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Correlation of structure and phase behaviour for a series of modular, chiral liquid crystal diacrylates based on lactic acid

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The mesogenic properties of a family of chiral liquid crystal (LC) diacrylates based on a 4-[4-(1*R*-methyl-2-hydroxyethoxy)phenyl]phenyl 4-hydroxybenzoate core were studied as a function of different tail lengths. In general, this family of LCs was found to exhibit a strong preference for adopting the chiral smectic A phase. Systematic variation of the alkyl spacer lengths on either side of the chiral core revealed that the onset of smectic A behaviour is highly sensitive to the length of the tail adjacent to the chiral unit. However, no correlation between phase transition temperatures and the length of the spacer on the other side of the core was observed. With a fixed spacer length on the chiral side of the core, systematic changes in the length of the other tail resulted in the formation of a monotropic smectic B phase and an increased tendency to supercool.

1. Introduction

Chiral liquid crystal (LC) diacrylates are useful for the construction of ordered non-centrosymmetric polymer networks and elastomers [1]. The resulting polymers have many useful device properties, such as pyroelectricity [2], piezoelectricity [3], and tunable optical reflection properties [4, 5]. In the synthesis of these polymers, the LC diacrylates are employed either as the actual chiral building blocks [2, 4, 6, 7], or as reactive chiral dopants for crosslinking other LC monomers [3, 5, 8, 9]. At present, there are only a limited number of methods for synthesizing intrinsically chiral LC diacrylates that exhibit the desired cholesteric or chiral smectic phases [2]. Because of this, virtually no systematic structure–property studies have been performed on these chiral LC monomers to determine the effects of the various molecular components on LC behaviour. Only one study has appeared in the literature describing the effect of varying the position of the chiral centre on the properties of a cholesteric diacrylate [6].

Recently, we developed a modular synthesis of a new chiral LC diacrylate based on lactic acid that exhibits smectic A* and C* phases [7]. The ease of synthesis afforded by this modular approach permits convenient, systematic changes to be made to the components in the molecule for detailed structure–property investigations. Herein, we describe the effect of different spacer lengths on the LC properties of this system. The influence of different tail lengths on either side of the chiral mesogenic core will be discussed.

2. Results and discussion

2.1. *Monomer synthesis*

All of the compounds synthesized are based on the same central core structure, as shown below. For ease of reference, this homologous series of LCs is denoted **C*p*C*n***, where ***p*** represents the number of methylene units in the hydrocarbon tail attached directly to the phenol, and ***n*** is the number of methylene units in the tail attached to the chiral moiety through an aliphatic ether linkage. (In the case of **C*p*C0**, it denotes homologues in which the acrylate group is directly attached to the chiral moiety via a standard ester linkage, not a peroxide linkage.) It is well known that LCs with tails containing even and odd numbers of carbons behave very differently even though they may differ only slightly with respect to overall molecular length [10, 11]. Thus, for this initial structure–property investigation, only LC diacrylates with tails containing even numbers of methylene units

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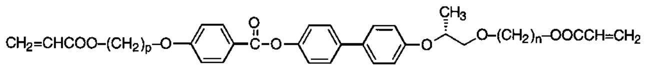
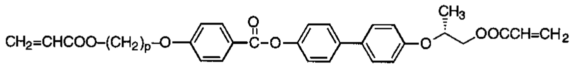
were synthesized and compared. Analogous LCs with tails containing odd numbers of methylene units will be investigated separately.


CpCn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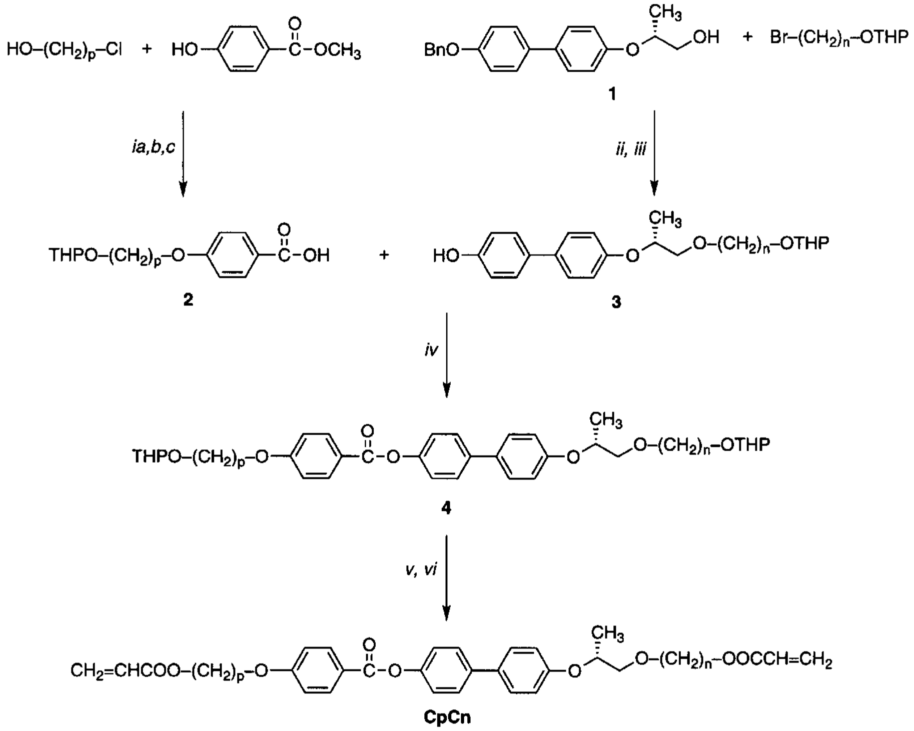
The molecules included in this study were synthesized as shown in the scheme below, using procedures described in a previous publication [7]. One half of each molecule in the series is first built up using chiral alcohol **1** as a central starting point. Compound **1** is synthesized by reacting the tosylate of *S*-ethyl lactate with the anion of monoprotected 4,4′-biphenol, followed by reduction with lithium aluminum hydride as described previously. Tetrahydropyranyl (THP) ether-protected ω-bromoalkanol is then added to **1** via a nucleophilic substitution reaction, and the resulting product is debenzylated via standard hydrogenation techniques to afford phenol **3**. The benzoic acid half of each molecule is built up separately from methyl 4-hydroxybenzoate and the appropriate ω-choroalkanol through a series of nucleophilic substitution, THP protection of the alcohol, and saponification of the ester to yield the acid **2**. Subsequent coupling of the fragments **2** and **3** using dicyclohexylcarbodiimide (DCC) affords the THP-protected form of the final diacrylates **4**. Removal of the THP groups using magnesium bromide, followed by reaction of the resulting diols with acryloyl chloride, affords the diacrylates **C*p*C*n***. For the series of homologues **C*p*C0** in which an acrylate group is directly attached to the core, the hydroxy group on the appropriate end of the chiral alcohol **1** is first protected as a THP ether. After coupling of the two halves of the molecule with DCC to form the central core as mentioned above, removal of the THP groups with magnesium bromide and reaction of the resulting diols with acryloyl chloride affords the desired diacrylates **C*p*C0**.

2.2. *Mesomorphic structure–property relationships*

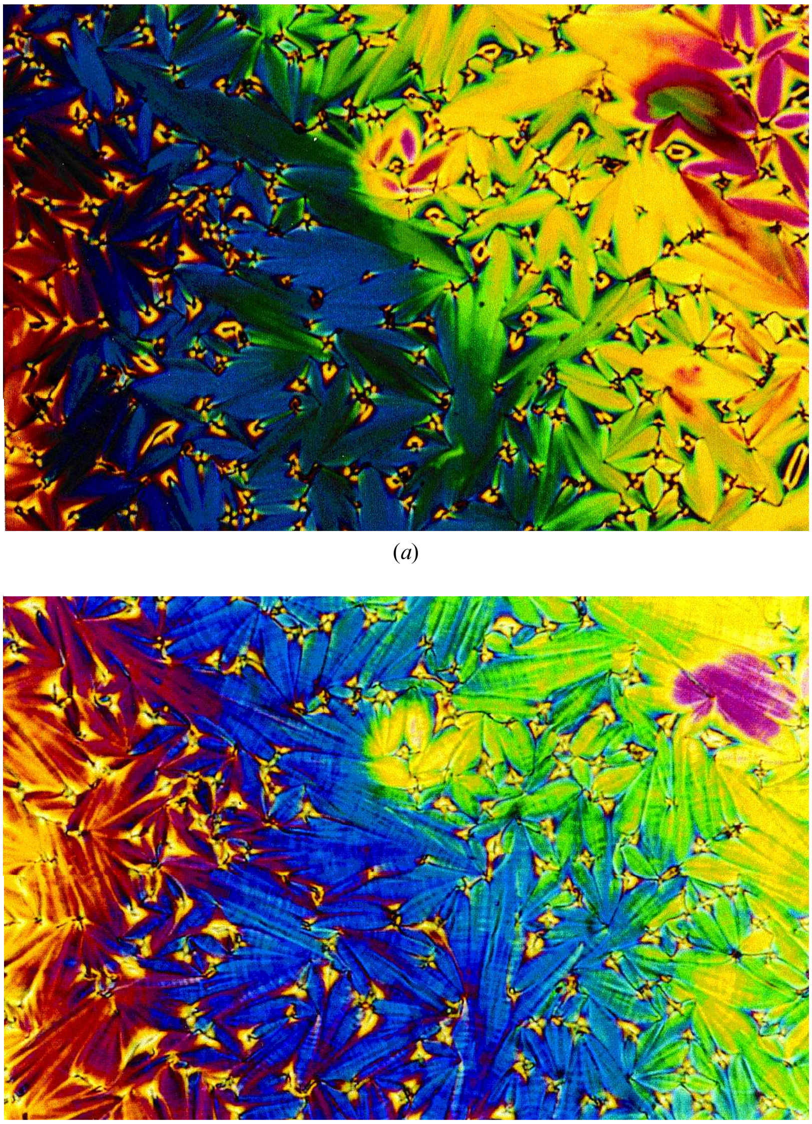
The new family of LC diacrylates discussed in this paper can be considered mesogenic molecules having a non-symmetrical core structure consisting of a central biphenyl unit linked to a chiral centre on one side and a benzoate moiety on the other side. The precursors of the resultant diacrylates, namely the corresponding diols, are mainly crystalline materials with only a slight tendency to form LC phases. The introduction of acrylate groups onto both ends of the molecule induces the



Scheme. *ia*) K_2CO_3, MEK, Δ; *ib*) DHP, CH_2Cl_2, H^+; *ic*) LiOH, MeOH, H_2O; *ii*) NaH, DMF, Δ; *iii*) H_2, 10% Pd/C; *iv*) DCC, CH_2Cl_2, DMAP; *v*) $MgBr_2$, Et_2O; *vi*) CH_2=CHC(O)Cl, NEt_3, CH_2Cl_2.

formation of an LC structure. For example, figure 1 shows representative fan-like optical textures for several of the diacrylates upon cooling the samples below their clearing temperature (T_i). These textures are consistent with smectic-like structures. Variable temperature X-ray diffraction analysis is able to elucidate further the type of the smectic phase formed by the chiral diacrylates: the X-ray diffraction profiles for all the samples under investigation are characterized by an intense diffraction peak at small angles and an amorphous halo at wide angles, consistent with a layered structure. The X-ray diffraction profiles of **C12C6** at different temperatures are presented in figure 2. As can be seen in figure 2, there is only a broad amorphous halo in the X-ray diffraction profile above the T_i, figure 2 (*a*). Below T_i, an intense small angle diffraction peak appears, figure 2 (*b*), the position of which does not change appreciably upon cooling (± 1 Å), figure 2 (*c*). The *d* spacing value for this peak (47 Å) is in good agreement with the calculated extended length of the diacrylate molecule (48 Å). Similar behaviour is exhibited by the other members of this series.

Figure 3 shows the primary X-ray diffraction spacing for the LC phases of several of the diacrylates plotted as a function of the number of methylene units in the two spacer chains. Superimposed on these plots are their calculated molecular lengths as a function of increasing spacer length, as dashed lines. One trend that is evident from figure 3 is that an increase in the length of either spacer (***p*** or ***n***) results in a corresponding increase in the observed *d* or layer spacing, consistent with an orthogonal SmA_1 monolayer structure [12]. The presence



(*a*)

(*b*)

Figure 1. Fan-like optical textures of compound **C12C6** at (*a*) 58.2°C and (*b*) 37.3°C. The magnifications are both 160 ×.

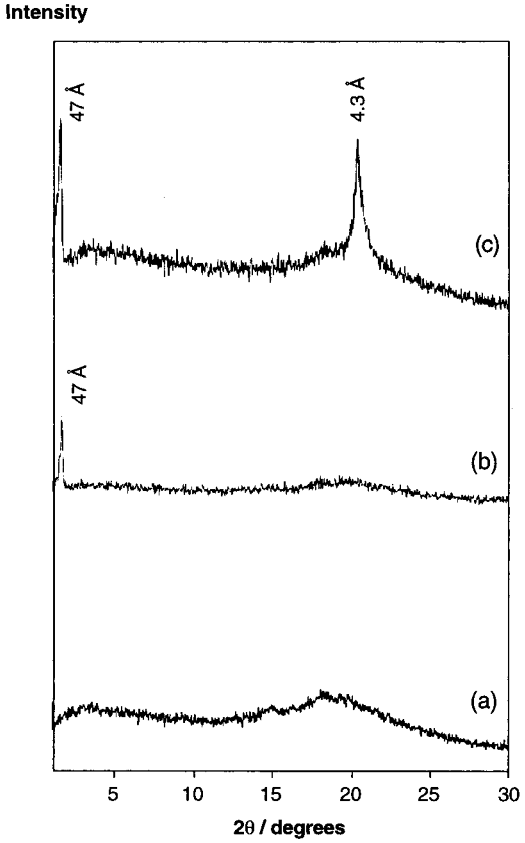


Figure 2. X-ray diffraction profiles of compound **C12C6** at (*a*) 66°C (isotropic), (*b*) 50°C (SmA*), and (*c*) 30°C (SmX).

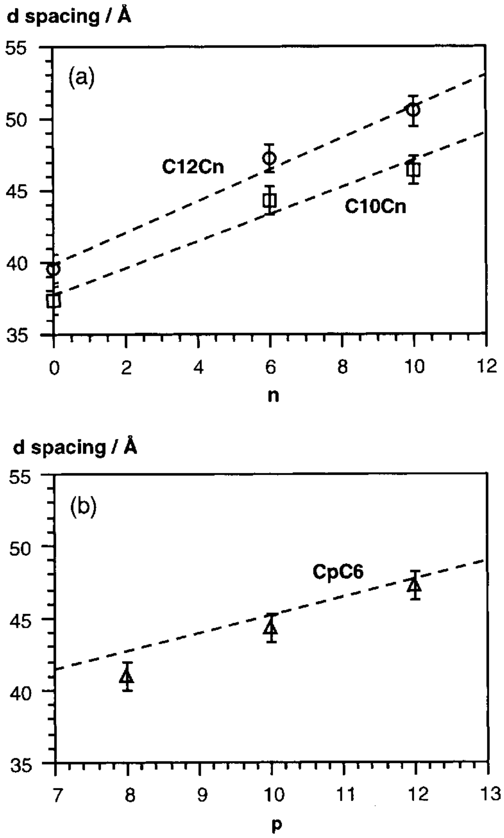


Figure 3. Plots showing correlation between observed diffraction layer spacing (solid data points) and calculated molecular length (dashed lines) for chiral LC diacrylates with (*a*) different tail lengths ***n***, and (*b*) different tail lengths ***p***.

of a SmA_1 phase has previously been proven for the diacrylate **C10C6** by performing two-dimensional X-ray diffraction on a magnetically oriented sample [7]. The Debye–Scherrer X-ray diffraction profile of a sample of **C10C6** aligned in a strong magnetic field exhibits only an intense low angle reflection split into two spot-like arcs along the *y*-axis and a similarly split diffuse wide angle reflection along the orthogonal *x*-axis, consistent with a SmA phase. Because these LC diacrylates also possess an enantiomerically pure stereocentre, the smectic phase should be considered a SmA_1^* phase [12].

Unfortunately, the presence of the stereocentre in these diacrylates does not induce sufficient tilting of the smectic structure to generate a stable SmC* phase, even with longer spacer lengths. Only the **C10C6** diacrylate forms a metastable, monotropic SmC* phase upon cooling, but it exists only over a very narrow temperature range [7]. The reason for the lack of a stable SmC* phase in these compounds is unclear at this time. One possibility is the location of the chiral centre with respect to the components of the mesogenic core. It has been found that non-polymerizable biphenyl benzoate containing mesogens with a chiral aliphatic tail often form chiral tilted smectic phases only if the chiral centre is located on the alkoxybenzoate part of the molecule [13–17]. In our LC diacrylates, the chiral centre is attached directly to the biphenyl core through an ether connection, a feature that has not been previously investigated.

A second structure–property relationship found for these compounds is that changing the spacer lengths (***p***, ***n***) results in a change of the T_i, but the effect of varying ***n*** on the onset of clearing is very different from the effect of varying ***p*** (see the table). An increase in the number of methylene groups in the spacer adjacent to the chiral centre (***n***) results in a systematic decrease in T_i, whereas there is no regularity in the change of T_i when the number of methylene units in the other spacer (***p***) is varied. Of particular interest in the correlation of spacer length with mesogenic properties in this series of diacrylates is the appearance of additional peaks in the (DSC) cooling curves when ***p*** is increased to 12 methylene groups (i.e. LCs with the structure **C12C*n***). As an example, the DSC cooling curves of two representative compounds **C12C0** and **C10C10** are shown in figure 4. For both compounds, the highest temperature transition

Table. Observed onsets of T_i (°C) for chiral LC diacrylates of varying tail lengths upon cooling from the isotropic melt. The onset temperatures were determined by variable temperature optical microscopy.

p	0	6	10
8	73	58	50
10	81	71	56
12	85	63	54

corresponds to an I–SmA$_\mathrm{I}^*$ transition (T_i), and the lowest temperature transition corresponds to a crystallization event. Although T_i does not change appreciably with cooling and heating rate, figures 4(*a*) and 4(*c*), the crystallization temperature was found to be highly dependent upon the cooling rate for these compounds. For **C12C0**, one can also observe an additional peak between T_i and the crystallization temperature upon cooling, figure 4(*a*), which is absent for **C10C10**. Simultaneous with this transition is a change in the observed fan-like optical texture characteristic of the SmA$_\mathrm{I}^*$ phase, figure 1(*a*) to a slightly different fan texture with striations in the fan-like domains, figure 1(*b*). This behaviour is consistent with a transition from the SmA$_\mathrm{I}^*$ phase to another smectic phase (SmA$_\mathrm{I}^*$–SmX). It is also important to note that all the systems studied show a strong tendency to supercool.

The kinetics of crystallization in these compounds were also found to be highly dependent upon the temperature at which crystallization is allowed to occur. At certain temperatures below the SmA$_\mathrm{I}^*$–SmX transition point, the crystallization time is long enough for the new SmX phase to be sufficiently long-lived to permit X-ray characterization of its structure. Instead of a single intense small angle diffraction peak with a broad low intensity amorphous halo, the X-ray diffraction profile of the SmX phase exhibits a small angle peak with a sharper wide angle peak of nearly equal intensity. The positions of these diffraction peaks do not change during the transition from the SmA$_\mathrm{I}^*$ to the SmX phase; only the intensities and the sharpness of the wide angle peaks do. For example, this phenomenon can be clearly seen when the X-ray diffraction profiles of **C12C6** at different temperatures are compared, figures 2(*b*) and 2(*c*). These data suggest that the SmX phase is a SmB* phase in which there is average hexagonal ordering of the mesogens in the layers [12]. It should be noted that this SmB* phase does not appear upon heating and that extended annealing of this phase, or cooling it below a certain temperature, readily initiates the onset of crystallization.

Non-polymerizable chiral LCs with a similar central core based on 4,4′-biphenol, hydroxybenzoic acid, and a related chiral centre lacking an ether connection to the terminal alkyl chain (i.e. not derived from lactic acid) have been reported and characterized by Furukawa

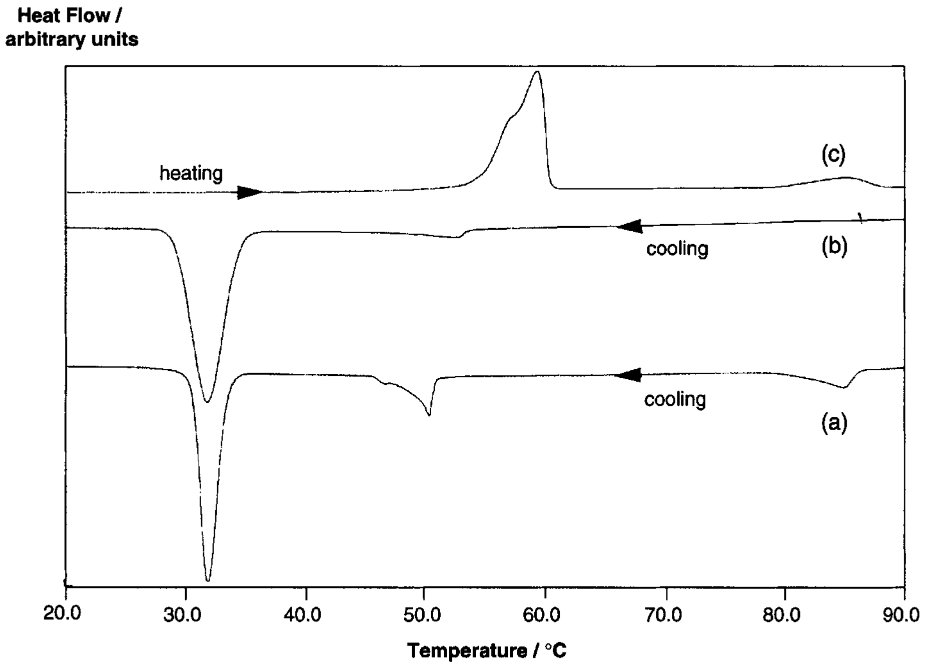


Figure 4. DSC profiles of (*a*) **C12C0** (cooling at 1°C min^{-1}), (*b*) **C10C10** (cooling at 4°C min^{-1}), and (*c*) **C12C0** (heating at 5°C min^{-1}).

et al. [18]. Depending on alkyl tail length, several molecules in this series display a similar tendency to form the SmA* phase and even occasionally a monotropic SmB* phase. In addition, the inclusion of a polar lateral substituent on the biphenol core unit adjacent to the chiral centre appears, in these systems, to afford enantiotropic SmC* phases with respectable spontaneous polarization values [18]. This provides an alternative method for enhancing the stability of the SmC* phase in our **C*p*C*n*** diacrylates based on lactic acid, and a direction for future work.

3. Conclusion

Chiral LC diacrylates based on a 4-[4-(1*R*-methyl-2-hydroxyethoxy)phenyl]phenyl 4-hydroxybenzoate core exhibit a strong tendency to form SmA* phases. Systematic variation of the alkyl spacer lengths on either side of the chiral core revealed two trends in the smectic LC behaviour of these molecules: (1) the onset of SmA* behaviour is highly sensitive to the length of the tail adjacent to the chiral unit; (2) a more ordered monotropic SmB* phase forms when the tail in the benzoate portion of the mesogen reaches 12 methylene units. Except for one member of the homologous series, variation of tail length is insufficient to induce tilt in these materials to generate ferroelectric SmC* phases for the convenient synthesis of piezoelectric materials. However, the presence of the chiral centre and dual acrylate groups allows these polymerizable mesogens to form chiral polymer matrices, which may be potentially useful in polymer-dispersed LC devices. When mixed with low molecular weight LCs, the chirality of the resulting LC networks may induce complex interactions on the encapsulated fluid mesogens, thereby modifying their orientation and switching behaviour. The LC diacrylates may also be used as chiral crosslinking agents in the polymerization of LC monoacrylates for the preparation of a new type of chiral LC elastomer. In these elastomers, the chiral mesogenic units will be the network junction points, rather than dangling side chains as in contemporary chiral LC elastomers. By varying the amount of chiral LC diacrylate incorporated, it should be possible to control simultaneously crosslink density and chiral content in these materials. This would in turn influence the LC structure and mechanical properties of these elastomeric networks, as well as any piezoelectric properties if these materials can be macroscopically aligned. Such investigations are currently in progress and will be discussed in subsequent publications.

4. Experimental

4.1. *Characterization techniques*

Initial phase determination and the corresponding transition temperatures were determined using a Leica DMRXP POL microscope equipped with a Linkam THMSE 600 hot stage controlled by a Linkam TP 92 temperature controller (accuracy ± 0.1°C). Photographs of the observed optical textures were obtained with a Wild MPS 48/52 automatic camera assembly. DSC data were obtained using a Perkin–Elmer DSC-7 under a nitrogen atmosphere. Low angle X-ray powder diffraction profiles were obtained using an Inel CPS 120 powder diffraction system using monochromatic CuK_α radiation. This system was equipped with an Inel programmable capillary oven with an accuracy of ± 1°C for variable temperature studies. Molecular lengths of the LCs were calculated using Chem3D Pro using MM2 energy minimization.

4.2. *Materials*

Homologues **C*p*C*n*** were synthesized using procedures similar to those published for **C10C6** but employing different length ω-bromoalkanols [7]. Characterization data collected (^{1}H NMR, ^{13}C NMR, FTIR, high resolution mass spectrometry) for all compounds and intermediates synthesized were consistent with their structures and similar to that published for **C10C6** [7]. All starting materials were purchased from the Aldrich Chemical Co. and used without further purification. All solvents were purchased from Fisher Scientific and used directly from the bottle.

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