Synthesis and properties of new mesomorphic side-on systems

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Synthesis and properties of new mesomorphic side-on systems

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New mesomorphic side-on materials containing high birefringent groups (tolanes and naphthalenes) have been designed and synthesized. We present the synthesis and characterization of 6-(4-acryloyloxybutanyloxy)-1,4{bis-[2-(6-propanoxynaphthyl)]diethyn}benzoate and 6-(4-acryloyloxybutanyloxy)-1,4{bis-[2-(6-((S)-2-butanoxy)naphthyl)]}diethyn}benzoate, and their corresponding polymers. The first monomer exhibits both enantiotropic smectic C and nematic mesophases, while the second monomer exhibits only a monotropic cholesteric mesophase. The effect of the second monomer on the birefringence of reflective cholesteric displays is reported.

1. Introduction

Liquid crystal displays have become essential as information displays. Since liquid crystalline materials switch between orientations with different optical properties, their use in display devices is particularly successful. In order to optimize the display parameters such as response time, contrast ratio, brightness and viewing angle, a high birefringent material is required. Moreover, polymer networks can be used to stabilize certain liquid crystal states and make the display operate properly [1]. Our aim was to synthesize liquid crystalline monomers exhibiting a large birefringence. The optically anisotropic nature of a nematic phase is due to the orientational order of molecules which have a greater polarizability along the molecular length than across the molecule. The birefringence exhibited is then dependent upon the degree of anisotropy of polarizability and the order parameter [2].

Liquid crystal materials of high optical anisotropy consist of moieties of high electron density in conjugation with each other along the molecular length [3,4]. Molecules which consist of high polarizability groups with high electron density such as benzene rings, polyaromatic systems and acetylene linking groups will therefore have high optical anisotropy. Moreover, a highly anisotropic nematogenic moiety can be generated by a typical architecture where the mesogenic group is laterally appended to a polymer backbone via a flexible spacer group [5–10]. These side-on fixed mesogenic polymers, unlike the side-end fixed ones [11,12], exhibit in the nematic phase a large anisotropy of the polymer conformation as evidenced by small angle neutron scattering experiments [13–16]. Indeed, the overall quadratic size along the direction of alignment was found to be much larger than in the perpendicular direction [17].

Our approach was to combine both effects together in order to obtain molecules with high optical anisotropy and high orientational order. We have designed new side-on monomers, 8 and 8a containing conjugative acetylene linking groups between naphthalenes and aromatic groups in the rigid core, and chiral and non-chiral chains in the aliphatic tails, as described in the following general formula.

2. Experimental

The synthesis of the monomers is shown in the scheme. Confirmation of the structures of the intermediates and products was obtained by ^{1}H NMR spectroscopy (Varian FT-200 spectrometer) and infrared spectroscopy (Nicolet Magna IR Spectrometer 550). Elemental analyses were performed by Oneida Research Services, Inc., New York. The purity of each monomer was checked by HPLC analysis (Waters). The specific rotations of the optically active compounds were measured using an automatic polarimeter AA-10 from Optical Activity Limited. A Perkin–Elmer DSC7 was used to determine the transition temperatures and the anisotropic textures were observed under a Leitz Laborlux S polarizing optical microscope fitted with a Mettler FP5 heating stage.

2.1. Preparation of the 2-bromo-6-propanoxynaphthalene (1)

Bromopropane (0·026 mol, 2·44 ml) was added dropwise to a stirred solution of 6-bromo-2-naphthol (6·00 g, 0·026 mol) and potassium carbonate (0·057 mol, 7·89 g)

N. Leroux and L.-C. Chien

8 with $R = CH_3CH_2CH_2$,
8a with $R = CH_3CH_2CH(CH_3)(s)$
　　　　　　　　*

Scheme 1.

(1)

(2)

(3)

(3) with $R = CH_3CH_2CH_2$ and (3a) with $R = CH_3CH_2CH$
　　　　　　　　　　　　　　　　　　　　　　　　　　*　(S)
　　　　　　　　　　　　　　　　　　　　　　　　　CH_3

(4)

(5)

(6)

(7)

(8)

(8) with $R = CH_3CH_2CH_2$ and (8a) with $R = CH_3CH_2CH$
　　　　　　　　　　　　　　　　　　　　　　　　　　*　(S)
　　　　　　　　　　　　　　　　　　　　　　　　　CH_3
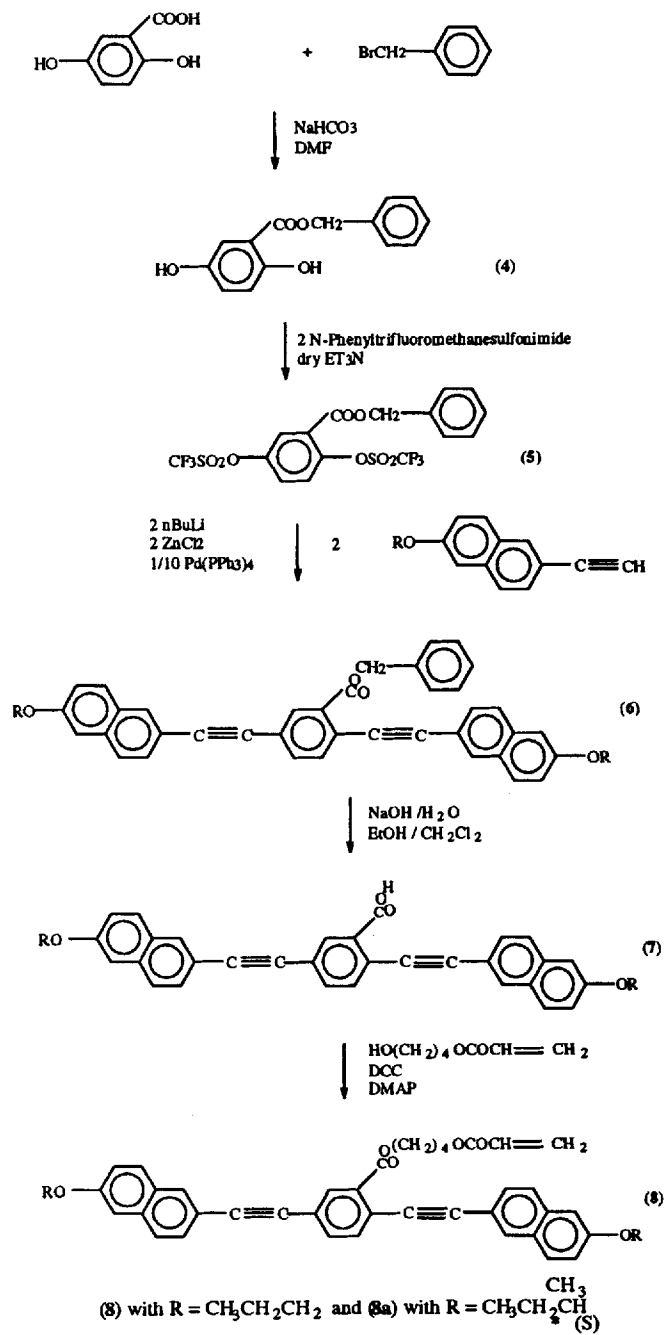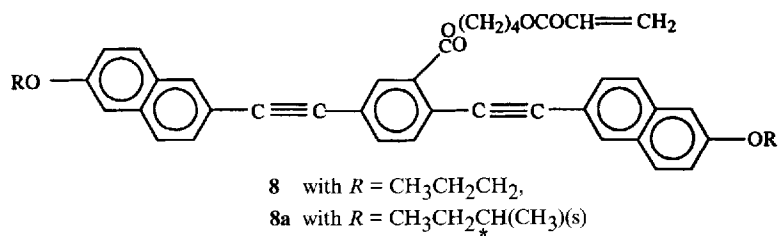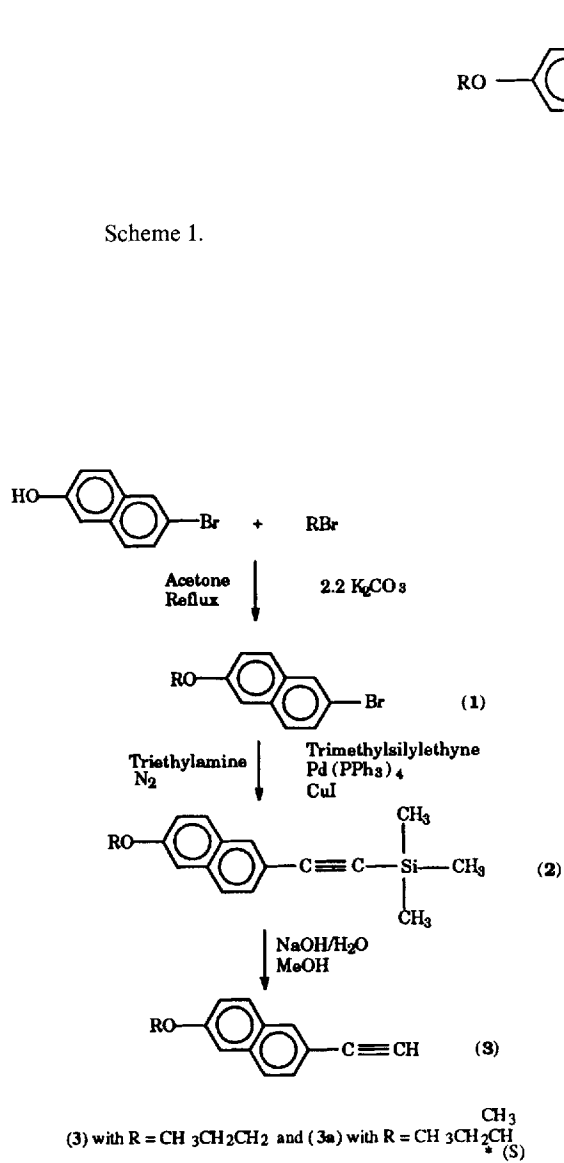
Scheme 2.

in 100 ml acetone. The reaction mixture was then stirred under reflux for 24 h and the product was extracted twice with diethylether, washed with water, 5 per cent sodium hydroxide, water and dried under magnesium sulphate. The solvent was removed *in vacuo* and the crude product was recrystallized from ethanol to yield a white crystal. Yield: 5·6 g (82 per cent); IR (Nujol): 1760 cm^{-1} (ether), 1480 and 1390 cm^{-1} (C–C aromatic); NMR ^{1}H (CDCl$_3$): 7·90 (s, 1 H, Ar), 7·56 (m, 3 H, Ar), 7·15 (m, 2 H, Ar), 4·02 (t, 2 H, CH$_2$OPh), 1·86 (m, 2 H, CH$_2$CH$_3$), 1·07 (t, 3 H, CH$_3$).

2.2. Preparation of the 2-bromo-6-((S)-2-butanoxy)naphthalene (1a)

Diethyl azodicarboxylate (7·06 ml, 0·044 mol) in 10 ml anhydrous tetrahydrofuran was added dropwise to a stirred, cooled (0°C) solution of (S)-butan-2-ol (4·15 ml, 0·044 mol) and 6-bromo-2-naphthol (10 g, 0·044 mol) with triphenylphosphine (11·75 g, 0·044 mol) in 150 ml anhydrous tetrahydrofuran. The reaction mixture was then stirred at room temperature for 24 h. The solvent was removed *in vacuo* and the product was purified by flash chromatography in dichloromethane to yield a yellowish oil. Yield: 5·8 g (80 per cent); IR (Nujol): 1760 cm^{-1} (ether), 1480 and 1390 cm^{-1} (C–C aromatic); NMR ^{1}H (CDCl$_3$): 7·87 (s, 1 H, Ar), 7·53 (m, 3 H, Ar), 7·01 (m, 2 H, Ar), 4·44 (q, 1 H, CHONaphth.), 1·75 (m, 2 H, CH$_2$CH), 1·34 (d, 3 H, CH$_3$CH), 1·00 (t, 3 H, CH$_3$CH$_2$); specific optical rotation $(\alpha)_{RT,CHCl3}= -2·44°$.

2.3. Preparation of 6-propanoxynaphth-2-ylethyne (3) [3]

A mixture of compound 1 (5·6 g, 0·021 mol), trimethyl-silylethyne (2·88 ml, 0·021 mol), tetrakis(triphenylphosphine)palladium(0) (1·5 g, 0·0013 mol) and copper(I) iodide (0·22 g, 0·0013 mol) in 40 ml of dry triethylamine was refluxed under dry nitrogen for 24 h. The product was then extracted twice into diethylether, washed with water and brine and dried under magnesium sulphate. The solvent was removed *in vacuo* and the product was purified by flash chromatography in hexane to yield a yellowish solid (2). Yield: 3·5 g (60 per cent); IR (Nujol): 2100 cm^{-1} (carbon–carbon triple bond), 1606 cm^{-1} (ether), 1383 and 1472 cm^{-1} (C–C aromatic); NMR ^{1}H (CDCl$_3$): 7·80 (s, 1 H, Ar), 7·55 (m, 3 H, Ar), 7·00 (m, 2 H, Ar), 3·93 (t, 2 H, CH$_2$OPh), 1·76 (m, 2 H, CH$_2$CH$_3$), 0·94 (3 H, t, CH$_3$CH$_2$), 0·15 (m, 9 H, (CH$_3$)$_3$–Si).

The product 2 was then dissolved into a mixture of acetone and methanol and stirred for 4 h with an excess of sodium hydroxide in water (10 per cent). The product was extracted twice into diethylether, washed with water and brine, and dried under magnesium sulphate. The solvent was removed *in vacuo* and the product was purified by flash chromatography in hexane to yield a

yellowish solid. Yield: 2·0 g (71 per cent); IR: 3296 cm^{-1} (ethyne), 2106 cm^{-1} (carbon–carbon triple bond), 1380 and 1470 cm^{-1} (C–C aromatic); NMR ^{1}H (CDCl$_3$): 7·90 (s, 1 H, Ar), 7·65 (m, 2 H, Ar), 7·48 (d, 1 H, Ar), 7·15 (m, 2 H, Ar), 3·97 (t, 2 H, CH$_2$OPh), 3·07 (s, 1 H, CH triple bond), 1·85 (m, 2 H, CH$_2$CH$_3$), 1·04 (t, 3 H, CH$_3$CH$_2$).

2.4. Preparation of 6-((S)-2-butanoxy)naphth-2-ylethyne (3a) [3]

The same procedure as described for compound 3 using compound (1a) was carried out to yield a yellowish oil. Yield: 72 per cent; IR: 3294 cm^{-1} (ethyne), 2110 cm^{-1} (carbon–carbon triple bond), 1385 and 1470 cm^{-1} (C–C aromatic); NMR ^{1}H (CDCl$_3$): 7·92 (s, 1 H, Ar), 7·65 (t, 2 H, Ar), 7·47 (m, 1 H, Ar), 7·09 (m, 2 H, Ar), 4·45 (m, 1 H, CHOPh), 3·09 (s, 1 H, CH triple bond), 1·75 (m, 2 H, CH$_2$) 1·35 (d, 3 H, CH$_3$CH), 1·00 (t, 3 H, CH$_3$CH$_2$); specific optical rotation $(\alpha)_{RT,CHCl3}= -31·07°$.

2.5. Preparation of benzyl 2,5-dihydroxybenzoate (4)

2,5-Dihydroxybenzoic acid (6·16 g, 0·04 ml) was stirred with sodium hydrogen carbonate (10 g, 0·04 mol) in 60 ml dimethylformamide at 70°C for 1 h. Benzylbromide (5·6 ml, 0·04 mol) was then added and the mixture was stirred at 70°C for 6 h. The reaction mixture was allowed to cool down to RT, and 140 ml of water was added. The product was extracted twice into a mixture hexane/ethylacetate (1 : 1), washed twice with water and dried under magnesium sulphate. The solvent was removed *in vacuo* and the crude product was recrystallized from ethanol to yield a white solid. Yield: 9·2 g (97 per cent); IR (Nujol): 3400 cm^{-1} (phenol), 1679 cm^{-1} (ester); NMR ^{1}H (CDCl$_3$): 10·33 (s, 2 H, OH), 7·39 (m, 5 H, Ar), 7·31 (m, 1 H, Ar), 7·05 (d, 1 H, Ar), 6·89 (m, 1 H, Ar), 5·35 (s, 2 H, CH$_2$Ph); m.p.: 85°C.

2.6. Preparation of benzyl 2,5-di-(trifluorosulphate)benzoate (5)

A solution of N-phenyltrifluoromethanesulphonimide (13·8 g, 0·038 mol) in 50 ml dry dichloromethane was added dropwise to a stirred, cooled solution (−78°C) of compound 4 (4·5 g, 0·018 mol) in 80 ml dry dichloromethane and 5·5 ml dry triethylamine under dry nitrogen. The stirred mixture was allowed to warm up to RT overnight. The mixture was then washed with an aqueous solution of sodium carbonate. The separated aqueous layer was washed with dichloromethane, and the combined organic phases were washed with water and dried under magnesium sulphate. The solvent was removed *in vacuo*, and the product was purified by chromatography in dichloromethane to yield a yellowish oil. Yield: 7·6 g (80 per cent); IR: 1729 cm^{-1} (ester); NMR ^{1}H (CDCl$_3$): 8·00 (d, 1 H, Ar), 7·43 (m, 7 H, Ar), 5·43 (s, 2 H, CH$_2$Ph).

2.7. *Preparation of benzyl 2,5-{bis-[2-(6-propanoxynaphthyl)]diethyn}benzoate (6)*
(R = CH₃CH₂CH₂)

(R = CH$_3$CH$_2$CH$_2$)

A solution of *n*-butyllithium (2·5 M in hexane) (4·6 ml) was added dropwise to a stirred, cooled (−5°C) solution of 6-propanoxynaphth-2-ylethyne (**3**) (2·44 g, 0·0116 mol) in 30 ml dry tetrahydrofuran under dry nitrogen. The mixture was stirred for 10 min and a solution of zinc chloride (1·6 g, 0·0116 mol) in 50 ml dry tetrahydrofuran was added dropwise between −5°C to 10°C. The mixture was then stirred at RT for 15 min and a solution of compound **5** (3 g, 0·0058 mol) in 30 ml dry tetrahydrofuran was added, followed by tetrakis(triphenylphosphine)palladium(0) (1·36 g, 0·0011 mol). The reaction mixture was then stirred under reflux for 48 h. The solvent was removed *in vacuo*, and the product was purified by flash chromatography in dichloromethane/hexane (1:1) to yield a yellowish solid. The product was dried under phosphorous pentoxide for two days. Yield: 1·8 g (50 per cent); IR (Nujol): 2216 cm⁻¹ (carbon–carbon triple bond), 1743 cm⁻¹ (ester); NMR ¹H (CDCl₃): 8·11 (m, 1 H, Ar), 8·00 (m, 2 H, Ar), 7·66 (m, 8 H, Ar), 7·41 (m, 5 H, Ar), 7·15 (m, 4 H, Ar), 5·4 (s, 2 H, CH₂Ph), 4·05 (t, 4 H, CH₂ONaphth.), 1·90 (m, 4 H, CH₂CH₂ONaphth.), 1·09 (t, 6 H, CH₃); m.p.: 130°C.

2.8. *Preparation of benzyl 2,5-{bis-[2-(6-((S)-2-butanoxy)naphthyl)]diethyn}benzoate (6 a)*
(R = CH₃CH₂CH(CH₃)(S))

The same procedure as described for compound **6** using compounds **3 a** and **5** was carried out to yield a yellowish solid. Yield: 67 per cent; IR (Nujol): 2210 cm⁻¹ (carbon–carbon triple bond), 1729 cm⁻¹ (ester); NMR ¹H (CDCl₃): 8·20 (m, 1 H, Ar), 8·00 (m, 2 H, Ar), 7·66 (m, 8 H, Ar), 7·50 (m, 5 H, Ar), 7·15 (m, 4 H, Ar), 5·45 (s, 2 H, CH₂Ph), 4·45 (m, 2 H, CHONaphth.), 1·75 (m, 4 H, CH₂), 1·36 (d, 6 H, CH₃CH), 0·88 (t, 6 H, CH₃CH₂); m.p.: 110–111°C; specific optical rotation (α)ᵣₜ,CHCl₃ = −25°C.

2.9. *Preparation of benzyl 2,5-{bis-[2-(6-propanoxynaphthyl)]diethyn}benzoic acid (7)*
(R = CH₃CH₂CH₂)

Compound **6** (1·53 g, 0·002 mol) in 10 ml dichloromethane was stirred under reflux for 24 h with an excess of sodium hydroxide (2·8 g) in 7 ml water and 50 ml of ethanol. The organic solvents were removed *in vacuo* and the crude product was poured into 200 ml water. The mixture was then acidified with concentrated hydrochloric acid until pH = 1. The yellow precipitate was filtered and rinsed with water. It was dried *in vacuo* under phosphorus pentoxide and was used without further purification. Yield: 1·35 g (98 per cent); IR (Nujol): 3385 cm⁻¹ (acid), 2216 cm⁻¹ (carbon–carbon

triple bond), 1771 cm⁻¹ (OH acid); NMR ¹H (CDCl₃): 8·45 (s, 1 H, Ar), 8·05 (d, 2 H, Ar), 7·70 (m, 8 H, Ar), 7·12 (m, 4 H, Ar), 4·05 (m, 4 H, CH₂ONaphth.), 1·87 (m, 4 H, CH₂CH₂), 1·08 (t, 6 H, CH₃CH₂); m.p.: 178–181°C.

2.10. *Preparation of benzyl 2,5-{bis-[2-(6-((S)-2-butanoxy)naphthyl)]diethyn}benzoic acid (7 a)*
(R = CH₃CH₂CH(CH₃)(S))

The same procedure as described for compound **7** using compound **6 a** was performed to yield a yellowish solid. Yield: 93 per cent; IR (Nujol): 3285 cm⁻¹ (acid), 2203 cm⁻¹ (carbon–carbon triple bond), 1709 cm⁻¹ (OH acid); NMR ¹H (CDCl₃): 8·45 (s, 1 H, Ar), 8·05 (d, 2 H, Ar), 7·70 (m, 8 H, Ar), 7·12 (m, 4 H, Ar), 4·45 (q, 2 H, CH), 1·68 (m, 4 H, CH₂), 1·38 (d, 6 H, CH₃CH), 1·03 (t, 6 H, CH₃CH₂); m.p.: 148–152°C.

2.11. *Preparation of the 6-(4-acryloyloxybutanyloxy)-1,4{bis-[2-(6-propanoxynaphthyl)]diethyn}benzoate (8)*
(R = CH₃CH₂CH₂)

Compound **7** (1·3 g, 0·0024 mol) and 4-hydroxybutyl acrylate (0·334 ml, 0·0024 mol) were stirred with (0·537 g, 0·0024 mol) 1,3-dicyclohexylcarbodiimide and (0·05 g) 4-dimethylaminopyridine in 20 ml dry tetrahydrofuran at room temperature for 24 h. The solvent was removed *in vacuo* and the hydrated dicyclohexylcarbodiimide was filtered off and rinsed with dichloromethane. The solvent was removed *in vacuo* and the product was purified by chromatography in dichloromethane/hexane (1:1) to yield a yellowish solid. The product was dried under phosphorous pentoxide 3 d. Yield: 0·7 g (53 per cent); IR (Nujol): 2203 cm⁻¹ (carbon–carbon triple bond), 1769 cm⁻¹ (ester); NMR ¹H (CDCl₃): 8·14 (s, 1 H, Ar), 8·01 (s, 2 H, Ar), 7·71 (m, 8 H, Ar), 7·13 (m, 4 H, Ar), 6·35 (d, 1 H, vinyl), 6·05 (q, 1 H, vinyl), 5·77 (d, 1 H, vinyl), 4·45 (m, 2 H, CH₂OCOPh), 4·18 (t, 2 H, CH₂OCOCH), 4·05 (t, 4 H, CH₂Ph), 1·89 (m, 8 H, CH₂CH₂), 1·09 (t, 6 H, CH₃CH₂); Elemental analysis: C 79·64 (calc. 79·52), H 6·21 (calc. 6·03) per cent.

2.12. *Preparation of the 6-(4-acryloyloxybutanyloxy)-1,4{bis-[2-(6-((S)-2-butanoxy)naphthyl)]diethyn}benzoate (8 a)*
(R = CH₃CH₂CH(CH₃)(S))

The same procedure as described for compound **8** using compound **7 a** was carried out. Yield: 54 per cent; IR (Nujol): 2205 cm⁻¹ (carbon–carbon triple bond), 1770 cm⁻¹ (ester); NMR ¹H (CDCl₃): 8·15 (s, 1 H, Ar), 8·00 (s, 2 H, Ar), 7·71 (m, 8 H, Ar), 7·13 (m, 4 H, Ar), 6·35 (d, 1 H, vinyl), 6·04 (q, 1 H, vinyl), 5·78 (d, 1 H, vinyl), 4·46 (m, 4 H, CH₂OCO), 4·18 (t, 2 H, CH), 1·8 (m, 8 H, CH₂CH₂ and CH₂CH), 1·38 (d, 6 H, CH₃CH), 1·03 (t, 6 H, CH₃CH₂); Elemental analysis: C 79·82 (calc. 79·77),

H 6·76 (calc. 6·36) per cent; specific optical rotation $(\alpha)_{RT, CHCl_3} = -21·48°$.

2.13. *Polymerization of the tolane side-on acrylates (8) and (8 a)*

The polymers were prepared by free radical polymerization using azobis isobutyronitrile (2 % mol) as initiator. For each polymerization, 200 mg of the appropriate monomer were used with 0·2 ml anhydrous toluene. The reactions were carried out under dry nitrogen at 70°C for 24 h. Upon completion, the reaction mixture was poured into 200 ml of cold methanol. The resulted precipitate was filtered, dissolved in 0·5 ml of tetrahydrofuran and poured into 200 ml of cold methanol. This procedure was repeated until no more monomers and oligomers were detected by thin layer chromatography (using dichloromethane as eluant). Additionally, the disappearance of the ^{1}H NMR bands associated with the vinyl group in all the synthesized polymers confirms the absence of residual monomer. The polymers were dried at 60°C under vacuum for 2 d. Their molecular weight (M_w) and polydispersity index (M_w/M_n) were determined by analytical gel permeation chromatography using a differential refractometer (Waters 410) with tetrahydrofuran as eluant and polystyrenes as calibrating standards.

3. Thermal properties

The characterization properties of the monomers and the polymers are listed in tables 1 and 2, respectively. The transition temperatures and the enthalpies of transition were determined by differential scanning calorimetry with decreasing temperature (rate: $10°C^{-1} min^{-1}$), and the mesophases were characterized by observation of the textures under polarizing optical microscopy.

Table 1. Phase transition temperatures (°C) and enthalpies of transitions (J g^{-1}) [in square brackets] for the tolane side-on monomers.

Monomers	Phase transition temperatures [and enthalpies]
8	Cr 117·8 [64·7] S_C 126·8 [3·88] N 162·2 [0·45] I
8 a	Cr (N* 46·8 [−0·36]) 92·1 [89·7] I

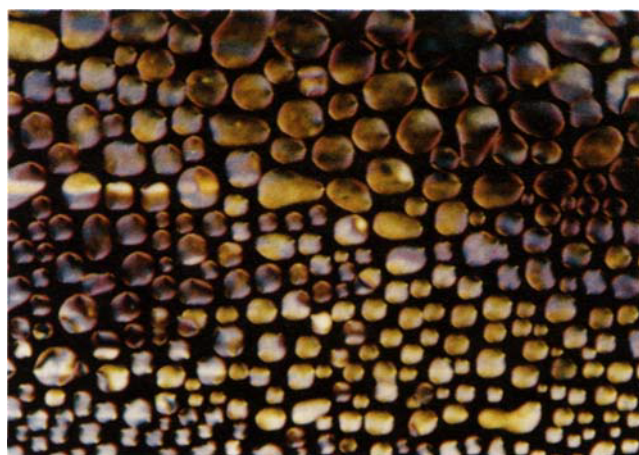Parentheses denote a monotropic transition.

3.1. *Monomers*

Both monomers **8** and **8 a** exhibit liquid crystalline phases. The non-chiral monomer **8** exhibits an enantiotropic smectic C mesophase from 117·8°C to 126·8°C and an enantiotropic nematic mesophase up to 162·2°C. Figure 1(a) shows the texture observed at the isotropic–nematic transition where typical nematic droplets appear from the isotropic state. Figure 1(b) shows the texture observed in the smectic mesophase which is a typical sandy-like smectic C texture. This is the first report of a smectic C mesophase for a symmetrical side-on liquid crystal monomer although strong smectic C fluctuations have been observed by X-ray experiments in the nematic mesophase of some side-on polysiloxanes [10]. The stabilization of the smectic C structure in the case of the side-on tolane acrylate is probably due to the presence of tolane groups in the rigid core which enhance the rigidity of the molecule. The chiral monomer **8 a** exhibits a monotropic cholesteric mesophase at $T = 46·8°C$. Figure 2 shows the texture observed by cooling from the isotropic state, which corresponds to a chiral nematic mesophase. In this case, the introduction of the two chiral aliphatic tails reduces the rigidity of the molecule and hence, the transition temperatures decrease. Moreover, the mesophase is destabilized, and no smectic phase is observed.

3.2. *Polymers*

Both polymers **P** and **P a** exhibit enantiotropic mesophases. As expected, the chiral polymer **P a** has a lower glass transition temperature and clarification temperature than the non-chiral polymer **P**. The smectic mesophase observed in the non-chiral monomer is no longer stable in the polymeric material, and the side-on tolane polyacrylate **P** exhibits only a nematic mesophase up to 115·2°C. Moreover, the chiral polymer **P a** exhibits a chiral nematic mesophase up to 77·9°C. In the case of the side-on tolane polymeric materials, the usual thermotropic behaviour of the side-on polymer is observed: both exhibit a nematogenic mesophase.

4. Display studies

To investigate the influence of the chiral side-on tolane acrylate on the birefringence of reflective cholesteric

Table 2. Phase transition temperatures (°C), enthalpies of transition (J g^{-1}) [in square brackets], average molecular weights and polydispersity index for the tolane side-on polymers.

Polymers	M_w	I_p	Phase transition temperatures [and enthalpies]
P $(R = CH_3CH_2CH_2)$	15 000	1·5	g 66·49 N 115·2 [0·59] I
P a $(R = CH_3CH_2CH)$ $\quad\quad CH_3$	12 300	1·6	g 37·3 N* 77·9 [1·02] I

(a)

(b)

Figure 1.   Micrograph under a polarizing optical microscope of the non-chiral monomer **8** at a magnification factor of × 320. (*a*) Isotropic–nematic transition from the isotropic state, (*b*) smectic C mesophase (117°C).

Figure 2.   Micrograph under a polarizing optical microscope of the chiral monomer **8 a** at a magnification factor of × 320. Cholesteric texture (38°C) observed by cooling from the isotropic state.

displays, samples of cholesteric mixtures with 4 per cent and 10 per cent (by weight) of the chiral monomer **8 a**, and 0·8 per cent (by weight) of a diacrylate cross-linker were prepared by vacuum filling ITO coated, surface rubbed polyimide glass cells which were separated with 10 μm spacers. The samples were prepared with commercially available chiral materials (CB15, CE1, R1011 (3 : 3 : 1)) (from BDH, England), at a concentration of 30 per cent (by weight) and 70 per cent of a nematic liquid crystal E48 (from BDH, England). This mixture resulted in a blue reflected colour. The samples were irradiated with 12·6 J cm^{-2} UV radiation while an electric field was applied to place the liquid crystal/monomer mixture in the homeotropic state.

The samples were illuminated with a 50 W tungsten–halogen light source, and a spectrascan meter (Photo Research PR704) was used to characterize the reflection

properties. The reflection spectra were measured for each display in the planar state at a normal incident angle.

Cholesteric liquid crystals in the planar texture exhibit the unique optical feature of separating incident light into its left and right handed circular components by reflecting one component and transmitting the other. The wavelength of the reflected component is governed by Bragg's reflection law [18], $\lambda_o = pn_a$, where λ_o is the reflected wavelength, p is the pitch, and n_a is the average reflective index.

The birefringence value Δn is calculated from the equation, $\Delta n = (\Delta\lambda/\lambda_o)n_a$, where λ_o is the reflective wavelength and $\Delta\lambda$ is the peak width of the reflection spectrum (see figure 3). The average refractive indices (n_a) were determined in the isotropic state with an Abbé refractometer. As n_a has almost the same value ($\sim 1\cdot 6$) for each sample, the study of the value of the ratio ($\Delta\lambda/\lambda_o$) is a good way to study the behaviour of the birefringence. The results are given in table 3.

An augmentation of the ratio $\Delta\lambda/\lambda$ is clearly observed when the chiral side-on tolane monomer **8 a** is used (samples 2, 3 and 4). The broadening of the reflection peak is observed before UV irradiation (sample 2), as well as after UV polymerization (sample 3). This behaviour clearly shows that the birefringence value of the reflective display has been improved using this new chiral side-on tolane acrylate.

Table 3. Influence of the chiral side-on tolane acrylate **8a** on the birefringence of polymer stabilized cholesteric texture displays.

Sample	wt % of chiral monomer (**8a**)	Reflective colour	λ_o/nm	$\Delta\lambda$/nm	$\Delta\lambda/\lambda_o$	Birefringence Δn
1	0	Blue	514	80	0·156	0·250
2	4[a]	Green	488	167	0·342	0·547
3	4[b]	Bluish green	519	157	0·303	0·485
4	10[b]	Peach	547	114	0·208	0·333

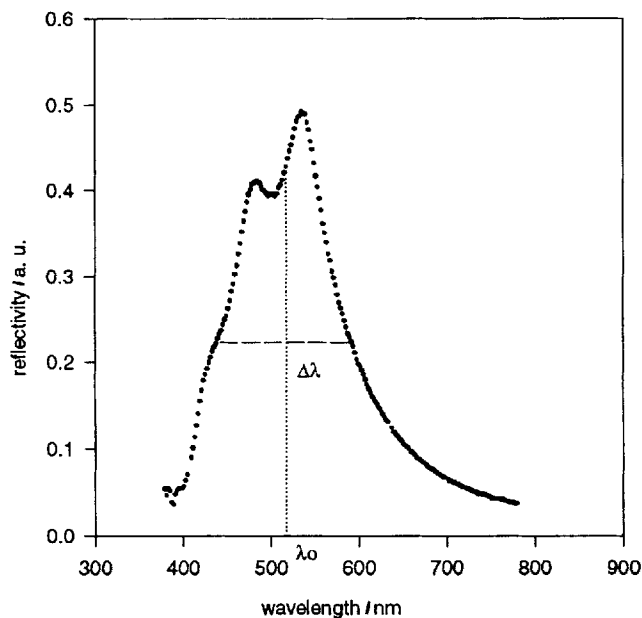[a] Before UV irradiation. [b] After UV irradiation.

Figure 3. Reflectivity versus wavelength for sample 3 (4 per cent of **8a**, after photopolymerization) in the planar state. λ_o: reflective wavelength. $\Delta\lambda$: peak width.

The evolution to higher reflective wavelengths, which reduces the chirality of the cholesteric mixture, is an indication of the helical twisting power and the opposite handiness of the chiral side-on tolane acrylate **8a**. An increase in the concentration of the chiral tolane network results in the decrease of the ratio $\Delta\lambda/\lambda$, and hence, the birefringence decreases. The birefringence value of the display containing 10 per cent of **8a** (sample 4) yields 0·333 which is still higher than in the absence of chiral tolane side-on monomer **8a** (sample 1).

5. Conclusions

New mesomorphic side-on tolane monomers and polymers have been synthesized and characterized. A smectic C mesophase has been observed in the monoacrylate material. Once polymerized, these side-on systems exhibit an enantiomeric nematogenic mesophase, following the usual tendency of the side-on polymeric systems.

Moreover, the use of the chiral tolane side-on material in reflective cholesteric displays shows clearly an improvement in the birefringence value. This material could be used to achieve a white reflective cholesteric display because it creates a wide spread of the reflective spectrum in the visible range.

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