**Liquid Crystals**
Publication details, including instructions for authors and subscription information:
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**To cite this Article** Shi, Hongqin and Chen, Shaw H.(1994) 'Novel glassy nematic and chiral nematic oligomers derived from 1,3,5-cyclohexanetricarboxylic and (1*R*,3S)-( )-camphoric acids', Liquid Crystals, 17: 3, 413 — 428
**To link to this Article: DOI:** 10.1080/02678299408036580
**URL:** http://dx.doi.org/10.1080/02678299408036580

LIQUID CRYSTALS, 1994, VOL. 17, NO. 3, 413–428

# Novel glassy nematic and chiral nematic oligomers derived from 1,3,5-cyclohexanetricarboxylic and (1*R*,3*S*)-( + )-camphoric acids

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(*Received 19 October 1993; accepted 10 February 1994*)

Novel nematic and chiral nematic liquid crystals capable of vitrification have been synthesized using 1,3,5-cyclohexanetricarboxylic and (1*R*,3*S*)-( + )-camphoric acids as the base structures to which cyanotolan, cyanobiphenyl, methoxybiphenylbenzoate nematogenic groups, (*S*)-( − )-1-phenylethylamine and (*S*)-( + )-1,3-butanediol chiral moieties are attached. Once the glassy state is induced by quenching or controlled cooling from the isotropic state, these liquid crystals showed no detectable tendency towards crystallization upon heating through the glass transition temperature. In all cases, the $\Delta C_p$ and $\Delta H_c$ values resulting from the DSC heating scans are comparable to those previously reported for polymer analogues and other low molar mass glassy liquid crystals. In the nematic series with varying spacer lengths, both $T_g$ and $T_c$ are consistently lower than the linear polymer counterparts, in contrast to the siloxane-based systems. It was also demonstrated that cholesteric mesomorphism can be induced following one of the three approaches: chiral nematic mixture, chiral nematic cyclic cooligomer, and pendant nematogenic groups attached to a chiral ring.

## 1. Introduction

Thermotropic liquid crystal polymers have been actively pursued in recent years for information storage and optical device applications due largely to mesophase stability that can be enhanced through vitrification, which is considered a privilege of polymeric materials. Several monographs [1–4] have been published on the fundamentals and potential applications of liquid crystal polymers. From a practical standpoint, the high viscosity value of polymeric materials in general has been recognized as a potential obstacle to applications where ease of processing into a large uniform area with a high degree of mesomorphic order is desired. Thus, ideal materials should possess low melt viscosity in addition to capabilities for mesophase formation and vitrification with glass transition temperature above the ambient.

To achieve this goal, interest in low molar mass glass-forming liquid crystals has been revived in the past few years with an inspiration from glassy liquid crystals first reported more than two decades ago [5]. A number of new materials have thus been synthesized with their chemical systems falling roughly into three categories. The first involves mesogenic units attached as pendant groups to benzene [6], cyclosiloxane [7]

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and cyclophosphazene [8–10] rings, the second includes mesogenic units as part of a macrocycle [11], and the third incorporates bulky and rigid structural elements in one-string or twin structures [12–15]. Although mesomorphism was consistently observed, it is important to point out that not all systems reported in the literature to date are capable of vitrification and that many are semicrystalline or tend to crystallize upon reheating through the glass transition temperature induced by prior quenching from the isotropic state. In fact, eutectic mixtures [13] were prepared to suppress tendencies towards crystallization.

In short, it is suspected that glassy liquid crystals represent a subtle balance between two seemingly opposing factors, one to discourage crystallization from occurring and the other to encourage liquid crystal mesomorphism. Nonetheless, except for some empirical rules proposed by Wedler *et al.* [14], there is little understanding of glassy liquid crystals from a chemical structure standpoint. Motivated in part by the curiosity as to the structural factors contributing to the realization of a glassy state in low molar mass liquid crystals and in part by the need for new materials to help advance laser and optical technologies, we have successfully synthesized and characterized a series of novel glassy nematics as well as chiral nematics based on cyclohexane and cyclopentane rings carrying pendant mesogenic and chiral moieties. Nematic systems based on cyanotolan, cyanobiphenyl, and methoxybiphenylbenzoate mesogenic groups as well as chiral nematic systems based on one of the nematogens plus (*S*)-( − )-1-phenylethylamine, (*S*)-( + )-1,3-butanediol, or (1*R*,3*S*)-( + )-camphoric acid are presented.

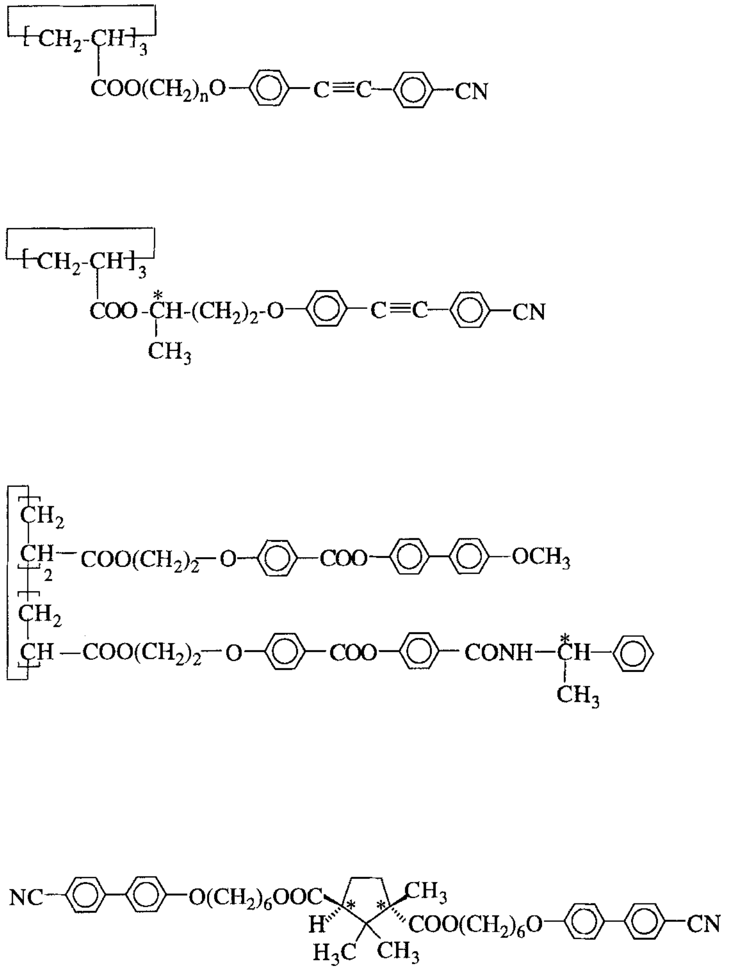
## 2. Experimental

### 2.1. *Materials*

4-Iodophenol (99 per cent), 3,4-dihydro-2-*H*-pyran (97 per cent), (trimethylsilyl)acetylene (98 per cent), copper(I) iodide (99·999 per cent), bis(triphenylphosphine)palladium (II) chloride (98 per cent), 4-bromobenzonitrile (99 per cent), *n*-butyllithium (2·5 M in hexanes), zinc chloride (98 per cent), oxalyl chloride (98 per cent), tetrakis(triphenylphosphine)palladium(0) (99 per cent), pyridinium *p*-toluenesulphonate (98 per cent), diethyl azodicarboxylate ( > 90 per cent) triphenylphosphine (99 per cent), 9-borabicyclo[3,3,1]nonane (0·5 M solution in hexanes or THF), 3-buten-1-ol (99 per cent), 4,4′-dihydroxyphenyl (97 per cent), dimethyl sulphate (99 per cent), 4-hydroxybenzoic acid (99 per cent), 4′-hydroxy-4-biphenylcarbonitrile (97 per cent), methyl chloroformate (99 per cent), 2-bromoethanol (95 per cent), 3-bromo-1-propanol (95 per cent), 6-bromo-1-hexanol (95 per cent), (*S*)-( + )-1,3-butanediol (98 per cent), (*S*)-( − )-1-phenylethylamine (98 per cent), (1*R*,3*S*)-( + )-camphoric acid (99 per cent), 1,3,5-cyclohexanetricarboxylic acid (99 per cent, a mixture of stereoisomers), and silica gel (40 $\mu$m flash chromatography packing), were all used as received from Aldrich Chemical Company. Solvent THF (100 per cent, J. T. Baker) was dried by refluxing over sodium spheres in the presence of benzophenone, and methylene chloride ( > 99·5 per cent, J. T. Baker) was dried by distillation over calcium hydride.

### 2.2. *Characterization techniques*

A Hitachi high performance liquid chromatography, HPLC, system comprising an L-2000 metering pump and an L-4200 UV–vis absorbance detector equipped with an LiChrosorb® column (RP-18, 5 $\mu$m) was employed to determine the number of components and purity of the products. Chemical structures of glassy nematics and chiral nematics were elucidated with the FTIR (Nicolet 20 SXC) and proton NMR (QE-300, GE) spectroscopic techniques. The chiral mole fractions in the chiral nematic systems were determined via an integration of appropriate proton NMR signals (typically 1 wt% in $CDCl_3$). Thermal transition temperatures were determined by differential scanning calorimetry, DSC (DuPont 910 interfaced with Thermal Analyst 2100 System) with mesophase textures identified under a polarizing optical microscope (Leitz Orthoplan-Pol) equipped with a hot stage (FP 80, Mettler). For the determination of selective reflection wavelength, a spectrophotometer (Perkin–Elmer Lambda 9) was employed to gather a UV–vis-NIR spectrum at room temperature on an optical element containing a chiral nematic material with a thickness on the order of 10 $\mu$m sandwiched between a pair of glass substrates (Corning 7059 near zero alkali baria alumina borosilicate glass with a refractive index of 1·53 at 589·3 nm). The element was first heated above the clearing temperature of the material followed by shearing to induce alignment and subsequently annealed at 95 per cent of its clearing temperature for 1 h.



**I**

**II**

**III**

**IV**

Figure 1. Chemical structures of glassy compounds **I** to **IV** synthesized and characterized for the present study; note that $n = 2, 3, 4$, or 6 in compound **I**.

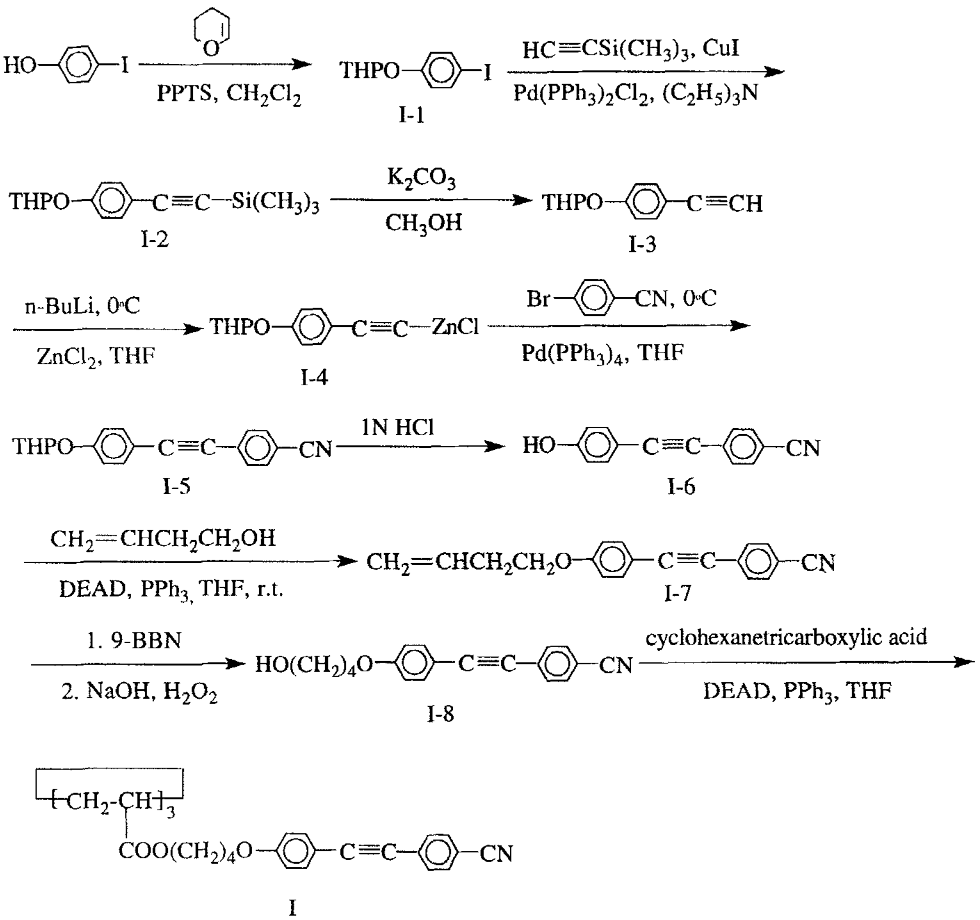
### 2.3. *Synthesis of glassy low molar mass materials*

Six glassy mesogenic compounds plus one glassy nonmesogenic compound depicted as **I** to **IV** in figure 1 were synthesized in accordance with synthetic routes as delineated in schemes I to IV with experimental procedures as described below.

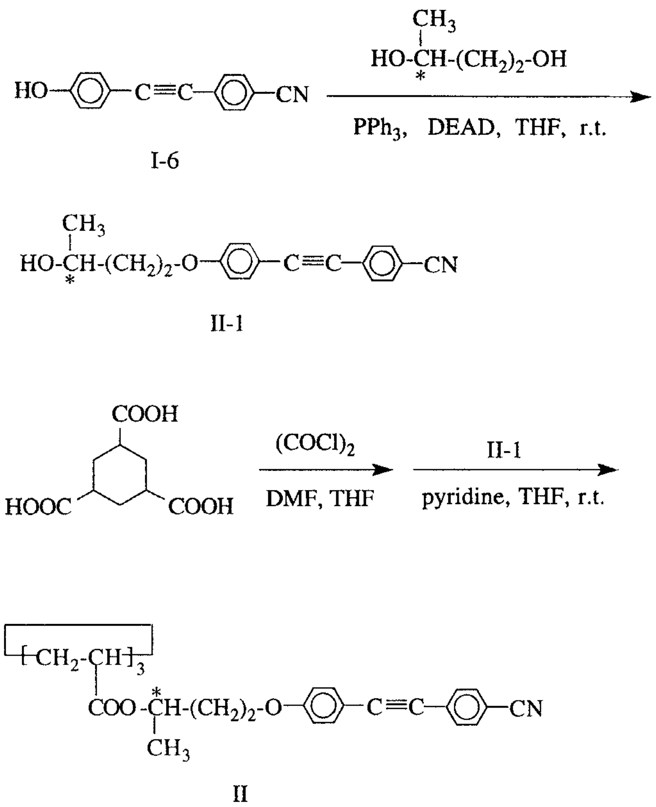
### 2.3.1. *Compound **I** with n = 4 as an example*

**I-1**: A solution of 4-iodophenol (74·4 g, 338 mmol) and 3,4-dihydro-2*H*-pyran (84·1 g, 1 mol) in 800 ml anhydrous methylene chloride containing pyridinium *p*-toluenesulphonate, PPTS, (17·5 g, 69·6 mmol) was stirred at room temperature for 5 h. Then the solution was diluted with ether and washed several times with half-saturated brine to remove the catalyst. Upon evaporation of the solvent, recrystallization from ethanol was accomplished to yield **I-1** (90 g, 85 per cent).

**I-2**: To a mixture of **I-1** (25 g, 82·2 mmol) and (trimethylsilyl)acetylene (12 g, 122 mmol) in 300 ml triethylamine were added bis(triphenylphosphine) palladium dichloride (1 g, 1·40 mmol) and copper(I) iodide (0·133 g, 0·70 mmol). The reaction mixture was stirred under nitrogen at room temperature for 3 h before the solvent was removed under reduced pressure. The residue was extracted with 500 ml petroleum



Scheme 1. Synthetic route for compound **I**.



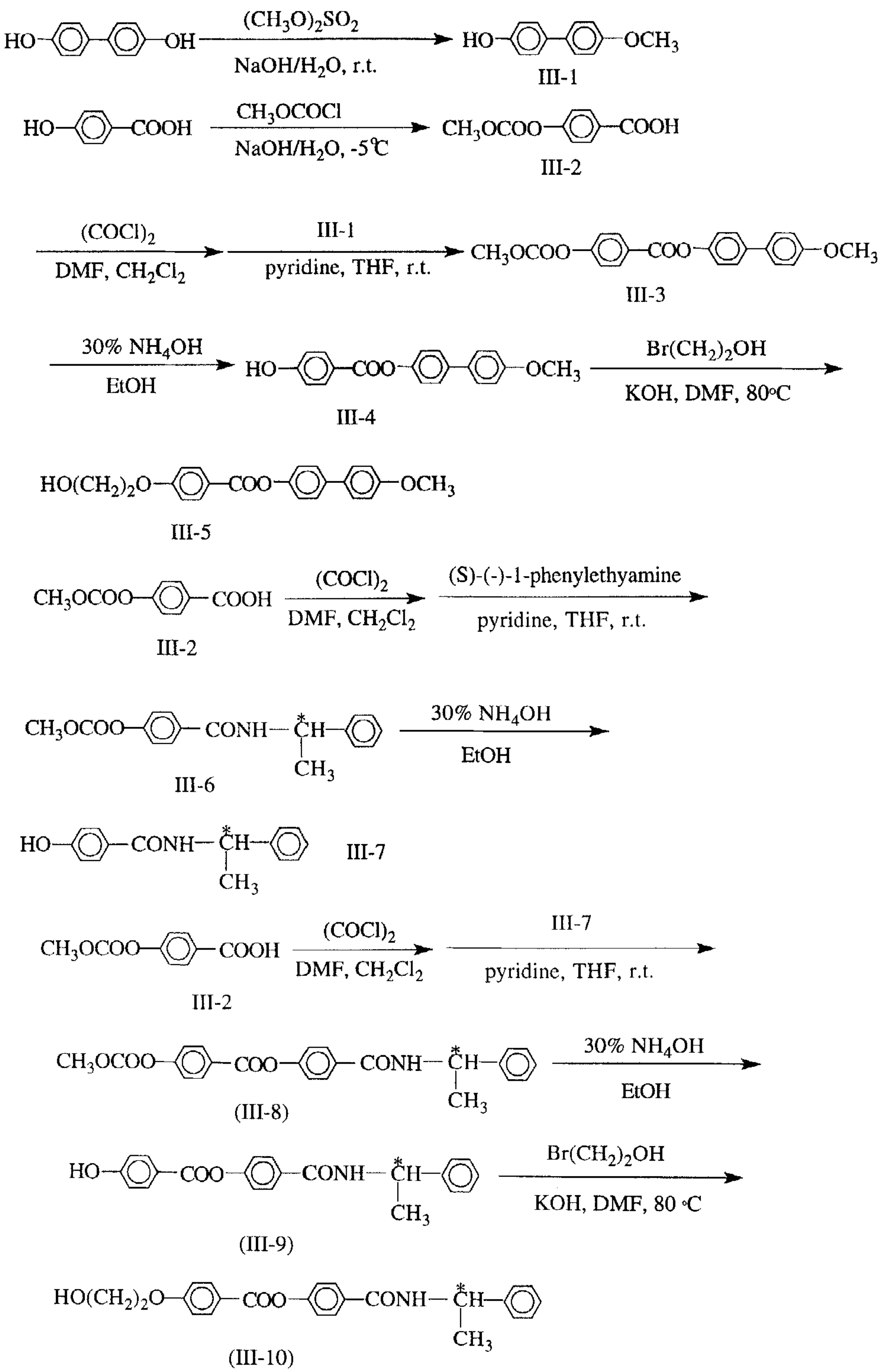
Scheme 2. Synthetic route for compound **II**.

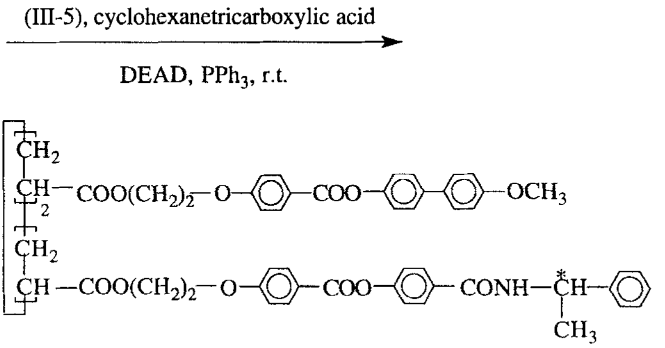
ether, and the solution was filtered, washed with water and then dried over anhydrous $MgSO_4$. Upon evaporating the solvent, the crude product was purified by flash chromatography on silica gel using 1 : 15 diethyl ether/petroleum ether as the eluent. The pale yellowish solid was recrystallized from ethanol to yield **I-2** (15 g, 66 per cent).

**I-3**: 5·0 g **I-2** (18·2 mmol) and anhydrous potassium carbonate (1·0 g, 7·23 mmol) were dissolved in 100 ml methanol and stirred for 2 h. The solvent was then evaporated off, and the residue was dissolved in 200 ml petroleum ether followed by washing with water and drying over anhydrous $MgSO_4$. Recrystallization from ethanol gave **I-3** (3·62 g, 98 per cent).

**I-4**: To a solution of **I-3** (3·4 g, 16·8 mmol) in 10 ml anhydrous THF at 0°C was added *n*-butyllithium (0·078 g, 16·8 mmol) in hexane (2 M). The solution was stirred for 5 min prior to adding anhydrous zinc chloride (2·29 g, 16·8 mmol) dissolved in anhydrous THF (20 ml). The mixture was stirred at room temperature for an additional 15 min.

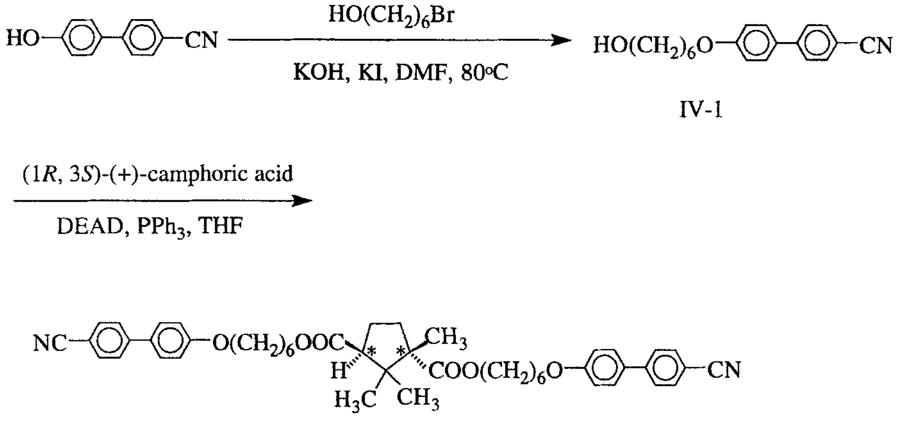
**I-5** and **I-6**: To the solution containing **I-4** cooled to 0°C, a solution of 4-bromobenzonitrile (3·07 g, 16·8 mmol) in anhydrous THF (20 ml) and that of tetrakis(triphenylphosphine) palladium(0) (0·5 g, 0·43 mmol) in anhydrous THF (20 ml), both at 0°C, were added sequentially to obtain **I-5**, which was not isolated. Instead, 30 ml 1 N HCl solution and 10 g ammonium chloride were added to form two clearly separated layers, which were stirred at room temperature for another 3 h to deprotect the hydroxyl group. The two layers were separated upon shaking with 50 ml


HO–Ph–Ph–OH
(CH3O)2SO2
NaOH/H2O, r.t.
HO–Ph–Ph–OCH3
III-1
HO–Ph–COOH
CH3OCOCl
NaOH/H2O, -5℃
CH3OCOO–Ph–COOH
III-2
(COCl)2
DMF, CH2Cl2
III-1
pyridine, THF, r.t.
CH3OCOO–Ph–COO–Ph–Ph–OCH3
III-3
30% NH4OH
EtOH
HO–Ph–COO–Ph–Ph–OCH3
III-4
Br(CH2)2OH
KOH, DMF, 80°C
HO(CH2)2O–Ph–COO–Ph–Ph–OCH3
III-5
CH3OCOO–Ph–COOH
III-2
(COCl)2
DMF, CH2Cl2
(S)-(-)-1-phenylethyamine
pyridine, THF, r.t.
CH3OCOO–Ph–CONH–*CH(CH3)–Ph
III-6
30% NH4OH
EtOH
HO–Ph–CONH–*CH(CH3)–Ph
III-7
CH3OCOO–Ph–COOH
III-2
(COCl)2
DMF, CH2Cl2
III-7
pyridine, THF, r.t.
CH3OCOO–Ph–COO–Ph–CONH–*CH(CH3)–Ph
(III-8)
30% NH4OH
EtOH
HO–Ph–COO–Ph–CONH–*CH(CH3)–Ph
(III-9)
Br(CH2)2OH
KOH, DMF, 80 °C
HO(CH2)2O–Ph–COO–Ph–CONH–*CH(CH3)–Ph
(III-10)



III

Scheme 3. Synthetic route for compound **III**.



IV-1

IV

Scheme 4. Synthetic route for compound **IV**.

petroleum ether, and the aqueous portion was extracted with petroleum ether. The organic portions were combined, washed with saturated aqueous solution of sodium bicarbonate, and dried over anhydrous $MgSO_4$. After the solvent was evaporated off under reduced pressure, the brown residue was purified by flash chromatography on silica gel with methylene chloride as the eluent. The yellowish product was recrystallized from chloroform to give **I-6** (2·35 g, 64 per cent).

**I-7**: To a stirred solution containing **I-6** (3·0 g, 13·68 mmol), triphenylphosphine (4·31 g, 16·41 mmol) and 3-buten-1-ol (1·42 ml, 16·4 mmol) in 30 ml anhydrous THF was added dropwise a 10 ml anhydrous THF solution of diethyl azodicarboxylate (2·01 ml, 16·4 mmol) under nitrogen atmosphere. The reaction mixture was stirred for 3 h before the solvent was evaporated off. The solid residue was purified by flash chromatography on silica gel with 10 : 1 methylene chloride/hexane as the solvent and the eluent. Further purification was accomplished via recrystallization from methanol spiked with methylene chloride to yield **I-7** (3·39 g, 91 per cent).

**I-8**: To a stirred solution of **I-7** (2·42 g, 8·86 mmol) in 10 ml anhydrous THF was added slowly 0·5 M solution of 9-borabicyclo[3,3,1]nonane (i.e. 9-BBN) in THF (21·27 ml, 10·64 mmol). The reaction mixture was stirred for 4 h at room temperature, and then 5 ml ethanol, 2 ml 6 M sodium hydroxide solution, and 4 ml 30 per cent hydrogen peroxide solution were added sequentially. The reaction was allowed to proceed for another hour before dilution with 100 ml methylene chloride. The solution was washed with water and then dried over anhydrous $MgSO_4$. Upon evaporating off the solvent, the solid residue was purified by flash chromatography on silica gel with methylene chloride as the eluent. Further purification was accomplished via recrystallization from ethanol to yield **I-8** (2·36 g, 92 per cent).

**I**: To a stirred solution containing **I-8** (0·606 g, 2·08 mmol), triphenylphosphine (0·55 g, 2·08 mmol) and 1,3,5-cyclohexanetricarboxylic acid (0·0136 g, 0·631 mmol) in 15 ml anhydrous THF was added dropwise a 5 ml anhydrous THF solution of diethyl azodicarboxylate (0·255 ml, 2·08 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 3 h before the solvent was evaporated off. The solid residue was purified by flash chromatography on silica gel with 40 : 1 methylene chloride/acetone as the solvent and the eluent. Further purification was accomplished via recrystallization from methanol spiked with methylene chloride to yield **I** (0·62 g, 95 per cent).

### 2.3.2. *Compound II*

**II-1**: To a stirred solution containing **I-6** (0·86 g, 3·93 mmol), triphenylphosphine (1·24 g, 4·71 mmol), and (*S*)-( + )-1,3-butanediol (0·42 g, 4·71 mmol) in 10 ml anhydrous THF was added dropwise a 5 ml anhydrous solution of diethyl azodicarboxylate (0·41 ml, 4·71 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 3 h before the solvent was evaporated off. The solid residue was purified by flash chromatography on silica gel with 20 : 1 methylene chloride/acetone as the solvent and the eluent to obtain **II-1** (0·8 g, 70 per cent).

**II**: To a solution containing 1,3,5-cyclohexanetricarboxylic acid (0·165 g, 0·76 mmol) and a few drops of *N*,*N*-dimethyl formamide in 10 ml anhydrous THF was added dropwise 2 M oxalyl chloride solution in anhydrous THF (1·37 ml) at room temperature. After stirring the reaction mixture for 1 h, the solvent was evaporated off, and excess oxalyl chloride was removed under vacuum. The resultant acid chloride was dissolved in 10 ml anhydrous THF, and the solution was added to a mixture of **II-1** (0·80 g, 2·75 mmol) and pyridine (0·22 ml, 2·75 mmol) in 10 ml anhydrous THF. The reaction mixture was stirred for 12 h before the solvent was evaporated off. The solid residue was purified by flash chromatography on silica gel with methylene chloride as the solvent and the eluent. Further purification was accomplished via precipitation from methanol to obtain **II** (0·71 g, 90 per cent).

### 2.3.3. *Compound III*

**III-1**: 4,4′-Dihydroxybiphenol (40·0 g, 0·215 mol) was dissolved in a solution containing sodium hydroxide (17·2 g, 0·43 mmol) in 160 ml water, to which dimethyl sulphate (27 g, 0·214 mol) was added. The solution was stirred at room temperature for 4 h. The precipitate was isolated by filtration and subsequently washed with 10 per cent aqueous sodium hydroxide solution. It was then dissolved in boiling water, and traces of insoluble 4,4′-dimethoxybiphenyl were separated by hot filtration. The crude product was precipitated upon addition of dilute hydrochloric acid, which was filtered off, washed with water, and recrystallized from ethanol to yield **III-1** (30 g, 70 per cent).

**III-2**: To a solution of sodium hydroxide (30·0 g, 0·75 mol) in 800 ml water was added 4-hydroxybenzoic acid (35·8 g, 0·259 mol). The solution was then cooled to − 10°C, to which methyl chloroformate (40·0 g, 0·423 mol) was slowly added for the temperature not to exceed − 5°C. The resulting slurry was stirred for 4 h before acidification to pH5 with concentrated hydrochloric acid. The crude product was isolated by filtration, and recrystallization from ethanol yielded **III-2** (35·0 g, 69 per cent).

**III-3**: To a solution containing **III-2** (10·0 g, 0·05 mol) and a few drops of *N,N*-dimethyl formamide in 200 ml methylene chloride was added dropwise oxalyl chloride (6·65 ml, 0·06 mol) at room temperature. The reaction mixture was stirred for 1 h. The solvent was then evaporated off, and excess oxalyl chloride was removed under vacuum. The resultant acid chloride in 100 ml anhydrous THF was added to a 100 ml anhydrous THF solution containing **III-1** (12·3 g, 0·06 mol) and pyridine (4·96 ml, 0·06 mol) at room temperature. The mixture was stirred for 12 h before dilution with 500 ml chloroform. The solution was washed with water and then dried over anhydrous sodium sulphate. Upon removing the solvent, the solid product was recrystallized from ethanol to yield **III-3** (11·5 g, 61 per cent).

**III-4**: To a solution of **III-3** (10·0 g, 0·026 mol) in 200 ml 95 per cent ethanol was added 30 per cent ammonium hydroxide (30 ml) at room temperature. The reaction mixture was stirred for 1 h and then acidified to pH5 with concentrated hydrochloric acid. The solution was diluted with 200 ml chloroform, and the organic portion was washed with water before drying over anhydrous sodium sulphate. The solvent was removed to yield **III-4** (7·6 g, 90 per cent).

**III-5**: To a solution at 80°C containing **III-4** (3·0 g, 9·38 mmol) plus potassium hydroxide (0·63 g, 11·3 mmol) in 10 ml *N,N*-dimethyl formamide was added dropwise 1-bromoethanol (0·94 ml, 11·3 mmol). The reaction mixture was allowed to stir at 80°C for 24 h before dilution with 100 ml methylene chloride. Then the solution was washed with water and dried over anhydrous sodium sulphate. Upon removing the solvent, the solid was recrystallized from ethanol to yield **III-5** (1·6 g, 46 per cent).

**III-6**: To a solution containing **III-2** (3·0 g, 15·3 mmol) and a few drops of *N,N*-dimethyl formamide in 30 ml methylene chloride was added dropwise oxalyl chloride (2·53 g, 20 mmol) at room temperature. After stirring for 1 h, the solvent was evaporated off, and excess oxalyl chloride was removed under vacuum. The resultant acid chloride was dissolved in 20 ml anhydrous THF, which was mixed with 20 ml anhydrous THF solution containing (*S*)-( − )-1-phenylethylamine (2·22 g, 18 mmol) and pyridine (1·57 g, 20 mmol) at room temperature. The reaction mixture was stirred for 12 h before dilution with 200 ml chloroform. The solution was washed with water and then dried over anhydrous sodium sulphate. Upon removing the solvent, the solid was recrystallized from ethanol to yield **III-6** (2·69 g, 73 per cent).

**III-7**: To a solution **III-6** (2·69 g, 9·0 mmol) in 150 ml 95 per cent ethanol was added 30 per cent ammonium hydroxide (30 ml) at room temperature. The reaction mixture was stirred for 1 h before being acidified to pH5 with concentrated hydrochloric acid. The solution was diluted with 150 ml chloroform, and the organic portion was washed with water before drying over anhydrous sodium sulphate. The solvent was then removed, yielding **III-7** (1·95 g, 90 per cent).

**III-8**: To a solution containing **III-2** (1·50 g, 7·65 mmol) and a few drops of *N,N*-dimethyl formamide in 10 ml methylene chloride was added dropwise oxalyl chloride (0·8 ml, 9·18 mmol) at room temperature. After stirring for 1 h, the solvent was evaporated off, and excess oxalyl chloride was removed under vacuum. The resultant acid chloride was dissolved in 10 ml anhydrous THF, which was mixed with 10 ml anhydrous THF solution containing **III-7** (2·20 g, 9·18 mmol) and pyridine (0·74 ml, 9·18 mmol). The reaction mixture was allowed to stir for 12 h before dilution with 100 ml chloroform. The solution was then washed with water and dried over anhydrous sodium sulphate. Upon removing the solvent, the solid was recrystallized from ethanol to yield **III-8** (2·0 g, 63 per cent).

**III-9**: To a solution of **III-8** (2·13 g, 5·03 mmol) in 100 ml 95 per cent ethanol was added 20 ml 30 per cent ammonium hydroxide at room temperature. The reaction mixture was stirred for 1 h before acidification to pH5 with concentrated hydrochloric acid. The solution was then diluted with 100 ml chloroform and dried over anhydrous sodium sulphate. The solvent was removed to yield **III-9** (1·73 g, 95 per cent).

**III-10**: To a solution at 80°C containing **III-9** (1·73 g, 4·78 mmol) plus potassium hydroxide (0·32 g, 5·73 mmol) in 10 ml *N*,*N*-dimethyl formamide was added dropwise 1-bromoethanol (0·48 ml, 5·73 mmol). The reaction mixture was stirred for 24 h at this temperature before dilution with 100 ml methylene chloride followed by drying over anhydrous sodium sulphate. Upon removal of the solvent, the solid was recrystallized from ethanol to yield **III-10** (1·0 g, 52 per cent).

**III**: To a stirred solution containing **III-5** (0·50 g, 1·37 mmol), **III-10** (0·279 g, 0·687 mmol), triphenylphosphine (0·54 g, 2·06 mmol) and 1,3,5-cyclohexanetricarboxylic acid (0·124 g, 0·573 mmol) in 15 ml anhydrous THF was added dropwise a 5 ml anhydrous THF solution of diethyl azodicarboxylate (0·253 ml, 2·06 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 3 h before the solvent was evaporated off. The solid residue was purified by flash chromatography on silica gel with 40 : 1 methylene chloride/acetone as the solvent and the eluent. Further purification was accomplished via precipitation from methanol to yield **III** (0·66 g, 90 per cent).

### 2.3.4. *Compound IV*

**IV-1**: To a solution at 80°C containing 4-hydroxy-4′-cyanobiphenyl (5·0 g, 25·6 mmol), potassium hydroxide (1·43 g, 25·6 mmol), plus a few crystals of potassium iodide in 10 ml *N*,*N*-dimethyl formamide was added dropwise 6-bromo-1-hexanol (3·35 ml, 25·6 mmol). The reaction mixture was stirred for 24 h at this temperature before dilution with 500 ml methylene chloride followed by drying over anhydrous sodium sulphate. Upon removal of the solvent, the solid was recrystallized from ethanol to yield **IV-1** (4·3 g, 57 per cent).

**IV**: To a stirred solution containing **IV-1** (0·74 g, 2·51 mmol), triphenylphosphine (0·658 g, 2·51 mmol) and (1*R*,3*S*)-( + )-camphoric acid (0·124 g, 0·573 mmol) in 15 ml anhydrous THF was added dropwise a 5 ml anhydrous THF solution of diethyl azodicarboxylate (0·31 ml, 2·51 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 3 h before the solvent was evaporated off. The solid residue was purified by flash chromatography on silica gel with 40 : 1 methylene chloride/acetone as the solvent and the eluent. Further purification was accomplished via precipitation from methanol to yield **IV** (0·76 g, 92 per cent).

## 3. Results and discussion

The structures of four representative nematic and chiral nematic systems are shown in figure 1. Note that compounds **I** to **IV** all carry single components according to reverse phase HPLC analysis. The FTIR spectroscopy was employed to verify the presence of $C\equiv C$ and $C\equiv N$ in terms of stretching modes at 2171 cm$^{-1}$ and 2214 cm$^{-1}$, respectively, as illustrated in figure 2 for compound **I-4**. The chemical structures were further elucidated with elemental analysis (performed by Oneida Research Services, Inc. in Whitesboro, New York) and proton NMR spectroscopy with relevant characterization data compiled in tables 1 and 2.

Let us look into the thermal behaviour of nematic compounds **I-*n***, where spacer length $n=2$, 3, 4, or 6. The threaded texture characteristic of the nematic mesomorphism was evident under hot-stage polarizing optical microscopy. As illustrated in figure 3 for compound **I-4**, the DSC thermograms reveal glass transition in both heating and cooling scans at ± 20°C min$^{-1}$, respectively, with a nitrogen purge of 50 ml min$^{-1}$. Note that there is no detectable tendency for **I-4** to crystallize upon heating through the glass transition temperature, which was induced via thermal quenching or controlled cooling. The DSC thermograms collected in figure 4 also indicate its thermal stability up to 160°C.

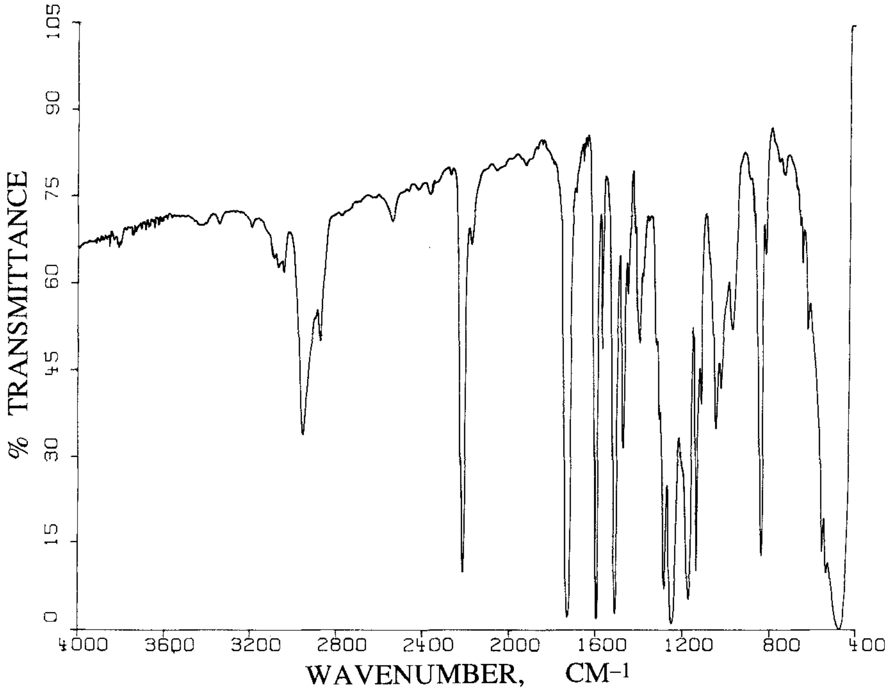


Figure 2. FTIR spectrum of a film prepared from neat compound **I** with a spacer length of 4.

Table 1. Elemental analysis of compounds **I** to **IV**.

| | Calculated(observed)/per cent | | |
|---|---|---|---|
| Compound | C | H | N |
| **I-2** | 75·70 (75·30) | 4·73 (4·67) | 4·41 (4·32) |
| **I-3** | 76·12 (74·76) | 5·14 (5·29) | 4·23 (4·23) |
| **I-4** | 76·50 (76·25) | 5·51 (5·72) | 4·06 (4·07) |
| **I-6** | 77·19 (76·82) | 6·17 (6·36) | 3·75 (3·74) |

| Compound | C | H | N |
|---|---|---|---|
| **II** | 76·50 (76·23) | 5·51 (5·68) | 4·06 (4·04) |
| **III** | 71·35 (71·16) | 5·33 (5·36) | 1·08 (1·13) |
| **IV** | 76·39 (76·06) | 7·16 (6·82) | 3·71 (4·14) |

Table 2. Proton NMR spectral data of compounds **I** to **IV**.

| **I-2**, per repeat unit | **I-3**, per repeat unit | **I-4**, per repeat unit | **I-6**, per repeat unit |
|---|---|---|---|
| 1·57–2·30 [m, 3 H, $-CH_2CH-$ on cyclohexane ring] | 1·50–2·45 [m, 5 H, $-CH_2CH-$ on cyclohexane ring plus $\mathrm{-CO_2CH_2}CH_2\mathrm{CH_2O-}$] | 1·52–2·43 [m, 7 H, $-CH_2CH-$ on cyclohexane ring plus $\mathrm{-CO_2CH_2(}CH_2\mathrm{)_2O-}$] | 1·50–2·45 [m, 11 H, $-CH_2CH-$ on cyclohexane ring plus $\mathrm{-CO_2CH_2(}CH_2\mathrm{)_4CH_2O-}$] |
| 4·28 [t, 2 H, $-CH_2\mathrm{O-}$] | 4·07 [t, 2 H, $-CH_2\mathrm{O-}$] | 4·01 [t, 2 H, $-CH_2\mathrm{O-}$] | 3·98 [t, 2 H, $-CH_2\mathrm{O-}$] |
| 4·48 [t, 2 H, $\mathrm{-CO_2}CH_2-$] | 4·30 [t, 2 H, $\mathrm{-CO_2}CH_2-$] | 4·20 [t, 2 H, $\mathrm{-CO_2}CH_2-$] | 4·11 [t, 2 H, $\mathrm{-CO_2}CH_2-$] |
| 6·87–7·63 [m, 8 H, arom.$^1$Hs] | 6·87–7·63 [m, 8 H, arom.$^1$Hs] | 6·88–7·63 [m, 8 H, arom.$^1$Hs] | 6·87–7·64 [m, 8 H, arom.$^1$Hs] |

| **II**, per repeat unit | **III**, entire molecule | **IV**, entire molecule |
|---|---|---|
| 1·28 [m, 3 H, $\mathrm{-C^*H(}CH_3\mathrm{)-}$] | 1·57–2·47 [m, 9 H, $-CH_2CH-$ 3 sets on cyclohexane ring] | 0·84 [s, 3 H, $-CH_3$] |
| 1·57–2·30 [m, 3 H, $-CH_2CH-$ on cyclohexane ring] | 4·29 [t, 6 H, $-CH_2\mathrm{O-}$, 3 sets] | 1·05 [s, 3 H, $-CH_3$] |
| 2·07 [m, 2 H, $\mathrm{-CH(CH)_3}CH_2\mathrm{CH_2-}$] | 4·42 [t, 6 H, $\mathrm{-CO_2}CH_2-$, 3 sets] | 1·31 [s, 3 H, $-CH_3$] |
| 4·02 [t, 2 H, $-CH_2\mathrm{O-}$] | 5·37 [m, 1 H, $\mathrm{-NHC}H\mathrm{(CH_3)Ph}$] | 1·52–1·86 [m, 20 H, $\mathrm{-CO_2CH_2(}CH_2\mathrm{)_4}$ $\mathrm{-CH_2O-}$, 2 sets, plus $\mathrm{-(CH_2)_2-}$ on ring] |
| 5·17 [m, 1 H, $\mathrm{-COC}H\mathrm{(CH_3)CH_2-}$] | 6·38 [d, 1 H, $\mathrm{-N}H-$] | 2·81 [t, 1 H, $\mathrm{-C}H\mathrm{(CO_2)-}$ on ring] |
| 6·82–7·63 [m, 8 arom.$^1$Hs] | 7·00–8·20 [m, 37 arom.$^1$Hs] | 4·02 [t, 4 H, $-CH_2\mathrm{O-}$, 2 sets]<br>4·09 [t, 4 H, $\mathrm{-CO_2}CH_2-$]<br>6·98–7·74 [m, 16 arom.$^1$Hs] |

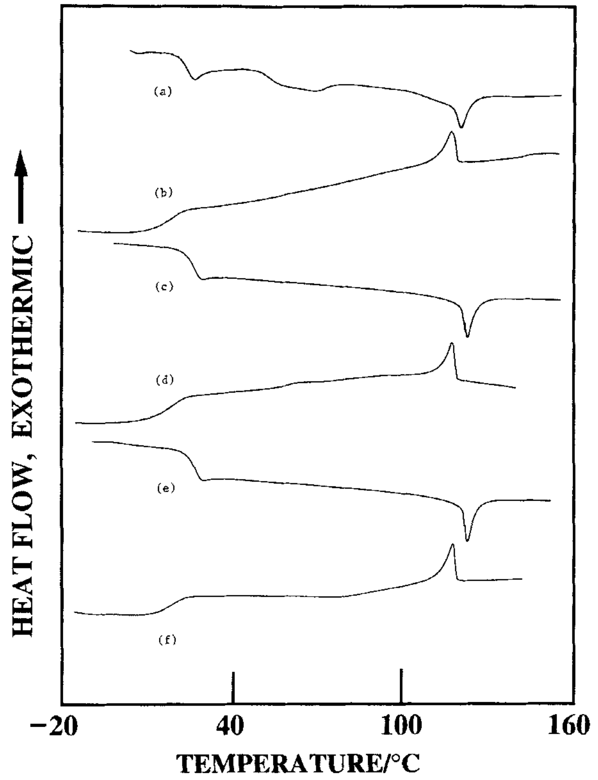


Figure 3. DSC thermograms at heating and cooling rates of 20°C min$^{-1}$ for compound **I** with a spacer length of 4: (*a*) first heating, (*b*) first cooling, (*c*) second heating, (*d*) second cooling, (*e*) third heating, and (*f*) third cooling.

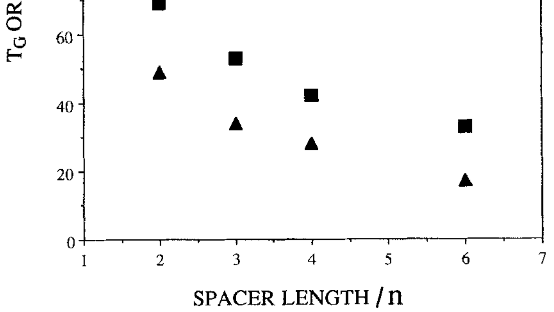


Figure 4. Thermal transition temperature determined with DSC (second heating scan) for nematic compound **I** with a spacer length of 4: $T_g$ and $T_c$ represented by solid and open triangles respectively; for nematic linear polymer analogues reported in [16]: $T_g$ and $T_c$ represented by solid and open squares, respectively.

Table 3. Thermal properties of glassy nematic **I** and nonmesogenic chiral **II**†.

| Compound | $T_g$/°C | $\Delta C_p$/W g$^{-1}$ | $T_c$/°C | $\Delta H_c$/J g$^{-1}$ |
|---|---|---|---|---|
| **I-2** | 49 | 0·19 | 73 | 0·88 |
| **I-3** | 34 | 0·12 | 126 | 3·18 |
| **I-4** | 28 | 0·18 | 124 | 3·33 |
| **I-6** | 17 | 0·17 | 114 | 4·53 |
| **II** | 33 | 0·19 | ‡ | ‡ |

† All thermal transition data were taken from the second DSC heating scales at 20°C min$^{-1}$ with a nitrogen purge of 50 ml min$^{-1}$.

‡ Compound **II** is a nonmesogenic, glassy material.

Table 4. Thermotropic and optical properties of glassy chiral nematic systems†.

| System | Chiral mol fraction | $T_g$/°C | $\Delta C_p$/W g$^{-1}$ | $T_c$/°C | $\Delta H_c$/J g$^{-1}$ | $\lambda_R$/nm | ΔO.D.‡ |
|---|---|---|---|---|---|---|---|
| **I-4/II** | 0·62 | 36 | 0·19 | 85 | 1·73 | 1355 | 0·29 |
| **III** | 0·33 | 69 | 0·12 | 137 | 0·46 | 425 | 0·20 |
| **IV** | 0·50§ | −5 | 0·16 | 42 | 2·86 | 1716 | 0·14 |

† All thermal transition data were taken from the second DSC heating scans at 20°C min$^{-1}$ with a nitrogen purge of 50 ml min$^{-1}$.

‡ ΔO.D. denotes optical density unit of the selective wavelength reflection band; perfect alignment will give a selective wavelength reflection band with 0·301 optical density unit.

§ Two asymmetric carbon centres residing on the ring for two pendant nematogens.

Included in table 3 are thermal characterization data for nematic series **I** and nonmesogenic chiral glass **II**. Note that the observed $\Delta C_p$ and $\Delta H_c$ values are typical of the glass and nematic–isotropic transitions of previously reported glassy liquid crystal [12–14] and of nematic acrylate homopolymers [16] containing pendant cyanotolan nematogen that have been investigated. Contrary to the siloxane series containing pendant cyanobiphenyl and cyanophenylbenzoate groups [17] with the number of repeat units no greater than 12, lower $T_g$ and $T_c$ were observed in cycloacrylate oligomers than linear polymer analogues, as demonstrated in figure 4. It is also noticed that while monotonic decrease in $T_g$ with an increasing spacer length is evident in both cyclic and linear series, the odd–even effect of spacer length on $T_c$ observed in the linear series is absent in the cyclic series. According to a recent report [7], there is no consistent trend in $T_c$ at increasing spacer length in liquid crystalline cyclosiloxane series.

Several approaches to the induction of cholesteric mesomorphism were tested. First, chiral nonmesogenic **II** was mixed with nematic **I-4** designated hereafter as **I-4/II**; second, both nematogenic and chiral pendant groups were attached to a single cyclohexane ring, i.e. **III**; and third, nematogenic pendant groups were attached to a chiral cyclopentane ring, i.e. **IV**. Chiral nematic systems are known to possess a unique optical property, i.e. selective wavelength reflection, causing an incident light beam to be circularly polarized and its intensity to be reduced by 50 per cent [18]. The DSC data (all based on the second heating scans at 20°C min$^{-1}$ with a nitrogen purge of 50 ml min$^{-1}$), chiral mole fraction, $x$, selective reflection wavelength, $\lambda_R$, and optical density of the selective reflection band, ΔO.D., are summarized in table 4. The following conclusions can be reached: (i) all three approaches lead to cholesteric mesomorphism as identified by hot-stage polarizing optical microscopy and by the selective wavelength reflection property, (ii) both **I-4/II** and **III** undergo glass transition above room temperature, whereas **IV** shows a $T_g$ below 0°C which is believed to be responsible for the low optical density of the selective wavelength reflection band, (iii) all three chiral nematic systems exhibit no tendency to crystallize upon reheating according to the DSC analysis, (iv) **III** appears to be more strongly twisting than **IV** and **I-4/II**, and (v) both $\Delta C_p$ and $\Delta H_c$ values are close to those observed for chiral nematic copolymers reported earlier [16].

## 4. Summary

Novel glassy nematic and chiral nematic liquid crystals with nematogenic and chiral pendant groups attached to cyclohexane and cyclopentane rings were synthesized and characterized in terms of elemental analysis, FTIR, proton NMR, and UV–vis-NIR spectroscopies, polarizing optical microscopy, and DSC. Key observations emerging from the present study are recapitulated below:

(i) All four series of compounds were found to be capable of vitrification upon quenching or controlled cooling from the clear temperature with no detectable tendency towards crystallization upon reheating across the glass transition temperature.

(ii) The observed $\Delta C_p$ and $\Delta H_c$ values turned out to be comparable to those previously reported for glassy low molar mass liquid crystals and linear polymer analogues; however, the nematic series containing pendant cyanotolan groups exhibited $T_g$ and $T_c$ both lower than the linear polymer counterparts, which is opposite to the siloxane-based liquid crystals.

(iii) Three different approaches to the induction of glassy cholesteric mesomorphism were demonstrated: chiral nematic mixture, chiral nematic cyclic cooligomer, and pendant nematogenic groups attached to a chiral ring. It appears that chiral nematic cyclic cooligomer is superior in terms of high glass transition temperature and strong helical twisting for selective wavelength reflection to occur in the visible region.

We acknowledge helpful discussions with S. D. Jacobs and technical assistance of K. L. Marshall of the Laboratory for Laser Energetics, University of Rochester. We also thank Professor A. S. Kende of the Chemistry Department, University of Rochester, for assistance with organic synthesis. We would like to express our gratitude to Kaiser Electronics for financial support of this work. Additional funding for our liquid crystal polymer program was provided by the U. S. Department of Energy, Division of Inertial Fusion under Agreement No. DE-FC03-92SF19460 with the Laboratory for Laser Energetics at the University of Rochester.

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