Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 06 August 2010

To cite this Article Hattori, Hideshi and Uryu, Toshiyuki(1999) 'Synthesis and characterization of polymerizable photochromic liquid crystals containing a spiro-oxazine group', Liquid Crystals, 26: 7, 1085 — 1095
To link to this Article: DOI: 10.1080/026782999204444
URL: http://dx.doi.org/10.1080/026782999204444

LIQUID CRYSTALS, 1999, VOL. 26, NO. 7, 1085–1095

Synthesis and characterization of polymerizable photochromic liquid crystals containing a spiro-oxazine group

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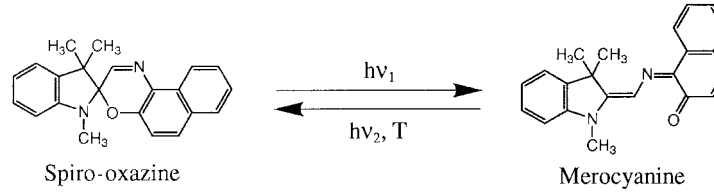
(*Received 23 December 1998; accepted 5 February 1999*)

Novel polymerizable photochromic liquid crystal materials containing either the 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b][1,4] oxazine] group or the 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] pyrido[3,2-f'][1,4] benzoxazine] group as the photochromic moiety, and the biphenylene unit as the mesogenic moiety, were synthesized. Thermal and physical properties of the compounds were examined using differential scanning calorimetry, optical polarizing microscopy, wide-angle X-ray diffractometry and UV-visible spectrophotometry. The photochromic compounds containing both photochromic and mesogenic moieties showed metastable mesophases; These tended to crystallize with time and on heating. The crystallization behaviours were strongly dependent on the structure of the terminal group of alkylene spacer and the position of the spiro-oxazine bound to the mesogen.

1. Introduction

Photochromic spiro-oxazines have been a subject of intensive investigation because of their potential applications, including light filters and optical devices [1, 2]. Spiro-oxazines belong to a class of photochromic compounds closely related to spiropyrans in which the carbon atom in the methine bridge is replaced by a nitrogen atom. Their photo fatigue resistance is much better than that of spiropyrans [3]. The photochromic transformation of spironaphthoxazine is shown in scheme 1.

Although low molecular mass liquid crystals and side chain liquid crystalline polymers containing azobenzenes as the photochromic moiety have been extensively studied, due to potential applications such as in display devices and optical data storage materials [4–9], much less attention has been paid to photochromic liquid crystals containing spiro-oxazines. Krongauz and co-workers reported the synthesis and liquid crystallinity of 5-[4-(4-heptylbenzoyloxy)benzoyloxy]-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b]-[1,4] oxazine] [10]. In addition, they reported the photochromic side chain liquid crystalline copolymers containing spiro-oxazine, which were prepared by copolymerization of a conventional liquid crystalline monomer and a non liquid crystalline photochromic



Spiro-oxazine Merocyanine

Scheme 1. The photochromic transformation of spironaphthoxazine.

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Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online
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monomer [11]. It has been reported that the liquid crystallinity of these photochromic copolymers was greatly decreased by an increasing proportion of the photochromic monomeric unit in the copolymers.

The purpose of this study was to obtain polymerizable spiro-oxazine-containing liquid crystals having a potential to produce a variety of photochromic side chain liquid crystalline copolymers. Thermal and physical properties of the compounds were examined by polarizing microphotography, differential scanning calorimetry (DSC), X-ray diffractometry, and UV-visible spectrophotometry.

The structures of the compounds described in this report are shown in figure 1.

2. Experimental

4-(Dimethylamino)pyridinium *p*-toluenesulphonate (DPTS) was synthesized according to the procedure described in reference [12]. 5-Hydroxy-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b]-[1,4] oxazine], 5-hydroxy-1,3-dihydro-1,3,3-trimethylspiro-[2H-indole-2,3′-[3H] pyrido[3,2-f][1,4] benzoxazine] and 9′-hydroxy-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b][1,4] oxazine] were synthesized according to the procedure reported in references [10, 13]. 4-(11-Acryloyloxy)undecyloxybenzoic acid was synthesized according to the procedure described in reference [14]. 4′-Dodecyloxy-4-biphenylcarboxylic acid was synthesized according to method of Gray *et al.* [15]. Synthetic routes for the target compounds are shown in schemes 2–4; the table gives key to compound designation.

2.1. *Ethyl 4-(4-hydroxyphenyl)benzoate (**1**)*

4-(4-Hydroxyphenyl)benzoic acid (50.0 g, 223.4 mmol) was dissolved in a mixture of EtOH (170 ml) and benzene (100 ml). After a catalytic amount of H_2SO_4 was added to the mixture, it was heated under reflux for 24 h.

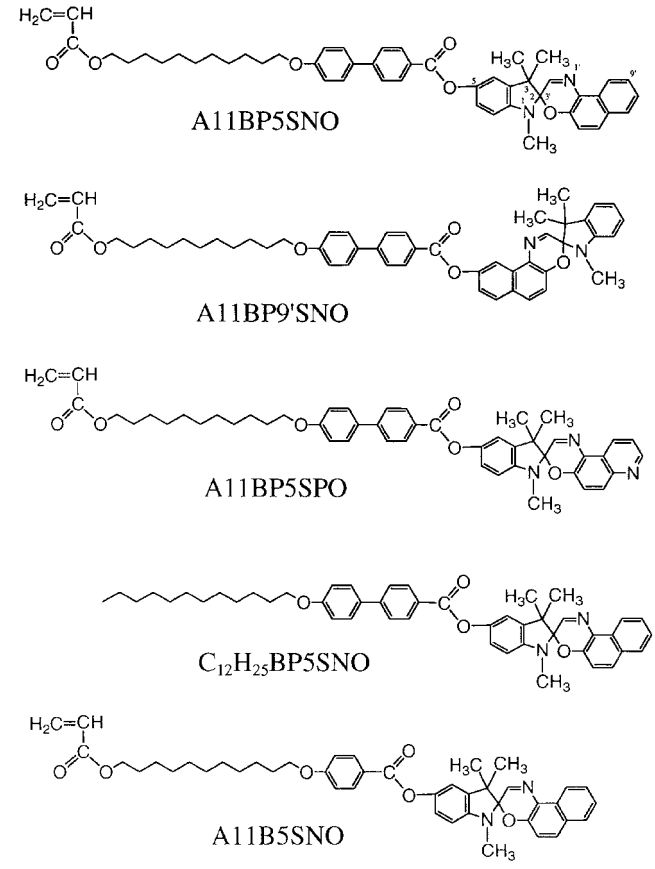


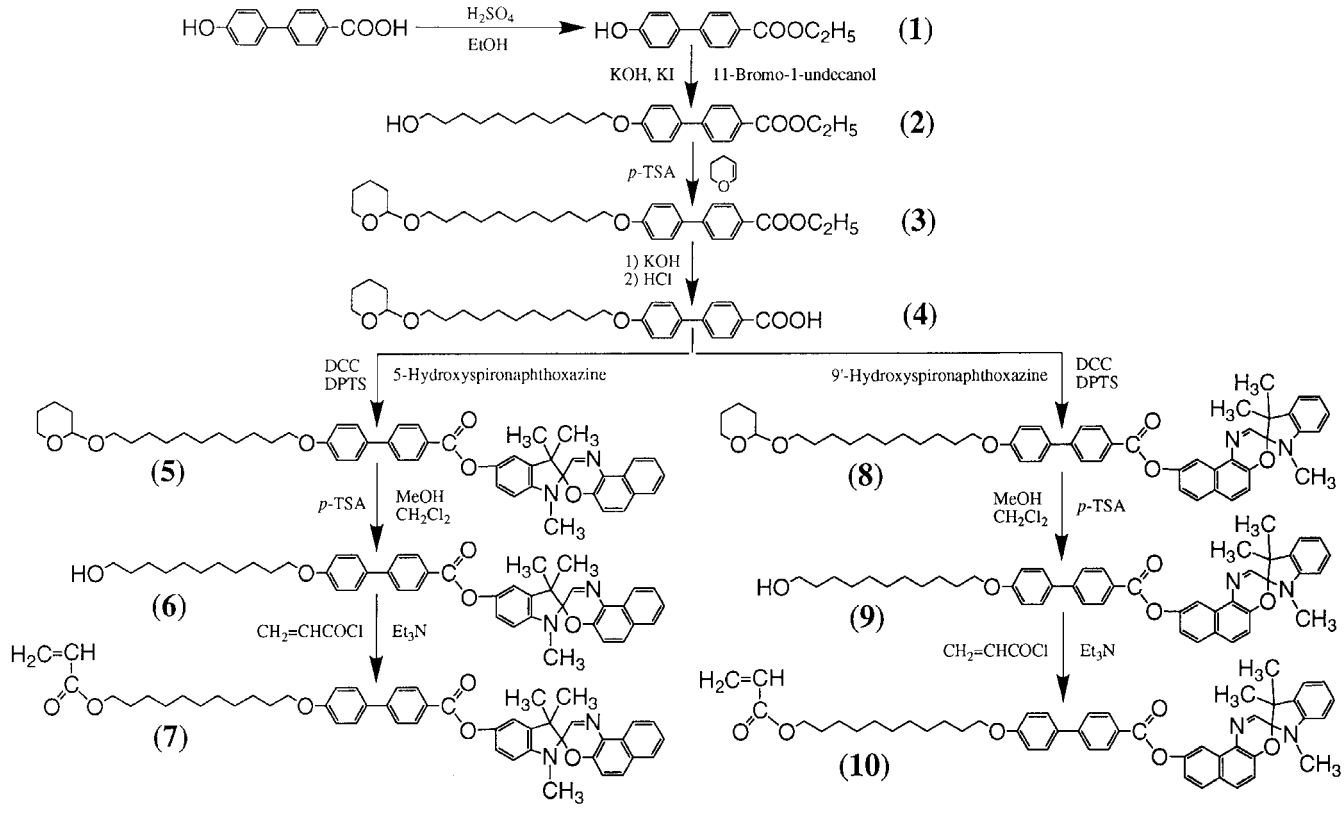
Figure 1. Structures of the photochromic compounds in this study.

The reaction mixture was then poured into water and extracted with CH_2Cl_2. The separated organic phase was washed with water, dried with Na_2SO_4, and evaporated to dryness. The resulting powder was recrystallized from EtOH. Yield 49.1 g (87%). ^{1}H NMR ($CDCl_3$): $\delta = 1.42$ (t, 3H), 4.40 (q, 2H), 6.95 (d, 2H), 7.50 (d, 2H), 7.59 (d, 2H), 8.07 (d, 2H).

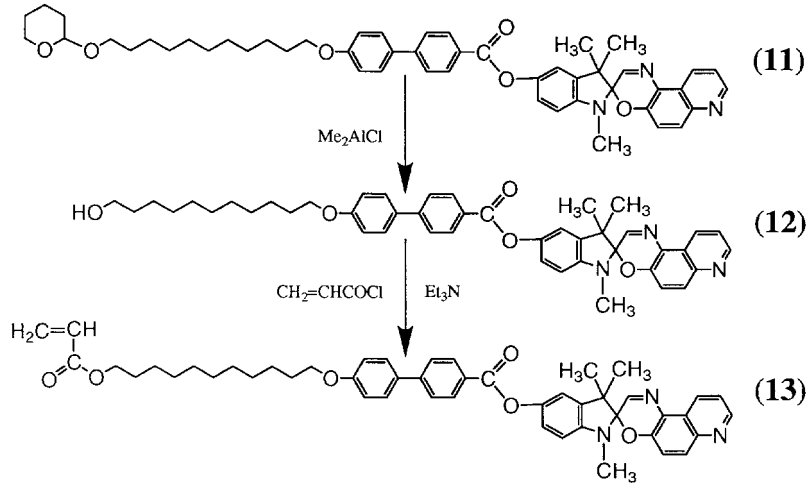
Table 1. Phase transition temperatures (°C) of compounds studied. Cr: crystalline; g: glassy; M: mesomorphic; I: isotropic; T_g: glass transition.

Compound[c]		Phase transition[a]		T_m[b]
A11BP5SNO	(**7**)	g 18.1 M 83.3 I	(1st cooling)	117.3
		g 13.4 M 86.3 Cr 118.0 I	(2nd heating)	
A11BP9′SNO	(**10**)	g 24.6 M 53.0 I	(1st cooling)	116.9
		g 21.7 M 53.6 I	(2nd heating)	
A11BP5SPO	(**13**)	g 18.5 M 60.3 I	(1st cooling)	110.2
		g 14.2 M 61.1 I 95.2 Cr 108.8 I	(2nd heating)	
$C_{12}H_{25}$BP5SNO	(**15**)	g 27.1 Cr_1 107.1 M 108.0 I	(1st cooling)	144.4
		g 30.0 Cr_1 81.3 Cr_2 140.4 I	(2nd heating)	
A11B5SNO	(**14**)	T_g – 8.7	(1st cooling)	96.3
		T_g – 2.5	(2nd heating)	

[a] Determined by DSC measurement at a scanning rate of 10°C min^{-1} and by optical polarizing microscopy.
[b] Determined by DSC measurement on the first heating at a scanning rate of 10°C min^{-1} and by optical polarizing microscopy.
[c] Only the crystalline-to-isotropic transition was observed on the first heating.



Scheme 2. Synthetic routes for A11BP5SNO and A11BP9'SNO.



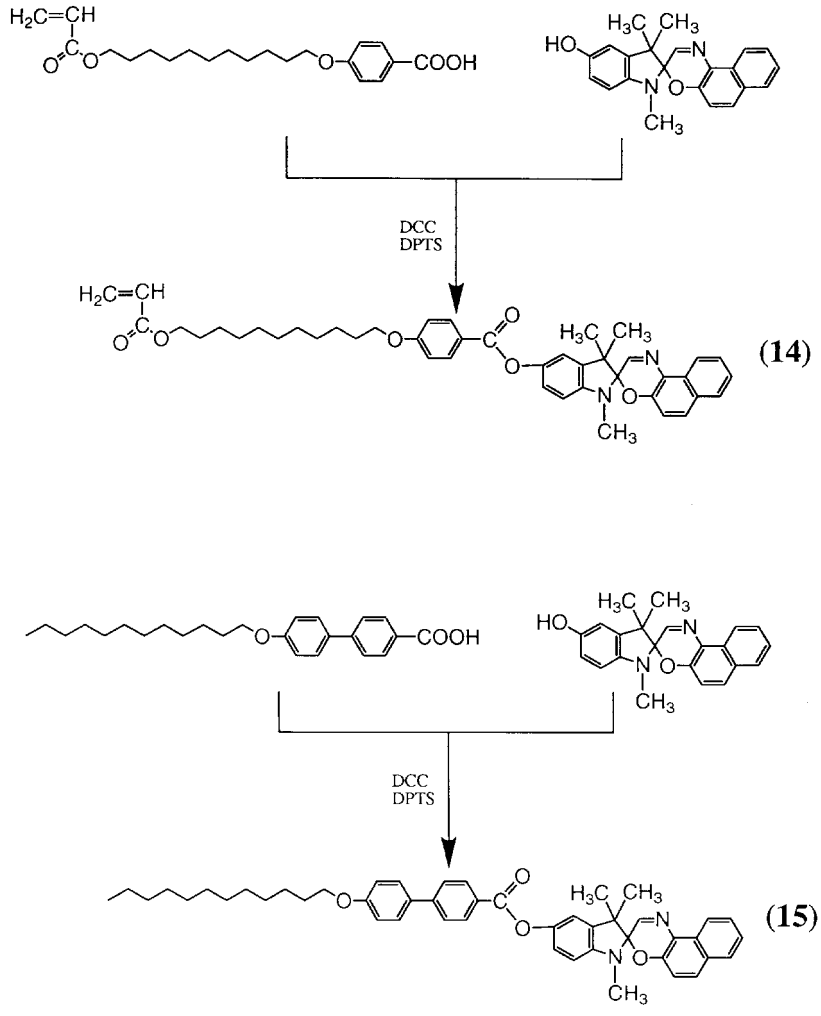
Scheme 3. Synthetic route for A11BP5SPO.

2.2. *Ethyl 4-[4-(11-hydroxyundecyl)oxyphenyl] benzoate (2)*

Compound **1** (18.4 g, 76.0 mmol) was dissolved in EtOH (150 ml). KOH (4.6 g, 82.0 mmol) dissolved in EtOH (100 ml) was added dropwise to the solution. KI (3.0 g, 18.1 mmol) and 11-bromo-1-undecanol (21.0 g, 83.6 mmol) were then added, and the solution was heated at reflux for 24 h. The resulting mixture was poured into water and extracted with $CHCl_3$. After the solvent was evaporated, the crude product was recrystallized twice from EtOH. Yield 24.1 g (77%). ^{1}H NMR ($CDCl_3$): $\delta = 1.30$–1.38 (m, 12H), 1.41 (t, 3H), 1.47 (m, 2H). 1.57 (m, 2H), 1.81 (m, 2H), 3.64 (t, 2H), 4.00 (t, 2H), 4.38 (q, 2H), 6.97 (d, 2H), 7.55 (d, 2H), 7.60 (d, 2H), 8.07 (d, 2H).

2.3. *Ethyl 4-{4-[11-(tetrahydro-2-pyranyl)-oxyundecyl] oxyphenyl}benzoate (3)*

Compound **2** (23.5 g, 57.0 mmol) was dissolved in CH_2Cl_2 (200 ml) with a catalytic amount of *p*-toluenesulphonic acid (*p*-TSA) at 30°C. 3,4-Dihydro-2H-pyran



Scheme 4. Synthetic routes for A11B5SNO and $C_{12}H_{25}$BP5SNO.

(23.7 g, 281.7 mmol) was added in a dropwise fashion and the solution stirred for 24 h. The reaction mixture was washed with 5% aqueous $NaHCO_3$ and water. It was then dried with Na_2SO_4, and the solvent evaporated. The product was purified by column chromatography (silica gel, hexane/ethyl acetate, 8/1) and recrystallized from EtOH/hexane (20/1). Yield 17.5 g (62%). ^{1}H NMR ($CDCl_3$): 1.30–1.61 (m, 20H), 1.41 (t, 3H), 1.69–1.85 (m, 4H), 3.37 (m, 1H), 3.50 (m 1H), 3.72 (m, 1H), 3.87 (m, 1H), 4.00 (t, 2H), 4.38 (q, 2H), 4.58 (t, 1H), 6.97 (d, 2H), 7.54 (d, 2H), 7.60 (d, 2H), 8.07 (d, 2H).

2.4. *4′-{11-[(Tetrahydro-2-pyranyl)oxy] undecyloxy}-4-biphenylcarboxylic acid (**4**)*

Compound **3** (17.0 g, 34.3 mmol) was dissolved in EtOH (120 ml). KOH (5.8 g, 103.4 mmol) dissolved in EtOH (120 ml) was then added and the solution heated at reflux for 3 h. The suspension was poured into EtOH containing 10% H_2O, and the solution was neutralized with HCl diluted with EtOH containing 10% H_2O. Since gelation occurred during neutralization, $CHCl_3$ was added to give the clear solution for complete neutralization. The solvents were then evaporated, and the product was dissolved in $CHCl_3$. This solution was washed with water, dried with Na_2SO_4, and evaporated. Yield 13.3 g (83%). ^{1}H NMR ($CDCl_3$): δ = 1.30 (m, 12H), 1.43–1.62 (m, 8H), 1.69–1.87 (m, 4H), 3.39 (m, 1H), 3.51 (m, 1H), 3.73 (m, 1H), 3.88 (m, 1H), 4.00 (t, 2H), 4.59 (t, 1H), 6.98 (d, 2H), 7.56 (d, 2H), 7.64 (d, 2H), 8.14 (d, 2H).

2.5. *5-{1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b] [1,4] oxazine]} 4-[11-(tetrahydro-2-pyranyloxy)undecyloxy] biphenyl-4′-carboxylate (**5**)*

Compound **4** (4.0 g, 8.6 mmol) and 5-hydroxy-1,3,3-trimethylspiro[indoline-2,3′-[3H] naphth[2,1-b] [1,4]-oxazine] (3.0 g, 8.7 mmol) were dissolved in CH_2Cl_2 at 25°C. *N,N′*-dicyclohexylcarbodiimide (DCC) (1.9 g, 9.2 mmol) and 4-(dimethylamino)pyridinium *p*-toluenesulphonate (DPTS) (0.26 g, 0.88 mmol) were added to the solution. The mixture was stirred for 7 h at 25°C; it was then washed with water, dried with Na_2SO_4, and

evaporated to dryness. The crude product was purified by column chromatography (silica gel, $CHCl_3$/MeOH, 80/1) and recrystallized from EtOH/$CHCl_3$ (20/1). Yield 4.7 g (69%). ^{1}H NMR ($CDCl_3$): $\delta = 1.30–1.40$ (m, 12H), 1.33 (s, 3H), 1.37 (s, 3H), 1.43–1.84 (m, 12H), 2.73 (s, 3H), 3.37 (m, 1H), 3.49 (m, 1H), 3.73 (m 1H), 3.86 (m, 1H), 4.00 (t, 2H), 4.57 (t, 1H), 6.58 (d, 1H, 2H-indole), 6.97 (d, 1H, 2H-indole), 7.02 (d, 2H, biphenyl), 7.05 (d, 1H, naphthoxazine), 7.06 (dd, 1H, 2H-indole), 7.40 (t, 1H, naphthoxazine), 7.54 (t, 1H, naphthoxazine), 7.58 (d, 2H, biphenyl), 7.66 (d, 1H, naphthoxazine), 7.67 (d, 2H, biphenyl), 7.73 (d, 1H, naphthoxazine), 7.74 (s, 1H, naphthoxazine), 8.24 (d, 2H, biphenyl), 8.59 (d, 1H, naphthoxazine).

2.6. *5-{1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b] [1,4] oxazine]} 4-(11-hydroxyundecyloxy) biphenyl-4′-carboxylate (**6**)*

Compound **5** (4.7 g, 5.9 mmol) was dissolved in CH_2Cl_2 (62 ml) and MeOH (83 ml) at 40°C. A catalytic amount of *p*-TSA was added to the solution and the mixture stirred for 8 h at 40°C. After the solvent was evaporated, CH_2Cl_2 was added to the resulting product. The solution was washed with water, dried with Na_2SO_4, and evaporated. The crude product was purified by column chromatography (silica gel, $CHCl_3$/MeOH, 80/1) and recrystallized from EtOH/$CHCl_3$ (20/1). Yield 3.3 g (79%). ^{1}H NMR ($CDCl_3$): $\delta = 1.30–1.41$ (m, 12H), 1.34 (s, 3H), 1.39 (s, 3H), 1.47 (m, 2H), 1.56 (m, 2H), 1.81 (m, 2H), 2.75 (s, 3H), 3.62 (t, 2H), 4.00 (t, 2H), 6.57 (d, 1H, 2H-indole), 6.97 (d, 1H, 2H-indole), 7.00 (d, 2H, biphenyl), 7.04 (d, 1H, naphthoxazine), 7.06 (dd, 1H, 2H-indole), 7.39 (t, 1H, naphthoxazine), 7.57 (t, 1H, naphthoxazine), 7.59 (d, 2H, biphenyl), 7.68 (d, 1H, naphthoxazine), 7.69 (d, 2H, biphenyl), 7.73 (d, 1H, naphthoxazine), 7.75 (s, 1H, naphthoxazine), 8.24 (d, 2H, biphenyl), 8.58 (d, 1H, naphthoxazine).

2.7. *5-{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 (**7**)*

Compound **6** (3.3 g, 4.6 mmol) was added to THF (50 ml) at room temperature. The solution was cooled with an ice/salt bath and then triethylamine (3.4 ml, 24.6 mmol) was added. Acryloyl chloride (1.0 ml, 12.3 mmol) dissolved in THF (20 ml) was added in a dropwise fashion to the solution under vigorous stirring and then the mixture was stirred for 3 h at room temperature. It was then poured into water and extracted with $CHCl_3$. This solution was washed with water, dried with Na_2SO_4, and evaporated. The crude product was purified by column chromatography (silica gel, $CHCl_3$) and recrystallized from EtOH/$CHCl_3$ (20/1). Yield 2.5 g (71%). ^{1}H NMR ($CDCl_3$): $\delta = 1.31–1.41$ (m, 12H), 1.35 (s, 3H), 1.40 (s, 3H), 1.48 (m, 2H), 1.67 (m, 2H), 1.81 (m, 2H), 2.77 (s, 3H), 4.02 (t, 2H), 4.15 (t, 2H), 5.82 (dd, 1H), 6.13 (dd, 1H), 6.42 (dd, 1H), 6.58 (d, 1H, 2H-indole), 6.97 (d, 1H, 2H-indole), 7.02 (d, 2H, biphenyl), 7.05 (d, 1H, naphthoxazine), 7.07 (dd, 1H, 2H-indole), 7.40 (t, 1H, naphthoxazine), 7.58 (t, 1H, naphthoxazine), 7.61 (d, 2H, biphenyl), 7.69 (d, 1H, naphthoxazine), 7.70 (d, 1H, biphenyl), 7.74 (d, 1H, naphthoxazine), 7.76 (s, 1H, naphthoxazine), 8.25 (d, 2H, biphenyl), 8.58 (d, 1H, naphthoxazine). Elemental analysis: calc. C 76.94, H 6.85, N 3.66; found C 77.02, H 6.96, N 3.54%.

2.8. *9′-{1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b] [1,4] oxazine]} 4-[11(tetrahydro-2-pyranyl) oxyundecyloxy] biphenyl-4′-carboxylate (**8**)*

Compound **8** was prepared according to the method for compound **5**. The crude product was purified by column chromatography (silica gel, $CHCl_3$) and recrystallized from EtOH/$CHCl_3$ (20/1). Yield 5.0 g (73%). ^{1}H NMR ($CDCl_3$): $\delta = 1.30–1.60$ (m, 20H), 1.32 (s, 3H), 1.33 (s, 3H), 1.67–1.80 (m, 4H), 2.73 (s, 3H), 3.39 (m, 1H), 3.48 (m, 1H), 3.75 (m, 1H), 3.86 (m, 1H), 3.96 (t, 2H), 4.57 (m, 1H), 6.55 (d, 1H, 2H-indole), 6.87 (t, 1H, 2H-indole), 6.98 (3H, naphthoxazine and biphenyl), 7.06 (d, 1H, 2H-indole), 7.19 (t, 1H, 2H-indole), 7.28 (d, 1H, naphthoxazine), 7.56 (d, 2H, biphenyl), 7.62–7.69 (m, 4H, naphthoxazine and biphenyl), 7.76 (d, 1H, naphthoxazine), 8.27 (d, 2H, biphenyl), 8.43 (d, 1H, naphthoxazine).

2.9. *9′-{1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b] [1,4] oxazine]} 4-(11-hydroxyundecyloxy) biphenyl-4′-carboxylate (**9**)*

Compound **9** was prepared according to the method for compound **6**. The crude product was purified by column chromatography (silica gel, $CHCl_3$/MeOH, 70/1) and recrystallized from EtOH/$CHCl_3$ (20/1). Yield 3.3 g (83%). ^{1}H NMR ($CDCl_3$): $\delta = 1.31–1.48$ (m, 12H), 1.35 (s, 3H), 1.36 (s, 3H), 1.45–1.58 (m, 4H), 1.82 (m, 2H), 2.77 (s, 3H), 3.65 (t, 2H), 4.02 (t, 2H), 6.59 (d, 1H, 2H-indole), 6.90 (t, 1H, 2H-indole), 7.00–7.02 (3H, naphthoxazine and biphenyl), 7.10 (d, 1H, 2H-indole), 7.22 (t, 1H, 2H-indole), 7.30 (dd, 1H, naphthoxazine), 7.63 (d, 2H, biphenyl), 7.67–7.73 (4H, naphthoxazine and biphenyl), 7.82 (d, 1H, naphthoxazine), 8.30 (d, 2H, biphenyl), 8.40 (d, 1H, naphthoxazine).

2.10. *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 (**10**)*

Compound **10** was prepared according to the method for compound **7**. The crude product was purified by column chromatography (silica gel, $CHCl_3$) and

recrystallized from EtOH/$CHCl_3$ (20/1). Yield 2.4 g (66%). ^{1}H NMR ($CDCl_3$): $\delta = 1.31–1.51$ (m, 14H), 1.36 (s, 6H), 1.67 (m, 2H), 1.82 (m, 2H), 2.77 (s, 3H), 4.02 (t, 2H), 4.16 (t, 2H), 5.83 (dd, 1H), 6.13 (dd, 1H), 6.42 (dd, 1H), 6.59 (d, 1H, 2H-indole), 6.90 (t, 1H, 2H-indole), 7.00–7.03 (3H, naphthoxazine and biphenyl), 7.10 (d, 1H, 2H-indole), 7.22 (t, 1H, 2H-indole), 7.30 (dd, 1H, naphthoxazine), 7.63 (d, 2H, biphenyl), 7.67–7.73 (4H, naphthoxazine and biphenyl), 7.82 (d, 1H, naphthoxazine), 8.30 (d, 2H, biphenyl), 8.39 (d, 1H, naphthoxazine). Elemental analysis calc. C 76.94, H 6.85, N 3.66; found C 76.90, H 6.74, N 3.98%.

2.11. *5-{1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] pyrido[3,2-f] [1,4] benzoxazine]} 4-[11-(tetrahydro-2-pyranyloxy)undecyloxy]-biphenyl-4′-carboxylate (**11**)*

Compound **11** was prepared according to the method for compound **5**. The crude product was purified by column chromatography (silica gel, $CHCl_3$/MeOH, 60/1) and recrystallized from EtOH/$CHCl_3$ (20/1). Yield 1.8 g (72%). ^{1}H NMR ($CDCl_3$): $\delta = 1.30–1.86$ (m, 24H), 1.36 (s, 3H), 1.41 (s, 3H), 2.77 (s, 3H), 3.39 (m, 1H), 3.50 (m, 1H), 3.74 (m, 1H) 3.88 (m, 1H), 4.02 (t, 2H), 4.58 (t, 1H), 6.60 (d, 1H, 2H-indole), 6.98 (d, 1H, 2H-indole), 7.02 (d, 2H, biphenyl), 7.08 (dd, 1H, 2H-indole), 7.29 (d, 1H, pyridobenzoxazine), 7.50 (dd, 1H, pyridobenzoxazine), 7.61 (d, 2H, biphenyl), 7.71 (d, 2H, biphenyl), 7.78 (s, 1H, pyridobenzoxazine), 8.00 (d, 1H, pyridobenzoxazine), 8.25 (d, 2H, biphenyl), 8.83 (dd, 1H, pyridobenzoxazine), 8.91 (dd, 1H, pyridobenzoxazine).

2.12. *5-{1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] pyrido[3,2-f] [1,4] benzoxazine]} 4-(11-hydroxyundecyloxy)biphenyl-4′-carboxylate (**12**)*

Although the preparation of compound **12** was attempted according to the method for compound **6**, the photochromic property of the product disappeared during the progress of the reaction. Dimethylaluminium chloride [16] was therefore chosen to replace *p*-TSA. Compound **11** (0.94 g, 1.2 mmol) was added to CH_2Cl_2 (30 ml) at room temperature. The solution was cooled with an ice/salt bath and then 1.05 mol l^{-1} dimethylaluminium chloride solution in *n*-hexane (6.5 ml, 6.8 mmol) was added in a dropwise fashion. The solution was then stirred for 3.5 h at room temperature and poured into cold 10% aqueous $NaHCO_3$ solution. The CH_2Cl_2 layer was separated and dried with Na_2SO_4. The solvent was evaporated and the crude product purified by column chromatography (silica gel, $CHCl_3$/MeOH, 60/1) and recrystallized from EtOH/$CHCl_3$ (20/1). Yield 0.51 g (38%). ^{1}H NMR ($CDCl_3$): $\delta = 1.30–1.57$ (m, 16H), 1.36 (s, 3H), 1.41 (s, 3H), 1.81 (m, 2H), 2.77 (s, 3H), 3.64 (t, 2H), 4.01 (t, 2H), 6.60 (d, 1H, 2H-indole), 6.98 (d, 1H, 2H-indole), 7.02 (d, 2H, biphenyl), 7.07 (dd, 1H, 2H-indole), 7.28 (d, 1H, pyridobenzoxazine), 7.48, 1H, pyridobenzoxazine), 7.61 (d, 2H, biphenyl), 7.70 (d, 2H, biphenyl), 7.77 (s, 1H, pyridobenzoxazine), 7.97 (d, 1H, pyridobenzoxazine), 8.25 (d, 2H, biphenyl), 8.82 (dd, 1H, pyridobenzoxazine), 8.89 (dd, 1H, pyridobenzoxazine).

2.13. *5-{1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] pyrido[2,1-b] [1,4] benzoxazine]} 4-[11-(acryloyloxy)undecyloxy] biphenyl-4′-carboxylate (**13**)*

Compound **13** was prepared according to the method for the compound **7**. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate, 2/1) and recrystallized from EtOH/$CHCl_3$ (20/1). Yield 0.36 g (64%). ^{1}H NMR ($CDCl_3$): $\delta = 1.31–1.44$ (m, 12H), 1.36 (s, 3H), 1.45 (s, 3H), 1.48 (m, 2H), 1.66 (m, 2H), 1.82 (m, 2H), 2.77 (s, 3H), 4.02 (t, 2H), 4.15 (t, 2H), 5.82 (dd, 1H), 6.13 (dd, 1H), 6.42 (dd, 1H), 6.60 (d, 1H, 2H-indole), 6.98 (d, 1H, 2H-indole), 7.02 (d, 2H, biphenyl), 7.08 (dd, 1H, 2H-indole), 7.28 (d, 1H, pyridobenzoxazine), 7.48 (dd, 1H, pyridobenzoxazine), 7.61 (d, 2H, biphenyl), 7.71 (d, 2H, biphenyl), 7.77 (s, 1H, pyridobenzoxazine), 7.97 (d, 1H, pyridobenzoxazine), 8.25 (d, 2H, biphenyl), 8.83 (dd, 1H, pyridobenzoxazine), 8.89 (dd, 1H, pyridobenzoxazine). Elemental analysis: calc. C 75.27, H 7.85, N 5.49; found C 75.33, H 7.82, N 5.40%.

2.14. *5-{1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b] [1,4] oxazine]} 4-[11-(acryloyloxy)undecyloxy] benzyl-4′-carboxylate (**14**)*

Compound **14** was prepared by the reaction of 5-hydroxy-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b][1,4] oxazine] and 4-[(11-acryloyloxy)undecyloxy] benzoic acid according to the method for compound **5**. The crude product was purified by column chromatography (silica gel, $CHCl_3$) and recrystallized from EtOH/$CHCl_3$ (20/1). Yield 1.5 g (69%). ^{1}H NMR ($CDCl_3$): $\delta = 1.30–1.45$ (m, 12H), 1.34 (s, 3H), 1.39 (s, 3H), 1.46 (m, 2H), 1.67 (m, 2H), 1.82 (m, 2H), 2.76 (s, 3H), 4.04 (t, 2H), 4.15 (t, 2H), 5.82 (dd, 1H), 6.13 (dd, 1H), 6.42 (dd, 1H), 6.57 (d, 1H, 2H-indole), 6.94 (d, 1H, 2H-indole), 6.98 (d, 2H, phenyl), 7.03 (dd, 1H, 2H-indole), 7.04 (d, 1H, naphthoxazine), 7.40 (t, 1H, naphthoxazine), 7.58 (t, 1H, naphthoxazine), 7.69 (d, 1H, naphthoxazine), 7.75 (s, 1H, naphthoxazine), 7.76 (d, 1H, naphthoxazine), 8.15 (d, 2H, phenyl), 8.57 (d, 1H, naphthoxazine). Elemental analysis: calc. C 74.98, H 7.02, N 4.07; found C 75.01, H 7.08, N 4.36%.

2.15. *5-{1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b] [1,4] oxazine] } 4-dodecyloxybiphenyl-4′-carboxylate (**15**)*

Compound **15** was prepared by the reaction of 5-hydroxy-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b] [1,4] oxazine] and 4-dodecyloxy-4′-biphenylcarboxylic acid according to the method for compound **5**. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate, 9/1) and recrystallized from EtOH/$CHCl_3$ (20/1). Yield 0.84 g (44%). ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, 3H), 1.27–1.41 (m, 19H), 1.35 (s, 3H), 1.40 (s, 3H), 1.46 (m, 2H), 1.82 (m, 2H), 2.76 (s, 3H), 4.01 (t, 3H), 6.58 (d, 1H, 2H-indole), 6.97 (d, 1H, 2H-indole), 7.01 (d, 2H, biphenyl), 7.05 (d, 1H, naphthoxazine), 7.06 (dd, 1H, 2H-indole), 7.40 (t, 1H, naphthoxazine), 7.58 (t, 1H, naphthoxazine), 7.61 (d, 2H, biphenyl), 7.69 (d, 1H, naphthoxazine), 7.70 (d, 2H, biphenyl), 7.75 (d, 1H, naphthoxazine), 7.76 (s, 1H, naphthoxazine), 8.25 (d, 2H, biphenyl), 8.57 (d, 1H, naphthoxazine). Elemental analysis: calc. C 79.63, H 7.39, N 3.95; found C 79.69, H 7.56, N 4.21%.

2.16. *Characterization*

^{1}H NMR spectra were recorded on a JEOL LA400 NMR spectrometer. A differential scanning calorimeter (Mettler DSC 30) was used to determine phase transition temperatures using heating and cooling rates of 10°C min^{-1}. An optical polarizing microscope (Olympus BH-2) equipped with a hot stage (Mettler FP84) and a temperature programmer (Mettler FP80) was also used to observe phase transitions. X-ray diffraction data were recorded on a Rigaku RINT 1500 X-ray diffractometer. Absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer equipped with UV irradiation and heating systems (figure 2) [17]. Films for absorption

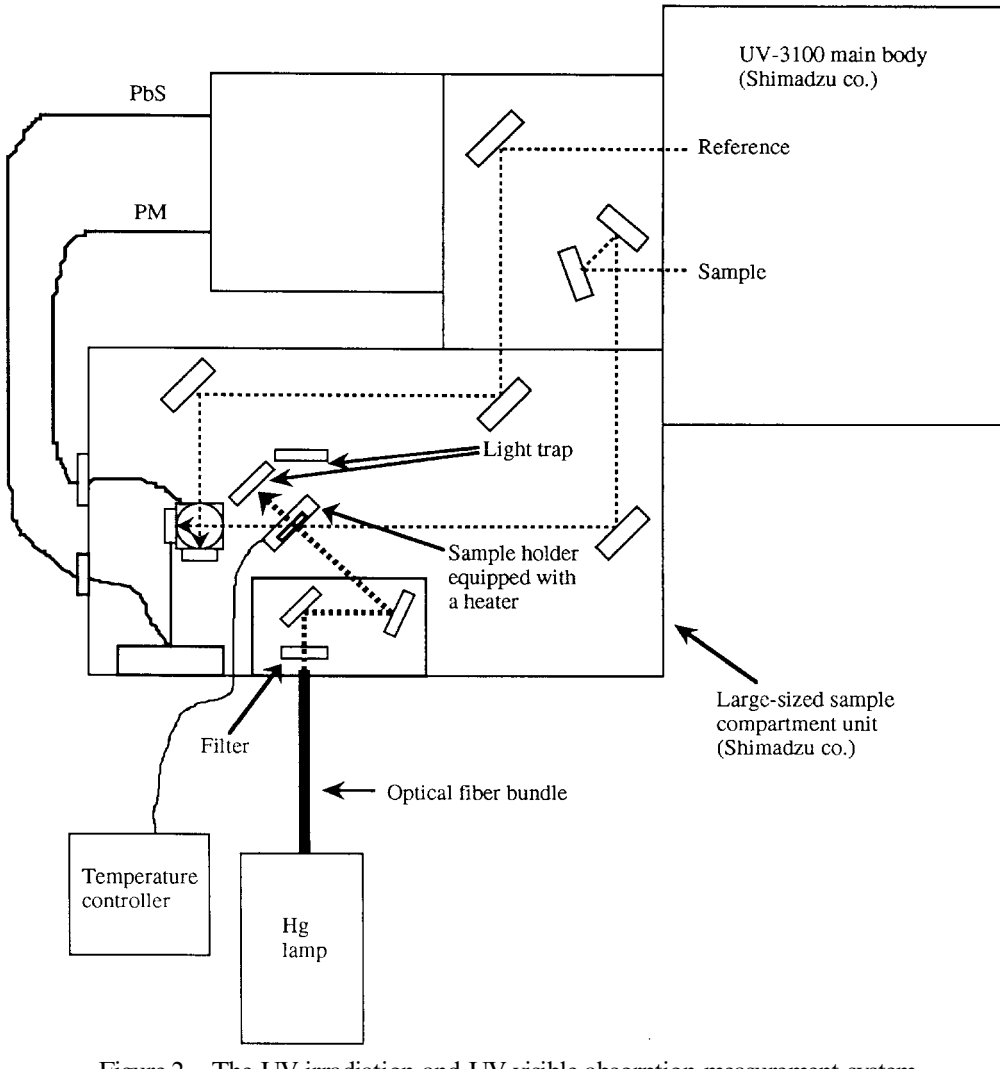


Figure 2. The UV irradiation and UV-visible absorption measurement system.

measurement were prepared between glass plates with a 25 μm spacer. The UV intensity through the filter was 0.95 mW cm^{-2} at 365 nm.

3. Results and discussion

3.1. *Phase transition behaviour of the compounds*

Phase transition temperatures of the compounds studied are shown in the table.

Although not all the compounds exhibited mesomorphic behaviour on the first heating stage, they began to show a mesophase at the first cooling and subsequent heating and cooling stages, except for A11B5SNO which had no mesophase. Since spiro-oxazines are known to exhibit thermochromism in addition to photochromism [18], it is clear that a small portion of the ring-opened merocyanine form of ring-closed spiro-oxazine derivatives might exist at higher temperatures. However, it is assumed that the appearance of the mesophase in the first cooling stage was caused by reorientation of the spiro-oxazine molecules in the molten state. Moreover, it has been reported that spiro-oxazines having alkyl and/or alkyloxy chains have a tendency to form undercooled melts [19].

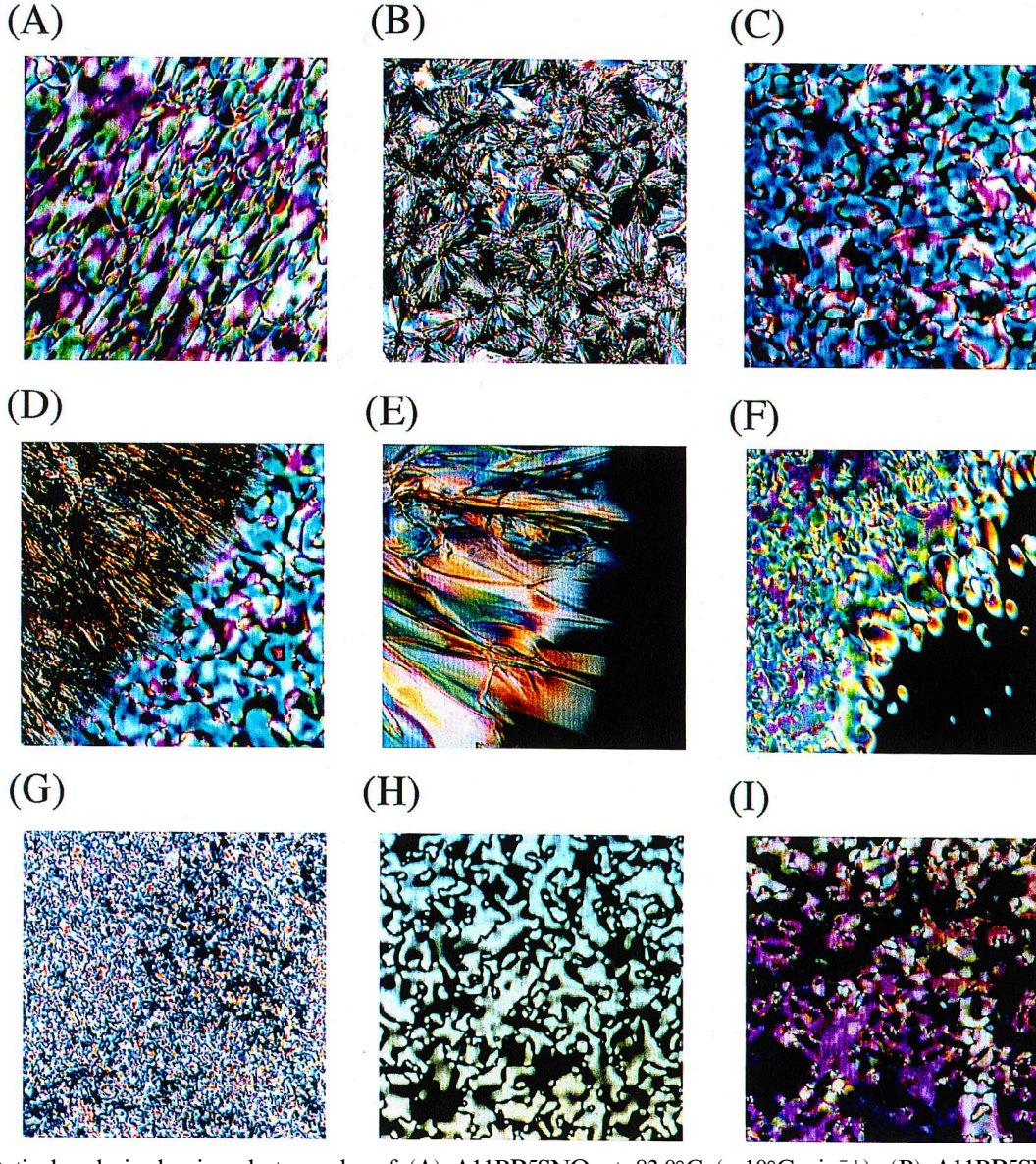


Figure 3. Optical polarized microphotographs of (A) A11BP5SNO at 83.0°C (– 10°C min^{-1}), (B) A11BP5SNO at 90.0°C (10°C min^{-1}), (C) $C_{12}H_{25}$BP5SNO at 108.0°C (– 10°C min^{-1}), (D) $C_{12}H_{25}$BP5SNO at 107.0°C (– 10°C min^{-1}), (E) $C_{12}H_{25}$BP5SNO at 128.2°C (slow cooling, dark area indicates isotropic region), (F) A11BP9′SNO at 53.0°C (– 10°C min^{-1}, dark area indicates isotropic region), (G) A11BP5SPO at 55.0°C (– 10°C min^{-1}), (H) A11BP5SPO at 99.7°C (slow cooling), and (I) A11BP5SPO at 99.7°C (annealing) under crossed polarizers.

Since it was revealed that the spiro-oxazine-containing compounds formed metastable supercooled mesomorphic melts, it was anticipated that their phase transition behaviours under DSC depend on the cooling and heating rates; Similarly in optical polarizing microscopy.

A11BP5SNO, containing the biphenylene mesogen, exhibited a mesophase from 83.3 to 18.1°C on the first cooling (Figure 3A) and crystallized from the mesophase at 86.6°C on the second heating (figure 3B). The temperature range of the mesophase lies about 30°C below the crystal melting point. Krongauz *et al.* reported similar thermal behaviour for 5-[4-(4-heptylbenzoyloxy)-benzoyloxy]-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H] naphth[2,1-b][1,4] oxazine] [10].

A11B5SNO, containing a phenylene ring, exhibited a glass transition alone on both first cooling and second heating. This result seemed to indicate that the liquid crystallinity of A11BP5SNO is mainly induced by the mesogenic biphenylene, while the spironaphthoxazine moiety does not have a mesogenic function.

Although $C_{12}H_{25}$BP5SNO exhibited a mesophase from 108.0 to 107.1°C at a cooling rate of 10°C min^{-1} (figure 3C and 3D), an isotropic-to-crystalline transition alone was observed at 128.2°C on a relatively slow cooling rate (figure 3E) under the optical polarizing microscopic observation. Thus, it is assumed that the molecular orientation of $C_{12}H_{25}$BP5SNO is much lower than that of A11BP5SNO. This result indicates that the introduction of the acryloyloxy group to the terminal position was effective in inducing a stable mesophase by helping orientation of the molecules.

A11BP9′SNO exhibited a mesophase from 53.0 to 24.6°C on cooling (figure 3F). The mesophase temperature range for A11BP9′SNO was narrow and a mesomorphic-to-isotropic transition temperature was low in comparison with that of A11BP5SNO (figure 4). The structural difference between A11BP9′SNO and A11BP5SNO exists in the binding position of a spironaphthoxazine to a biphenyloyloxy group. According to molecular models calculated by the molecular force field method (CAChe), the conformation of A11BP9′SNO is bent compared with that of A11BP5SNO (figure 6). This structural difference might cause the difference in thermal properties between the two compounds.

The isotropic-to-mesomorphic transition temperature (60.3°C) of A11BP5SPO was 23°C lower than that of A11BP5SNO at a cooling rate of 10°C min^{-1} (figure 3G and 4) and unusual thermal behaviour was observed on the second heating at a rate of 10°C min^{-1} (see the table and figure 5). However, as shown in figure 3H and 3I, A11BP5SPO demonstrated isotropic-to-mesomorphic transition at 99.7°C at a relatively slow cooling rate, and spontaneous crystallization was caused in this compound by annealing at 99.7°C.

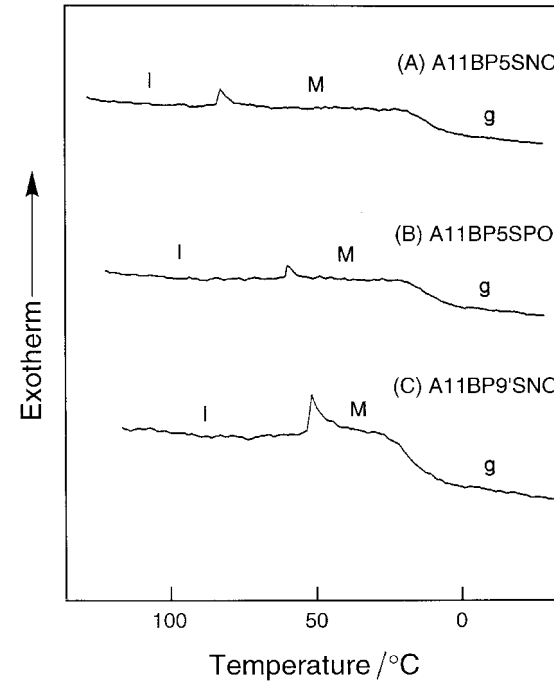


Figure 4. DSC thermograms of (A) A11BP5SNO, (B) A11BP5SPO, and (C) A11BP9′SNO on the first cooling at a scanning rate of 10°C min^{-1}.

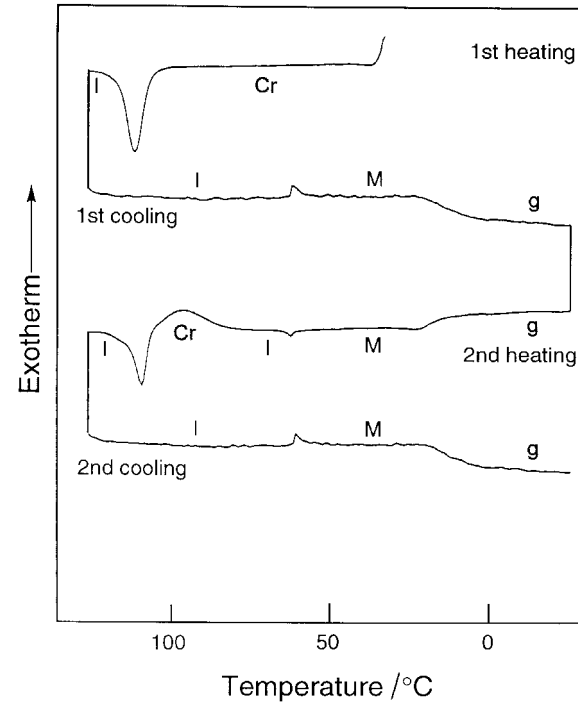


Figure 5. DSC thermograms of A11BP5SPO at a scanning rate of 10°C min^{-1}. The scale of the enthalpy axis was not normalized. The isotropic-to-mesomorphic transition enthalpy was 0.5 J g^{-1} on both cooling and heating cycles.

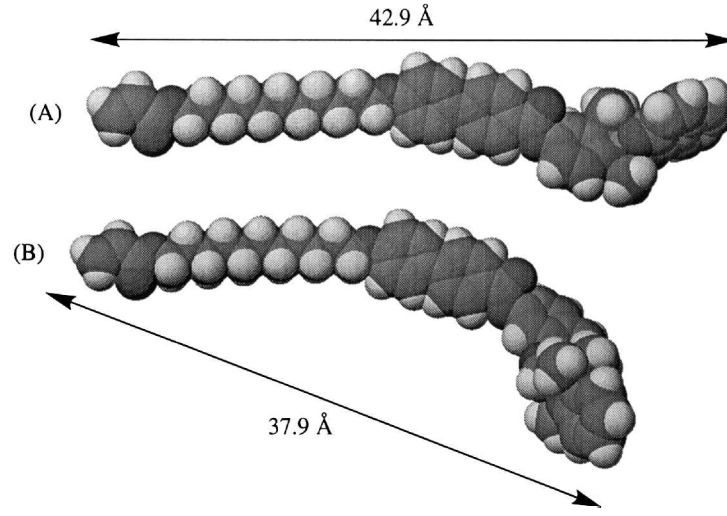


Figure 6. Molecular models calculated by the moleculae force field method (CAChe) of (A) A11BP5SNO and (B) A11BP9′SNO. The biphenylene moiety was fixed in the planar conformation before calculation.

3.2. *Wide-angle X-ray diffraction patterns of the compounds*

Wide-angle diffraction patterns of the compounds studied are shown in figure 7. All samples were quenched from the mesomorphic state by means of a liquid nitrogen bath. For the non liquid crystalline $C_{12}H_{25}$ BP5SNO, a sharp peak and very broad reflection appeared in a small angle region at 2.16° (40.9 Å) and around 19° (4.65 Å), respectively. The distance of the former peak was close to the calculated length (39.5 Å) based on the stretched molecule.

On the other hand A11BP5SPO, quenched from the liquid crystalline state at 59°C, exhibited a broad peak centred around 19° which was assignable to the distance between layers formed by the mesogenic molecules nematically ordered on the planes [20]. No small angle reflection appeared for this compound.

Both A11BP5SNO and A11BP9′SNO exhibited a relatively small peak in a small angle region at 2.16° and 2.47°, respectively, and a broad peak around 19°. Since both compounds showed nematic texture in the optical polarizing microscopic observation, this X-ray diffraction pattern seems to indicate a small amount of crystallization arising from the quenching procedure.

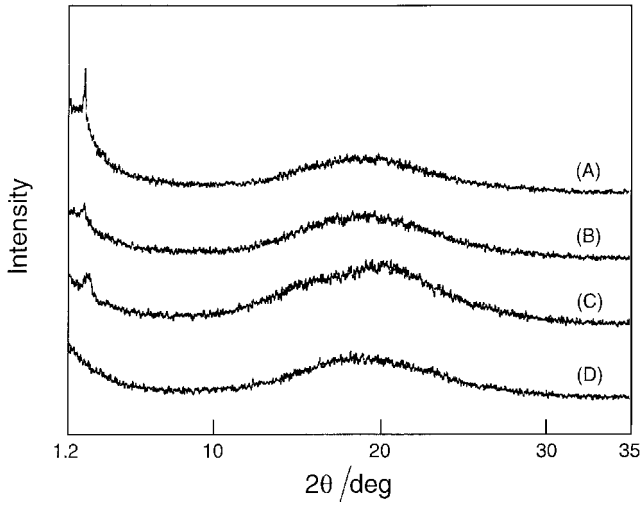


Figure 7. Wide-angle X-ray diffraction patterns of quenched samples: (A) $C_{12}H_{25}$ BP5SNO, (B) A11BP5SNO, (C) A11BP9′SNO, (D) A11BP5SPO.

3.3. *Thermochromism and photochromism of A11B5SNO*

A demonstration of thermochromism and photochromism in a A11B5SNO film are shown in figure 8. Absorbance derived from the ring-opened merocyanine form of the spiro-oxazine moiety is clearly dependent on temperature (figure 8A). The A11B5SNO film reached the photostationary state after UV irradiation for 90 s at 23°C (figure 8B). The absorbance derived from the ring-opened A11B5SNO by thermochromism at 80°C was 0.068 at 609 nm. On the other hand, the absorbance by photochromism at the photostationary state at 23°C was 0.957 at 609 nm. The concentration of the ring-opened A11B5SNO due to thermochromism at 80°C was 7.1% of that due to photochromism at the photostationary state at 23°C.

4. Conclusions

In conclusion, the first polymerizable photochromic liquid crystals containing the spiro-oxazine moiety have been synthesized. Their mesophases are metastable, exhibiting a tendency to depend on the cooling rate and the annealing condition. Polymerization studies on the acrylic monomers and their physical properties will be published elsewhere.

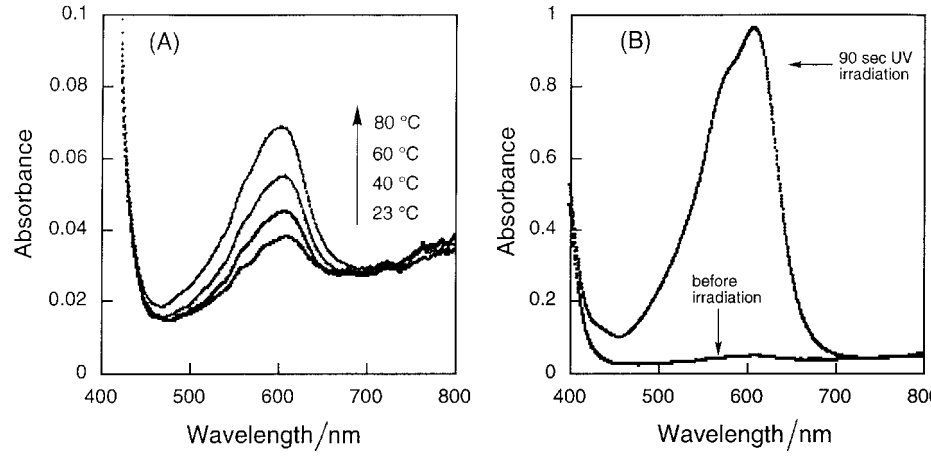


Figure 8. Absorption spectra of thermochromism (A) and photochromism at 23°C (B) of an A11B5SNO film.

We thank Dr. Takashi Kato of the University of Tokyo for DSC measurements and Mr. Kiyohisa Takizawa of the Analysis Center, Dai Nippon Printing Co. Ltd., for wide-angle X-ray measurements.

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