16–5.34 (m, $\mathrm{CH_2{=}C}$, 2H), 5.85–5.99 (m, $\mathrm{CH{=}C}$, 1H), 7.03 (d, aromatic H's ortho to OC*, 2H), 7.50–7.54 (d, aromatic H's ortho to CN, 2H), 7.61–7.71 (m, meta H's, 4H).

Synthesis of the Phenyl Cinnamate Monomer 3. 4-(5-Hexenoxy)cinnamic Acid. To a stirred solution of sodium hydroxide (7.0 g, 0.18 mol) and 300 mL of 95% ethanol was added 4-hydroxycinnamic acid (12.5 g, 0.076 mol). The mixture was refluxed for 30 min before 6-bromo-1-hexene (10.0 g, 0.061 mol) was added dropwise. Reflux was continued for 24 h, then NaOH pellets (3.5 g, 0.09 mol) were added, and the mixture was refluxed for an additional 3 h. The reaction mixture was poured into ice water. This solution was acidified with 3 N HCl and stirred vigorously for 30 min to give the white precipitate which was collected, washed several times with cold water, and dried in a vacuum oven. This material was used without further purification. Yield: 11.48 g (79%). IR (Nujol, cm^{-1}): 3381 (br, str, OH); 1675 ($\mathrm{O{-}C({=}O)}$); 1631 ($\mathrm{C{=}C}$); 1608, 1514 (aromatic $\mathrm{C{-}C}$); 1254 ($\mathrm{C{-}O{-}Ph}$).

^{1}H NMR ($\mathrm{CDCl_3}$, δ, ppm): 1.52–1.88 (m, $\mathrm{(CH_2)_2}$, 4H), 2.10–2.18 (m, $\mathrm{CH_2C{=}C}$, 2H), 3.96–4.02 (2, $\mathrm{CH_2O}$, 2H), 4.95–5.07 (m, $\mathrm{CH_2{=}C}$, 2H), 5.75–5.89 (m, $\mathrm{CH{=}C}$, 1H), 6.20–6.33 (d, $\mathrm{C{=}CH{-}COOH}$, 1H), 6.83–6.91 (d, aromatic H's ortho to $\mathrm{OCH_2}$, 2H), 7.36–7.48 (d, aromatic H's ortho to $\mathrm{CH{=}CH}$, 2H), 7.56–7.65 (d, $\mathrm{C_{Ar}{-}CH{=}C}$, 1H).

4-Methoxyphenyl 4-(5-Hexenoxy)cinnamate (3). Dicyclohexylcarbodiimide (DCC) (10.5 g, 0.051 mol) and (*N*,*N*-dimethylamino)pyridine (DMAP) (0.60 g, 0.0049 mol) were added to a stirred solution of the acid (11.48 g, 0.047 mol) in sieve-dried dichloromethane. 4-Methoxyphenol (6.56 g, 0.053 mol) was then added, and the resulting milky suspension was stirred overnight at room temperature. *N*,*N*′-Dicyclohexylurea was filtered off, and the filtrate was washed with 5% HCl and then water and dried. The solvent was removed, and the crude material was purified by flash column chromatography using CH_2Cl_2 as the eluent. The product was recrystallized in hexane. The DSC heating scan for this compound showed a melting point at 83.3 °C and a clearing point at 111.1 °C. Yield: 6.2 g (37.5%). IR (Nujol, cm^{-1}): 1730 (O—C(=O)) 1636 (C=C) 1608, 1509 (aromatic (C—C). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.54–1.61 (m, CH_2, 2H), 1.78–1.86 (m, CH_2, 2H), 2.12–2.16 (m, CH_2—C=C, 2H), 3.89 (s, OCH_3, 3H), 4.01 (t, CH_2O, 2H), 4.96–5.09 (m, CH_2=C, 2H), 5.71–5.95 (m, CH=C, 1H), 6.44–6.51 (d, CH—C(=O)O, 1H), 6.89–6.93 (d, aromatic H's ortho to OCH_2– and OCH_3, 4H), 7.06–7.11 (d, aromatic H's ortho to O—C(=O), 2H), 7.50–7.54 (d, ortho H's to CH=CH, 2H), 7.77–7.85 (d, C_{Ar}—CH=C, 1H).

Synthesis of Siloxane-Based Copolymers 1a-e. A stirred mixture of poly(hydromethylsiloxane) (PHMS) (0.5 g, 7.2 mmol (Si—H)), vinyl monomers 2 and 3 (7.9 mmol; mol % of chiral monomer is 10, 20, 40, 60, and 95, respectively), 5% hexachloroplatinic acid in isopropyl alcohol (2 drops), and sodium-dried toluene (5 mL) was heated under N_2 and anhydrous conditions at 110 °C for 20–24 h. The solution was cooled to room temperature, and the solvent was removed under reduced pressure. The crude polymer was purified by several reprecipitations from the CH_2Cl_2 solution into cold diethyl ether or methanol. This procedure was repeated until the product was shown by TLC to be free from monomer. Average yield: (86.4%). IR (film, cm^{-1}): 2223 (CN); 1725 (O—C(=O)); 1635 (C=C); 1600, 1500 (aromatic C—C); 1250 (C—O—Ph). ^{13}C NMR ($CDCl_3$, δ, ppm): (peaks due to the chiral side chain) 158.81 (C_{Ar}—O), 145.21 (aromatic C-4 to CN), 132.87 (aromatic C-2 to CN), 131.81 (aromatic C-4 to OC*), 128.64 (aromatic C-3 to OC*), 127.26 (aromatic C-3 to CN), 119.27 (CN), 116.64 (aromatic C-2 to OC*), 110.50 (C_{Ar}—CN), 74.55 (C*), 74.16 (O—C—C*), 73.41 (O—C—$(CH_2)_3$–), 23.53, 17.34, 13.85 (aliphatic C's); (peaks due to the cinnamate side chain) 166.16 (O—C(=O)–), 161.24 (C_{Ar}—O—$(CH_2)_6$–), 157.29 (C_{Ar}—OCH_3), 146.03 (C_{Ar}—C=), 144.44 (C_{Ar}—O—C(=O)–), 132.69 (C_{Ar}—C=), 130.13 (aromatic C-2 to C=C, 122.56 (aromatic C-3 to OCH_3), 115.08 (O—C(=O)—C=), 114.91 (aromatic C-2 to OCH_3), 114.57 (aromatic C-2 to O—$(CH_2)_6$–), 68.19 (O—C—$(CH_2)_6$–), 55.71 (OCH_3), 26.04, 29.41, 33.32, 33.39, 33.53 (aliphatic C's).

Photo-Cross-Linking of the Copolymer 1a. For determination of the kinetics of photochemical cross-linking, a thin film of copolymer 1a was deposited on a sodium chloride plate. The film was irradiated with the 4-W mercury lamp (365 nm, 2 mW/cm^2) for certain durations of time. After each time increment, the IR spectrum of the sample was taken. The temperature of the sample during irradiation was maintained at 90 ± 2 °C.

To investigate the effect of cross-linking in the mesomorphic and in the isotropic states, two sets of thin-film samples of copolymers 1a–d were cast into DSC sample pans. One set was irradiated with a xenon lamp (40 mW/cm^2) for 50 min at 90 °C, and the other set was irradiated at the temperatures 10 deg above the respective clearing points of the different copolymers. The irradiated samples were analyzed by DSC. No NMR analysis was done because of the solubility problem of the resulting irradiated materials.

Results and Discussion

Mesomorphic Properties of Monomers. The synthesis of chiral compound 2 was carried out by following the synthesis in Scheme 1. ^{1}H NMR spectra of monomers 2 and 3 are shown in Figure 1. The optical activity of the chiral monomer ($[\alpha]_D{}^{24} = +17.28$) was found to be higher and of the opposite sense compared to that of the starting ethyl lactate ($[\alpha]_D{}^{24} = -8.70$). Theses data suggest that the last step in the synthetic scheme occurs via a S_N2 mechanism with the inverstion of configuration at the chiral center. The less probable S_N1 mechanism leads to racemization which could have otherwise reduced the optical activity of the compound.

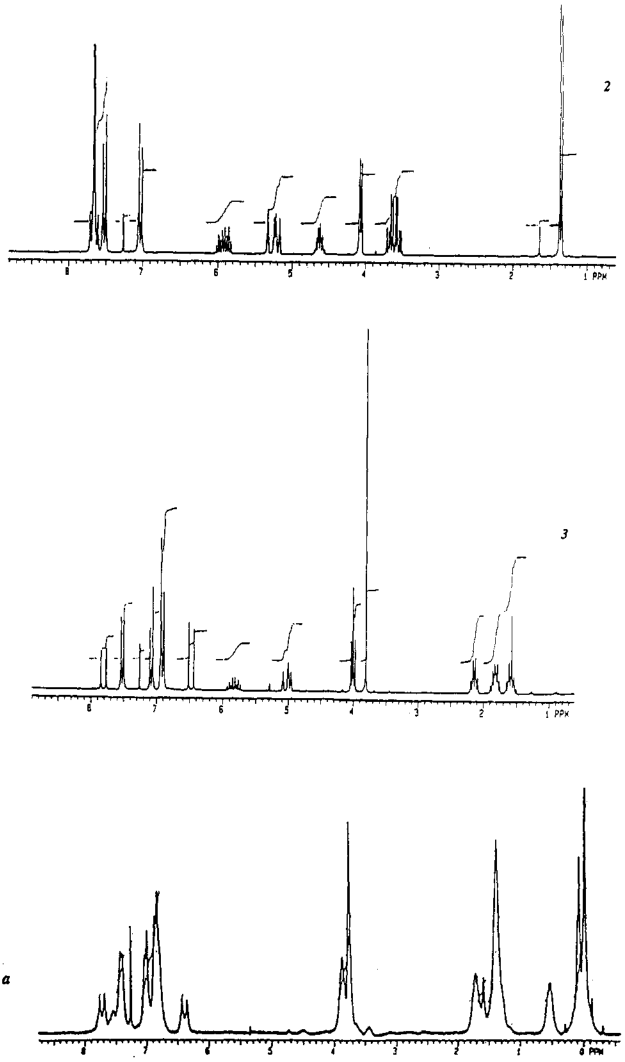
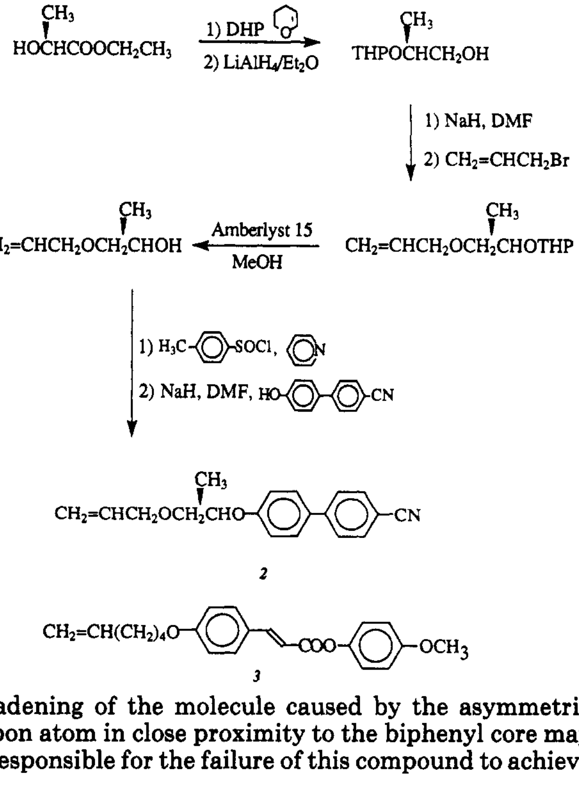


Figure 1. ^{1}H NMR spectra of monomers 2 and 3 and copolymer 1a.

Scheme 1



The optically active product, however, was found to be isotropic at room temperature according to the DSC study from −30 to +50 °C. The combined effects of the low melting point caused by the specific alkoxy group and the broadening of the molecule caused by the asymmetric carbon atom in close proximity to the biphenyl core may be responsible for the failure of this compound to achieve

Table 1. Transition Temperatures of Copolymers 1a–e[a]

copolymer	*f*	transition temp (°C)	ΔH_{S_c*-I}(J/g)
1a	0.1	g 26.6 S_c* 147.3 I	2.6
1b	0.2	g 22.6 S_c* 137.6 I	5.1
1c	0.4	g 15.9 S_c* 132.8 I	6.4
1d	0.6	g 11.3 S_c* 113.1 I	4.1
1e	0.95	g 2.2 I	

[a] Mole ratio of monomer **2** in the monomer feed. g: glass transition. S_c*: chiral smectic C. I: isotropic phase.

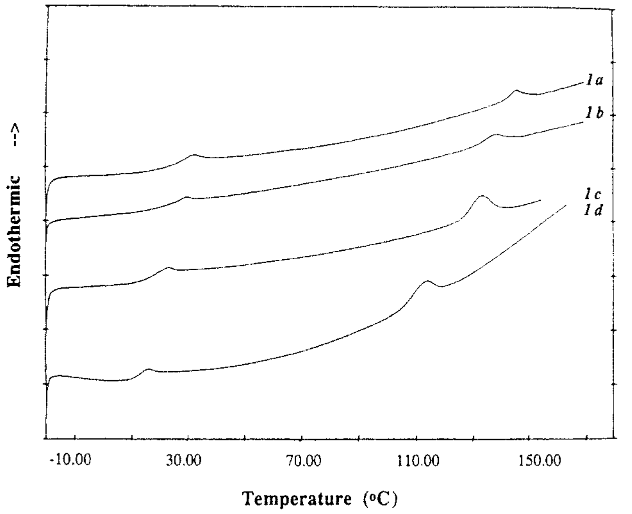


Figure 2. DSC thermograms of the copolymer **1a–d**, obtained from the second heating scans.

any mesomorphic order. Although this phenomenon has not been confirmed for the specific type of molecules, the disruptive effect of terminal groups with a second oxygen atom and of branched alkoxy groups on the thermal stability of mesophases has been reported for other types of molecules.[22] The phenyl cinnamate-containing monomer **3**, prepared in a two-step synthesis,[19] was found to be nematogenic in a temperature range of 83.3–111.1 °C.

Mesomorphic Properties of Copolymers. In the preparation of these polymers, a 10 mol % stoichiometric excess of the reacting alkenes was employed to ensure full reaction of the Si–H units on the PHMS backbone. The extent of completion of hydrosilation had been assessed by IR and NMR spectroscopy. The ^{1}H NMR spectrum of copolymer **1a** is shown in Figure 1. In this spectrum the Si–H peak at 4.7 ppm is negligible, although it is still detectable. The time of reaction was extended (>24 h) in an attempt to push the hydrosilylation reaction to completion. But this failed due to the gelation problem encountered in the reaction mixture. It is also difficult to quantify the extent of hydrosilylation for the different copolymers by IR spectroscopy.[23] But suffice it to say that all the reactions had gone near completion, as evidenced by the negligible Si–H absorptions at 2160 cm^{-1}.

Thermal analysis results of the prepared side-chain polysiloxanes **1a–e** are summarized in Table 1. The DSC heating curves for these copolymers exhibited a wide mesophase range, as shown in Figure 2. The data showed that an increase in the nonmesogenic chiral monomer **2** content in the reaction mixture resulted in a lower glass transition and clearing temperature copolymer. The increasing content of the nonmesogenic chiral side chains dilutes the content of mesogenic side chains and decreases the transition temperatures. At a mole ratio of 0.95:0.5 of monomer **2** to monomer **3** in the feed, copolymer **1e** was found to be nonmesomorphic. It is expected that the homopolymer containing the chiral substrate will be nonmesomorphic due to the disruptive effect of the oligo(ethylene oxide) spacer on the ability of the cyanobiphenyl side groups to interdigitate.

The mesogenic copolymers exhibited the schlieren textures indicative of the S_C* phase. Microscopy investigations showed that these copolymers exhibit the pseodohomeotropic texture. The change in the birefringence colors with temperature (usually associated with changes in the tilt angle) was noted particularly in copolymer **1a** (Figure 3a,b). The existence of some biphasic regions was observed as the fully isotropic liquid was being cooled. The observed biphase region consisted of small birefringent needles either on an isotropic medium or on a thinly diffused grained texture. This biphasic phenomenon has been reported with other side-chain polymers[20,21,24,25] and has been attributed to the high viscosity and polydispersity of the material.

The identification of the smectic mesophase was supported by an X-ray diffraction study. The X-ray pattern for the unoriented sample of copolymer **1a** (Figure 4) showed one sharp inner ring corresponding to a lamellar thickness of 25.8 Å and a diffused outer ring reflecting the absence of ordering within the layer planes. Although there was no significant change of the layer spacing obtained from 50 to 145 °C, it is reasonable to assign the S_C* phase on the basis of texture observation. The calculated length of the mesogenic side chain (including the Si–CH$_3$) is 18.2 Å. This value, compared with that obtained from the X-ray study (25.8 Å), suggests an interdigitated tilted double-layer structure.

There is an increase in the order of the system in going from the vinylic precursors to the copolymers. This is shown by the higher clearing temperatures of the copolymers and their more ordered chiral smectic phase relative to the nematic cinnamate precursor. These results are supportive of the reported observation on the enhancement effect of phenyl cinnamate groups[19] on the tendency of side-chain polysiloxanes to give smectic C phases.[26,27]

Photo-Cross-Linking of Coplymer 1a. The photo-cross-linking reaction was carried out on thin films of the prepared polymers using either a hand-held UV lamp or the UV light of a differential photocalorimeter. The progress of the reaction was monitored by the decrease in the –C=C– IR absorption at 1635 cm^{-1}. Figure 5 shows the FTIR spectra of polymer **1a** before and after UV irradiation (2 mW/cm^2) at 90 °C for 50 min. The absorption of the peak at 1635 cm^{-1} decreased after photoirradiation. This indicates that the photoreaction has occurred and that the concentration of the C=C adjacent to the carbonyl group has decreased. This decrease reflects the overall reactivity of the cinnamate chromophores involving all possible photochemical reactions of the excited cinnamate, i.e., photodimerization ([$2\pi + 2\pi$] cycloaddition), photo-Fries reaction, and photoisomerization. The [$2\pi + 2\pi$] cycloaddition reaction between the carbon—carbon double bonds of the cinnamate ester side chains is believed to be the mechanism for the photo-cross-linking process in this type of polymeric materials.[28-32] The extent of photo-cross-linking was found by evaluating the decrease in absorbance of C=C at 1635 cm^{-1} (A_{1635}) relative to an internal standard absorbance. The C—H absorbance at 2933 cm^{-1} (A_{2933}) was chosen as the internal standard since it is not affected by the photoirradiation. The result of these measurements is shown in Figure 6, where the percent of conversion, expressed as $1 - A_t/A_0$ ($A_0 = A_{1635}/A_{2933}$ at time t and $A_0 = A_t$ at $t = 0$), is plotted as a function of the irradiation time t (minutes) in the S_C* phase. It can be derived from the plot that, after 1.7 h of UV irradiation, 24% of the

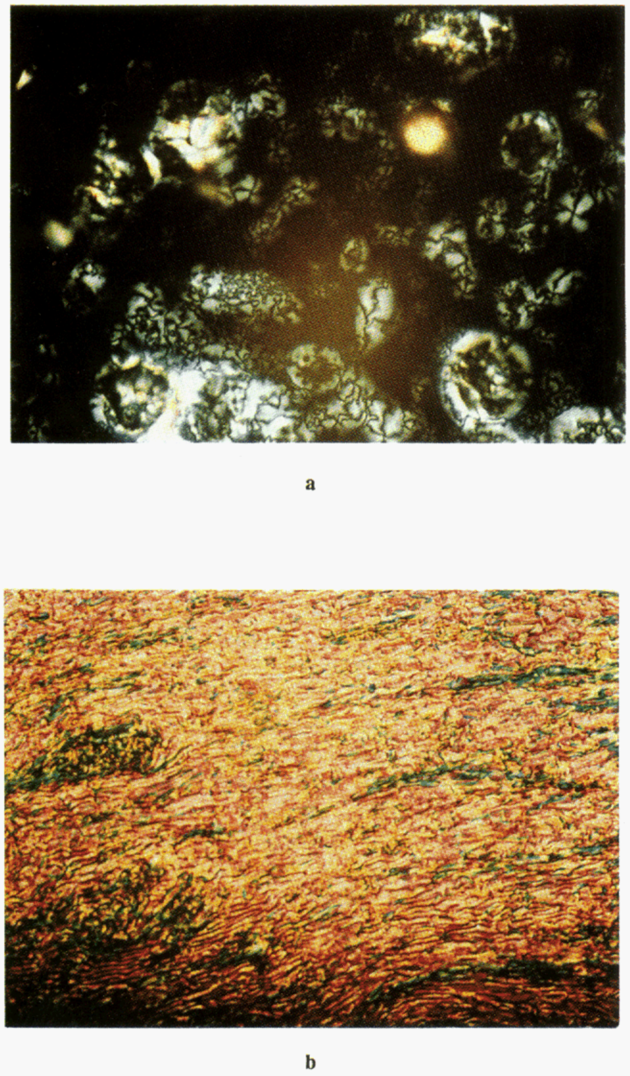


Figure 3. Photomicrographs of copolymer **1a**: (a) pseudohomeotropic schlieren texture of the chiral smectic C phase; (b) color schlieren texture of the chiral smectic C phase.

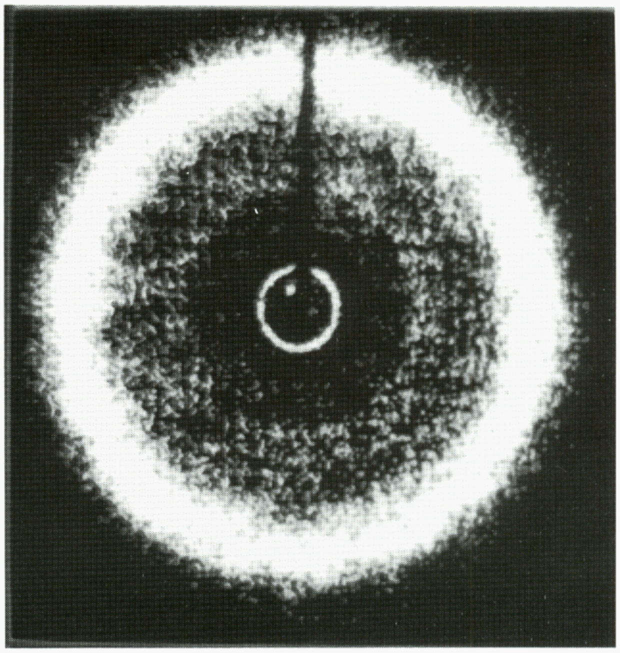


Figure 4. WAXD pattern of a S_c* phase of the unoriented copolymer **1a**.

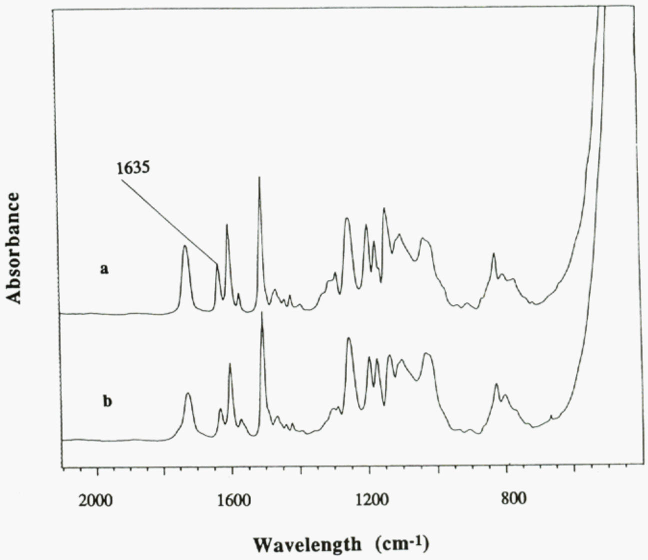


Figure 5. FT-IR spectra of the copolymer **1a**: (a) before irradiation; (b) after irradiation at 90 °C for 50 min.

cinnamate has reacted. Further irradiation does not increase the conversion. This is expected that the dimerization in the mesomorphic state depends on the geometrical orientation of the neighboring cinnamate groups and the intensity of the UV light.

The effect of photoirradiation on the transition temperatures of the copolymers was investigated with a 50-min irradiation of their mesomorphic states (90 °C). As expected, the state of order during the cross-linking reaction should affect the phase transition of the final network.[33] Stabilization of the ordered state was observed from the increase in the clearing temperature of the copolymers while being irradiated in their liquid-crystalline states. This indicates that the distribution of the net points stabilizes the smectic order during the cross-linking reaction. It is also possible that stabilization may have been due to the increase in the molecular weight associated with the cross-linking reaction.[34] The result is summarized in the Table 2.

However, irradiation performed at the temperature 10 deg above the isotropic phase gave no significant change in the clearing points of copolymers **1b** and **1c**. With copolymers **1a** and **1d**, a slight decrease in clearing points (1–2 deg lower) was noted. The observed decrease in phase transition temperature after irradiating the copolymers at temperatures above T_{cl} suggests that cross-linking of the polymer matrix at the isotropic temperature destabilizes the ordered state and suppresses the reorientation of the mesogenic side groups.

The irradiated materials turned yellow as the irradiation time is increased. This has been attributed to the photo-Fries rearrangement[35] which results in the formation of a hydroxychalcone derivative. This yellowing was also reported in recent studies with cinnamate-based polyesters[31] and polymethacrylates.[36] The extent of this photo-fries rearrangement could not be verified by NMR analysis since the photoirradiated materials are insoluble in the available solvents. This side reaction can be minimized by using long wavelength ($\lambda \geq 313$ nm) UV light for photo-cross-linking.

Conclusion

The absence of a chiral nematic phase in the synthesized copolymers suggests that the phenyl cinnamate side chain is the dominant component in the chiral smectic C phase formation. Increasing the content of mesogenic cinnamate

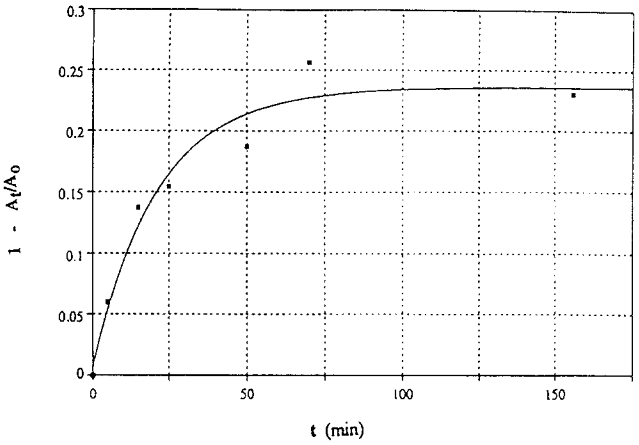


Figure 6. Plot of photochemical reactivity vs the UV irradiation time for copolymer **1a**.

Table 2. Changes in Transition Temperatures of Copolymers 1a–d[a] after Photoirradiation at Their Mesomorphic State

copolymer	ΔT_g (°C)	$\Delta T_{S_c^*-I}$ (°C)	$\Delta H_{S_c^*-I}$ (J/g)
1a	1.5	4.0	1.0
1b	0.8	1.5	4.1
1c	3.0	3.4	5.4
1d	2.5	4.6	4.1

[a] ΔT_g: increase in the glass transition temperature. $\Delta T_{S_c^*-I}$: increase in the isotropization temperature.

side groups resulted in high-clearing-temperature copolymers. The high degree of smectic order was also reflected in the relatively high ΔH values for the isotropization transition. In addition to the induction of chirality in the polymeric system, the low-viscosity chiral monomer dilutes the content of the mesogenic side chains and leads to lowering the glass transition temperatures. Photo-cross-linking the liquid-crystalline polymers at their mesomorphic state stabilizes the ordered state. These photosensitive LCPs have the potential to form liquid-crystalline elastomers and to be used as binders for polymer-dispersed liquid crystal displays.

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