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Synthesis and characterization of symmetrical banana shaped liquid crystalline polyethers

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ABSTRACT

A series of banana shaped allyl terminated liquid crystalline bis{[4'(10-undecenoyloxy)-1,1'biphenyl-4carboxylate]s varied with H, COOCH₃, Cl and NO₂ substituents in the central phenyl ring were synthesized and characterized by FT-IR, ¹H NMR and ¹³C NMR spectroscopy. Effect of substituents on the mesomorphic property was examined by polarized optical microscopy (POM) and exhibited B₁ and nematic mesophases. Differential scanning calorimetry (DSC) measurements confirmed the LC property. Allyl group in the terminal position was epoxidized and polymerized to get banana shaped liquid crystalline ladder polyethers by ring opening polymerization and characterized spectroscopically. POM investigations displayed the development of enantiotropic grainy textures for polyethers and confirmed by DSC. Thermogravimetric analysis revealed that they were decomposed at high temperatures with good char yield.

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1. Introduction

Thermotropic liquid crystals are formed by calamitic or discotic liquid crystals, wherein both exhibit nematic phase, calamitic mesogen constitute smectic (laminar) while discotic imprint columnar phase [1–6]. One of the most exiting developments in liquid crystal research in the past few years was the discovery of ferroelectricity and antiferroelectricity in liquid crystal with a non-chiral banana shaped molecular structure by Noiri et al. [7-10]. The polar order of bent molecule in smectic layer can induce chirality of smectic layer, although the individual molecule is achiral; it seems that the bent or banana shaped liquid crystal induce new sub-field of liquid crystals. Such new materials, consisting of achiral molecule, can be packed in smectic chiral layer by different ways which in turn produces a diversified mesophases, namely B mesophases [11–14]. They are designated as B_1-B_7 , wherein some of them exhibit unusual physical properties [15-17], like B₂, B₅ and B₇ phases render electro-optical switching property. The high-temperature smectic B₁ phase formed at lower chain homolog whereas switchable B₂ phase attributed to longer-chained homolog [18–19]. The low-temperature phases of the same compounds are designated as B_3 or B_4 .

Recently, several low molecular mass bent-core liquid crystals have been synthesized and characterized [20]. They possess macroscopic polar order with variety of useful properties, such as piezo, pyroelectricity and second-order nonlinear optical activity. Especially ferroelectric (FE) and antiferroelectric (AF) liquid crystalline materials are of interest, because they can be rapidly switched between different states by external electrical field [21– 22]. Most of the bent-shaped mesogens are based on 1,3-phenylene unit in the central core. The liquid crystalline polymers (LCPs) combine the typical features of polymers and their application as organic switching in external fields [23]. The first report on bentcore main chain liquid crystalline polymers has been appeared recently [24]. It was found that lateral substitution in the core and in outer rings influences the formation and different type of mesophases. Structure–property relationships on banana-shaped mesogens have also recently been summarized [25]. Number of banana-shaped liquid crystals reported based on five-ring symmetrical [26] and unsymmetrical [27] derived from resorcinol.

The structural modification of bent-core molecules achieved by introducing various lateral substituents such as H, COOCH₃, Cl, and NO₂ group into the central 1,3-phenylene ring at 2 and 4 positions would furnish different materials that in turn may help to empathize the relation between molecular structure and thermal behavior. Herein, we report the influence of chemical variations on central ring and connecting group of terminal chain with ester link containing bent-core mesogenic molecules. The linking group at the terminal chain to mesogen implies a major role in the formation of mesophases and transition temperatures. The terminal allyl group was epoxidized to get banana shaped liquid crystalline monomers succeeded ladder type polyethers by ring opening polymerization and characterized.





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2. Experimental

2.1. Materials

Benzene, methanol, ethanol, dichloromethane and acetone were purified by the reported procedure [28,29]. HBr 47% (SRL), 1,6-hexanediol (Merck), potassium hydroxide, sodium hydroxide, potassium carbonate, hydrochloric acid (Merck, Mumbai), 4-hydroxybenzoic acid (Spectrochem, India), BF₃-etharate (SD fine), *N*,*N*-dicyclohexylcarbodiimide (DCC) (Aldrich), 4-(dimethylamino)pyridine (DMAP) (Aldrich), hydroquinone (SRL, India) and 3-chloroperbenzoic acid (Aldrich) were used as received.

2.2. Measurements

The inherent viscosity of polymers was determined using Ubbelohde viscometer using chloroform as solvent at 30 °C. Elemental analysis was carried out on a Carlo-Erba 1106 system. Infrared spectra were obtained on a Thermo Electron Corporation Nicolet 380 FT-IR spectrometer. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) were recorded on a Bruker AM-400 spectrometer with Me₃Si (¹H NMR) as internal standard and in CDCl₃. Differential scanning calorimetry (DSC) was conducted on a Perkin-Elmer model DSC Pvris 1 system calibrated with indium and zinc standards. Dynamic thermogravimetric analysis was performed on Perkin-Elmer model TGA Pyris 1 system on film or powder samples at a heating rate of 20 °C/min in Nitrogen. The polarizing microscope study was performed using Euromex polarizing optical microscope (POM) with an image analyzer equipped with Linkem HFS91 heating stage and a TP-93 temperature programmer. Samples were placed between two thin microscopic slides. The textures were observed during heating and cooling at the rate of 5 °C min⁻¹ with the magnification of $20\times$. The photographs were taken with a Nikon FM 10 camera and printed on a Konica film.

2.3. Synthesis of 10-undecenoyl chloride (1)

10-Undecenoic acid (0.2117 mol) was dissolved in benzene (150 ml) with one drop of dimethylformamide, then thionyl chloride (75 ml; 0.6351 mol) added drop wise to the reaction mixture. The resultant mixture was refluxed for 6 h with constant stirring. The benzene and excess thionyl chloride were removed under vacuum to get acid chloride as colorless liquid [30] (yield 95%). ¹H NMR(400 MHz, CDCl₃, δ): 1.31–1.38 (m, 10H, –CH₂–), 1.62–1.69 (m, 2H, –CH₂–), 2.01–2.14 (m, 2H, –CH₂–), 2.87 (t, 2H, –CH₂–), 4.97 (dd, 1H, –CH–), 5.05 (dd, 1H, –CH), 5.75 (dd, 1H, –CH–). 13C NMR (75 MHz, CDCl₃): δ = 172.1, 137.2, 115.9, 46.9, 33.5, 29.6, 28.1, 25.2. IR (KBr): 3046 (alkene–CH–), 1799(–C–Cl), 2926(–CH–), 1718(–C=O). 1643(–C=C–).

2.4. Synthesis of 4-(10-undecenoyloxy)-1-biphenyl-4-carboxylic acid (2)

10-Undecenoyl chloride (0.1 mol) diluted with dry tetrahydrofuran (100 ml) and 4-hydroxybiphenyl-4-carboxylic acid (0.1 mol) followed by dry triethylamine (0.12 mol) were added and stirred at 20 °C for 12 h under nitrogen atmosphere. The precipitated triethylamine hydrochloride was removed and product was dissolved in THF and filtered. The filtrate was evaporated under vacuum to get crude product then recrystallized in ethanol yield white crystals (yield 92%) [31]. ¹H NMR(400 MHz, CDCl₃, δ): 1.32–1.38 (m, 10H, –CH₂—), 1.62–1.69 (m, 2H, –CH₂—), 2.05– 2.14 (m, 2H, –CH₂—), 2.81 (t, 2H, –CH₂—), 4.97 (dd, 1H, –CH–), 5.08 (dd, 1H, –CH), 5.76 (dd, 1H, –CH–), 7.15 (d, 2H, ArH), 7.63 (d, 4H, ArH), 8.02 (d, 2H, ArH), 11.05 (s.1H, –COOH). 13C NMR (75 MHz, CDCl₃): δ = 176.0, 172.1, 150.7, 144.0, 139.0, 137.5, 130.2, 129.6, 128.5, 121.99, 115.9, 33. 6, 29.1, 29.0, 24.8. IR (KBr): 3045 (alkene–CH–), 2926(–CH–), 2852 (–OH–), 1685(–C=O), 1641(–C=C–).

2.5. Synthesis of 1,3-substituted phenylene bis{[4'-(10undecenoyloxy)-1,1'-biphenyl-4-carboxylate}s (**ia-ie**)

A typical procedure for the synthesis of *ia* is as follows: 4-(10undecenoyloxy)-1-biphenyl-4-carboxylic acid (0.0038 mol), resorcinol (0.0019 mol) and dicyclohexylcarbodiimide (DCC)(0.0087 mol) were dissolved in dry dichloromethane (25 ml), to this solution 4-(dimethylamino)pyridine (DMAP; 0.005 mol) added and then stirred at room temperature for 5 h. The precipitate thus obtained was removed by filtration and the precipitate was dissolved in dichloromethane and filtered. The filtrate was washed with 5% HCl (3×50 ml), saturated NaCl (3×50 ml), and followed by water. The separated organic layer was dried over anhydrous sodium sulphate and solvent removed under reduced pressure. The product was purified by column chromatography using chloroform as eluent, and recrystallized from ethanol to give white solid (yield 85%). The above synthetic procedure was adopted for all other homologs and the analytical data presented as follows:

ia: 1H NMR(400 MHz, CDCl₃, δ): 1.31–1.37 (m, 10H, –CH₂–), 1.64–1.69 (m, 2H, –CH₂–), 2.02–2.14 (m, 2H, –CH₂–), 2.86 (t, 2H, –CH₂–), 4.96 (dd, 1H, –CH–), 5.02 (dd, 1H, –CH), 5.78 (dd, 1H, –CH–), 7.06 (s, 1H, ArH), 7.16 (d, 2H, ArH), 7.63 (d, 5H, ArH), 8.08 (d, 2H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 172.1, 165.3, 150.7, 139.0, 137.5, 130.2, 129.6, 129.2, 128.5, 121.9, 118.4, 115.9, 115.1, 33.6, 29.1, 29.0, 24.8. IR (KBr): 3046 (alkene–CH–), 2926(–CH–), 1721(–C=O), 1642 (–C=C–).

ib: (Yield 83%) ¹H NMR(400 MHz, CDCl₃, δ): 1.31–1.37 (m, 10H, –CH₂–), 1.62–1.68 (m, 2H, –CH₂–), 2.01–2.15 (m, 2H, –CH₂–), 2.85 (t, 2H, –CH₂–), 83.94 (s, 3H, ArH), 4.95 (dd, 1H, –CH–), 5.07 (dd, 1H, –CH), 5.76 (dd, 1H, –CH–), 7.03 (s, 1H, ArH), 7.17 (d, 1H, ArH), 7.64 (d, 5H, ArH), 8.08 (d, 2H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 172.1, 166.0, 165.3, 150.7, 139.0, 137.5, 130.2, 129.6, 129.2, 128.5, 121.9, 117.4, 115.9, 115.1, 51.5, 33.6, 29.1, 29.0, 24.8. IR (KBr): 3046 (alkene–CH–), 2926(–CH–), 1720(–C=O), 1642(–C=C–).

ic: (Yield 82%) ¹H NMR(400 MHz, CDCl₃, δ): 1.31–1.38 (m, 10H, –CH₂—), 1.62–1.69 (m, 2H, –CH₂—), 2.01–2.14 (m, 2H, –CH₂—), 2.87 (t, 2H, –CH₂—), 4.97 (dd, 1H, –CH–), 5.05 (dd, 1H, –CH), 5.75 (dd, 1H, –CH–), 7.02(s, 1H, ArH), 7.16 (d, 1H, ArH), 7.62 (d, 5H, ArH), 8.09 (d, 2H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 172.1, 165.3, 150.7, 139.0, 137.5, 130.2, 129.6, 129.2, 128.5, 121.9, 119.0, 115.9, 115.1, 33.6, 29.1, 29.0, 24.8. IR (KBr): 3046 (al-kene–CH–), 2926(–CH–), 1790 (–Ar–Cl–), 1720(–C=O), 1643 (–C=C–).

id: (Yield 85%) ¹H NMR(400 MHz, CDCl₃, δ): 1.32–1.38 (m, 10H, –CH₂—), 1.62–1.68 (m, 2H, –CH₂—), 2.01–2.13 (m, 2H, –CH₂—), 2.86 (t, 2H, –CH₂—), 4.96 (dd, 1H, –CH–), 5.04 (dd, 1H, –CH), 5.76 (dd, 1H, –CH–), 7.14 (d, 2H, ArH), 7.61 (d, 5H, ArH), 8.05 (d, 2H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 172.1, 165.3, 150.7, 139.0, 137.5, 130.2, 129.6, 129.2, 128.5, 121.9, 118.4, 115.9, 114.6, 33.6, 29.1, 29.0, 24.8. IR (KBr): 3046 (alkene–CH–), 2928(–CH–), 1722(–C=O), 1641 (–C=C–), 1525 (asymmetric-Nitro).

ie: (Yield 80%) ¹H NMR(400 MHz, CDCl₃, δ): 1.31–1.38 (m, 10H, –CH₂—), 1.62–1.69 (m, 2H, –CH₂—), 2.01–2.14 (m, 2H, –CH₂—), 2.87 (t, 2H, –CH₂—), 3.92 (s, 3H, –CH₃), 4.97 (dd, 1H, –CH₋), 5.05 (dd, 1H, –CH), 5.75 (dd, 1H, –CH–), 7.16 (d, 1H, ArH), 7.62 (d, 5H, ArH), 8.09 (d, 2H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 172.1, 166.0, 165.3, 150.7, 139.0, 137.5, 130.2, 129.6, 129.2, 128.5, 121.9, 117.8, 115.9, 114.6, 51.5, 33.6, 29.1, 29.0, 24.8. IR



Scheme 1. Synthesis of monomers and polymers Ia–Ie.



Scheme 2. Molecular modeling of ladder type banana shaped polyethers.

Table 1	
Yield, viscosity, solubility and elemental analysis of polymer Ia	-Ie.

Polymer Yield (%) η_{int}		η_{inh}^{a} (dL/g)	Solubility ^b			Emp. formula	Elemental analysis			
			DMF CHCl ₃ /DCM	Acetone	MeOH/EtOH/Benzene		Calc. Found	С	Н	Ν
la	88	0.81	+/+	-/+	-/-	$(C_{54}H_{60}O_{10})_n$	Calc. Found	74.63 74.25	6.96 6.82	-
Ib	87	0.89	+/+	_/+	-/-	$(C_{56}H_{62}O_{12})_n$	Calc. Found	72.55 72.06	6.74 6.70	-
Ic	89	0.85	+/+	-/+	-/-	$(C_{54}H_{59}ClO_{10})_n$	Calc. Found	71.79 71.55	6.58 6.44	-
Id	85	0.83	+/+	-/+	-/-	$(C_{54}H_{59}NO_{12})_n$	Calc. Found	70.96 70.70	6.51 6.38	1.53 1.46
le	90	0.87	+/+	_/+	-/-	$(C_{56}H_{61}NO_{14})_n$	Calc. Found	69.19 69.08	6.33 6.27	1.44 1.41

^a Measured at 30 °C with c = 0.2 g/dL in chloroform.

^b Solubility (0.05 g in 10 ml). +/+, soluble at room temperature; -/+, soluble at heating; -/-, insoluble.



Fig. 1. FT-IR spectrum of ia and Ia.

(KBr): 3046 (alkene—CH—), 2926(—CH—), 1722(—C=O), 1643 (—C=C—), 1527 (asymmetric–Nitro).

2.6. Synthesis of 1,3-substituted phenylene bis{[4'-(10-epoxyundecyloxy)-1,1'-biphenyl-4-carboxylate}s

A solution of 1,3-phenylene bis{[4'-(10-undecenoyloxy)-1,1'biphenyl-4-carboxylate} (**ia**; 0.001 mol) and pure 3-chloroperbenzoic acid (0.00017 mol) dissolved in dry dichloromethane (30 ml) and stirred at room temperature for 24 h. The dichloromethane solution was extracted successively with 5% aqueous solution of Na₂SO₄ (3 × 20 ml), 5% aqueous Na₂CO₃ (3 × 20 ml), and concentrated aqueous NaCl (3 × 20 ml) solution. After drying over MgSO₄, dichloromethane evaporated under vacuum gave corresponding epoxy monomer as white solid which was polymerized *in situ* without further purification. A similar procedure was adopted for the preparation of remaining monomers.



Fig. 2. ¹H NMR spectrum of ia.

2.7. Synthesis of poly{1,3-phenylenebis{[4'-(9-(2-oxiranoyloxy)-1,1'-biphenyl-4-carboxylate}s (Ia–Ie)

A typical procedure for the synthesis of **Ia** is as follows: 1,3-phenylene bis{[4'-(10-epoxyundecyloxy)-1,1'-biphenyl-4-carboxylate} (0.001 mol) was dissolved in dry dichloromethane (5 ml) and 0.1 ml of BF₃-etharate added and stirred at room temperature for 24 h under nitrogen atmosphere. At the end of reaction, mixture was concentrated, and poured in to dry methanol (100 ml). A white colored precipitate formed was purified by reprecipitation using chloroform–methanol, filtered and dried in vacuum oven at 75 °C (Yield 88%). This synthetic procedure was adopted for the synthesis of remaining polymers and the analytical data presented as follows:

Polymer **Ia**: ¹H NMR (400 MHz, CDCl₃, δ): 1.32–1.36 (m, 10H, –CH₂—), 1.62–1.68 (m, 2H, –CH₂—), 2.01–2.16 (m, 2H, –CH₂—), 2.88 (t, 2H, –CH₂—), 4.96 (dd, 1H, –CH–), 5.05 (dd, 1H, –CH), 5.75 (dd, 1H, –CH–), 7.01(s, 1H, ArH), 7.15 (d, 2H, ArH), 7.64 (d, 5H, ArH), 8.08 (d, 2H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 172.1, 165.3, 150.7, 139.0, 137.5, 130.2, 129.6, 129.2, 128.5, 121.9, 118.4, 115.9, 115.1, 33.6, 29.1, 29.0, 24.8. IR (KBr): 2925(–CH–), 1720(–C=0), 1247(C–O–C).

Polymer **Ib**: (Yield 87%) ¹H NMR (400 MHz, CDCl₃, δ): 1.31–1.38 (m, 10H, -CH₂--), 1.62–1.69 (m, 2H, -CH₂--), 2.01–2.14 (m, 2H, -CH₂--), 2.87 (t, 2H, -CH₂--), 4.97 (dd, 1H, -CH--), 5.05 (dd, 1H, -CH), 5.75 (dd, 1H, -CH--), 7.02(s, 1H, ArH), 7.16 (d, 2H, ArH), 7.62 (d, 5H, ArH), 8.09 (d, 2H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 172.1, 165.3, 150.7, 139.0, 137.5, 130.2, 129.6, 129.2, 128.5, 121.9, 118.4, 115.9, 115.1, 33.6, 29.1, 29.0, 24.8. IR (KBr): 2926(-CH--), 1720(-C=0), 1248(C-O--C).

Polymer **Ic**: (Yield 89%) ¹H NMR(400 MHz, CDCl₃, δ): 1.33–1.38 (m, 10H, -CH₂--), 1.63–1.69 (m, 2H, -CH₂--), 2.01–2.14 (m, 2H, -CH₂--), 2.85 (t, 2H, -CH₂--), 4.97 (dd, 1H, -CH--), 5.07 (dd, 1H, -CH--), 5.07

--CH), 5.73 (dd, 1H, --CH--), 7.08(s, 1H, ArH), 7.15 (d, 1H, ArH), 7.62 (d, 5H, ArH), 8.05 (d, 2H, ArH). 13 C NMR (75 MHz, CDCl₃): δ = 172.1, 165.3, 150.7, 139.0, 137.5, 130.2, 129.6, 129.2, 128.5, 121.9, 119.0, 115.9, 115.1, 33.6, 29.1, 29.0, 24.8. IR (KBr): 3046 (alkene--CH--), 2924(--CH--), 1790 (--Ar--Cl--), 1720(--C=O), 1247(C-O--C).

Polymer **Id**: (Yield 85%) ¹H NMR(400 MHz, CDCl₃, δ): 1.32–1.38 (m, 10H, –CH₂–), 1.62–1.69 (m, 2H, –CH₂–), 2.02–2.14 (m, 2H, –CH₂–), 2.87 (t, 2H, –CH₂–), 4.97 (dd, 1H, –CH–), 5.05 (dd, 1H, –CH), 5.77 (dd, 1H, –CH–), 7.16 (d, 2H, ArH), 7.62 (d, 5H, ArH), 8.09 (d, 2H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 172.1, 165.3, 150.7, 139.0, 137.5, 130.2, 129.6, 129.2, 128.5, 121.9, 118.4, 115.9, 114.6, 33.6, 29.1, 29.0, 24.8. IR (KBr): 3046 (alkene–CH–), 2925(–CH–), 1720(–C=O), 1244(C–O–C), 1528 (asymmetric-Nitro).

Polymer **le**: (Yield 90%) ¹H NMR(400 MHz, CDCl₃, δ): 1.31–1.36 (m, 10H, –CH₂–), 1.62–1.69 (m, 2H, –CH₂–), 2.01–2.16 (m, 2H, –CH₂–), 2.87 (t, 2H, –CH₂–), 3.95 (s, 3H, –CH₃), 4.97 (dd, 1H, –CH–), 5.08 (dd, 1H, –CH), 5.75 (dd, 1H, –CH–), 7.19 (d, 1H, ArH), 7.62 (d, 5H, ArH), 8.10 (d, 2H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 172.1, 166.0, 165.3, 150.7, 139.0, 137.5, 130.2, 129.6, 129.2, 128.5, 121.9, 117.8, 115.9, 114.6, 51.5, 33.6, 29.1, 29.0, 24.8. IR (KBr): 3046 (alkene–CH–), 2926(–CH–), 1722(–C=O), 1248(C–O–C), 1527 (asymmetric–Nitro).

3. Results and discussion

3.1. Synthesis

The banana shaped 1,3-substituted phenylene $bis{[4'-(10-undecenoyloxy)-1,1'-biphenyl-4-carboxylate}s were prepared and then epoxidized to get the monomers and polymers (Scheme 1). The allyl terminated banana shaped precursors were studied for$



Fig. 3. ¹³C NMR spectrum of ia.



Fig. 4. ¹H NMR spectrum of *Ia*.

their POM investigation based on their better chemical stability than their epoxy counterparts. The polyethers (Scheme 2) were synthesized by epoxidation of allyl group followed by ring opening polymerization in the presence of BF₃-etherate as an initiator. The polymers are soluble in DMF, CHCl₃, CH₂Cl₂, and acetone and insoluble in methanol, ethanol, 2-propanol, benzene and toluene (Table 1). The intrinsic viscosity of the polymers was determined using an Ubbelohde viscometer using chloroform as solvent at 30 °C and data shown in Table 1. The inherent viscosity was in the range of 0.81–0.89 dL/g. The data reveals that they are of reasonably high molecular weight materials.

The structures of **ia**–**ie** and **Ia**–**Ie** were confirmed by FT-IR, ¹H and ¹³C NMR, and elemental analysis. The spectral values are in accordance with the assigned structures. The representative FT-IR spectrum of **ia** and **Ia** is shown in Fig. 1. The strong absorption bands at 3046, and 1643 cm⁻¹ corresponds to alkene—C—H, and —C=C— stretchings respectively and these two absorptions are disappeared in **Ia** ascribed to completeness of polymerization. The bands appearing at 2926 and 1722 cm⁻¹ as a result of asymmetric stretching of methylene spacers and carbonyl (C=O) stretching, respectively. The alky and aryl ether stretching appeared around 1253 cm⁻¹. The absorption around 832–727 cm⁻¹ represents to aromatic ring vibrations.

The representative ¹H NMR spectrum of **ia** is illustrated in Fig. 2. The aromatic protons of precursor were resonated in the range of 7.02–8.09 ppm and aliphatic protons resonated in the range of 1.31–2.87 ppm. Three olefinic protons resonated at 4.97, 5.05 and

5.75 ppm. The ¹³C NMR spectrum of **ia** is shown in Fig. 3. The C=O signal of ester group at 165.3 ppm, the aliphatic protons are appeared in the range of 33.6–24.8 ppm and aromatic protons resonated in the range of 115.1–172.1 ppm. ¹H NMR spectrum **Ia** is shown in Fig. 4, the disappearance of olefinic protons shows the formation of polymer. All the polymers displayed similar FT-IR, ¹H and ¹³C NMR spectra. The elemental analysis values obtained for **Ia–Ie** are in accordance with the calculated values and listed in Table 1.

3.2. Mesophases and thermal properties of precursors ia-ie

The transition temperatures and associated enthalpy values for **ia-ie** are summarized in Table 2. They differ from one another with respect to substituents (H, Cl, NO₂, and COOCH₃) in 2 and 4 position of central phenyl ring. The **ia**, **ic** and **id** shows enantiotropic B₁ phase on cooling from isotropic liquid and there was no significant change in the mesophase on lowering the temperature. The enthalpy value of isotropization was 11.38j/g with mesophase duration (ΔT) of 71.9 °C, nevertheless, compound **ib** unable to exhibit mesophase attributable to destabilization of substituent in the center core. However, **ie** was displayed nematic phase on cooling from isotropic temperature because of the presence of NO₂ group which reduce the perturbation effect of COOCH₃.

The DSC thermograms were measured at the rate of 5° C/min with heating and cooling cycles, DSC curve of **ia**–**ie** shown in Fig. 5 and phase transitions listed in Table 2. Except **ib**, the remain-

Table 2	2
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Transition temperatures (°C) and associated enthalpies (J/g) observed in DSC for $ia\mathchar`a\ma\mathchar`a\mathchar`a\mathchar`a\mathchar`a$

Precursor	R^2/R^4	Transit	Transition temperature (°C)						
		Cr		B1		Ν		Ι	
ia	H/H	*	69.5 (3.83 J/g)	*		_	144.5 (11.38 J/g)	*	75
ib	H/COOCH ₃	*		-		-	116 (16.32 J/g)	*	-
ic	H/Cl	*	99 (2.79 J/g)	*		-	137 (9.8 J/g)	*	38
id	NO ₂ /H	*	119 (3.48 J/g)	*		-	140 (10.56 J/g)	*	21
ie	NO ₂ /COOCH ₃	*		-	78 (3.46 J/g)	*	122 (9.85 J/g)	*	44

Cr, crystalline phase, B1, columnar phase, N, nematic phase, I, isotropic liquids.





Fig. 6. Graphical representation of the phase transition temperatures of ia-ie.

ing precursors show two endothermic peaks corresponds to crystalline-liquid crystalline (T_m) and liquid crystalline–isotropic transition (T_i) respectively. The T_m of the series was observed in the range of 69.5–144.5 °C. Fig. 6 shows correlation between the series and transition temperatures (T_m and T_i) observed from DSC measurement. The **ia–ie** indicate two endothermic peaks (except **ib**). The **ia** exhibited large mesophase duration of 75 °C where as **id** displayed little mesophase duration of 21 °C.

3.3. Mesophase and thermal property of polymers *Ia–Ie*

The polymers **Ia**, **Ic** and **Id** were found to form grainy phases as found in POM and the representative LC texture grainy phases (Fig. 7). The polymer **Ib** and **Ie** substituted with methyl ester and nitro group did not exhibit any LC phase. In case of polymer Ie, the reason that do not show LC phase is attributed to the steric hindrance of NO₂ and COOCH₃ groups which could not provide mobility to the polymeric chain. But the same monomer (ie) exhibited LC phase since the steric hindrance was nullified by each other (NO₂ and COOCH₃). The LC property of **Ia**, **Ic** and **Id** was evaluated with DSC measurement and their thermograms of **Ia**, **Ic** and **Id** shown in Fig. 8 and phase transition data given in Table 3. Here again, except **Ib** and **Ie**, the remaining polymers evidenced three endothermic peaks corresponds to glass transition temperature (T_g), cystallineliquid crystalline (T_m) and liquid crystalline–isotropic transition (T_i) respectively.

The T_m of the series was observed in the range of 138–145 °C. In general, T_g value of LCPs is influenced not only by the polymeric chain flexibility but also the substitutents in the aromatic ring. The POM observations confirmed (Fig. 7) the grainy LC phase was formed between the temperature range of T_m and T_i in both cooling and heating cycles. The transition observed under POM was found to be in accordance with DSC results.

The thermal behavior of polyethers was evaluated by TGA under nitrogen atmosphere at a heating rate of 10 °C/min; the representative TGA thermogram of Ia shown in Fig. 9, the data illustrated in Table 4. The thermal stability was evaluated by 5%



Fig. 7. HOPM photographs of ia, ic, id and Ia at 20× magnifications.



Fig. 8. DSC thermograms of Ia-Ie.

Table 3DSC and POM data of **Ia–Ie**.

Polymer	DSC (°C) ^a				POM (°C) ^b			
	T_g	T_m	T_i	ΔT	T_m	T_i	ΔT	Mesophase
la	78	138	175	37	136	175	39	Grainy
Ib	108	159	-	-	160	-	-	-
lc	110	145	181	36	142	180	38	Grainy
Id	97	141	169	28	138	168	30	Grainy
Ie	86	162	-	-	160	-	-	-

^a Observed in POM during cooling cycle.

^b Obtained in DSC during heating cycle.

and 50% weight loss at minimum temperature. The results disclosed they were stable upto 302 °C and start degrading thereafter in nitrogen atmosphere. The thermal stability increases in the order of the le > lb > lc > ld > la. The char yield was measured at 800 °C and data shown in the Table 4. The polymers rendered good char yield due to the presence of aromaticity.

4. Conclusions

A series of structurally similar with varying substituents containing bent-core liquid crystalline precursors, monomers and



Fig. 9. TGA thermogram of Ia.

Table 4

IGA	udld	0I	Id-IC.	

Polymer	Temperature corr	esponding to	Carbon residue at 800 °C (
	5% Weight loss	50% Weight loss			
la	327	440	20		
Ib	302	438	22		
lc	345	456	27		
Id	316	432	31		
le	325	437	24		

polymers (**Ia–Ie**) were synthesized and characterized. The molecular structures were identified by FT-IR and NMR spectroscopy, and are in accordance with the targeted molecular formula. The variations in substituents (H, COOCH₃, Cl and NO₂) on central phenyl ring have been correlated with thermal and mesomorphic properties. The **ia**, **ic** and **id** have been designated as columnar B₁ phase and **ie** identified as nematic phase. The **ia** exhibited large mesophase duration. The **Ia**, **Ic** and **Id** shows a grainy phase on heating and cooling, whereas **Ib** and **Ie** unable to show mesophases because of the steric hindrance of both the bulky groups (NO₂ and COOCH₃) while the monomer **ie** showing LC phase in which the steric hindrance was nullified resulted from the free mobility in the molten state. All the polymers possess high T_g in the range of 78–110 °C. The thermal stability of the polymers increases in the order as Ie > Ib > Ic > Id > Ia.

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