Effect of molecular structure on mesomorphism XXI. Monodisperse tetrameric model compounds for liquid crystalline polymers

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Effect of molecular structure on mesomorphism

XXI†. Monodisperse tetrameric model compounds for liquid crystalline polymers

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Twinned dimeric mesogens having a rigid-flexible-rigid molecular structure have been shown to be appropriate models for some properties of regularly alternating (rigid-flexible)$_n$ main chain liquid crystalline polymers (lcps). A family of tetrameric monodisperse liquid crystalline model compounds chemically related to known main chain liquid crystalline polymers of the 4-alkoxyphenyl 4′-alkoxybenzoate type has been synthesized. The tetramers are nematogenic. Alternations in thermodynamic parameters (ΔH, ΔS) for the N–I transition as a function of spacer chain length indicate conformational behaviour of the internal spacers dominates mesophase properties.

1. Introduction

Oligomeric model compounds for liquid crystalline polymers are of interest because, by progressive buildup of monomeric units, it should be possible to approximate some of the thermal properties of the corresponding polymers. This concept has been shown to be effective in comparative studies relating dimeric compounds to their polymeric counterparts [2–8]. Synthesis of higher oligomeric models should give an even better approximation. The terms 'monomer' and 'oligomer' are used here in the conceptual sense [4] and do not refer to actual monomers and oligomers. The real oligomers in actual polymerizations have unreacted functional groups which can dominate their liquid crystalline properties. We feel that our conceptual oligomers are more analogous chemically to the polymers. The 4-alkoxyphenyl 4′-alkoxybenzoate group was chosen as the mesogenic unit because of its thermal stability and resistance to hydrolysis and oxidation, and further because of its ubiquity in monomers, polymers [6, 8–11], and recently in dimers [2, 4, 8, 12].

Tetrameric model compounds have been the synthetic targets of several groups. Keller [8] prepared a monodisperse compound incorporating 4-alkoxyphenyl 4′-alkoxybenzoate cores in an *A–B* sequence, but this tetramer was not mesogenic. Fradet and Heitz [13] synthesized oligomeric models using five *bis*-phenyl terephthalate cores with methylene spacers, which exhibited liquid crystallinity but were polydisperse. Kothe and Müller [14] have prepared a triaromatic-cored tetramer which is mesogenic. We wish to report here the synthesis and characterization of a series of tetrameric model compounds for liquid crystalline polymers. These compounds are monodisperse, and consist of four 4-alkoxyphenyl 4′-alkoxybenzoate mesogenic cores separated by a fixed spacer of ten methylene units in the outside
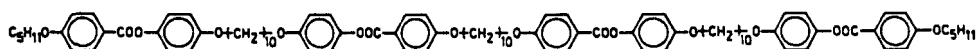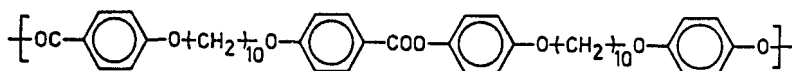
† For part XX see [1].
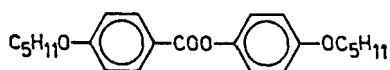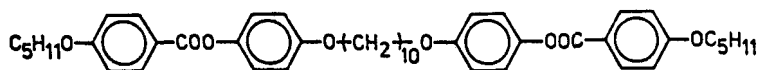
Figure 1. Structures of 4-alkoxyphenyl 4'-alkoxy benzoate monomer, dimer, tetramer and polymer.

two spacer segments, while the central spacer segment is varied from seven to ten methylene units. The terminal tails were held constant as pentyloxy. These tetramers are chemically similar to dimers and polymers made previously by our group. The analogous monomer was originally synthesized by Van Meter and Klanderman [15] (figure 1).

2. Experimental
2.1. *General*

Thermal transitions and enthalpies of the tetramers were measured on a DuPont 9900 Thermal Analysis System using a model 910 D.S.C. cell at a heating rate of 10°C per minute under a flow of dry nitrogen. Optical textures were determined using a Reichert Thermovar microscope with a Mettler FP5/52 programmable heating stage. X-ray samples were contained in a 1.5 mm diameter quartz capillary tube and the samples were run on a General Electric XRD-700 diffractometer using fast Polaroid film, ASA 3000. Samples were run as room temperature solids after having been heated to the isotropic phase or as untreated powders. Infrared spectra were run on a Mattson FTIR Infrared Spectrophotometer. Carbon-13 N.M.R. data for the tetramer of central spacer $x = 8$ was obtained on a Bruker MSL 200 solid-state

N.M.R. Proton N.M.R. data for compound *A* was obtained on a Bruker 250 MHz N.M.R.

2.2. *Preparation of materials*

The synthetic route to the tetramers is shown in figure 2. The diacid chlorides (B) and the diphenol were prepared by known routes [9].
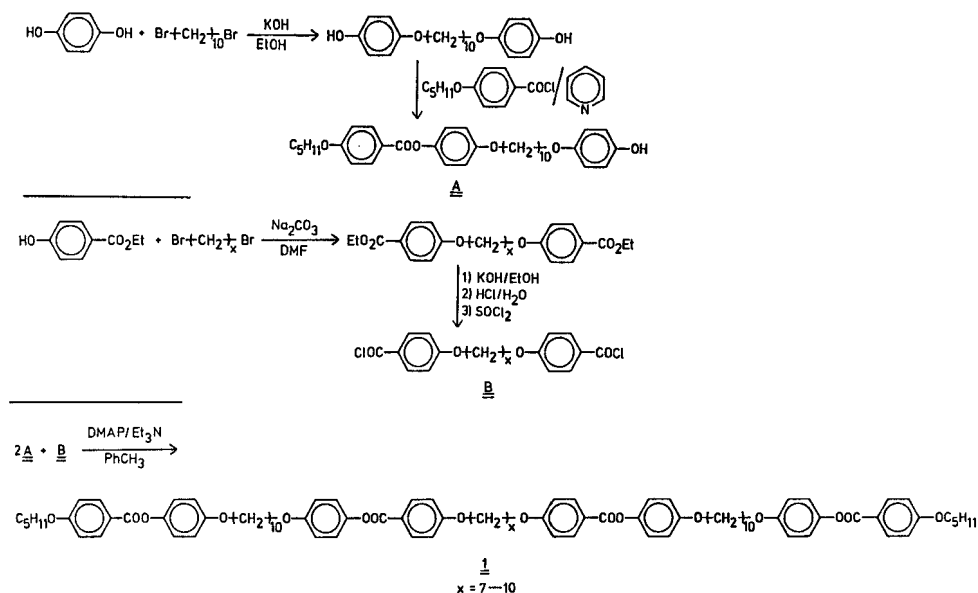

Figure 2. Synthetic route to tetramers, **1**, $x = 7$–10.

4-[[10-(4-hydroxyphenoxy)decyl]oxy]phenyl 4-(pentyloxy)benzoate, *A*, was prepared according to the following procedure. 2·15 g (6 mmol) of the 1,10-bis(4′-hydroxy-phenoxy) decane was dissolved in minimal dry pyridine (about 30 ml) at room temperature. 1·00 g (4·4 mmol) of 4-pentyloxybenzoyl chloride (Kodak) was added dropwise with stirring and the mixture was stoppered and stirred overnight. Next day, the mixture was poured into excess 3M HCl, stirred for ten minutes, filtered and washed with water. The solid product was slurried with saturated NaHCO₃ for one hour, filtered, washed well with water and air-dried. The compound was recrystallized, first from benzene and then from absolute ethanol, at least three times from each. Purity was monitored by thin layer chromatography (CH₂Cl₂, silica gel; $R_f = 0.28$). The compound exhibited a monotropic nematic phase. The highest yield obtained was 37 per cent, due to dimer formation and material loss in purification.

(*A*) K 118·2 N (78·5) I; IR (KBr) cm^{-1} 3677–3001 (broad), 2881, 2833, 1761, 1608, 1487, 1431, 1297, 1264, 1211, 1160, 1089, 1035, 832.

¹H N.M.R. (CDCl₃) δ 0·95 (t, CH₃), 1·45 (m, aliph.), 3·88 (m, CH₂–O), 4·51 (s, O–H), 6·73 (m, arom.), 6·94 (m, arom.), 7·09 (m, arom.), 8·12 (m, arom.); mass spectrometry: m/z 548 (M⁺).

The bis[4-[[10-[4-[[4-(pentyloxy)benzoyl]oxy]phenoxy]decyl]oxy]phenyl]4,4′-[α, ω-alkanediylbis(oxy)]bis(benzoate)]s, the tetramers, were prepared from compound *A* and the diacid chlorides as follows. Ten mmoles of compound *A* were placed in dry toluene (about 75 ml) under a flow of dry nitrogen. Five mmoles triethylamine,

0·5 mmoles 4-dimethylaminopyridine (DMAP), and 5 mmoles of the appropriate diacid chloride were added in that order. The mixture was refluxed for one hour (upon heating, all solids went into solution), then cooled, stoppered and stirred overnight. The solution was then filtered and the filtrate was evaporated to isolate the crude product. For the tetramers of $x = 8$ and 10, repeated recrystallizations from chloroform produced pure tetramer. For $x = 7$ and 9, purification was more difficult, requiring column chromatography (CHCl$_3$, silica gel). Yields were quite low, never greater than 12 per cent, due to separation difficulties caused by the chemical similarity between the tetramers, the precursors and byproducts. Purity was assessed by thin layer chromatography (silica gel, CHCl$_3$).

1, x = *7.* K 152·9 N 186·4 I; I.R. (KBr)—peaks virtually identical to those listed for $x = 8$. Anal. Calcd for C$_{89}$H$_{108}$O$_{16}$: C, 74·56; H, 7·59. Found: C, 74·33; H, 7·59.

1, x = *8.* K 150·4 N 192·7 I; I.R. (KBr) cm^{-1} 2910, 2850, 1738, 1608, 1511, 1283, 1254, 1205, 1171, 1083; ^{13}C N.M.R. δ 15·3, 25·4, 33·2, 87·4, 110, 115·8, 124·5, 132·6, 145·0, 155·6, 161·39. Anal. Calcd for C$_{90}$H$_{110}$O$_{16}$: C, 74·66; H, 7·66. Found: C, 74·77; H, 7·89.

1, x = *9.* K 147·2 N 182·3 I; I.R. (KBr)—peaks virtually identical to those listed for $x = 8$. Anal. Calcd for C$_{91}$H$_{112}$O$_{16}$: C, 74·77; H, 7·72. Found: C, 74·67; H, 7·82.

1, x = *10.* K 149·7 N 185·5 I; I.R. (KBr)—peaks virtually identical to those listed for $x = 8$. Anal. Calcd for C$_{92}$H$_{114}$O$_{16}$: C, 74·87; H, 7·79. Found: C, 74·44; H, 7·83.

3. Results and discussion

Table 1 lists N–I transition temperatures and enthalpies for the tetramers. Figure 3 shows a typical DSC curve for a tetramer, $x = 8$. All tetramers were nematic. The corresponding polymers and dimers also show only a nematic mesophase. It is seen from figure 4 that the nematic-isotropic transition temperatures for the tetramers are quite similar to those of the polymers, much more so than are the dimers. This is to be expected since the tetramer is structurally more analogous to the repeating rigid-flexible chemistry of the polymers. Tetramers with central spacers of seven and nine methylene units showed crystal-crystal transitions below the crystal-nematic transition while tetramers with even carbon central spacers have no such solid-solid transition. Nematic–isotropic transition temperatures, changes in enthalpy at the N–I transition, and the corresponding N–I entropy change all show an odd-even alternation (figures 4, 5, 6).

Table 1.   Enthalpies, entropies, and temperatures at N–I transition for tetramers.

1, x	ΔH_{N-I}/kJ/mol	ΔS_{N-I}/J/mol K	T_{N-I}/°C
7	18·8	40·8	186·4
8	22·5	48·2	192·7
9	20·3	44·6	182·3
10	23·0	50·2	185·5

In contrast to the decreasing N–I temperature with increasing spacer length, the magnitude of the changes in enthalpy and entropy at this transition show an increasing trend. The tetramer with a ten methylene spacer has a relatively low transition temperature but the largest enthalpy and entropy change of the four. This large entropy change indicates a very ordered mesophase, more so than that of the other three. As has been found previously in dimer and polymer compounds with
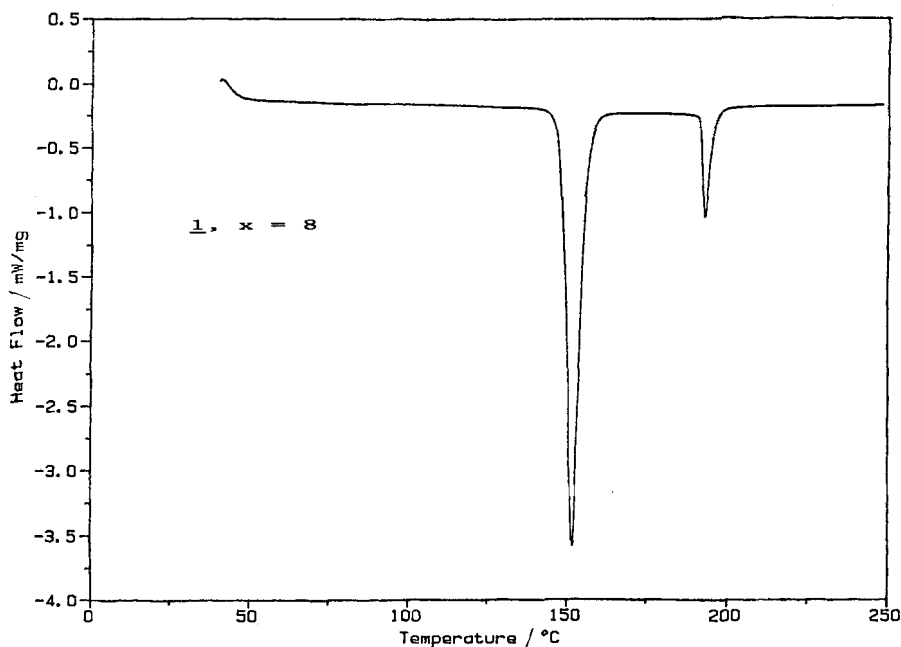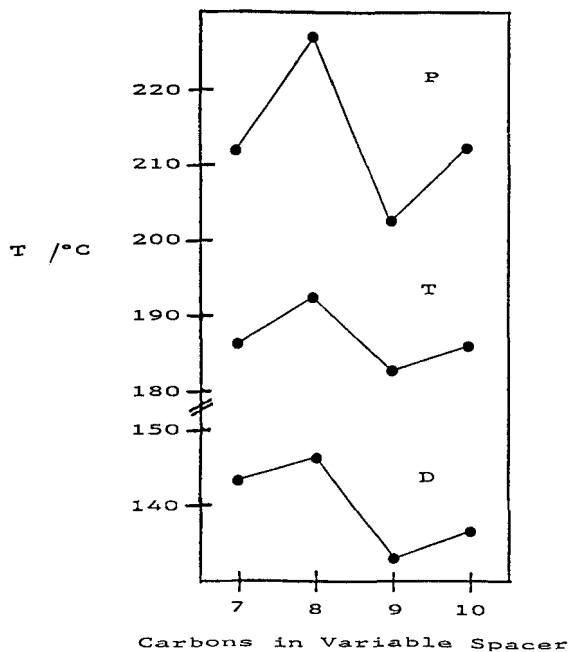
Figure 3.   D.S.C. scan of tetramer, 1, $x = 8$.

Figure 4.   Transition temperatures (N–I) for dimers (D), tetramers, (T) and polymers (P).

flexible methylene ether spacers [4, 10, 16–20], the even members of the series show the higher values of enthalpy and entropy changes. This is likely due to the differences in conformational populations between even and odd numbered spacer segments [21], with the even carbon spacers having the more extended conformational population.
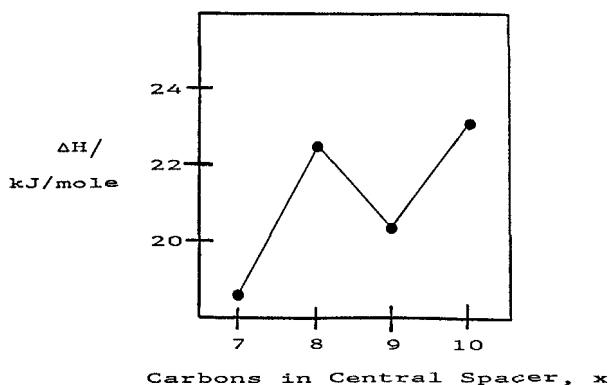
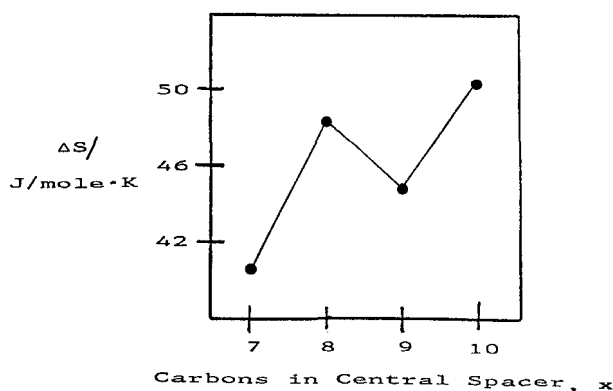Figure 5.   Enthalpy change at N–I transition for tetramers.

Figure 6.   Entropy change at N–I transition for tetramers.

The N–I transition is very sharp for these tetramers. The nematic–isotropic biphase is only approximately 1°C by optical microscopy. Comparison of the entropy at the N–I transition of the $x = 10$ tetramer ($\Delta S = 50\cdot24\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$) with the corresponding dimer ($\Delta S = 17\cdot92\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$) and monomer ($\Delta S = 1\cdot51\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$) shows a large increase in ΔS from monomer to dimer to tetramer. Normalization of the data gives values of 12·56 (tetramer), 8·96 (dimer) and 1·51 (monomer), in $\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$ per mer unit. The initial increase from monomer to dimer is large as order is imposed upon the rigid cores by linking through the flexible spacer. In the progression from two rigid cores to four, there is still a definite though smaller increase in ΔS but not so great a change; more cores are linked together and more order is imposed.

In the X-ray diffraction study, each tetramer showed a small angle maximum corresponding to about 21 Å, ranging from 20·6–22·3 Å. Model measurements show that this corresponds approximately to the length of one 'monomeric unit', if the spacer segments are extended. The X-ray data is given in table 2. X-ray diffraction studies by Azároff *et al.* [22] on the dimers and polymers corresponding to the tetramer of $x = 10$ produced values similar to these.

The tetrameric models show in general the behaviour anticipated from previous studies on the analogous dimers. However, the large alternation in N–I transition temperatures and also in the associated thermodynamic parameters resulting from such a small structural modification in the parity of the central spacer underscores the
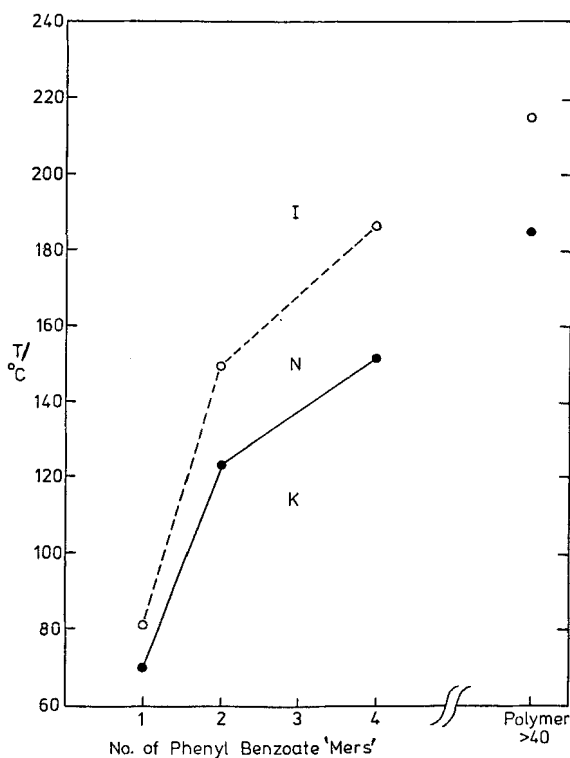
Figure 7.   Transition temperatures vs. number of 'mer' units for structures shown in figure 1.

Table 2.   X-ray diffraction data for tetramers.

x	Powder $d/\text{Å}$	Crystal from melt $d/\text{Å}$
7	21·6	20·6
8	21·9	21·9
9	22·3	21·1
10	21·9	22·3

dramatic effect of spacer conformation on mesophase behaviour. Figure 7 illustrates the trend in N–I temperatures of the analogous monomer, dimer and tetramer (of central spacer $x = 10$) towards that of the polymer as the mesogenic structure is increasingly repeated. Deuterium N.M.R. studies on the conformation of the different internal spacer segments would show how nearly the spacers of the tetramers mimic those of the polymers.

References

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