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Photochromic chiral liquid crystalline systems containing spiro-oxazine with a chiral substituent I. Synthesis and characterization of compounds

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Photochromic chiral liquid crystalline systems containing spiro-oxazine with a chiral substituent I. Synthesis and characterization of compounds

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Photochromic acrylates containing both biphenylene and spiro-oxazine moieties with a chiral substituent and the related polymers were prepared and yielded photochromic chiral liquid crystalline systems. The photochromic acrylates containing both an undecamethylene group and a (2*S*, 3*S*)-2-chloro-3-methylpentanoyloxy group (A11SOP) or a (−)-menthoxyacetoxy group (A11SOM) gave a supercooled mesophase; the latter reflected right-handed visible light (blue colour) at room temperature. On the other hand, the photochromic acrylate containing both the (*R*)-(−)-2-methylpropylene and (2*S*, 3*S*)-2-chloro-3-methylpentanoyloxy groups (A3SOP) showed no mesophase. The related homopolymers, PA11SOP and PA11SOM, did not exhibit mesophases because of steric hindrance between the side groups of the polymers. However, only PA11SOM exhibited shear-induced birefringence under 100–104°C. Several copolymers consisting of the nematogenic monomer, 4-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-benzonitrile (A6CN), and A11SOP or A11SOM possessed a smectic phase due to reduction of the steric hindrance between the potentially smectogenic A11SOP or A11SOM moieties.

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1. Introduction

Recently, the manipulation of chiral liquid crystalline systems by means of light-induced irreversible and reversible reactions of chiral photosensitive compounds has attracted much attention because of the potential for applications in areas including optical switches, optical filters, and optical memory devices [1–7]. Helical pitch induction [3] or its change [1, 2, 4, 5] in chiral nematic liquid crystalline systems and spontaneous polarization change [6, 7] in ferroelectric liquid crystalline systems have been demonstrated.

In chiral nematic liquid crystals, the wavelength of maximum reflection (λ_R) is related to the pitch (p) of the chiral nematic helix by

$$\lambda_R = \bar{n}p$$

where $\bar{n}$ is the average refractive index of the chiral nematic system. A photochromic chiral nematic liquid crystal may be prepared by doping a chiral photochromic compound into a nematic liquid crystal. In this case, it is expected that the pitch is inversely proportional to the concentration of chiral photochromic dopant (x_{ch}) in a certain concentration range of the chiral dopant as given by the following equation:

$$1/p = \beta x_{ch}$$

where β is called the helical twisting power. If photoreaction of the chiral dopant occurs, β will change because the value is dependent upon the chemical structure of the chiral dopant. Therefore, it is possible to manipulate the pitch by controlling the photoreaction of the chiral dopant.

We have been studying spiro-oxazine-containing liquid crystal materials systematically [8–10]. As far as we know, there has been no study of a photochromic chiral nematic liquid crystalline system doped with a spiro-oxazine with a chiral substituent. Although spiro-oxazines have a spiro-carbon atom as a chiral centre, they usually exist as racemates. Even if enantiomers are separated, each enantiomer is racemized by thermal

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[11] and optical interconversions. Thus, spiro-oxazines are not usually able to act as chiral dopants. To use spiro-oxazines as chiral dopants, their synthesis with a chiral substituent is required. The concept of our system is represented in scheme 1 [12]. This paper describes the synthesis and characterization of the novel spiro-oxazine-containing monomers with the chiral substituents shown in figure 1 and the related polymers. Investigations of the potential of the spiro-oxazine derivatives to act as photochromic chiral dopants will appear elsewhere [13].

2. Experimental

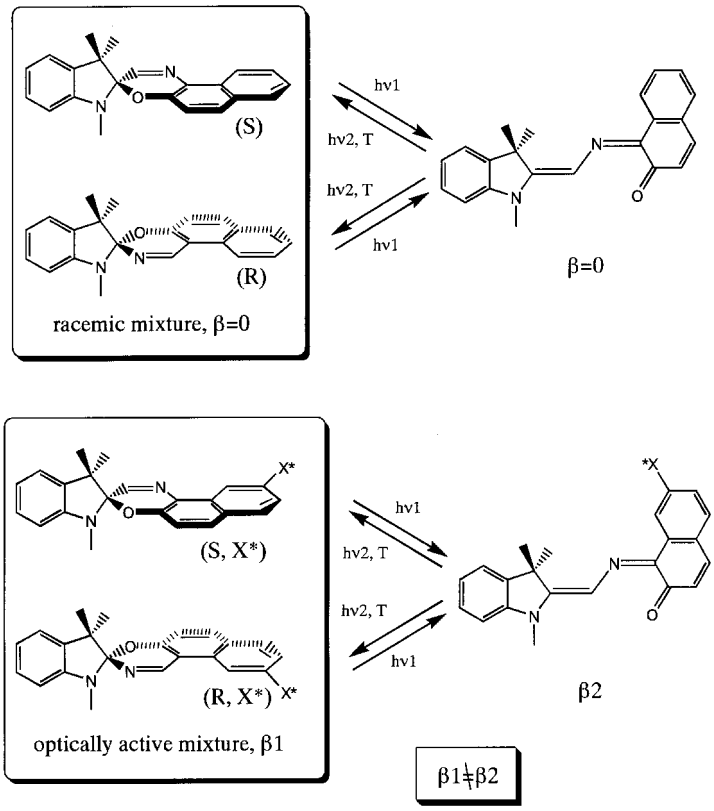
4-[4-(6-Acryloyloxyhexyloxy)benzoyloxy]benzonitrile (A6CN) was prepared according to the procedure described in [14]. The spiro-oxazine-containing monomers with chiral substituents were prepared according to the procedure reported in [8]. The synthetic route to the hydroxyl-containing spiro-oxazine with a chiral substituent is referred to as Krongauz's method [15] and shown in scheme 2. The synthesis of 5-(−)-menthoxyacetoxy-9′-hydroxy-(1,3-dihydro-1,3,3-trimethylspiro-[2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine]) is described here in detail.

2.1. *5-Methoxy-2,3,3,-trimethylindolenine (**1**)*

4-Methoxyphenylhydrazine hydrochloride (50.0 g, 286.3 mmol) and methyl isopropyl ketone (28.0 g, 325.1 mmol) were added to abs. ethanol (500 ml) and the mixture was heated at reflux with stirring for 5 h. After filtration, the solvent was evaporated and CH_2Cl_2 was added to the resulting product to precipitate impurities. After a second filtration, the solution was washed with water, dried with Na_2SO_4, and the solvent evaporated. The resulting product was used directly in the following step without further purification. ^{1}H NMR ($CDCl_3$): $\delta = 1.28$ (s, 6H), 2.24 (s, 3H), 3.83 (s, 3H), 6.81 (dd, 1H), 6.83 (d, 1H), 7.42 (d, 1H).

2.2. *5-Hydroxy-2,3,3-trimethylindolenine (**2**)*

A solution of compound **1** in sieve-dried CH_2Cl_2 (100 ml) was cooled in a dry ice/ethanol bath. Boron tribromide (150.0 g, 598.7 mmol) in sieve-dried CH_2Cl_2 (100 ml) was added dropwise to the solution. After the mixture had been stirred for 6 h, the dry ice/ethanol bath was removed and the mixture left with stirring at room temperature overnight. The mixture was carefully neutralized by saturated Na_2CO_3 solution. To maintain stirring, CH_2Cl_2 (200 ml) and a small amount of water were added to the mixture during neutralization. After neutralization the mixture was filtered and the CH_2Cl_2 layer was separated. The solution was washed with water, dried with Na_2SO_4, and the CH_2Cl_2 evaporated. The resulting product was recrystallized twice from ethanol; yield 30.1 g (60%). ^{1}H NMR ($CDCl_3$): $\delta = 1.28$



Scheme 1. Schematic representation of the concept.

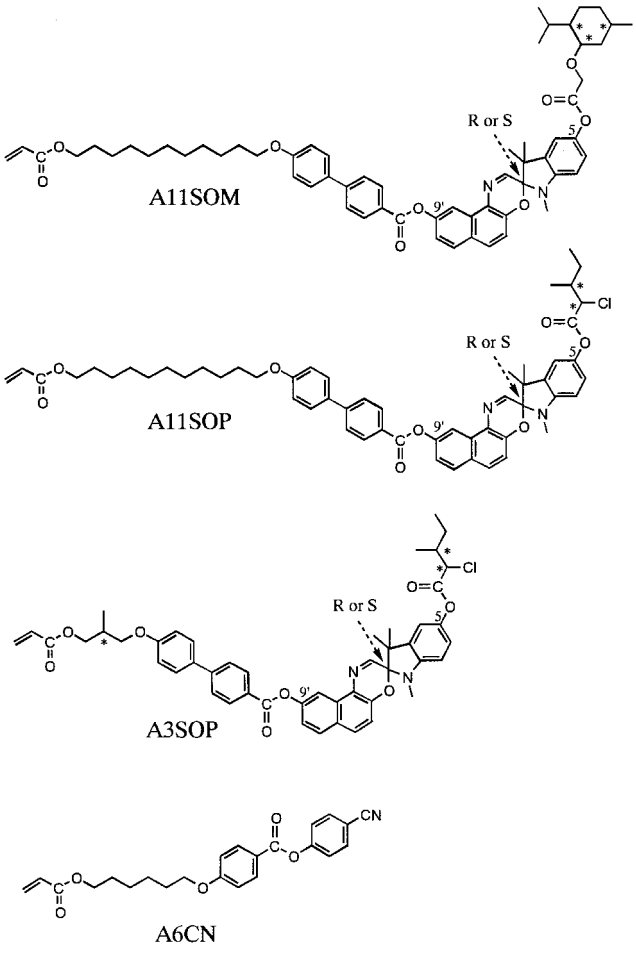


Figure 1. Structures of the compounds in this study.

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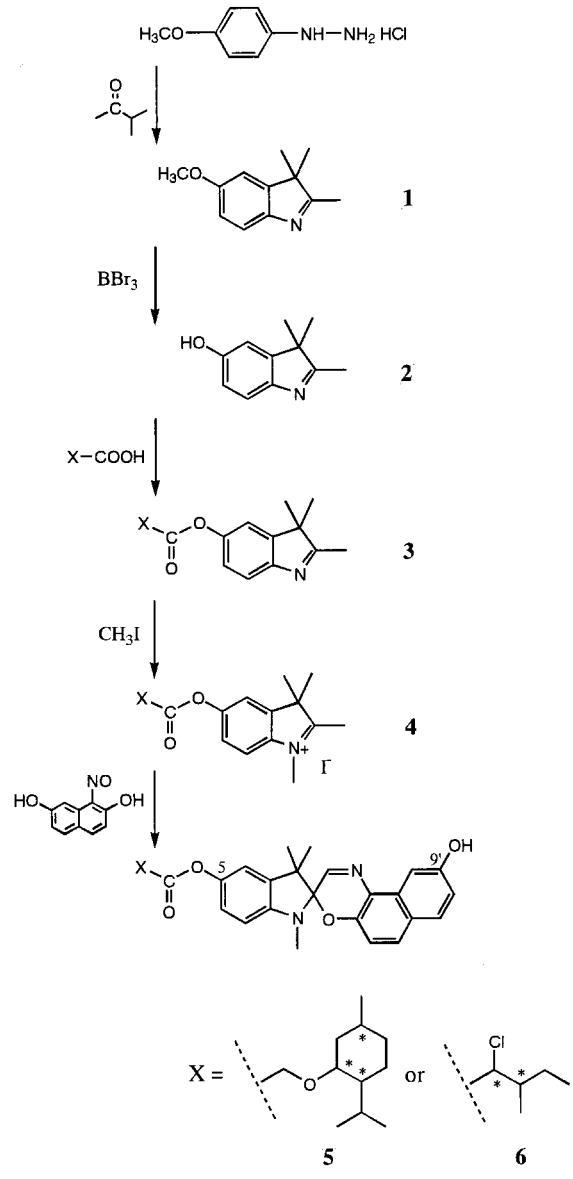
(s, 6H), 2.26 (s, 3H), 6.79 (dd, 1H), 6.86 (d, 1H), 7.30 (d, 1H), 10.18 (1H, −O<u>H</u>).

2.3. *5-(−)-Menthoxyaceto xy-2,3,3-tr imethylindolenine (**3**)*

Compound **2** (18.4 g, 105.0 mmol), (−)-menthoxyacetic acid (25.0 g, 116.7 mmol), and 4-dimethylaminopyridine (4-DMAP) (2.0 g, 16.4 mmol) were dissolved in sieve-dried CH_2Cl_2 (200 ml) at room temperature. *N,N′*-Dicyclohexylcarbodi-imide (DCC) (25.3 g, 122.6 mmol) dissolved in sieve-dried CH_2Cl_2 (200 ml) was added to the mixture which was then stirred for 3 h at room temperature. After filtration the solution was washed with water, dried with Na_2SO_4, and the solvent evaporated. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane, 2/5); yield 33.8 g (87%). ^{1}H NMR ($CDCl_3$): δ = 0.82 (d, 3H), 0.92 (d, 3H), 0.94 (d, 3H), 0.86–1.04 (m, 3H), 1.24–1.27 (m, 1H), 1.29 (s, 6H), 1.31–1.42 (m, 1H), 1.64–1.68 (m, 2H), 2.13–2.17 (m, 1H), 2.26 (s, 3H), 2.31–2.38 (m, 1H), 3.25–3.30 (m, 1H), 4.35 (q, 2H), 7.02 (dd, 1H), 7.05 (d, 1H), 7.49 (d, 1H).



Scheme 2. Synthesis of the hydroxyl-containing spiro-oxazines with chiral substituents.

2.4. *5-(−)-Menthoxyacetoxy-1,2,3,3-tetramethyl-3H-indolium iodide (**4**)*

Compound **3** (33.8 g, 91.0 mmol) was dissolved in sieve-dried CH_2Cl_2 (40 ml). Methyl iodide (28.3 g, 454.6 mmol) was added dropwise to the solution and the mixture was heated at reflux with stirring for 12 h. The resulting solid was washed with benzene and recrystallized from ethanol; yield 40.5 g (87%). ^{1}H NMR (DMSO): δ = 0.84 (d, 3H), 0.94 (d, 3H), 0.98 (d, 3H), 0.86–1.09 (m, 3H), 1.25–1.30 (m, 1H), 1.40–1.47 (m, 1H), 1.61 (s, 6H), 1.60–1.71 (m, 2H), 2.24–2.26 (m, 1H), 2.31–2.37 (m, 1H), 2.84 (s, 3H), 3.33–3.38 (m, 1H), 4.05 (s, 3H), 4.52 (q, 2H), 7.50 (dd, 1H), 7.77 (d, 1H), 8.03 (d, 1H).

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2.5. *5-(−)-Menthoxyacetoxy-9′-hydroxy-{1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine]} (**5**)*

Compound **4** (24.2 g, 47.2 mmol) and 1-nitroso-2,7-dihydroxynaphthalene (9.0 g, 47.6 mmol) were added to dry toluene (500 ml). The mixture was heated to 85°C with stirring. Piperidine (5.1 ml, 52.3 mmol) dissolved in dry toluene (50 ml) was added dropwise to the mixture which was then stirred for 30 min at 85°C; the solvent was then evaporated. Some hydrolysis of compound **4** might occur during reaction. The crude product was purified twice by column chromatography (silica gel, ethyl acetate/hexane, 1/3); yield 1.6 g (6.1%). ^{1}H NMR ($CDCl_3$): $\delta = 0.83$ (d, 3H), 0.93 (d, 3H), 0.96 (d, 3H), 0.87–1.04 (m, 3H), 1.34 (s, 3H), 1.35 (s, 3H), 1.32–1.43 (m, 2H), 1.64–1.69 (m, 2H), 2.18–2.21 (m, 1H), 2.35–2.41 (m, 1H), 2.76 (s, 3H), 3.29–3.34 (m, 1H), 4.43 (q, 2H), 6.45 (1H, −OH), 6.51 (d, 1H), 6.83 (s, 1H), 6.84 (d, 1H), 6.92 (dd, 1H), 7.02 (dd, 1H), 7.58 (d, 1H), 7.64 (d, 1H), 7.68 (s, 1H), 7.87 (d, 1H).

2.6. *5-{[(2S, 3S)-2-Chloro-3-methylpentanoyloxy]-9′-hydroxy-(1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine]} (**6**)*

Only the last synthetic step is described here. 5-[(2*S*, 3*S*)-2-Chloro-3-methylpentanoyloxy]-1,2,3,3-tetramethyl-3H-indolium iodide (21.6 g, 48.0 mmol) and 1-nitroso-2,7-dihydroxynaphthalene (9.1 g, 48.0 mmol) were added to dry toluene (500 ml). The mixture was heated to 85°C with stirring. Piperidine (5.1 ml, 52.3 mmol) dissolved in dry toluene (50 ml) was added dropwise to the mixture which was then stirred for half an hour at 85°C and the solvent evaporated. The crude product was purified twice by column chromatography (silica gel, ethyl acetate/hexane, 1/3) and recrystallized twice from ethanol; yield 3.9 g (16%). ^{1}H NMR ($CDCl_3$): $\delta = 0.99$ (t, 3H), 1.13 (d, 3H), 1.33 (s, 3H), 1.36 (s, 3H), 1.39–1.45 (m, 1H), 1.80 (s, 3H), 2.20–2.24 (m, 1H), 2.74 (s, 3H), 4.36 (d, 1H), 6.10 (1H, −OH), 6.51 (d, 1H), 6.83 (s, 1H), 6.84 (d, 1H), 6.92 (dd, 1H), 7.02 (dd, 1H), 7.58 (d, 1H), 7.65 (d, 1H), 7.69 (s, 1H), 7.86 (d, 1H).

2.7. *9′-{5-(−)-Menthoxyacetoxy-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphth-[2,1-b][1,4]oxazine]} 4-[11-(acryloyloxy)-undecyloxy]biphenyl-4′-carboxylate (A11SOM)*

^{1}H NMR ($CDCl_3$): $\delta = 0.83$ (d, 3H, menthyl), 0.92 (d, 3H, menthyl), 0.94 (d, 3H, menthyl), 0.87–1.02 (m, 3H, menthyl), 1.32 (s, 3H), 1.35 (s, 3H), 1.31–1.39 (m, 14H including 2H assigned menthyl), 1.45–1.51 (m, 2H), 1.65–1.69 (m, 4H including 2H assigned menthyl), 1.79–1.85 (m, 2H), 2.15–2.18 (m, 1H, menthyl), 2.33–2.38 (m, 1H, menthyl), 2.74 (s, 3H), 3.25–3.30 (m, 1H, menthyl), 4.02 (t, 2H), 4.16 (t, 2H), 4.35 (q, 2H, menthyl −O−CH$_2$−), 5.81 (dd, 1H), 6.12 (dd, 1H), 6.39 (dd, 1H), 6.51 (d, 1H, 2H-indole), 6.84 (d, 1H, 2H-indole), 6.93 (dd, 1H, 2H-indole), 7.01 (3H, 1H assigned naphthoxazine and 2H assigned biphenyl), 7.29 (dd, 1H, naphthoxazine), 7.61 (d, 2H, biphenyl), 7.63–7.73 (4H, 2H assigned naphthoxazine and 2H assigned biphenyl), 7.81 (d, 1H, naphthoxazine), 8.28 (d, 2H, biphenyl), 8.38 (d, 1H, naphthoxazine). The ^{1}H NMR spectrum of A11SOM is given in figure 2. Elemental analysis: calc. for $C_{61}H_{72}N_2O_9$ C 74.97, H 7.43, N 2.87; found C 75.05, H 7.55, N 2.64%.

2.8. *9′-{5-[(2S, 3S)-2-Chloro-3-methyl-pentanoyloxy]-1,3-dihydro-1,3,3-trimethylspiro-[2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine]} 4-[11-(acryloyloxy)undecyloxy]biphenyl-4′-carboxylate (A11SOP)*

^{1}H NMR ($CDCl_3$): $\delta = 0.99$ (t, 3H, chiral moiety), 1.13 (d, 3H, chiral moiety), 1.34 (s, 3H), 1.36 (s, 3H), 1.31–1.43 (m, 13H including 1H assigned chiral moiety), 1.45–1.50 (m, 2H), 1.65–1.70 (m, 2H), 1.76–1.79 (m, 1H, chiral moiety), 1.79–1.85 (m, 2H), 2.20–2.25 (m, 1H, chiral moiety), 2.75 (s, 3H), 4.02 (t, 2H), 4.16 (t, 2H), 4.37 (d, 1H, chiral moiety), 5.81 (dd, 1H), 6.12 (dd, 1H), 6.39 (dd, 1H), 6.52 (d, 1H, 2H-indole), 6.84 (d, 1H, 2H-indole), 6.93 (dd, 1H, 2H-indole), 7.01 (3H, 1H assigned naphthoxazine and 2H assigned biphenyl), 7.29 (dd, 1H, naphthoxazine), 7.61 (d, 2H, biphenyl), 7.69–7.73 (4H, 2H assigned naphthoxazine and 2H assigned biphenyl), 7.81 (d, 1H, naphthoxazine), 8.28 (d, 2H, biphenyl), 8.39 (d, 1H, naphthoxazine). Elemental analysis: calc. for $C_{55}H_{61}ClN_2O_8$ C 72.31, H 6.73, N 3.07; found C 71.54, H 6.75, N 2.84%.

2.9. *9′-{5-[(2S, 3S)-2-Chloro-3-methylpentanoyloxy]-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine]} (R)-(−)-4-[(3-acryloyloxy-2-methylpropyl)oxy]-biphenyl-4′-carboxylate (A3SOP)*

^{1}H NMR ($CDCl_3$): $\delta = 0.99$ (t, 3H, chiral moiety), 1.13 (d, 3H, chiral moiety), 1.14 (d, 3H), 1.34 (s, 3H), 1.36 (s, 3H), 1.38–1.46 (m, 1H, chiral moiety), 1.75–1.80 (m, 1H, chiral moiety), 2.20–2.25 (m, 1H, chiral moiety), 2.38–2.45 (m, 1H), 2.75 (s, 3H), 3.95–4.02 (m, 2H), 4.22–4.30 (m, 2H), 4.37 (d, 1H), 5.84 (dd, 1H), 6.15 (dd, 1H), 6.41 (dd, 1H), 6.52 (d, 1H, 2H-indole), 6.84 (d, 1H, 2H-indole), 6.93 (dd, 1H, 2H-indole), 7.01–7.03 (3H, 1H assigned naphthoxazine and 2H assigned biphenyl), 7.29 (dd, 1H, naphthoxazine), 7.61 (d, 2H, biphenyl), 7.69–7.72 (4H, 2H assigned naphthoxazine and 2H assigned biphenyl), 7.81 (d, 1H, naphthoxazine), 8.29 (d, 2H, biphenyl), 8.39 (d, 1H, naphthoxazine). Elemental analysis: calc. for $C_{48}H_{47}ClN_2O_8$ C 70.71, H 5.81, N 3.44; found C 69.44, H 5.81, N 3.04%.

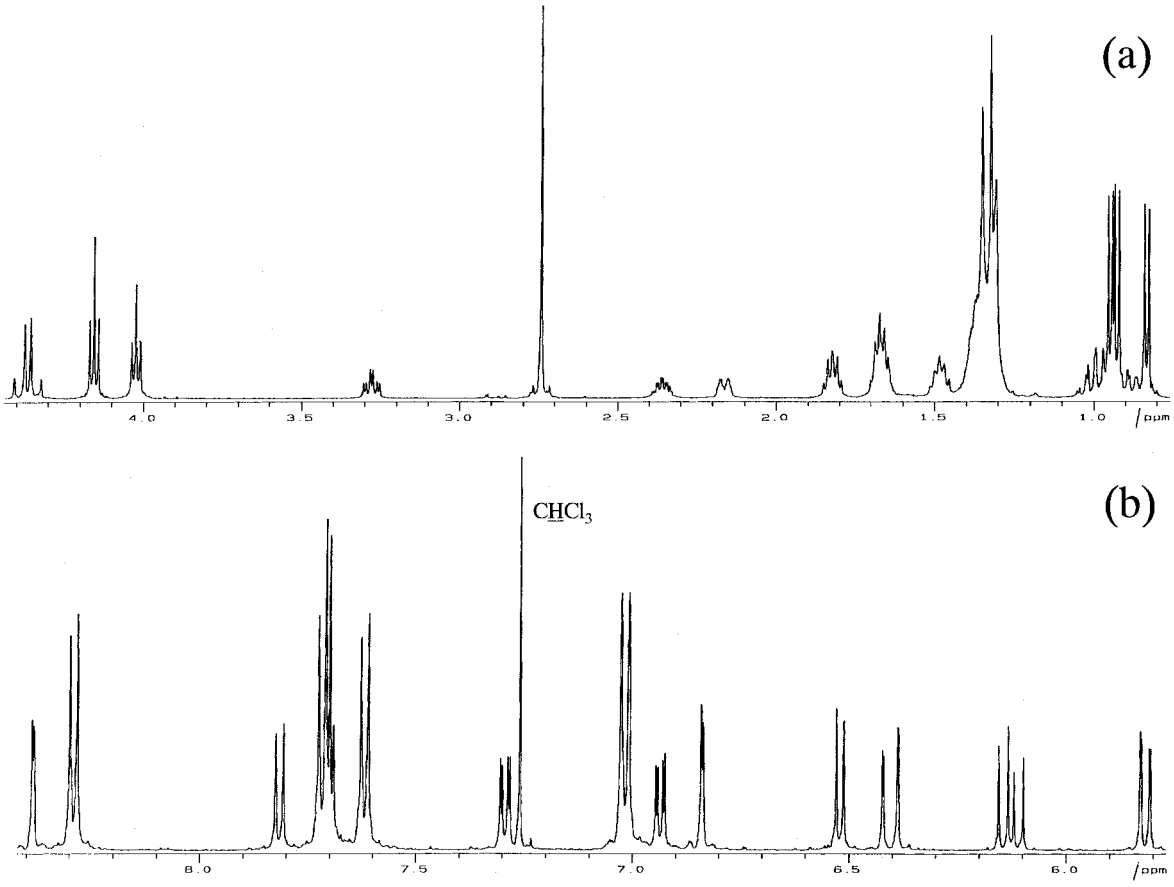

Figure 2. ^{1}H NMR spectra of (*a*) the small and (*b*) the large chemical shift regions of A11SOM in $CDCl_3$ with TMS as standard (TMS signal is not shown). Assignment of each peak is described in the text.

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2.10. *Polymerization*

Polmerizations were carried out using solutions in *N*,*N*-dimethylformamide with 2,2′-azobisisobutyronitrile (3 mol % relative to the monomer) as initiator at 60°C for 40 h under vacuum. To prepare relatively low molecular mass polymers, 1-decanethiol was used as chain transfer reagent. The resulting polymers were purified by reprecipitation using a chloroform/methanol system.

2.11. *Characterization*

^{1}H NMR spectra were recorded using a JEOL LA500 NMR spectrometer. Specific rotations of the monomers were measured with a Perkin-Elmer 241 polarimeter, using a 1 dm cell at 20°C. Each sample was prepared as a 1 wt % chloroform solution. Molecular masses of the polymers were measured using HLC-802A (Tosoh Co.), THF as eluent and standard polystyrenes as reference. Differential scanning calorimetry (DSC) was carried out to determine phase transition temperatures by using a Perkin-Elmer DSC-7 calorimeter at heating and cooling rates of 10°C min^{-1}. A polarizing optical microscope (POM) (Olympus BH-2) equipped with a Mettler FP-82 hot stage and a temperature programmer FP-80 was used to observe phase transitions. Wide angle X-ray diffraction (WAXD) data for glassy-state samples were recorded on a Rigaku RINT 1500 X-ray diffractometer at room temperature. Before the measurement, the samples were heated to 150°C and then annealed for about 1.5 h at an appropriate temperature, which was a few degrees lower than mesomorphic–isotropic transition temperature for liquid crystalline polymers and about 10°C higher than the glass transition temperature for amorphous polymers.

3. Results and discussion

3.1. *Phase transition behaviour of the monomers*

As shown in table 1, A11SOM and A11SOP having long spacers, each showed a supercooled mesophase which was enantiotropic with respect to the glassy state. In addition, A11SOM showed a relatively large optical rotation value due to the menthyl moiety and thus reflected right-handed blue light at room temperature. On the other hand, A3SOP having a short spacer did not show a mesophase.

Table 1. Thermal and optical properties of monomers studied. Cr = crystalline; g = glassy; M = mesomorphic; I = isotropic; T_g = glass transition; T_i = isotropic transition.

Designation	Phase transition temperature/°C[a]						T_i/°C[b]	$[\alpha]_D^{20}$/°[c]
A11SOM	g	20.5	M	34.9	I	(1st cooling)	75.8	− 24.4
	g	24.7	M	40.7	I	(2nd heating)		
A11SOP	g	22.0	M	53.2	I	(1st cooling)	100.9	2.6
	g	23.4	M	55.0	I	(2nd heating)		
A3SOP	T_g	64.5				(1st cooling)	139.8	− 2.9
	T_g	67.3				(2nd heating)		
A6CN	Cr	59.7	I			(1st cooling)	79.1	—
	Cr	77.2	I			(2nd heating)		

[a] Determined by DSC measurement at a scanning rate of 10°C min^{-1} and by optical polarizing microscopic observation.
[b] Determined by DSC measurement on the first heating run at a scanning rate of 10°C min^{-1} and by optical polarizing microscopic observation.
[c] Measured for a solution in chloroform (*c* 1%).

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As far as we know, all spiro-oxazine-containin g mesogens reported, after first heating, exhibit supercooled mesophases, enantiotropic with respect to the glass transition which occurs without crystallization [8, 9, 15]. We note that the compounds do tend to recrystallize on heating *above* the mesophase to isotropic temperature.

3.2. *Phase transition behaviour of the homopolymers*

As shown in table 2, all the photochromic chiral homopolymers were non-mesomorphic, similarly to poly-{9′-{1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine]} 4-[11-(acryloyloxy)-undecyloxy]biphenyl-4′-carboxylate} [9], which corresponds to the unsubstituted form of PA11SOM and PA11SOP. It is stressed that all the corresponding monomers exhibited a supercooled mesophase. Since the spiro-oxazine moiety is bulky and each conformation of the monomers is bent with a large angle at the 9′-position of the spiro-oxazine moiety according to molecular force field calculations, the side groups of the polymers cannot apparently arrange in mesomorphic order due to the steric hindrance between the side groups. Only PA11SOM exhibited birefringence by applying shear-stress under 100 to 104°C and this disappeared at 107°C. In the case of shearing at 125°C, birefringence was not observed.

3.3. *Phase transition behaviour of the copolymers*

In table 3, the compositions of the copolymers (poly-1 to poly-11) formed from one of the photochromic chiral monomers and A6CN (see figure 1) are given.

Both poly-4 and poly-5 showed mesophases and the values of the enthalpy change at the mesomorphic to isotropic transition were relatively large, 2.08 J g^{-1} and 2.20 J g^{-1}, respectively. Also, as shown in figure 3 (*a*), both poly-4 and poly-5 exhibited a relatively weak peak in the small angle range of the WAXD spectra corresponding to the layer spacings 36.9 and 39.2 Å, respectively. These values correspond to the length of A11SOP (42.4 Å) calculated by the molecular force field method. In addition, the copolymers showed colourful sand-like textures under POM observation; these were

Table 2. Properties of homopolymers studied and their yields. g = glassy; N = nematic; I = isotropic; T_g = glass transition.

Designation	Yield/%	Molecular mass[a]		Phase transition temperature/°C[b]
		$10^4 \bar{M}_n$	$10^4 \bar{M}_w$	
PA11SOM	74	2.78	4.73	T_g 85.7
PA11SOP	80	2.85	4.11	T_g 101.1
PA3SOP	81	2.44	4.05	T_g 147.9
PA6CN	78	1.89	3.02	g 23.9 N 118.0 I
$PA6CN_{low}$[c]	64	0.40	0.52	g 0.4 N 54.7 I

[a] Determined by GPC measurement.
[b] Determined by DSC measurement on the second heating run at a scanning rate of 10°C min^{-1} and by optical polarizing microscopic observation.
[c] Polymerized with 1-decanethiol (30 mol% per monomer).

Table 3. Thermal and other properties of copolymers consisting of photochromic chiral monomer and A6CN.

Designation	Chiral monomeric unit: designation	Chiral monomeric unit: proportion: in feed	Chiral monomeric unit: proportion: in copolymer[a]	1-decanethiol mol % per monomer in feed	yield/%	Molecular mass[b]: $10^4\bar{M}_n$	Molecular mass[b]: $10^4\bar{M}_w$	Phase transition temperature/°C[c]	ΔH_i^d/ J g^{-1}
Poly-1	A3SOP	0.30	0.30	0	76	1.37	2.58	g 67.8 N* 88.9 I	0.29
Poly-2	A3SOP	0.60	0.62	0	69	1.58	2.70	T_g 101.3	—
Poly-3	A3SOP	0.30	0.36	30	62	0.48	0.59	T_g 45.2	—
Poly-4	A11SOP	0.15	0.15	0	66	1.69	3.45	g 42.3 Sm 110.4 I	2.08
Poly-5	A11SOP	0.30	0.30	0	77	1.76	3.65	g 52.6 Sm 96.4 I	2.20
Poly-6	A11SOP	0.60	0.60	0	56	1.54	2.69	T_g 83.4	—
Poly-7	A11SOP	0.30	0.35	30	18	0.48	0.58	g 28.8 Sm 57.8 N* 62.0 I	2.34[e]
Poly-8	A11SOM	0.15	0.16	0	92	1.84	3.66	g 44.3 Sm 102.0 I	0.60
Poly-9	A11SOM	0.30	0.30	0	70	1.67	3.02	g 54.7 X 83.8 I	not clear
Poly-10	A11SOM	0.40	0.40	0	93	1.55	2.63	T_g 63.0	—
Poly-11	A11SOM	0.30	0.31	7	87	0.94	1.27	g 44.9 N* 75.9 I	0.53

[a] Determined by ^{1}H NMR.
[b] Determined by GPC.
[c] Determined by DSC measurement on the second heating run at a scanning rate of 10°C min^{-1} and optical polarizing microscopic observation.
[d] Determined by DSC measurement on the second heating run at a scanning rate of 10°C min^{-1}; ΔH_i = enthalpy change on clearing.
[e] Enthalpy change from smectic through to isotropic.

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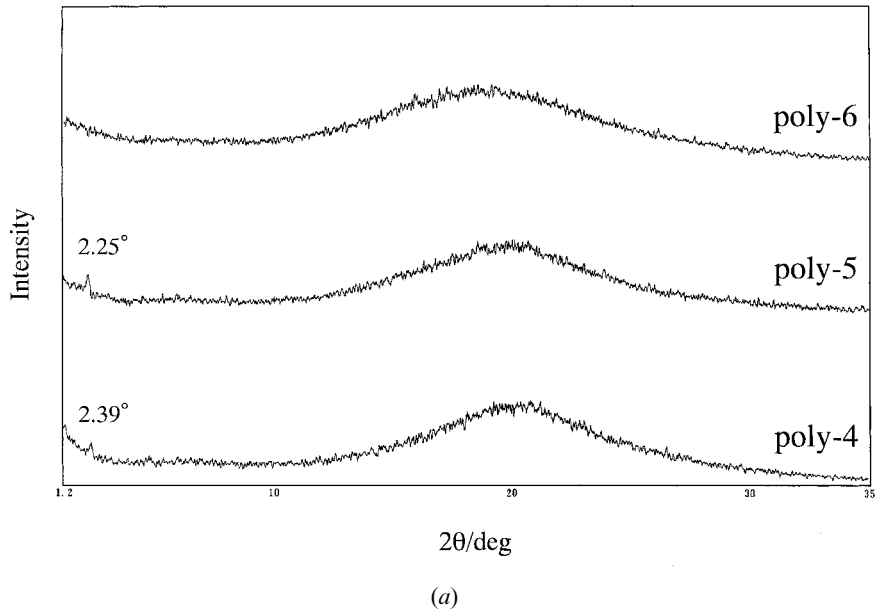
similar to that of the smectic homopolymer, poly-{5-{1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]-pyrido[2,1-b][1,4]benzoxazine]} 4-[11-(acryloyloxy)-undecyl-oxy]biphenyl-4′-carboxylate} [9]. However, each of the mesomorphic–isotropic transition temperatures of poly-4 and poly-5 was lower than that of the nematic homopolymer, PA6CN, despite the fact that the copolymers showed smectic order as described above. Taking these results into consideration, we conclude that the A11SOP moiety is potentially smectogenic and that the A6CN and A11SOP moieties in the copolymers tend to arrange cooperatively. The cooperative arrangement induces a reduction of the steric hindrance between the potentially smectogenic A11SOP moieties. Therefore, the copolymers exhibited higher order compared with PA6CN. However, there is no remarkable interaction such as donor–acceptor interaction [16–20] between the A6CN and A11SOP moieties and therefore no increase of the mesomorphic–isotropic transition temperature compared with that of PA6CN was observed.

On the other hand, the enthalpy changes at the mesomorphic–isotropic transitions of both poly-8 and poly-9 consisting of A6CN and A11SOM moieties were significantly smaller than those of poly-4 and poly-5 as shown in table 3. In addition, the birefringence of poly-8 and poly-9 under POM observation was weaker than that of poly-4 and poly-5. However, as shown in figure 3(*b*), the WAXD spectrum of poly-8 exhibited a relatively weak peak at 2.33° (37.9 Å). This layer spacing is 9.1 Å smaller than the calculated length of A11SOM (48.0 Å). Taking these results into consideration, the A6CN and A11SOM moieties in poly-8 also appear to tend to arrange cooperatively in a smectic order due to reduction of the steric hindrance between the potentially smectogenic A11SOM moieties. But the smectogenic capability is poorer than that of A11SOP, because the menthyl-containing substituent in A11SOM is bulky. Therefore, the enthalpy change and the birefringence of poly-8 were much smaller and weaker, respectively. The mesophase of poly-9 could not be indentified. However, at least it does not seem to be a crystalline state because there is no peak in the small angle range nor a sharpening of the halo in wide angle range of the WAXD spectrum.

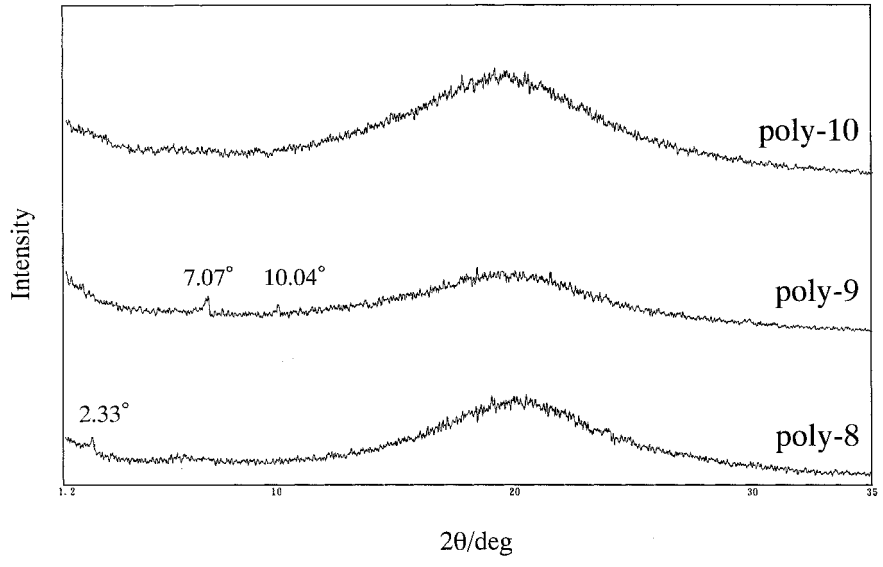
Note that the amorphous polymers containing the smectogenic photochromic side groups in this study do not exhibit the amorphous chiral smectic A phase reported in [21]. Although these copolymers exhibited enthalpy changes of 7–9 kJ mol^{-1} due to amorphous chiral smectic A–isotropic transition, our amorphous polymers did not show by DSC any enthalpy change due to such a phase transition.

3.4. *Phase transition behaviour of the relatively low molecular mass copolymers*

As shown in table 3, the phase behaviours of the relatively low molecular mass copolymers, poly-3, poly-7, and poly-11, were different from those of the corresponding large molecular mass copolymers, poly-1, poly-5,



(*a*)



(*b*)

Figure 3. WAXD spectra of copolymers containing (*a*) the A11SOP moiety and (*b*) the A11SOM moiety.

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and poly-9, respectively. Poly-3 did not show any mesophase, in contrast with poly-1. The DSC thermograms in figure 4 reveal that poly-7 exhibited a chiral nematic (N*) phase in addition to a smectic phase in contrast with poly-5 which is purely smectic. The WAXD spectrum of poly-7 in figure 5 exhibited a stronger peak at 1.99° than poly-5 in figure 3 (*a*). In addition, the layer spacing of poly-7 (44.4 Å) was 6.5 Å larger than that of poly-5. These results for poly-7 seem to indicate that the narrow chiral nematic phase above the smectic phase assisted a higher order of packing of the smectogenic A11SOP moieties. On the other hand, poly-11 showed not an unidentified X phase like that of poly-9, but a chiral nematic phase. The WAXD spectrum of poly-11 in figure 5 indicates clearly that no layer order exists.

3.5. *Discussion*

Wolff *et al.* have found a phase transition from a metastable monolayer SmA phase to a bilayer SmC phase or to an unidentified phase, depending upon the annealing temperature, in one azobenzene-containing liquid crystalline polymethacrylate having the alkylene spacer and the alkoxy tail group of nearly the same length [22]. The result has been interpreted by postulating

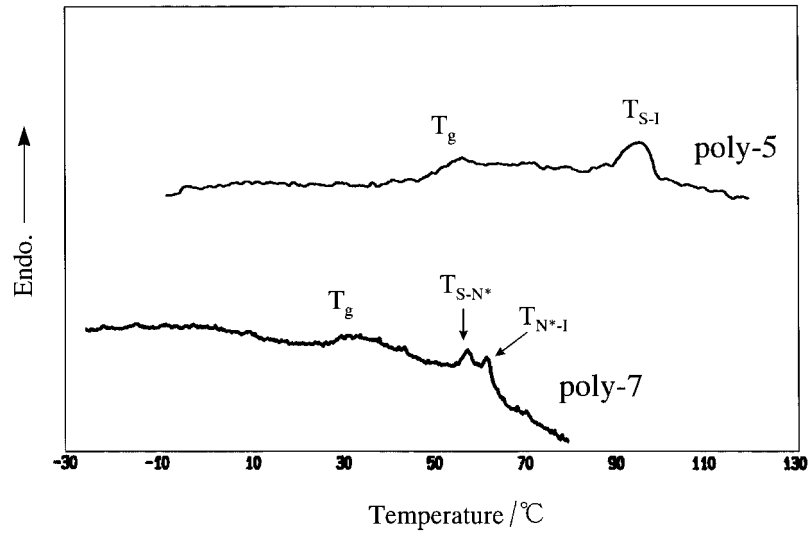

Figure 4. DSC thermograms of high molecular mass copolymer, poly-5 and low molecular mass copolymer, poly-7. Each copolymer contains 30 mol % and 35 mol % of the A11SOP moiety, respectively.

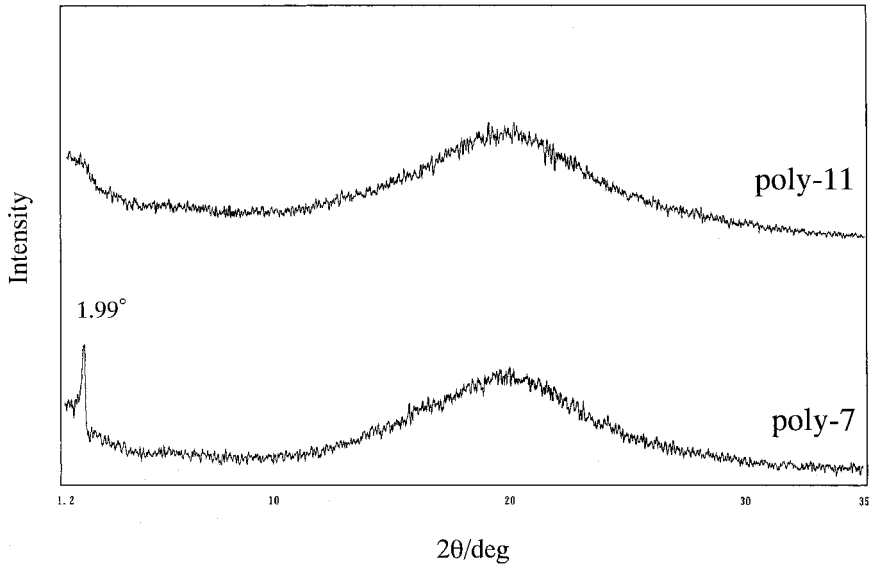

Figure 5. WAXD spectra of copolymers containing 35 mol % A11SOP moiety, poly-7, and 31 mol % A11SOM moiety, poly-11. The value of $10^4 \bar{M}_w$ for each copolymer is 0.58 and 1.27, respectively.

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that the SmA–SmC transition occurs to reduce the steric *hindrance* between the spacer of one side group and the tail of a neighbouring side group. Recently too, Bobrovsky *et al.* have reported on an induced SmA phase due to steric *correspondence* between side groups in copolymers built up from phenyl benzoate monomers and menthyl-containing benzoyloxybiphenyl monomers [23]. As described in § 3.3 for the smectic copolymers in this study, the steric hindrance between the potentially smectogenic A11SOP or A11SOM moieties was reduced by copolymerization with the nematogenic A6CN; therefore, a 'hindered' smectic phase appeared.

4. Conclusions

Photochromic acrylates containing both biphenylene and spiro-oxazine moieties with a chiral substituent and the related polymers were prepared and gave photochromic chiral liquid crystalline systems. A11SOP and A11SOM each showed a supercooled mesophase and the latter reflected right-handed visible light (blue colour) at room temperature. Several copolymers consisting of A6CN and A11SOP or A11SOM showed induced smectic phases due to reduction of the steric hindrance between the potentially smectogenic A11SOP or A11SOM moieties through copolymerization with nematogenic A6CN.

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