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Synthesis and Thermal Transitions of Some Liquid Crystalline Oligomers

W.-C. Chan [a], J. A. Mooney [a] & A. H. Windle [a]
[a] Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, England
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Synthesis and Thermal Transitions of Some Liquid Crystalline Oligomers

W.-C. CHAN, J. A. MOONEY and A. H. WINDLE

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ England

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Fourteen aromatic ester oligomers have been synthesised, the majority of which have not been described previously. They can be considered as model compounds for liquid crystalline polyesters, and as such give useful information regarding the relationship between chemical structure and thermal properties. Such oligomers are also potentially important as precursors to liquid crystalline monomers.

1. INTRODUCTION

Thermotropic liquid crystalline polymers (LCPs) represent a new class of materials with an unparalleled combination of thermal, chemical, and mechanical properties.[1] LCPs can be readily aligned in flow fields, for example those obtained during extrusion, and melt spinning produces fibres with a high degree of axial orientation giving impressive tensile properties.[2] Liquid crystalline polymers can also be effectively aligned in magnetic or electric fields.[3–6] They possess very low apparent viscosities in the mesophase and the transition from an isotropic to liquid crystalline state is often accompanied by a decrease in viscosity.[7] They thus make ideal candidates for complex moulding operations and for blending with conventional polymers to lower viscosity and ease processing.[8,9]

Many polymer manufacturers have active research programmes on these high performance materials, and a number of formulations are now commercially available. Furthermore, the liquid crystalline state has opened up several new scientific questions, and this paper describes the synthesis and thermal properties of a number of aromatic ester oligomers designed as model materials to address these underlying issues. The oligomers studied, shown in Figure 1, are based on the repeat units commonly found in commercial LCPs, the most common being the *p*-oxybenzoate unit. The corresponding homopolymer, polyhydroxybenzoic acid cannot be melted much below its decomposition temperature. Processibility is achieved through the use of other chemical units which are copolymerised with the *p*-oxybenzoate unit, thus disrupting the periodicity and frustrating crystallisation. In this way the effective melting point can be reduced to an accessible temperature.

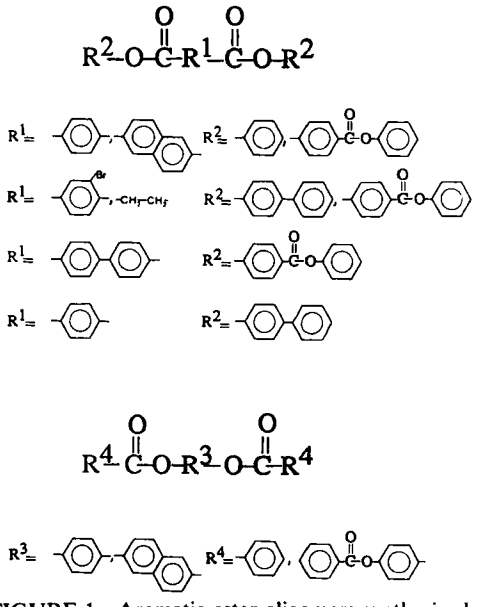


FIGURE 1 Aromatic ester oligomers synthesized.

In scientific terms, the cost of achieving a polymeric liquid crystalline phase and thus materials which can approach equilibrium is an additional level of complexity associated with the random copolymerisation. The oligomer route however, can provide an alternative approach.[10,11] Furthermore, problems of molecular weight distribution are avoided and it is possible to control the chemical structure exactly which means that particular unit sequences can be obtained and difficulties associated with active end groups eliminated. The possibility of studying cocrystallisation of either identical or subtly different chemical sequences is also opened up. Structure/property relationships for conventional low molecular weight liquid crystals have been detailed in the literature,[12,13] here we focus on the materials intermediate in character between these and LCPs.

It is also significant that the ease with which liquid crystalline oligomers can be oriented in electric or magnetic fields, compared to that of LCPs, may lead to new methods of processing in which polymerisable end groups are incorporated and the molecules are chain extended after orientation.[14,15]

2. EXPERIMENTAL

2.1 Synthesis

Except where reference is made to other work, there are no reports of the molecules being synthesised before.

The following reagents were used as received:

Aldrich: Hydroquinone 99%; Benzoyl chloride 99%; Terephthaloyl chloride 99+%; Phenol 99+%; 2,6-Naphthalenedicarboxylic acid, dipotassium salt 95%;

2,6-Dihydroxynaphthalene 98%; 2-Bromoterephthalic acid 97%; Succinoyl chloride 95%; 4-Phenylphenol 97%; Thionyl chloride 99%; Pyridine, anhydrous 99%; Triethylamine 99%; Oxalyl chloride 99+%.

Apin Chemicals: Phenyl 4-hydroxybenzoate; 4,4'-Bisbenzoic acid; 4-Benzoyloxybenzoic acid.

Solvents were dried where appropriate, following standard procedures.

Precursors

2-Bromoterephthaloyl chloride, $C_8H_3O_2BrCl_2$ (281.92)
CAS Reg. No. 13815-89-9

Thionyl chloride (200g, 1.68 mol) and dimethylformamide (DMF) (3ml) were added to 2-bromoterephthalic acid (50.0g, 204.1mmol) and the mixture heated at reflux under nitrogen until clear. The excess of thionyl chloride was evaporated under reduced pressure and the product vacuum distilled to give a yellow tinged oil. Yield = 41.33g, 71.8%, b.p. 185–190°C @ 11mm Hg, *cf* 158°C @ 11mm Hg.[16]
IR(KBr, cm^{-1}): 1775, 1745 (s, C=O)
C,H: Calc. 34.08C 1.07H; found 33.86C 1.15H

4,4'-Biphenyl dicarbonyl chloride, $C_{14}H_8O_2Cl_2$ *(279.12)*
CAS Reg. No. 2351-37-3

Thionyl chloride (200g, 1.68mol) and DMF (3ml) were added to 4,4'-bisbenzoic acid (25.0g, 103.2mmol) and the mixture heated at reflux under nitrogen until clear. On cooling, a beige solid crystallised. The excess of thionyl chloride was removed (rotary evaporator) and the crude product recrystallised from toluene to give off-white needles. Yield = 19.0g, 65.9%, m.p. 180–186°C, *cf* buff crystals, 24%, 180–182°C.[17]
IR(KBr, cm^{-1}): 1775 (s, C=O) 1598 (m, C=C)
C,H: Calc. 60.24C 2.89H; found 60.24C 2.88H

2,6-Naphthalene dicarbonyl chloride, $C_{12}H_6O_2C_{12}$ *(253.08)*
CAS Reg. No. 2351-36-2

Oxalyl chloride (32.0g, 252.1mmol) was dissolved in toluene (60ml), and to this 2,6-naphthalene dicarboxylic acid, dipotassium salt (25.0g, 85.5mmol) was added slowly. The mixture was heated at reflux under nitrogen for 3 h, and on cooling, a beige solid crystallised. The mixture was dissolved in boiling toluene (400ml) and left to cool slowly to give small yellow needles. Yield = 12.14g, 56.0%, m.p. 183–188°C, *cf* 182–185°C.
IR(KBr, cm^{-1}): 1745 (s, C=O), 1590 (m, C=C)
C,H: Calc. 56.95C 2.39H; found 56.40C 2.39H

4-Benzoyloxybenzoyl chloride, $C_{14}H_9O_3Cl$ *(260.68)*
CAS Reg. No. 58860-87-7

4-Benzoyloxybenzoic acid (9.9g, 41mmol) was converted into its acid chloride by heating at reflux under nitrogen for 3 h with an excess of thionyl chloride (200g,

1.68mmol) and DMF (3ml). After distilling off the excess of reagent, the resulting chloride was crystallised from toluene and dried *in vacuo*. Yield = 8.3g, 78%, m.p. 133–134°C, *cf* 133–134°C.[19]
IR(KBr, cm^{-1}): 1765, 1719 (s, C=O), 1602 (m, C=C)
C,H: Calc. 64.49C 3.45H; found 64.69C 3.64H

Oligomers

A *1,4-Phenylene bis(benzoate), $C_{20}H_{14}O_4$ (318.33)*
CAS Reg. No. 14210-97-0

To an argon filled flask, hydroquinone (2.75g, 25mmol) was added with pyridine (30ml) and stirred until dissolved. Benzoyl chloride (7.0g, 50mmol) was then added with vigorous stirring. The white solid was filtered, washed with water and dried *in vacuo* before being crystallised from 1,4-dioxan to give a white powder. Yield = 4.61g, 58%, m.p. 203°C, *cf* 204°C.[20]
IR(KBr, cm^{-1}): 1732 (s, C=O), 1597 (m, C=C)
C,H: Calc. 75.47C 4.40H; found 75.16C 4.62H

B *1,4-Phenylene terephthalate $C_{20}H_{14}O_4$ (318.33)*
CAS Reg. No. 1539-04-4

To a solution of phenol (9.4g, 100mmol) in ice cold water (150ml) containing sodium hydroxide (4.0g, 100mmol), terephthaloyl chloride (10.15g, 50mmol) in diethylether was added dropwise with vigorous stirring. The mixture was stirred for a further 30 min at the end of which the solid was collected, washed with water and dried *in vacuo* before crystallised from 1,4 dioxan to give small white platelets. Yield = 4.2g, 53%, m.p. 197°C, *cf* 196–198°C.[21]
IR(KBr, cm^{-1}): 1732 (s, C=O), 1592 (m, C=C)
C,H: Calc. 75.47C 4.40H; found 75.48C 4.55H

C *2,6-Naphthalene bis(benzoate), $C_{24}H_{16}O_4$ (368.39)*
CAS Reg. No. 58635-09-9

To an argon filled flask was added 2,6-dihydroxynaphthalene (3.2g, 20mmol) in pyridine (25ml). The mixture was ice cooled before benzoyl chloride (5.9g, 42mmol) was added with rapid stirring. The ice bath was removed and the mixture stirred for a further 30 min. The solid was collected, washed with water and dried *in vacuo* before being crystallised from 1,4-dioxan to give a white powder. Yield = 4.7g, 64%, m.p. 218°C *cf* 220°C.[22]
IR(KBr, cm^{-1}): 1729 (s, C=O), 1597 (m, C=C)
C,H: Calc. 75.47C 4.40H; found 75.48C 4.55H

D *Diphenyl 2,6-naphthalene dicarboxylate, $C_{24}H_{16}O_4$ (368.39)*
CAS Reg. No. 2412-00-2

Sodium hydroxide (2.22g, 55.4mmol) was dissolved in water (100ml) and cooled in ice to below 10°C after which, phenol (5.21g, 55.4mmol) was added. To this,

2,6-naphthalene dicarbonyl chloride (7.70g, 30.4mmol) dissolved in tetrahydrofuran (400ml) was added dropwise with stirring. A white precipitate formed immediately. The mixture was stirred at room temperature for 30 min and then filtered. The solid was washed with distilled water and dried *in vacuo*. The crude product was crystallised from toluene to give small white platelets. Yield = 6.40g, 62.7%

IR(KBr, cm^{-1}): 1728 (s, C=O), 1590 (m, C=C)
C,H: Calc. 78.25C 4.38H; found 77.79C 4.41H

E *1,4-Bis[(4-benzoyloxyl)benzoyloxy]phenylene, $C_{34}H_{22}O_8$ (558.54)*

To an argon filled flask containing a solution of hydroquinone (0.825g, 7.5mmol) in pyridine (50ml) was added 4-benzoyloxybenzoyl chloride (3.9g, 1.5mmol) in pyridine (50ml), with stirring. The mixture was allowed to stand for 24 h, after which the white precipitate was filtered off, washed with water and acetone and dried *in vacuo*. It was then crystallised from dimethylsulphoxide (DMSO) to give a white powder. Yield = 2.71g, 65%.

IR(KBr, cm^{-1}): 1737 (s, C=O), 1599 (m, C=C)
C,H: Calc. 73.12C 3.94H; found 73.03C 4.13H

F *1,4-Bis[(4-phenyloxycarbonyl)phenyloxycarbonyl]phenylene, $C_{34}H_{22}O_8$ (558.54)*

To an ice-cold solution of phenyl 4-hydroxybenzoate (2.5g, 11.7mmol) in water (30ml) containing sodium hydroxide (0.47g, 11.7mmol), was added terephthaloyl chloride (1.38g, 6.8mmol) in diethyl ether, with stirring. The white precipitate was filtered off, washed with water and acetone, and dried *in vacuo*. The solid was then crystallised from DMSO to give a white powder. Yield = 1.36g, 42%, m.p. 254°C, *cf* 257°C.[23]

IR(KBr, cm^{-1}): 1733 (s, C=O), 1596 (m, C=C)
C,H: Calc. 73.12C 3.94H; found 72.49C 4.10H

G *1,4-Bis[(4-phenyloxycarbonyl)phenyloxycarbonyl]-2-bromophenylene, $C_{34}H_{21}O_8Br$ (637.44)*

Phenyl 4-hydroxybenzoate (13.82g, 64.5mmol) was dissolved in dichloromethane (1 l) containing triethylamine (8g, 79.1mmol). To this, 2-bromoterephthaloyl chloride (10.0g, 35.5mmol) was added dropwise with stirring. The solution was heated at reflux for 4 h and then the solvent removed under reduced pressure to leave a white solid which was left to dry fully overnight at room temperature. Subsequently, it was washed with 10% by wt. hydrochloric acid (2 × 1 litre), 1M sodium hydroxide solution (2 × 1 litre), distilled water (3 × 1 litre) and then dried *in vacuo*. The crude product was crystallised from toluene to give a white powder. Yield = 11.1g, 53.8%.

IR(KBr, cm^{-1}): 1725 (s, C=O), 1590 (m, C=C)
C,H: Calc. 64.06C 3.32H; found 63.86C 3.40H

H *2,6-Bis[(4-benzoyloxy)benzoyloxy]naphthalene, $C_{38}H_{24}O_8$ (608.60)*

To an argon filled flask was added 2,6-dihydroxynaphthalene (1.2g, 7.5mmol) and pyridine (50ml). To this stirred solution, 4-benzoyloxybenzoyl chloride (3.9g, 1.5mmol)

in pyridine (50ml) was added. The mixture was left to stand for 24 h at room temperature, after which the white precipitate was filtered off, washed with water and acetone and dried *in vacuo*. The solid was crystallised from DMSO to give a white powder. Yield = 1.83g, 40%.

IR(KBr, cm^{-1}): 1735 (s, C=O), 1598 (m, C=C)
C,H: Calc. 75.00C 3.95H; found 74.63C 4.13H

I *2,6-Bis[(4-phenyloxycarbonyl)phenyloxycarbonyl]naphthalene,* $C_{38}H_{24}O_8$ *(608.60)*

Phenyl 4-hydroxybenzoate (7.70g, 35.9mmol) was dissolved in DCM (400ml) containing triethylamine (4.5g, 44.5 mmol). To this, a solution made up of 2,6-naphthalene dicarbonyl chloride (5.0g, 19.8mmol) in DCM (400ml) was added dropwise with stirring. A white precipitate formed on addition. The mixture was heated at reflux for 2 h, and the solid filtered and dried *in vacuo*. It was subsequently washed with 10% by wt. hydrochloric acid (2 × 500ml), 1M sodium hydroxide solution (2 × 500ml), distilled water (3 × 500ml) and then dried *in vacuo*. The crude product was crystallised from DMSO to give a white powder. Yield = 5.34g, 48.8%.

IR(KBr, cm^{-1}): 1728 (s, C=O), 1590 (m, C=C)
C,H: Calc. 74.99C 3.97H; found 74.06C 3.91H

J *4,4'-Bis(phenoxycarbonyl-1,4-phenyl)biphenyldicarboxylate,* $C_{40}H_{26}O_8$ *(634.64)*

Phenyl 4-hydroxybenzoate (13.96g, 65.2mmol) was dissolved in DCM (600ml) containing triethylamine (8.0g, 79.1mmol). To this, a solution of 4,4'-biphenyl dicarbonyl chloride (10.0g, 35.8mmol) in DCM (600ml) was added dropwise with stirring. A white precipitate formed upon addition. The mixture was heated at reflux for 2 h under nitrogen, the solvent removed at reduced pressure, and the solid left to dry *in vacuo*. The solid was then ground, washed with 10% by wt. hydrochloric acid (2 × 1 l), 1M sodium hydroxide solution (2 × 1 l), distilled water (4 × 1 litre) and dried *in vacuo*. The crude product was crystallised from DMSO to give a white powder. Traces of the crystallisation solvent could not be removed even at high temperatures under very low pressures; the product was therefore washed with DCM in a Soxhlet apparatus. Even then, small traces of solvent could still be detected. Yield = 7.28g, 35.2%.

IR(KBr, cm^{-1}): 1732 (s, C=O), 1598 (m, C=C)
C,H: Calc. 75.70C 4.13H; found 75.78C 4.05H

K *Bis(phenoxycarbonyl-1,4-phenyl)succinate,* $C_{30}H_{22}O_8$ *(510.50)*

Phenyl 4-hydroxybenzoate (15.20g, 71.0mmol) was dissolved in DCM (600ml) containing triethylamine (7g, 69.2mmol). To this, succinoyl chloride (5.0g, 32.3mmol) was added dropwise with stirring. A light brown precipitate formed upon addition. The mixture was heated at reflux for 4 h under nitrogen and then all the solvent evaporated at reduced pressure to leave a brown solid which was left to dry at room temperature overnight. Subsequently the solid was washed with 10% by wt. hydrochloric acid (2 × 1 l), 1M sodium hydroxide solution (2 × 1 l), distilled water (3 × 1 l) and then dried *in vacuo*. The crude product was crystallised from toluene to give off-white crystal flakes. Yield = 8.20g, 49.7%.

IR(KBr, cm^{-1}): 1760, 1735 (s, C=O), 1595 (m, C=C)
C,H: Calc. 70.58C 4.34H; found 70.68C 4.40H

L *Bis(4,4'-biphenyl)terephthalate, $C_{32}H_{22}O_4$ (470.52)*
CAS Reg. No. 52256-89-0

4-Phenylphenol (15.0g, 88.1mmol) was dissolved in ether (800ml) containing triethylamine (8.92g, 88.1mmol). To this, a solution of terephthaloyl chloride (8.95g, 44.1mmol) in ether (100ml) was added dropwise with stirring. A white precipitate formed upon addition. The mixture was stirred at room temperature for 4 h, the solid filtered off, washed with ether, and then left to dry overnight at room temperature. Subsequently the solid was washed with 10% by wt. hydrochloric acid (2 × 800ml), distilled water (4 × 1 l) and then dried *in vacuo*. The crude product was crystallised from DMSO to give small white crystal platelets. Yield = 8.18g, 39.44%.

IR(KBr, cm^{-1}): 1725 (s, C═O), 1598 (m, C═C)
C,H: Calc. 81.69C 4.73H; found 81.44C 4.77H

M *Bis(4,4'-biphenylyl) 2-bromoterephthalate, $C_{32}H_{21}O_4Br$ (549.42)*

4-Phenylphenol (10.98g, 64.5mmol) was dissolved in ether (400ml) containing triethylamine (8.0g, 79.1mmol). To this, 2-bromoterephthaloyl chloride (10.0g, 35.5mmol) was added dropwise with stirring. A white precipitate formed upon addition. The mixture was stirred at room temperature for 30 min, the solid filtered off and then *in vacuo*. Subsequently the solid was washed with 10% by wt. hydrochloric acid (2 × 1 l), 1M sodium hydroxide solution (2 × 1 l), distilled water (4 × 1 l) and then dried *in vacuo*. The crude product was crystallised from toluene to give white crystals. Yield = 8.55g, 48.3%.

IR(KBr, cm^{-1}): 1732 (s, C═O), 1595 (m, C═C)
C,H: Calc. 69.96C 3.85H; found 70.76C 3.92H

N *Bis(4,4'-biphenylyl) succinate, $C_{28}H_{22}O_4$ (422.48)*

4-Phenylphenol (19.97g, 117.3mmol) was dissolved in ether (400ml) containing triethylamine (13.5g, 133.4mmol). To this, succinoyl chloride (10.0g, 64.5mmol) was added dropwise with stirring. A beige precipitate formed upon addition. The mixture was stirred at room temperature for 30 min, the solid filtered off and then dried *in vacuo*. Subsequently the solid was washed with 10% by wt. hydrochloric acid (2 × 1 l), 1M sodium hydroxide solution (2 × 1 l), distilled water (4 × 1 l) and dried *in vacuo*. The crude product was crystallised from toluene to give large beige crystal platelets. Yield = 12.44g, 50.2%.

IR(KBr, cm^{-1}): 1752 (s, C═O), 1595 (m, C═C)
C,H: Calc. 79.60C 5.25H; found 79.49C 5.38H

2.2 Characterisation of oligomers

The samples were subjected to a detailed calorimetric analysis using a Perkin Elmer DSC 7. The instrument was calibrated against the melting points of indium and zinc, and the enthalpy of indium at 20°C/min. Experiments were carried out under a continuous flow of nitrogen and in general, heating and cooling rates of 20°C/min were used.

Rapid heating (150°C/min) was sometimes employed to avoid degradation at elevated temperature when the liquid crystalline to isotropic transition was being studied. The instrument was separately calibrated against indium for rates of 150°C/min and −20°C/min and in all cases the transition temperatures were taken at the maximum peak positions.

On first heat, samples were taken 30°C above the crystal melting transition temperature and then subjected to a controlled cool at −20°C/min in order to produce a "standard state". Although the second heating was taken as the definitive run, it showed only minor changes with respect to the first, and there was no evidence that a cooling rate of −20°C/min was sufficient to suppress crystallinity, an observation confirmed by subsequent hot-stage X-ray analysis.

2.3 Optical microscopy

Samples were also examined by hot stage polarising microscopy. They were contained in cells 10 μm thick, the glass slides having been cleaned by a Decon, distilled water, 10% hydrochloric acid, distilled water, ethanol, warm air sequence. Microscopy was used to distinguish between liquid crystalline and isotropic melts, and where possible to identify the transition between them.

3. RESULTS

The thermal transition data for all the molecules synthesised are recorded in Table I. A typical uncorrected DSC trace is shown in Figure 2 for oligomer M. The larger peak on heating at 214°C is the crystal to liquid crystalline phase transition, des-

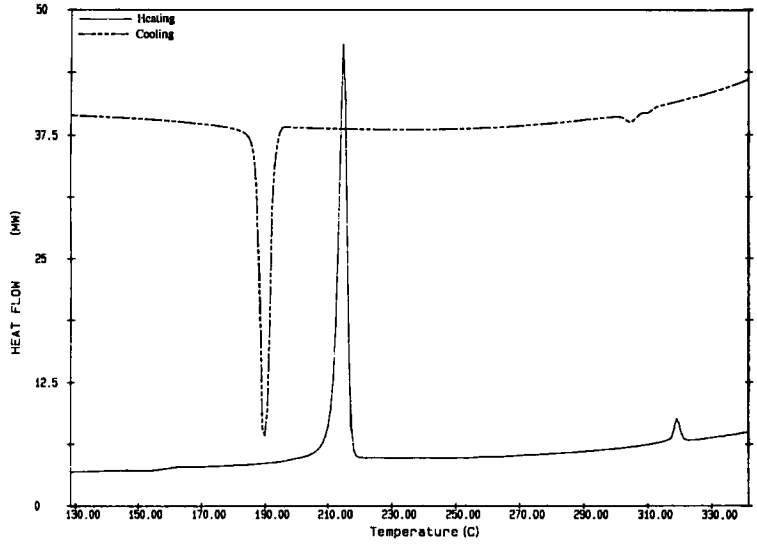


FIGURE 2 DSC trace for oligomer M at 20°C/min.

TABLE I

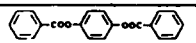
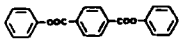
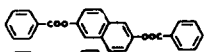
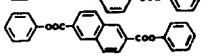
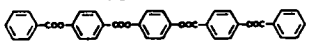
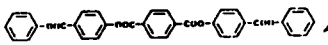
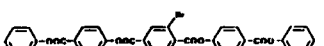
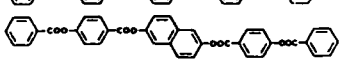
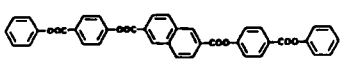
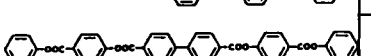
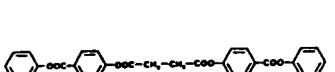
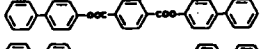
	SAMPLE	Reference	DSC TRANSITION TEMPERATURES/°C and (ENTHALPIES/Jg^{-1}) @20°C/min. 1st HEAT	1st COOL	2nd HEAT	UNDER-COOLING	@150°C/min. 1st HEAT	MESOPHASE
A		20	203(149.8)k→i	185(-127.5)i→k	203(148.3)k→i	18	211(149.2)k→i	Not LC
B		21	197(139.1)k→i	184(-126.6)i→k 191(-0.9)	197(134.6)k→i 205(0.7)	13	194(148.0)k→i	Not LC
C		22	218(126.4)k→i	194(-120.6)i→k	217(119.9)k→i	23	218(130.7)k→i	Not LC
D		24	216(130.3)k→i	202(-113.7)i→k	216(129.4)k→i	14	218(138.1)k→i	Not LC
E			276(83.9)k→lc	265(-71.8)lc→k	271(68.6)k→lc	6	279(92.2)k→lc 397(8.3)lc→i	Nematic
F		23	254(94.4)k→lc	240(-70.9)lc→k	250(74.3)k→lc	10	250(92.2)k→lc 392(4.0)lc→i	Nematic
G			178(75.0)k→lc	153(-62.2)lc→k	155, 169 177(69.4)k→lc	24	179(76.6)k→lc 345(8.6)lc→i	LC
H			264(71.9)k→lc	251(-67.9)lc→k	263(70.3)k→lc	12	263(75.9)k→lc 433(8.5)lc→i	LC
I			250(94.0)k→lc	237(-72.1)lc→k	250(105.3)k→lc	13	247(98.9)k→lc 428(10.1)lc→i	LC
J			221shoulder 238(74.4)k→lc	226(-53.0)lc→k 197(-2.4)	219shoulder 227shoulder 238(80.4)k→lc	12	241(80.5)k→lc lc→i>500°C	LC
K			182shoulder 186shoulder 195(139.1)k→i	146(-117.9)i→k	186shoulder 194(128.7)k→i	48	198(140.7)k→i	Not LC
L		25	319(141.1)k→lc	311(-136.5)lc→k	319(137.9)k→lc	8	322(144.1)k→lc 373(4.9)lc→i	LC
M			214(82.3)k→lc	204(-80.0)lc→k	214(81.4)k→lc	10	214(87.1)k→lc 314(4.9)lc→i	Nematic
N			228(151.7)k→i	205(-142.9)i→k	228(150.2)k→i	23	229(160.5)k→i	Not LC

FIGURE 3 Texture observed between crossed polarisers for oligomer G at 210°C.

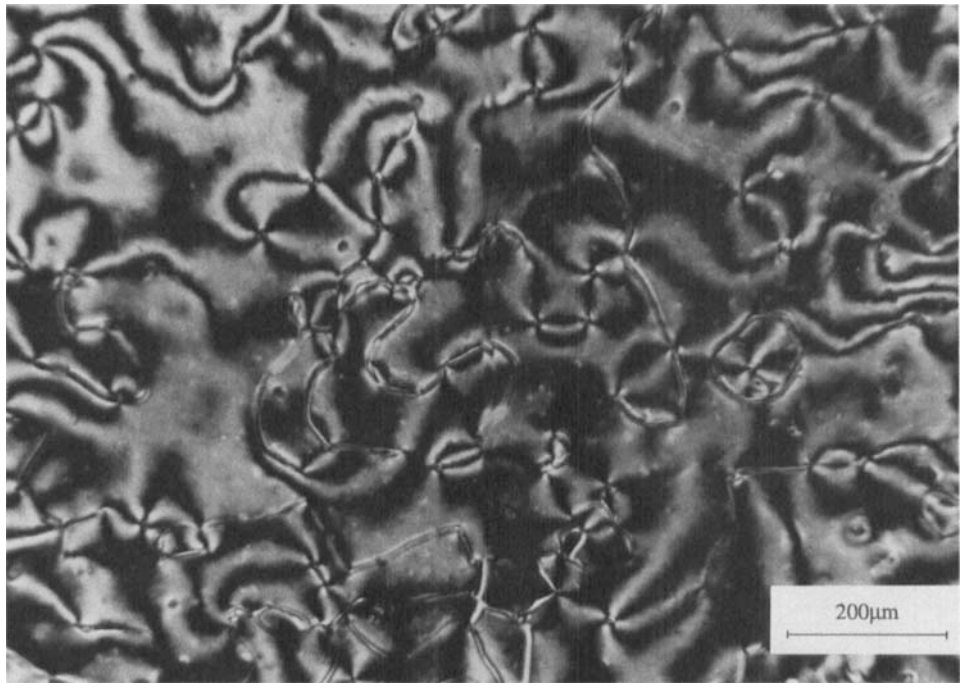


FIGURE 4 Texture observed between crossed polarisers for oligomer M at 270°C.

ignated $T_{k\rightarrow lc}$, whereas the smaller one at 314°C is the liquid crystalline to isotropic phase transition, denoted by $T_{lc\rightarrow i}$. Owing to degradation, the higher heating rate (150°C/min) was normally used to observe the liquid crystalline to isotropic transition. However, it was found that this transition could also be observed at 20°C/min for oligomers G and L as well as M. In some cases, additional transitions were seen and these are discussed below.

For G, at a rate of 20°C/min, the first heat shows a broad peak as does the first cool. However, the second heat shows 3 peaks at the temperatures quoted in Table I.

For K, at a rate of 20°C/min, 2 peaks are seen for the first heat; one at 182°C and the main one at 195°C. The lower peak can be removed by annealing at 183°C for 2 h and is attributed to an alternative crystal form.

For J, at a rate of 20°C/min, two peaks can be seen. The lower one is attributed to solvent evaporation, so the results quoted are for samples annealed at 180°C for 30 min to ensure all the DMSO is removed. However, after annealing, although the heating profile displays one transition, the cooling profile (− 20°C/min) displays two. The higher one is attributed to crystallisation as confirmed by microscopy. The lower one is still under investigation although no transition could be seen under the microscope.

Oligomers H, I, J and L appeared dark between cross polars except under shear when there was a transient brightening of the field. The liquid crystalline texture was thus identified as homeotropic. Oligomers G and M, namely those with a bromo- substituent on the central ring, showed conventional liquid crystalline textures (Figures 3 and 4); that of M is a schlieren texture typical of a nematic, whereas that of G is possibly more characteristic of a smectic. Oligomers E and F also showed schlieren textures on initial melting but these rapidly became homeotropic.

4. DISCUSSION

4.1 Trimeric oligomers. Comparing A, B, C and D.

The oligomers A, B, C and D melt to isotropic liquids. Although it was possible to reduce the crystallisation temperature by around 100°C by rapid cooling there was no DSC evidence of an isotropic to liquid crystalline transition even though it would not be expected to be as sensitive to cooling rate. In fact, the absence of liquid crystallinity in these trimer molecules is not especially surprising as their axial ratio is of the order of three which is clearly less than the critical value of 5.44 predicted by Flory[26] on purely geometrical grounds.

Replacement of the central benzene by a naphthalene moiety (oligomers C and D compared with A and B), leads to an increase in the melting point of the order of 15°C. Again this is not unexpected as for rigid molecules, the enthalpy change on melting increases more rapidly with size than the associated entropy change.

The significant influence of the direction of the ester groups on the thermal transition properties is illustrated by the observation that the trimers with the ester oxygens attached to the central group, a diol centre, (A and C), show a larger

undercooling at $-20°C$/min than the molecules with the diacid centre (B and D). This may be associated with different packing in the crystal structure.

For compound B an additional endotherm is seen on second heat, with an enthalpy value approximately twenty times less than the main endotherm. This second transition was also observed for a bought-in sample (Lancaster Synthesis), and in both cases its enthalpy can be substantially enhanced by annealing at 200°C.

4.2 Pentameric oligomers. Comparing E, F, H and I.

These compounds were identified as liquid crystalline by DSC and optical microscopy. Comparing E with F and H with J, it can be seen that the diol centred oligomers (E and H) have higher crystal to liquid crystalline transition temperatures than the diacid centred ones (F and I). As with the trimers, the difference is thought to be associated with contrasting modes of molecular packing in the crystalline phase and X-ray diffraction evidence in support of this view will be discussed in a future paper.

The consequence of substituting a central benzene (E and F) by a naphthalene moiety to give H and I, is to increase the liquid crystalline to isotropic temperature by 36°C in each case. This effect is characteristic of the well established relationship between axial ratio and mesophase stability. It is interesting to note that replacement of one of the five units by one of greater length and thickness does not prevent crystallisation; indeed comparable stability is indicated by similar values for the crystal melting point and the enthalpy change on melting. This observation is relevant to the concept of Non Periodic Layer crystallites.[27] The solid state structure of LCPs is a research area of much interest and activity. The fibre diffraction patterns of certain main-chain thermotropic copolyesters have been shown to contain features indicative of a much higher order than might be expected from packing of molecules with a random distribution of monomer units. Models to account for this order have been put forward; Non Layer Crystallites are consistent with experimental observations.[28,29] Studies on the oligomers made here show how chain sequences that are non periodic yet identical, are able to form crystalline order.

4.3 Addition of a bromine atom to the central ring. Comparing G with F and M with L.

The influence of the added bromine atom is to reduce both the crystal to liquid crystalline and liquid crystalline to isotropic transition temperatures. The effect on the crystal melting point is the more marked, and is presumably associated with the difficulty of incorporating the bulky bromine group into a lattice, while providing efficient packing for the remainder of the molecule.[30] The reduction in the liquid crystalline to isotropic transition temperature can again be explained in terms of the relationship between axial ratio of the molecule and mesophase stability.[31] It is worthy of note that the molecule G has a liquid crystalline temperature range which corresponds to that in which a number of known heat-induced polymerisations are initiated. This molecule is thus seen as a good starting point for additional study and further synthetic experiments are underway to attach polymerisable end groups.

4.4 Replacement of an end phenyl-4-benzoate group by a biphenyl group. Comparing F with L and G with M.

The effect of this biphenyl substitution is to remove the end ester links from each molecule. The consequence is that the crystal melting points are increased, pointing to the influence of the greater rigidity of the molecule in the liquid crystal phase and possibly better packing in the crystal. In contrast the liquid crystalline to isotropic transition temperature is reduced, again in accord with the expected trend with axial ratio.

4.5 Oligomers with flexible links. Comparing K with F and N with L.

The effect of replacing the central benzene ring with a flexible sequence such as $-(CH_2)_2-$—to give molecules K and N, is to prevent the formation of a liquid crystalline phase. The crystal melting temperature is also reduced as a result, (compare K with F and N with L) in fact by about the same amount as caused by the introduction of a bromine atom as discussed in 4.3. The amount of undercooling for oligomer K is 48°C at −20°C/min and is significantly greater than for any of the other oligomer models, although that for N is also substantial. This effect is probably associated with the increased number of conformations available to oligomers with flexible centres.

4.6 Biphenyl replacement of central benzene ring. Comparing J with F.

For oligomer J, the liquid crystalline to isotropic transition cannot be seen below 500°C where degradation becomes dominant even at a heating rate of 150°C/min. This particularly high liquid crystalline to isotropic transition is seen as a natural consequence of the large axial ratio.

4.7 Examining the liquid crystalline to isotropic transition.

The liquid crystal to isotropic transition has been observed for all liquid crystalline oligomers except J. It can be seen that the larger the axial ratio, the higher the $T_{lc\rightarrow i}$. For example the effect of adding the bromine atom is to reduce the axial raito and thus the liquid crystalline to isotropic transition temperature.

5. CONCLUSIONS

We conclude:

(1) For the symmetrical series studied here, liquid crystallinity is not seen for oligomers with either central flexible units or for models with only three aromatic moieties.

(2) The replacement of the central benzene by a naphthalene moiety leads to an extension of the liquid crystalline temperature range, mostly as a result of higher upper transition temperatures to the isotropic phase.

(3) The direction of the ester group, comparing diol with diacid centred oligo-

mers, is shown to affect thermal transition temperatures. It is proposed that this difference may be due to different crystalline packing.

(4) Addition of a bromine to the central ring results in a marked depression of the crystal melting point and a small reduction in $T_{lc \rightarrow i}$. The liquid crystalline temperature range is thus broadened.

(5) The replacement of a phenyl-4-benzoate group with a biphenyl moiety results in a reduction in the liquid crystalline temperature range, mostly caused by a higher crystal melting point.

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