Liquid crystal dimers and higher oligomers: between monomers and polymers

Corrie T. Imrie* and Peter A. Henderson

The underlying theme of this *Critical Review* is the relationship between molecular structure and liquid crystalline behaviour in a class of materials referred to as liquid crystal oligomers. For the purposes of this review, a liquid crystal oligomer will be defined as consisting of molecules composed of semi-rigid mesogenic units connected *via* flexible spacers. Much of the review will be devoted to structure–property relationships in the simplest oligomers, namely dimers, in which just two mesogenic units are connected by a single spacer. Along the way we will see how this molecular architecture has been exploited to address issues in a range of quite different areas and has given rise to potential applications for these materials. On the whole, only compounds in which the mesogenic units are linked essentially in a linear fashion will be considered while structures such as liquid crystal dendrimers and tetrapods fall outside the scope of this review. The review will be of interest not only to scientists working directly in this area but in particular to those interested in understanding the relationships between structure and properties in polymers, and those designing materials for new applications (231 references).

A historical perspective—why the interest?

Today's considerable research activity in liquid crystal oligomers can be traced back to the early 1980s and specifically the development of semi-flexible main chain liquid crystal polymers.[1] These polymers consisted of mesogenic units separated by flexible spacers, most commonly alkyl chains, and were the focus of intense research activity arising not only because of their technological potential[2] but also on a more fundamental level because they exhibited a range of unusual liquid crystalline behaviour. The most striking example of such behaviour was the dramatic dependence of their transitional properties on the length and parity of the flexible spacers linking the mesogenic units; for example, Fig. 1 shows the dependence of the nematic–isotropic transition temperature and the associated entropy change (expressed as the dimensionless quantity $\Delta S/R$) on the number of carbon atoms in the flexible spacer for a homologous series of polymers, the α,ω-[4,4′-(2,2′-dimethylazoxyphenyl)]alkanedioates,[3] **1**.

The pronounced dependence of both these quantities on the length and parity of the flexible spacer was quite different to the behaviour of conventional low molar mass materials consisting of molecules comprising a single mesogenic core attached to which were one or two alkyl chains. Varying the number of carbon atoms in these terminal chains was known

Chemistry, School of Natural and Computing Sciences, University of Aberdeen, Meston Building, Aberdeen, UK, AB24 3UE
E-mail: c.t.imrie@abdn.ac.uk; Fax: 44 1224 273105; Tel: 44 1224 272910

Corrie T. Imrie

Corrie Imrie is presently a Professor of Chemistry and Head of the School of Natural and Computing Sciences at the University of Aberdeen. After graduating from the University of Southampton in 1984 he remained there to undertake a PhD under the supervision of Geoffrey Luckhurst focussed on liquid crystal dimers. In 1987 he was awarded a Fellowship by the Royal Commission for the Exhibition of 1851 which he held in Southampton. In 1989 he moved to the University of Massachusetts at Amherst to work as a research fellow with Frank Karasz looking at side-group liquid crystal polymers. He joined the University of Aberdeen in 1992 as a lecturer in chemistry. His research interests now include liquid crystals, polymer chemistry, ionic conductivity and thermal analysis.

Peter A. Henderson

Peter Henderson is currently a Teaching Fellow at the University of Aberdeen. He recently completed a post-doctoral position at the Military University of Technology in Warsaw, Poland, with Roman Dąbrowski, looking at ortho-conic antiferroelectric liquid crystals. He received his PhD from Aberdeen under the supervision of Corrie Imrie. His thesis was on structure–property relationships in liquid crystal dimers and oligomers. His research interests now include liquid crystal oligomers, novel molecular architectures and the biaxial nematic phase.

1
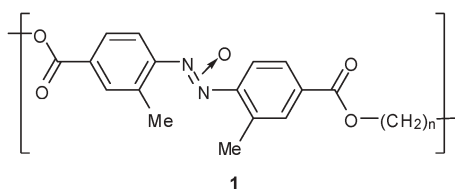
to have, by comparison, a very weak effect on the transitional properties.[4] Other examples of unusual behaviour seen for these polymers included nematic–nematic transitions[5] and novel alternating smectic phases.[6]

The semi-flexible polymers, therefore, provided a demanding challenge to our understanding of self-assembly in condensed phases and this was tackled by both experimental investigations and the development of molecular theories. The inherent structural heterogeneity of such polymers, however, greatly complicated both these tasks. An alternative approach was identified by Griffin and Britt who sought a monodisperse low molar mass compound whose behaviour encapsulated the essential molecular physics of the polymeric system.[7] They proposed that the fundamental structural repeat unit of the polymer contained two mesogenic units connected *via* a spacer and studied the behaviour of such compounds. Several names

have been used to refer to these materials including dimesogens or Siamese twins but these have now been superseded by the preferred name of liquid crystal dimers. Griffin and Britt's premise proved to be correct in that, and as we will see, the behaviour of dimers is indeed strongly reminiscent to that of the polymers. It is worth noting that Griffin and Britt did not in fact discover liquid crystal dimers but rather that the two previous reports of such materials had made little impact and essentially been overlooked.[8,9]

The initial interest in liquid crystal dimers was triggered, therefore, by their role as model compounds for semi-flexible main chain polymers[10] and later as model compounds for side group liquid crystal polymers,[11] but it soon became apparent, however, that dimers were of significant interest in their own right and exhibited quite different behaviour to conventional low molar mass mesogens.[12–14] These studies have now resulted in the discovery of a range of new phase behaviour and this will be described in this review. Although there are many striking similarities between the transitional behaviour of the dimers and semi-flexible polymers, there are also many differences and more recently in order to investigate how the liquid crystal properties evolve from dimers to polymers a range of higher monodisperse oligomers have been reported. We will also see how these molecular architectures are being used to develop new materials to study a range of other issues such as, for example, in the search for the biaxial nematic phase. The focus of this review, therefore, is principally molecules in which liquid crystal groups are interconnected *via* flexible spacers and on the whole in a linear sense. Other types of assemblages including mesogenic groups and flexible spacers, for example dimers[15] and tetrapodes,[16] and non-linear discotic[17] and rod/disc[18] oligomers fall outwith the scope of this review.

Archetypal behaviour of liquid crystal dimers: dramatic odd–even effects

The vast majority of low molar mass liquid crystals are composed of molecules consisting of a single semi-rigid or mesogenic core attached to which are one or two terminal alkyl chains.[4] In essence, it is the anisotropic interactions between the cores, normally consisting of phenyl rings linked through short unsaturated groups, that give rise to the observation of liquid crystallinity, while the alkyl chains tend to lower the compound's melting point so allowing for the observation of liquid crystalline behaviour. Indeed, for many years such a structure was considered to be a prerequisite for the observation of liquid crystalline behaviour but this situation changed dramatically during the 1980s when many non-conventional molecular structures were shown to support liquid crystallinity.[19] Liquid crystal dimers were one of these new molecular architectures and as we have seen, contravened conventional wisdom by consisting of molecules having a highly flexible core rather than a semi-rigid one. Indeed in this respect, the structure of a liquid crystal dimer actually represented an inversion of the conventional molecular design for low molar mass mesogens.

Liquid crystal dimers can be divided into two broad classes: symmetric and non-symmetric. In a symmetric liquid crystal
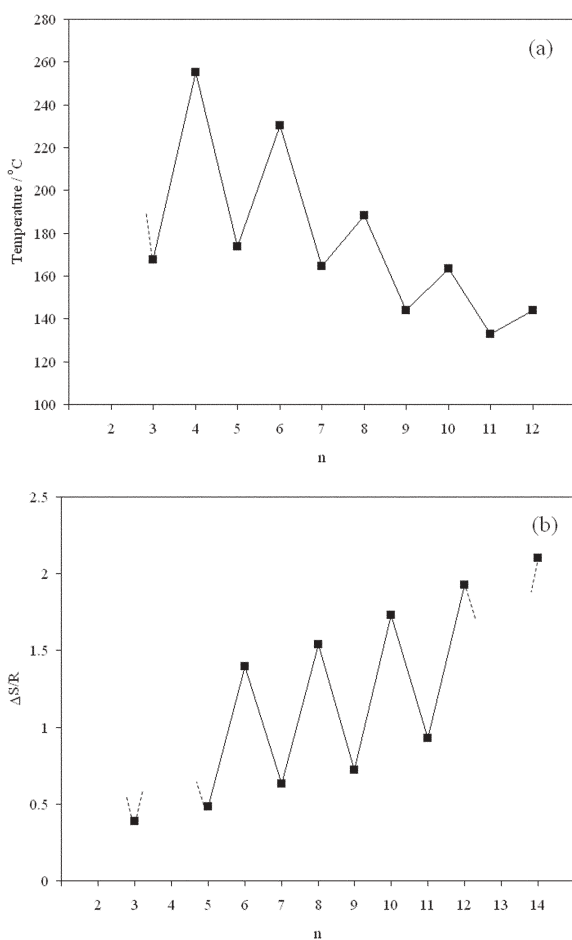

Fig. 1 The dependence of (a) the nematic–isotropic transition temperatures, T_{NI}, and (b) the associated entropy change, $\Delta S_{NI}/R$, on the number of methylene groups in the flexible spacers for the α,ω-[4,4′-(2,2′-dimethylazoxyphenyl)]alkanedioates.[3]

This journal is © The Royal Society of Chemistry 2007

Chem. Soc. Rev., 2007, **36**, 2096–2124 | 2097

dimer the two mesogenic units are identical whereas they differ in structure in a non-symmetric dimer. The most extensively studied series of liquid crystal dimers is the BCBOn series, the α,ω-bis(4-cyanobiphenyl-4′-yloxy)alkanes, **2**,
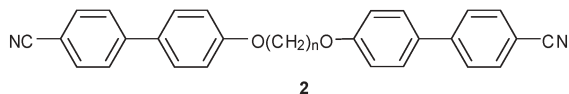
and this is the only series for which such a large range of spacer chain lengths, spanning a single to twenty two methylene units, have been prepared.[20,21] Normally, and mainly for synthetic considerations, only dimers containing spacers having between 3 and 12 carbon atoms are reported in the literature and thus, this series is particularly valuable in helping us understand the behaviour of liquid crystal dimers. All 22 homologues belonging to this series exhibit nematic behaviour and the dependences of their melting and nematic–isotropic transition temperatures, T_{NI}, and the entropy change associated with the nematic–isotropic transition, $\Delta S_{NI}/R$, on the length of the spacer are shown in Fig. 2. The nematic–isotropic transition temperatures can be seen to clearly alternate for short spacer
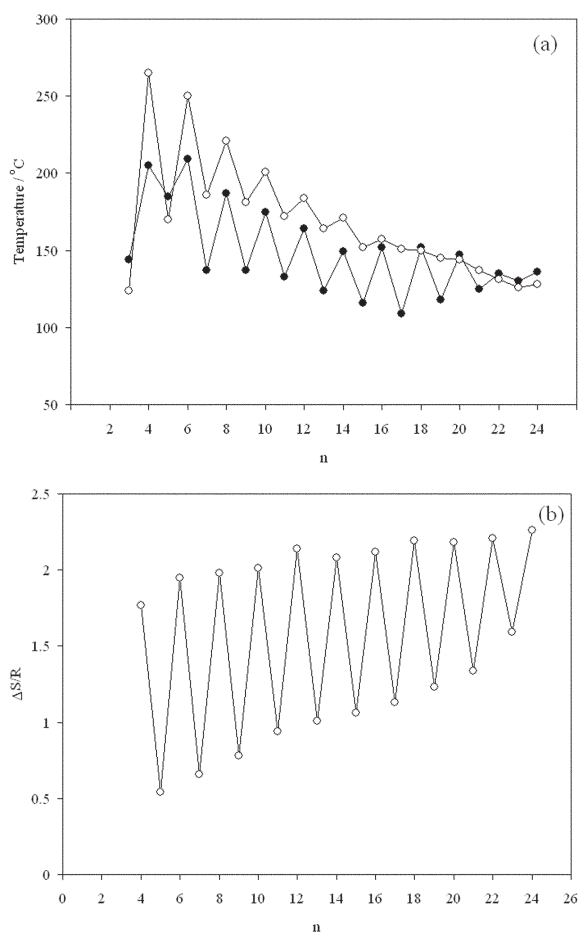

Fig. 2 The dependence of (a) the melting (●) and nematic–isotropic (○) transition temperatures, T_{NI}, and (b) the entropy change associated with the nematic–isotropic transition, $\Delta S_{NI}/R$, on the number of methylene groups in the flexible spacer for the α,ω-bis(4′-cyanobiphenyl-4′-yloxy)alkanes.[21]

lengths with the even members exhibiting the higher values but this alternation is attenuated strongly on increasing spacer length. Indeed, for spacer lengths of 14 and higher the effect has been extinguished and T_{NI} decreases essentially monotonically on increasing the number of carbon atoms in the spacer. It is worth noting that the melting points of the dimers also show an alternation in which again the even members of the series exhibit the higher values but which tends not to be attenuated on increasing spacer length. The entropy change associated with the nematic–isotropic transition, $\Delta S_{NI}/R$, also shows a pronounced alternation on varying the length and parity of the spacer which remains marked even for the longest spacers. Typically the transitional entropy change for an even member is about three times larger than that exhibited by an odd member. There is, however, a small decrease in the absolute size of the alternation. It may also be argued that the alternation is attenuated in a relative sense on increasing the spacer length because the values of $\Delta S_{NI}/R$ increase with increasing spacer length but the difference between the n and $n + 1$ homologue does not. Hence, the ratio of the values of $\Delta S_{NI}/R$ for n and $n + 1$ homologues decreases as n increases. In summary, the behaviour shown in Fig. 2 represents what might be considered to be archetypal behaviour for a series of liquid crystal dimers.

The dramatic odd–even effects seen in the transitional properties of dimers on varying the length and parity of the spacer are most often attributed to the dependence of the molecular shape on the number of atoms linking the two mesogenic units, and by considering the spacer to exist in its all-*trans* conformation, see Fig. 3. Specifically, an even-membered dimer has a zigzag shape in which the mesogenic units are anti-parallel whereas an odd-membered dimer has a bent shape in which the mesogenic units are inclined to each other. The structure for an even-membered dimer is then considered to be more compatible with the molecular organisation found in the nematic phase than is the bent shape seen for odd-membered dimers, and it is this greater compatibility which results in, for example, the higher nematic–isotropic transition entropies found for the even members. This often invoked but overly simplistic interpretation would predict, however, that the transitional entropy for an even-membered dimer with its parallel mesogenic groups
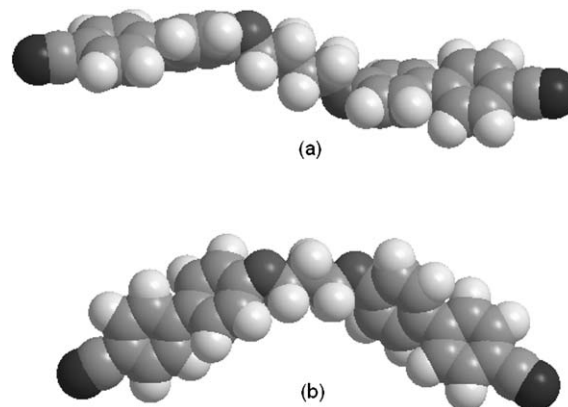

Fig. 3 The molecular shape of (a) an even- and (b) an odd-membered liquid crystal dimer with the spacer in the all-*trans* conformation.

should be comparable to that of a conventional low molar mass mesogen while that shown by an odd-membered dimer should be considerably smaller. This in fact is not the case and it is the odd-membered dimer which behaves like a conventional low molar mass mesogen while the even-membered dimers exhibit considerably higher entropy changes.

This interpretation of the transitional properties of dimers has completely neglected the flexibility of the spacer and a more realistic interpretation of the dependence of the transitional properties on the length and parity of the spacer must include a wide range of conformations and not solely the all-*trans* arrangement.[12] In the isotropic phase approximately half the conformers of an even-membered dimer are essentially linear whereas for an odd-membered dimer just 10% are linear. The conformational distribution will change at the isotropic–nematic phase transition with the more anisotropic conformers being favoured in the nematic phase. The extent to which the conformational distribution will be modified depends on the conformational energy of the anisotropic conformers which proves to be higher for odd than for even-membered dimers. Hence, at the transition to the nematic phase for even-membered dimers many of the bent dimers are converted to a linear form which enhances the orientational order of the nematic phase resulting in a larger nematic–isotropic entropy than would be expected for a conventional low molar mass mesogen. By comparison, for an odd-membered dimer the difference in free energy between the bent and linear conformers is such that the orientational order of the nematic phase is insufficient to convert bent conformers into linear conformers. Thus, the orientational order of the nematic phase is not enhanced and a smaller nematic–isotropic entropy is observed.

A number of molecular field theories have been developed, most notably by Luckhurst and his co-workers, for these flexible molecules which encapsulate this synergy between conformational and orientational order.[21] A key feature of these theories is how the conformational state of the spacer is described from which the conformational energies may be calculated. The two extreme models used to do this either allow for a continuous variation in the torsional angles along the spacer or restrict the torsional angles to three discrete values corresponding to the *trans*, *gauche*(+) or *gauche*(−) conformations of a given link in the chain, the so-called rotational isomeric state model. Both approaches have been used in predicting the properties of nematic liquid crystal dimers and the most striking difference in these predictions is that the discrete model predicts a far greater alternation in both the transition temperatures and entropies than the continuous model. In addition these alternations are attenuated much faster in the continuous model than in the discrete model as the spacer length is increased. Comparing these predictions to the data shown in Fig. 2, which, as we have already noted, constitute the most complete set in the literature by which to test these theories, it is clear that the transitional properties of dimers are better represented using the continuous model for the conformational states. Within such a framework, the attenuation in the alternation seen for the transitional temperatures can be accounted for in terms of torsional fluctuations about the energy minima which results in a loss of orientational correlations. The alternation seen in
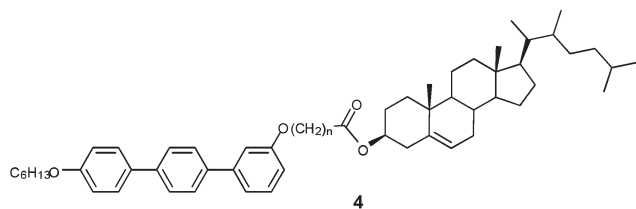
the melting point of these dimers, see Fig. 2, may indicate that the change in the conformation statistical weights of the spacer on melting is small for even-membered spacers but large for odd-membered compounds. Alternatively, it may reflect the ease of packing of even dimers with their elongated shape into a crystal lattice in comparison to the bent shape of the odd dimers. It should be noted, however, that this regular dependence of the melting point on the length of the spacer does not extend to all dimer series but typically only those showing nematic behaviour.

The magnitudes of the alternations seen for the nematic–isotropic transition temperatures and associated entropy changes as the length and parity of the spacer are varied are strongly dependent on the nature of the group linking the spacer to the mesogenic units. Changing the spacer, for example, from being ether-linked, *i.e.* $O(CH_2)_nO$, to methylene-linked, *i.e.* $(CH_2)_{n+2}$, results in decreased transition temperatures but this reduction is greater for odd-membered spacers than for even.[22–24] By contrast, the entropy change is higher for an even-membered methylene linked dimer than for the corresponding ether-linked material but this trend is reversed for odd members. Thus the magnitudes of the alternations seen in these properties are greater for the methylene- than the ether-linked materials. These rather surprising differences in transitional behaviour have been interpreted by Luckhurst and co-workers in terms of the differences in molecular geometry and specifically, the bond angle between the *para* axis of the mesogenic group and the first bond in the spacer.[25–27] For the ether-linked materials this bond angle is 126.4° while for methylene-linked dimers it is 113.5°. This difference means that the all-*trans* conformation of an ether-linked dimer is more linear than that of the corresponding methylene-linked dimer and this greater shape anisotropy is expected to give rise to the higher transition temperatures. This suggestion has been tested using a molecular field theory in which the only difference between the calculations for the methylene- and ether-linked series was this bond angle and the predictions of the theory were in good agreement with the experimental data. Furthermore, the same approach also showed that it was possible to account for the differences in the entropy changes between the ether- and methylene-linked dimers in terms of geometrical factors alone.

The sense of the alternation in the transitional properties exhibited by dimers may be inverted by changing the point of attachment of the spacer to the mesogenic units. Marcelis *et al.*[28] reported the properties of two series of non-symmetric dimers consisting of a terphenyl-based moiety linked *via* a spacer to a cholesteryl unit for which the only difference in structure was that the spacer was attached in a *para* position in one, **3**, and in a *meta* position in the other, **4**.

3
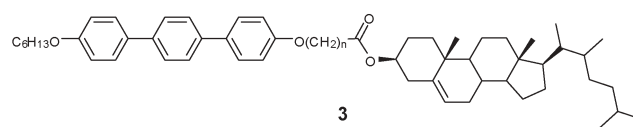
The sense of the alternation in the clearing temperatures and entropies differs for the two series. For the *para*-linked materials the even members of the series show the higher

This journal is © The Royal Society of Chemistry 2007

Chem. Soc. Rev., 2007, **36**, 2096–2124 | 2099

4

values of the clearing temperature and associated entropy changes. By contrast, however, it is the odd rather than the even members of the *meta*-linked materials which exhibit the higher transition temperatures and larger transitional entropies. This may be interpreted in terms of the average molecular shapes of these molecules and the change in the linking position means that there are now more conformations for the odd-membered *meta*-linked materials which hold the two mesogenic units more or less parallel than there are for an even-membered spacer. This difference in shape is shown schematically in Fig. 4 for the all-*trans* conformations of an odd and even member of each series.

The majority of liquid crystal dimers contain flexible alkyl spacers but other types of spacer are attracting increasing attention, in particular, oligo(ethylene oxide) and siloxane-containing chains. The first systematic study of the dependence of the transitional properties of liquid crystal dimers on the chemical nature of the spacer was undertaken by Creed *et al.* in an investigation of two sets of dimers shown in Fig. 5.[29] For both sets of materials, the clearing temperature was highest for the pentamethylene chain and lowest for the disiloxane spacer. This trend suggests an inverse relationship between the clearing temperature and the flexibility of the spacer.
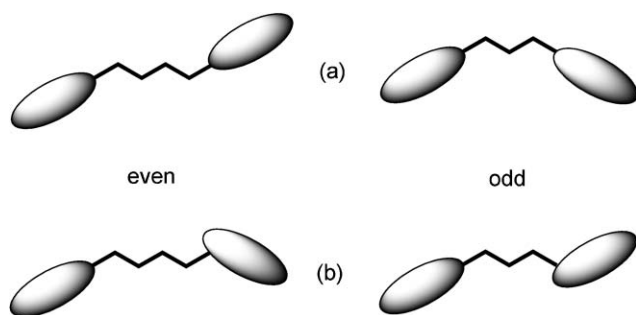

Fig. 4 Schematic representations of the molecular shapes of odd and even-membered dimers containing (a) two *para*-linked and (b) a *para* and a *meta*-linked mesogenic groups.
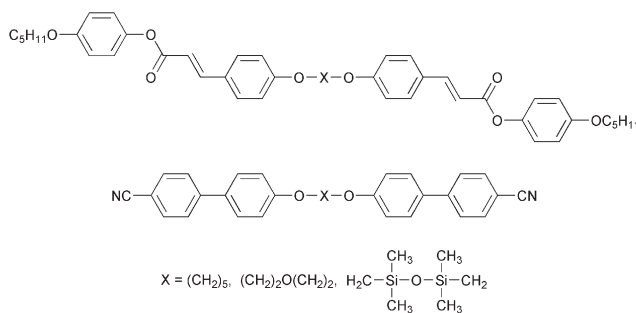

Fig. 5 Molecular structures of liquid crystal dimers in which the chemical nature of the spacer was varied.[29]

More recently, interest has focussed on dimers containing oligo(ethylene oxide) spacers, in part because of their application potential as anisotropic ionic conductors. For example, Kato and co-workers have reported the properties of the series,[30] **5**, and these show smectic and nematic phases.


5
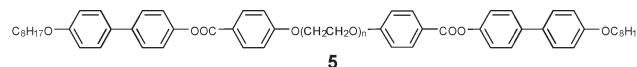
On the addition of lithium triflate, the nematic behaviour is extinguished and this is attributed to the preferential solvation of the lithium ions by the oligo(ethylene oxide) segments which enhances the tendency for microphase separation and hence the formation of a smectic phase. Anisotropic conductivities of approximately 10^{-4} S cm^{-1} have been measured in the smectic A phase of these materials. These dimers may be considered as low molar mass analogues of ionically conducting side chain liquid crystal polymers.[31]

Interest in liquid crystal dimers containing siloxane moieties within the spacer has also increased sharply in recent years and largely because of their electro-optic properties.[32–35] These will be discussed in more detail later. Other types of spacer used in liquid crystal dimers have included a perfluoroalkyl segment,[36] a malonic acid linking unit,[37,38] and *via cis*-2-buten-1,4-diol.[39]

Between conventional low molar mass mesogens and liquid crystal dimers

We have now seen that the characteristic behaviour of a homologous series of liquid crystal dimers in which the length and parity of the flexible spacer is varied consists of dramatic alternations in the thermodynamic transitional properties at the liquid crystal–isotropic transition. It has been commonly overlooked, however, that there are other examples of low molar mass mesogens which exhibit similarly large transitions in their clearing temperatures and these compounds tend to have a common molecular architecture comprising an anisometric terminal group, often a phenyl ring, attached to a mesogenic moiety *via* a flexible spacer. Clearly if we allow the anisometric group to increase in size to the point at which it may be described as a liquid crystal unit then we have a liquid crystal dimer. Thus this class of compounds may be considered to be structurally intermediate between conventional low molar mass liquid crystals and dimers, and here we will discuss the properties of such compounds and explore the extent to which their properties do resemble those of dimers. We will also see why having been overlooked for some thirty or so years this molecular architecture has again become the subject of research interest.

In the early 1970s Gray and his co-workers undertook a detailed study of the liquid crystalline properties of the phenyl- and ω-phenylalkyl 4-(4′-substituted-benzylidene-amino)cinnamates,[40–43] **6**,

6
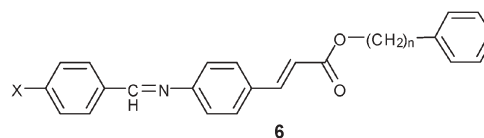
The dependence of the transition temperatures on the length of the alkyl chain for the ω-phenylalkyl 4-(4′-cyanobenzylideneamino)cinnamates is shown in Fig. 6.[40] Immediately apparent is the very pronounced alternation in the nematic–isotropic transition temperatures which appears to attenuate on increasing chain length, behaviour strongly reminiscent to that observed for liquid crystal dimers, see Fig. 2. This alternation was attributed to the shapes of the molecules and specifically for even-membered spacers the terminal phenyl ring is co-linear with the liquid crystal group whereas for odd members the two anisometric units are inclined at some angle, see Fig. 7. In order to test this intuitively appealing explanation, although it ignores the flexibility of the spacer, that the large alternation in the nematic–isotropic transition temperatures reflects the smaller anisometric unit moving on and off the long axis of the rest of the molecule, Gray and his co-workers synthesised a range of compounds which contained either chloro or methyl substituents in the 3″ or 4″ positions of
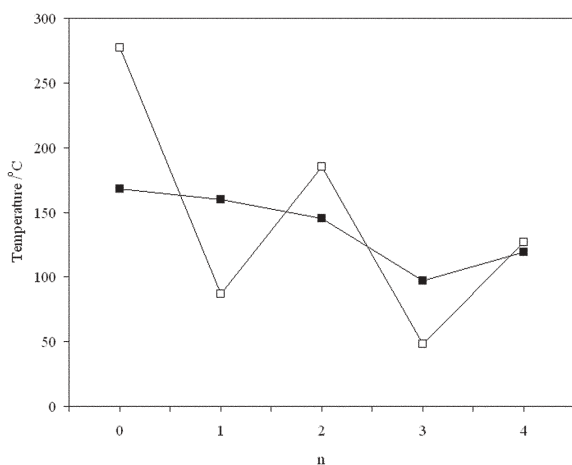

Fig. 6 The dependence of the transition temperatures on the number of methylene units in the alkyl chain for the ω-phenylalkyl 4(4′-cyanobenzylideneamino) cinnamates; ■ indicates the melting point and □ denotes the nematic–isotropic transition temperature.[40]
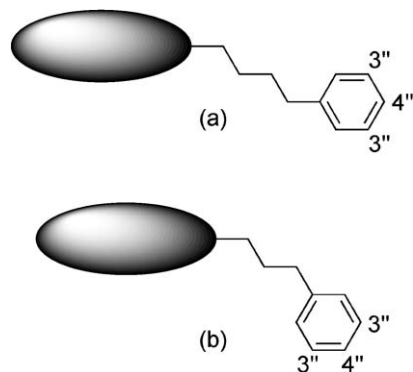

Fig. 7 Schematic representation of the molecular shape of (a) an even and (b) an odd-membered molecule consisting of a mesogenic unit and a phenyl ring interconnected *via* an alkyl chain in the all-*trans* conformation. The positions marked as 3″ and 4″ are referred to in the text.

the terminal phenyl ring;[42,43] these positions are indicated on the structures shown in Fig. 7. The effect of substitution in the 4″-position on the clearing temperature was found to depend on the parity of the linking alkyl chain: for even members the nematic–isotropic transition temperature increased while for odd members it decreased. This is wholly consistent with the view that for even members the molecule is essentially linear so that a 4″-substituent enhances the molecular length to breadth ratio and hence, increases the clearing temperature. For odd members, however, a 4″-substituent broadens the molecule because the phenyl ring is lying off the long molecular axis and hence a reduction in the nematic–isotropic transition temperature is anticipated and indeed observed. Furthermore, substitution in the 3″-position generally decreases the nematic–isotropic transition temperatures for both odd- and even-membered compounds. This reduction, however, is sometimes smaller for the odd members and in one case an increase in the clearing temperature is observed.[42] To explain these observations, Gray noted that if rotation about the O-ring (n = 0) or CH$_2$-ring bond is possible then for substitution in the 3″-position there are two extreme molecular conformations when the ring is co-planar with the rest of the molecule. For an even member, irrespective of which conformation is adopted, a 3″-substituent broadens the molecule and a concurrent decrease in the clearing temperature is easily understood. By contrast, for an odd member a 3″-substituent can actually serve to increase the length to breadth ratio of the molecule and so an increase in the clearing temperature would be anticipated. Gray further commented that since there is no consistent effect for substitution in the 3″ position for an odd member then it is unlikely that free rotation can occur about the CH$_2$-ring bond in the nematic phase and that the amounts of the different rotational conformers differ with substituent type and alkyl chain length. This is somewhat surprising as the rotation of a phenyl group is normally expected to occur. The experimental results, however, appear to have been fully accounted for by restricting the alkyl chain to an all-*trans* conformation and then by considering the spatial dispositions of the anisometric groups.

This explanation of the transitional properties of these compounds does, however, have its limitations. If we remember that both methyl and chloro substituents enhance the clearing temperature relative to a hydrogen atom[4] then as the small anisometric group is increased in size, we would expect the transition temperatures to approach those of the corresponding dimer. This is indeed the case for compounds containing an even-membered spacer. By contrast, for an odd-membered spacer we have seen that a 4″-substituent decreases the clearing temperature relative to the unsubstituted material and within the framework of the model proposed increasing the size of the group would serve to reduce the clearing temperature further, such that the clearing temperature of the dimer would in fact be lower than that of the corresponding monomer. This is not the case and in reality large increases are always observed when comparing the clearing temperatures of both odd- and even-membered dimers with those of the corresponding monomers. We will return to this issue later.

As we have seen, compounds containing a single mesogenic group and a small anisometric group linked *via* an alkyl chain appear to mimic the large alternation in the clearing temperatures observed on varying the parity of the spacer in liquid crystal dimers but what about the dependence of the associated entropy changes? Fig. 8 shows the dependence of the transition temperatures on the length of the alkyl spacer for the cholesteryl ω-phenylalkanoates,[44] 7, and a very large alternation in the chiral nematic–isotropic transition temperature on varying the spacer length is immediately apparent.

7
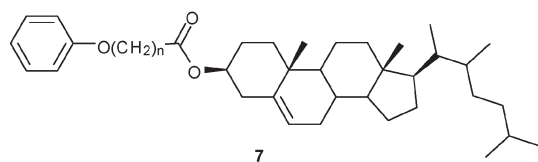
This alternation attenuates on increasing the length of the spacer in a manner strongly reminiscent of that seen for the dimers, see Fig. 2. Fig. 9 shows the dependence of the entropy change associated with the chiral nematic–isotropic transition on the length and parity of the spacer and a large odd–even effect is evident in which the even members have the higher values, and which does not attenuate on increasing chain length. It should also be noted that the values of the entropy changes shown in Fig. 9 are larger than those exhibited by the corresponding conventional monomers. This reinforces the view that the behaviour of this class of materials is indeed intermediate between that of conventional low molar mass liquid crystals consisting of molecules containing just a single semi-rigid core and liquid crystal dimers.

If we return to the question of how the transitional properties evolve from the monomer to the dimer through what may be considered as these intermediate molecular architectures we need to consider more carefully the nature of the substituents chosen in these studies. Chloro and methyl substituents tend to make relatively small changes to the anisometric properties of a molecule such as, for example, the
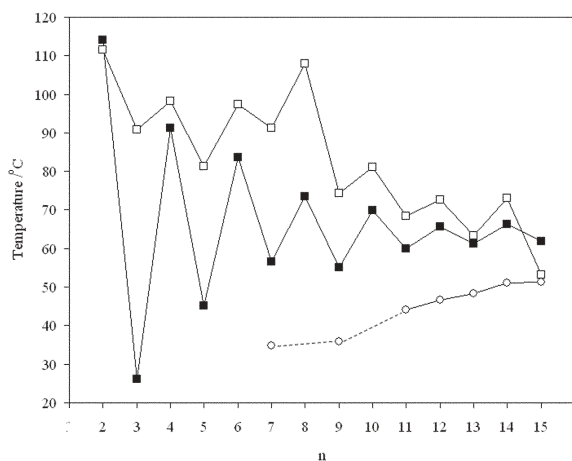

Fig. 8 The dependence of the transition temperatures on the number of carbon atoms in the alkyl spacer for the cholesteryl ω-phenylalkanoates; ■ indicates the melting point, □ the chiral nematic–isotropic transition and ○ the smectic–chiral nematic transition.[44]
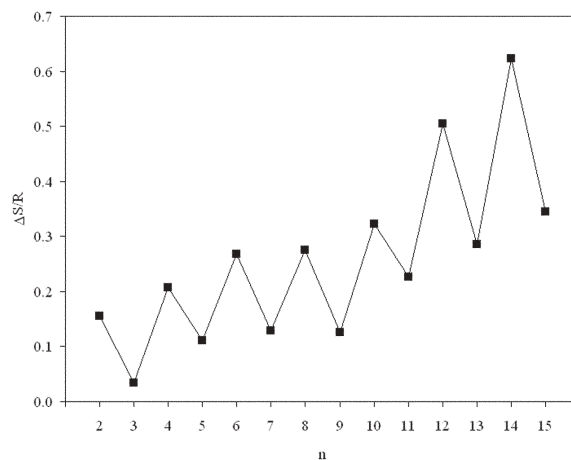

Fig. 9 The dependence of the entropy change associated with the chiral nematic–isotropic transition on the number of carbon atoms in the alkyl spacer for the cholesteryl ω-phenylalkanoates.[44]

anisometric polarisability. Thus, for an odd-membered spacer the enhanced interaction of the bulky terminal group with the molecular field on substituting a hydrogen atom by either a chloro or methyl group is more than offset by the concurrent increase in molecular volume and so the overall effect is a reduction in the clearing temperature. If we consider instead substituents such as a cyano group which are readily polarisable and therefore can interact strongly with the phenyl ring, these give rise to an appreciably larger contribution to the anisotropic properties of the molecule. The resulting increased interaction of this segment with the molecular field is further enhanced in the nematic phase offsetting the increased molecular volume and gives rise to an increased clearing temperature for both even- and odd-membered compounds. Within this framework, enhancing the anisotropic properties of the terminal group still further and to the point at which it is a recognisable mesogenic unit in its own right, would lead to increased clearing temperatures as indeed are observed for the liquid crystal dimers. More recent examples of this type of liquid crystal have been reported by Itahara and are based on 4-cyanobiphenyl as the mesogenic unit.[45]

Recently Zannoni and co-workers used molecular dynamics simulation techniques to study the properties of the first four homologues of the phenyl alkyl-4-(4′-cyanobenzylidene)aminocinnamate series.[46] This involved modelling the molecules with full atomistic detail and complete conformational freedom and subsequently undertaking molecular dynamics simulations. This was in fact the first example of nematic–isotropic transition temperatures being reproduced using molecular dynamics simulation techniques. The study revealed that the pronounced odd–even effect seen on varying the number of carbon atoms linking the phenyl ring to the mesogenic group, see Fig. 6, could be attributed to two factors: firstly, on passing from an even to an odd number of carbon atoms there is essentially no change in molecular length but the breadth increases and it is well known that the length to breadth ratio influences transitional behaviour and secondly, for the odd-membered spacer the phenyl ring cannot align preferentially along the phase director. The authors also note

that their study reveals the significance of considering conformations which are not fully extended because these are responsible for the decrease in transition temperatures on ascending the homologous series.

More recently interest in this class of liquid crystals has resurfaced through the work of Goodby and his colleagues[47–51] in which the properties of chiral and racemic liquid crystals incorporating bulky terminal groups have been investigated. This work has focussed on the role of the bulky terminal group in disrupting and weakening the layer interactions in smectic phases which can have quite remarkable effects on the properties of the material. Cowling *et al.* showed, for example, that modifying a racemic mixture of the classical MHPOBC material by the addition of a terminal cyclohexyl ring to give, **8**, yielded a compound which showed smectic C and A phases.[48]

8
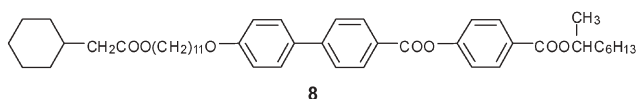
Remarkably, this achiral smectic C phase exhibited the electro-optic switching behaviour typical of a ferroelectric smectic C phase *i.e.* an apparent chiral response! The molecular significance of this observation is at present unclear but this work has shown that the bulky terminal group can be used to modify the interlayer interactions and hence, phase structures.[47]

In this section we have highlighted for the first time that molecules containing a bulky terminal group attached to a mesogenic unit *via* a flexible spacer may be considered as structural precursors to liquid crystal dimers and that there appears to be a continuum of behaviour from the monomer to the dimer through these intermediate structures. Indeed this study of these materials highlights the shortcomings in the most common approach used to explain the transitional properties of liquid crystal dimers in terms of the shape of a single conformation of the molecules. Indeed, not only is the average molecular shape an important consideration but attention must also be paid to other anisotropic properties and how these contribute to and interact with the molecular field in the liquid crystal phase.

Symmetric dimers and smectic phases

The rediscovery of liquid crystal dimers in the early 1980s was followed quickly by many other reports of new dimers. Curiously the vast majority of these compounds exhibited only nematic behaviour leading to the suggestion that the dimeric architecture inherently suppressed the formation of smectic phases.[7] This was a rather surprising view given that smectic phase formation is most often considered in terms of molecular inhomogeneity with the disparity in the strengths of the various interactions between the differing molecular segments providing the driving force for microphase separation and hence a smectic molecular organisation. A liquid crystal dimer consists of molecules with chemically distinct regions and therefore, smectic phase behaviour would be predicted. It was not until 1992, however, that the first family

of liquid crystal dimers to exhibit rich smectic polymorphism was reported, the α,ω-bis(4-*n*-alkylanilinebenzylidine-4′-oxy)-alkanes,[52] **9**, and these were referred to using the mnemonic *m*.O*n*O.*m* in which *n* indicates the number of methylene units in the flexible spacer and *m* the number of carbon atoms in each of the terminal chains.
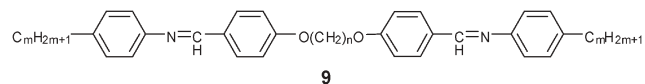

9

Fig. 10 shows the dependence of the transition temperatures on the length of the flexible spacer, *n*, for the 4.O*n*O.4 series which exhibits both smectic and nematic behaviour. Immediately apparent is the pronounced alternation in the clearing temperatures which attenuates as *n* is increased, and we have seen already that this may be considered as archetypal behaviour for dimers as discussed in a previous section. The shorter members of the series (*n* = 2, 3, 4) exhibit exclusively smectic behaviour, intermediate spacer lengths (*n* = 5, 6) show both smectic and nematic phases while for the longer members (*n* ≥ 7) only nematic behaviour is observed. Thus, increasing spacer length appeared to promote the observation of nematic over smectic behaviour. The transitional properties of 11 homologous series belonging to this general family of compounds were reported (*n* = 1–12; *m* = 0–10) leading to the observation of a range of smectic phases including smectic A, C and F phases and hexatic B and crystal G phases. Rare phase transitions such as the smectic F–smectic A and crystal G–isotropic transitions were also observed. In addition novel modulated hexatic phases were identified[53] and these will be described in a later section. This study revealed a simple empirical relationship relating the observation of smectic phases to molecular structure: specifically, for smectic behaviour to be observed the terminal chain length must be greater than half the spacer length. Furthermore, X-ray diffraction studies showed that all the smectic phases possessed a monolayer structure.

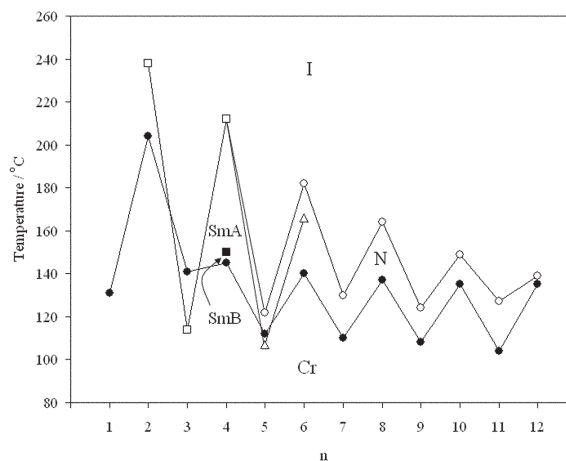**Fig. 10** The dependence of the transition temperatures on the number of methylene units, *n*, in the flexible spacer for the 4.O*n*O.4 series;[52] ● indicates melting points, □ smectic A–isotropic transitions, ○ nematic–isotropic transitions, △ smectic A–nematic transitions, and ■ smectic B–smectic A transitions.

This journal is © The Royal Society of Chemistry 2007

Chem. Soc. Rev., 2007, **36**, 2096–2124 | 2103

This relationship between molecular structure and smectic behaviour was a surprising result but one which has been shown to be true for a wide range of symmetric dimers. Indeed there are very few known exceptions to it. To understand why this was an unexpected observation, we must first consider why smectic phases form. We have noted earlier that smectic phase formation is often thought of in terms of a microphase separation in which the chemically different segments of the molecules are arranged in domains. Thus, the mesogenic units form one domain while the alkyl chains constitute another. The driving force for this microphase separation may be thought of either in energetic or entropic terms. Energetically, if the mean of the mesogenic unit–mesogenic unit and chain–chain interactions is more favourable than the mixed mesogenic unit–chain interaction then phase separation will occur or entropically, the interaction between a mesogenic unit and a chain acts to order the chain and hence is unfavourable. Again, this will give rise to microphase separation. Thus, for conventional low molar mass materials the very general observation is that increasing the length of a terminal alkyl chain promotes smectic behaviour. This relationship holds also on increasing the length of alkyl chains in polymeric systems such that increasing the length of the spacer in either a semi-flexible main chain liquid crystal polymer or a side chain liquid crystal polymer promotes smectic over nematic behaviour.

We now return to the dimers and perform a simple thought experiment. In forming a smectic arrangement composed of dimers we might first place the mesogenic units into layers, see Fig. 11(a), and then ask the question as to how to connect these units to form dimers. Such an approach reveals two plausible structures if we ignore the possibility that the dimers can form horseshoe-like conformations which would be highly unfavourable energetically. In the first of these structures the spacers and terminal chains are added in a random fashion giving the arrangement shown in Fig. 11(b) such that the spacers and terminal chains are mixed within the chain regions; this is termed an intercalated smectic phase. Alternatively, the spacers and terminal chains are added in such a way that all the mesogenic units in one layer are attached to a mesogenic unit in the same adjacent layer, see Fig. 11(c). In this arrangement, there are effectively three domains composed of either the mesogenic units, the spacers or the terminal chains. Energetically, the lateral interactions between the mesogenic units which are important in the formation of the smectic phase are identical in both structures whereas entropically, the random mixing of the chains in the intercalated structure would appear to be more favourable than their effective microphase separation in the monolayer structure. We will see in the next section that an intercalated structure is characterised by a layer spacing which is approximately half the molecular length while in the mono-layer variant the layer spacing should be approximately the molecular length. The data for the m.OnO.m series showed that only monolayer smectic phases are formed so ruling out the possibly of the intercalated structure. In addition, the empirical observation that for smectic phases to be observed the terminal chain length must be greater than half the spacer length precludes the possibility that these symmetric dimers form an intercalated structure simply because the terminal
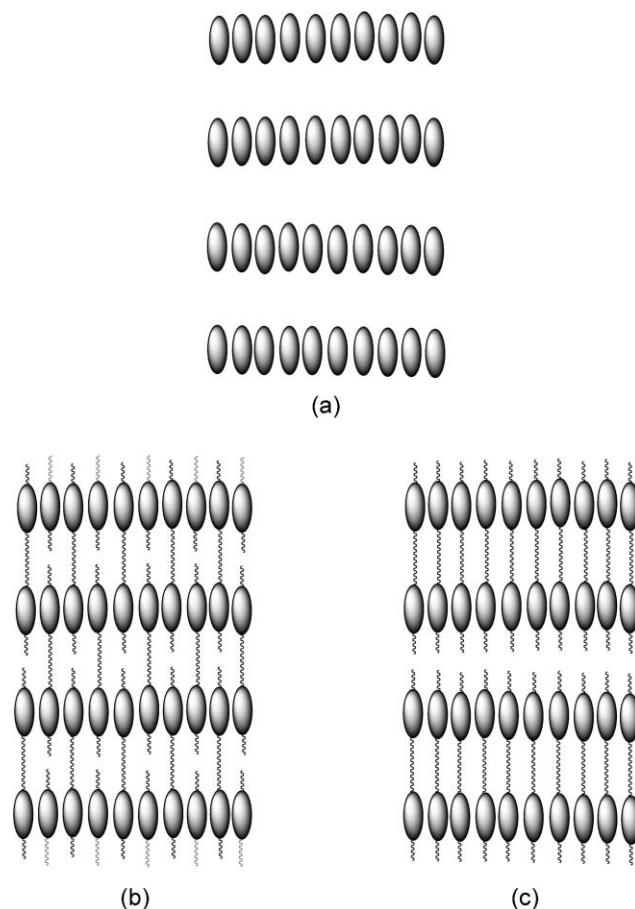

Fig. 11 Sketches showing possible ways to construct a smectic phase using liquid crystal dimers. (a) First the mesogenic units are arranged into layers and linked (b) mixing the spacer and terminal alkyl chains giving an intercalated phase or (c) without mixing of the different types of chain giving a monolayer arrangement.

chains can only be accommodated within such a structure if the combined length of the two chains is equal to or less than that of the spacer.

Thus, the very general observation is that symmetric dimers have a strong tendency to exhibit monolayer smectic phases and to do so the length of the terminal chains normally exceed half that of the spacer. To rationalise this observation, it was suggested that the interaction between a spacer and a terminal chain is an unfavourable one and so destabilises the intercalated arrangement. This unfavourable enthalpic term would then offset the favourable entropic term which would drive the formation of an intercalated phase. A molecular interpretation of why this is the case is still not clear.

Non-symmetric dimers and intercalated smectic phases

We have seen already that a non-symmetric dimer consists of molecules containing two different mesogenic units linked *via* a flexible spacer, see Wu[54] and Do *et al.*[55] for recent examples. In the majority of reported cases the differing mesogenic units have been chosen because they are known to exhibit a specific favourable molecular interaction. This normally involves

linking together electron rich and electron deficient mesogenic groups. The first and most extensively studied family of such compounds were the α-(4-cyanobiphenyl-4′-yloxy)-ω-(4-n-alkylanilinebenzylidine-4′-oxy)alkanes,[56–59] **10**, and the mnemonic used to describe these is CB.OnO.m where m refers to the number of carbon atoms in the terminal alkyl chain and n the number in the spacer.

10
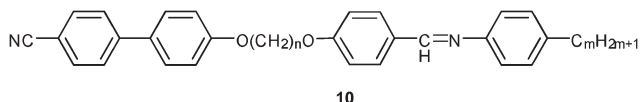
This particular dimer structure was chosen, in part, because binary mixtures of conventional low molar mass liquid crystals containing these mesogenic units were know to exhibit unusual phase behaviour; it was observed, for example, a binary mixture of two nematogens could show smectic behaviour, the so-called induced smectic phases.[60–62] In addition, the phase behaviour of the corresponding parent symmetric dimers was known, allowing the behaviour of the non-symmetric dimers to be compared with binary mixtures of the symmetric dimers.[21,52]

The dependence of the transition temperatures on the number of carbon atoms in the flexible spacer, n, for the CBOnO.10 series is shown in Fig. 12.[57,58] The liquid crystal–isotropic transition temperatures show a dramatic alternation which attenuates on increasing the spacer length, which as we saw earlier is archetypal behaviour for liquid crystal dimers. In contrast to such expected behaviour, however, the dependence of the smectic behaviour on the length of the spacer is highly unusual. The early members of the series, n = 3–7, exhibit a smectic A phase as do the longest members, n = 10–12. For intermediate values of the spacer length, n = 8, 9, however, only nematic behaviour was observed. This is quite unlike the behaviour of symmetric dimers for which increasing
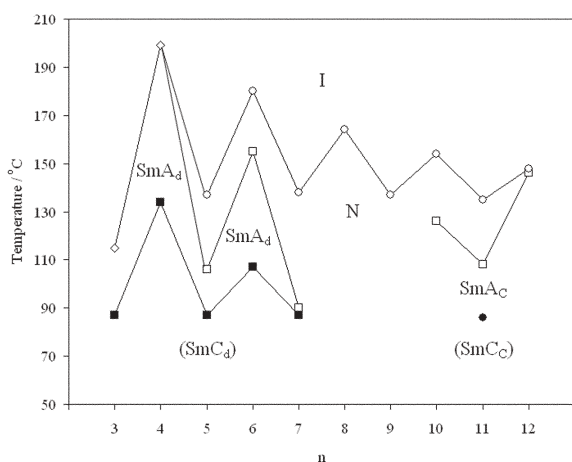
the spacer length simply tends to promote nematic behaviour.[52] We will return to this observation later.

The effect of varying the terminal chain length in a series of non-symmetric dimers is shown for CBO4O.m in Fig. 13.[57] All eleven members of this series exhibit enantiotropic liquid crystal phases. The dependence of the nematic–isotropic transition temperature on the number of carbon atoms, m, in the terminal alkyl chain mirrored the behaviour observed for a conventional low molar mass mesogen having high transition temperatures.[63] The smectic A–nematic transition temperature can be seen to increase for the first three members of the series but then falls over the next two members. This decrease presumably continued over the next three homologues for which smectic behaviour could not be observed even though the nematic phases could be extensively super-cooled. Smectic behaviour then reappears with the octyl homologue and the smectic A–nematic transition temperature increases over the highest three homologues. Indeed the decyl member actually shows a smectic A–isotropic transition temperature. This behaviour was unprecedented and quite unlike that of conventional low molar mass liquid crystals for which the tendency to exhibit smectic behaviour simply increases on increasing the length of a terminal chain.

To understand the highly unusual phase behaviour seen in Fig. 12 and Fig. 13, we must consider the molecular arrangements within the smectic phases observed. For the CBOnO.10 series the ratio of the smectic periodicity or layer spacing, d, to the estimated all-trans molecular length, l, is strongly dependent on the length of the flexible spacer. Thus, for the smectic A phase seen for n = 3–7, d/l = 1.8, whereas for n = 10–12, this value falls to just 0.5. The larger value of d/l is indicative of an interdigitated smectic A phase in which the like parts of the molecules overlap, see Fig. 14(a). The driving force for the formation of this phase was attributed to the electrostatic interaction between the polar and polarisable cyanobiphenyl groups while the smectic phase results from the molecular inhomogeneity arising from the long terminal alkyl

Fig. 12 The dependence of the transition temperatures on the number of methylene units, n, in the flexible alkyl spacer for the CBOnO.10 series;[57,59] ◇ indicates interdigitated smectic A–isotropic transitions, ○ nematic–isotropic transitions, ■ interdigitated smectic A–interdigitated smectic C transitions, □ interdigitated smectic A–nematic transitions, ▫ intercalated smectic A–nematic transitions and ● intercalated smectic A–intercalated smectic C transitions.

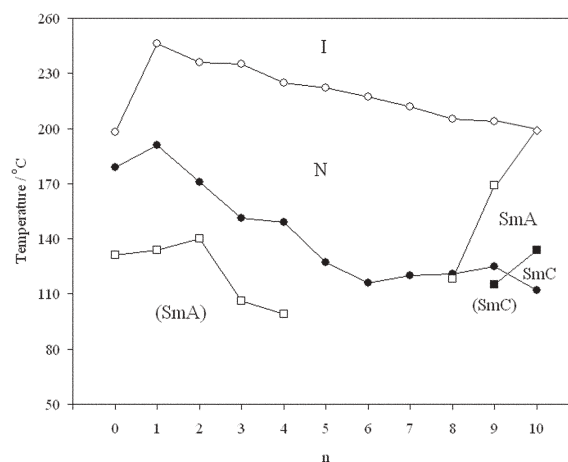**Fig. 13** The dependence of the transition temperatures on the number of carbon atoms, m, in the terminal alkyl chain for the CBO4O.m series.[57] The melting points are denoted by ●; ○ indicates nematic–isotropic transitions, ◇ the smectic A–isotropic transitions, ■ the interdigitated smectic C–interdigitated smectic A transition and □ the smectic A–nematic transitions.
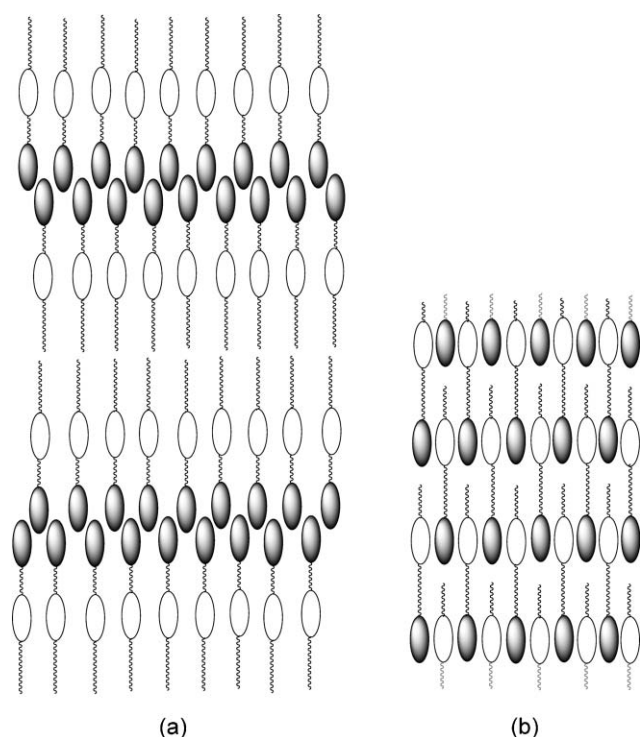
Fig. 14 Schematic representations of (a) an interdigitated smectic A phase and (b) and intercalated smectic A phase composed of non-symmetric dimers.

chains. The apparent voids in the structure are presumably filled by the flexibility of the terminal chains. As we noted earlier, the much smaller value of d/l observed for the smectic A phase seen for $n = 10–12$ indicates the formation of an intercalated smectic A phase in which it is now the differing parts of the molecules which overlap, see Fig. 14(b). The driving force for the formation of this phase is attributed, in part, to a specific favourable interaction between the unlike mesogenic groups thought to be an electrostatic quadrupolar interaction between groups having quadrupole moments of opposite signs.[64] In addition, mixing the unlike mesogenic units within a layer rather than allowing them to phase separate into adjacent layers is entropically favourable, although this entropic contribution and the enthalpic interactions between the unlike mesogenic groups in fact would be identical in both the proposed intercalated arrangement and a conventional monolayer structure. Indeed, it is often over-looked when interpreting the behaviour of this type of non-symmetric dimer that the unlike mesogenic unit interactions alone cannot explain the formation of intercalated smectic phases. Presumably, the entropic gain derived from mixing the terminal chains and spacers must also be important. We noted earlier, however, that the behaviour of symmetric dimers implied that this mixing of terminal chains and spacers was enthalpically unfavourable. Thus, for these non-symmetric dimers the reduction of terminal chains to just one must reduce the unfavourable enthalpic term to the point at which it may be offset by the entropic gain achieved by their mixing. It is important to note that the sketch of the intercalated smectic A phase shown in Fig. 14(b) implies that the phase has

ferroelectric ordering but this is presumably removed by a random arrangement of such domains at the macroscopic level. Indeed, attempts to detect a macroscopic polarization for intercalated smectic phases shown by differing compounds failed. It is apparent from Fig. 14(b) that the ability to accommodate terminal chains in the space between the layers of mesogenic groups in an intercalated arrangement is determined largely by the length of the spacer implying that the intercalated structure will only be observed if the terminal chain length is equal to or shorter than that of the spacer. If we now return to the phase behaviour seen in Fig. 12 and Fig. 13 for the CBOnO.10 and CBO4O.m series respectively, this prediction is borne out. Thus, intercalated smectic A phases are observed for the CBOnO.10 series when $n = 10–12$ and for the CBO4O.m series when $m = 0–4$. Conversely, when the terminal chain length is much longer than that of the spacer interdigitated smectic A phases would be predicted, and again such behaviour is observed. Thus, interdigitated smectic A phases are observed for the CBOnO.10 series when $n = 3–7$ and for the CBO4O.m series when $m = 8–10$. For intermediate n/m ratios smectic behaviour is extinguished in both series suggesting that neither smectic modification is favourable and hence, nematic behaviour is observed. There is a strong similarity here to re-entrant nematic behaviour which is also driven by two different length scales. It is important to stress that while this discussion has focussed solely on the CBOnO.m family of compounds for which this dependence of smectic phase formation on the relative lengths of the spacer and terminal chain was first observed, similar behaviour has now been seen for many other non-symmetric dimers consisting of unlike mesogenic units with one being electron rich and the other electron deficient.

To test the suggestion that a specific interaction between unlike mesogenic groups was important in driving the formation of intercalated smectic phases by non-symmetric dimers rather than other considerations, for example, effects of excluded volume or space filling constraints, Blatch and Luckhurst prepared a family of non-symmetric dimers in which the lack of symmetry derived only from differences in the lengths of the terminal chains,[65] **11**.

11
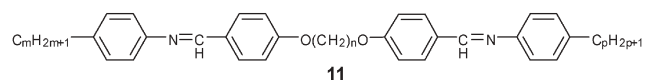
In these non-symmetric dimers the mesogenic groups were identical so removing the possibility of a specific interaction between them. The behaviour of these dimers was essentially in accord with that of the m.OnO.m series described earlier and only monolayer smectic phases were observed. This strongly suggests that the specific interaction between the two unlike mesogenic units is required in order to stabilize the intercalated arrangement. Quantitative estimates of the nematic–isotropic transition temperatures of the CBOnO.m non-symmetric dimers based on the Marcelja–Luckhurst theory provided further evidence for a specific interaction between the unlike mesogenic groups.[57,58]

The proposed structure of the intercalated smectic A phase shown in Fig. 14(b) does not fully account, however, for the behaviour of these non-symmetric dimers. Of particular note is

the behaviour of the CBO*n*O.2 series for which the stability of the intercalated smectic A phase unexpectedly increases as the spacer length is increased. Thus, CBO12O.2 shows the intercalated smectic A phase but given the mismatch in length between the spacer and terminal chain it is difficult to see how the molecules pack efficiently into the intercalated arrangement without a considerable concentration of voids. This observation led to the suggestion that the dimers may adopt horseshoe-like conformations which are stabilized by the favourable interactions between the unlike mesogenic groups. It is easy to visualise how these horseshoe-shaped structures can be packed into a smectic arrangement in which the periodicity is approximately half the all-*trans* molecular length.[12] This view was not supported, however, by the observation that the intercalated smectic A phase has considerably higher rotational viscosities in comparison to those of the interdigitated smectic phases at comparable temperatures which is consistent with the network structure of the intercalated smectic A phase shown in Fig. 14(b).[65]

The intercalated smectic phases are not only observed for these non-symmetric dimers but are also seen for binary mixtures of the corresponding symmetric dimers.[57,58] Binary mixtures of members of the 2.O*n*O.2 series with $n = 2$–6 and BCBO10, for example, each show a smectic A phase with a d/l ratio of 0.5, where l now denotes the arithmetical mean of the estimated all-*trans* molecular lengths of the two symmetric dimers, even though the constituent symmetric dimers are exclusively nematogens. This d/l value strongly suggests the formation of an intercalated phase. It is difficult to visualise, however, the molecular arrangement within such a structure given the disparity in the lengths of the flexible spacers of the two symmetric dimers and presumably implies a relatively low degree of translational order within the phase. This observation, however, does tend to support the proposed intercalated arrangement of the dimers shown in Fig. 14(b) rather than one consisting of horseshoe conformations because it is far from clear why these symmetric dimers should adopt such horseshoe arrangements.

The intercalated smectic A phase was the first intercalated smectic phase to be discovered but examples of intercalated smectic C and smectic I phases and intercalated B and J phases were also seen for the CBO*n*O.m series.[57,58] Of particular interest was the intercalated smectic C phase shown by, for example, CBO9O.6, and for which a Schlieren optical texture containing both types of point singularity was observed implying that the tilt direction alternated between the layers. The value of d/l for the phase was approximately 0.5 indicating an intercalated arrangement of the molecules and Fig. 15 shows a schematic representation of the proposed molecular organisation within the phase. The alternation of the tilt direction on passing from one layer to the next means that the global tilt angle of the phase is, in fact, zero but locally, within a layer, is non-zero. This proposed structure for the intercalated smectic C phase was supported by the results of a study using electron spin resonance spectroscopy in which Le Masurier and Luckhurst showed that within the phase there are two distinct directors with tilt directions differing by 180°.[66] The maximum value of the tilt angle within a layer was shown to be 18° which is consistent with the molecular
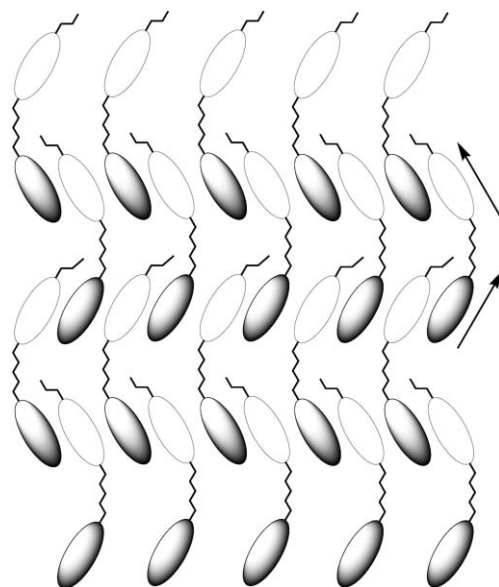

Fig. 15 Sketch of the molecular organisation found within an intercalated smectic C phase composed of odd-membered non-symmetric dimers.

geometry of an odd-membered dimer in which the mesogenic groups make an angle of about 15° with the spacer. A possible model with which to describe the transition from an intercalated smectic A to an intercalated smectic C phase involves a biasing of the distribution of the tilt directions of the mesogenic units resulting in a long range correlation of the tilt angle. This alternation of the tilt direction between layers is a structural feature also observed for a smectic phase shown by semi-flexible main chain liquid crystal polymers[6] and of the antiferroelectric smectic C phase.[67] In each of these cases the requirement for the observation of this alternation in the tilt direction must be a correlation of the mesogenic groups. For the antiferroelectric smectic C phase the origin of this correlation is dipolar forces between the chiral molecules, for the polymers it is provided by the flexible spacer and the polymeric structure of the system, while for the dimers the correlation may originate from the specific interaction between the unlike mesogenic groups. The alternating intercalated smectic phases are typically only observed for dimers possessing long odd-membered spacers suggesting that the difficulty that these bent molecules experience in packing into an intercalated arrangement may provide the driving force for the formation of the phase.

Intercalated smectic phases have now been seen for a wide range of non-symmetric dimers.[68] It is important to note, however, that this description of intercalated smectic phases has been solely in terms of non-symmetric dimers while in fact, such phases have also been observed for a small number of symmetric dimers.[69–72] It is not clear what drives the formation of the intercalated arrangement for these materials, although it has been suggested that specific dipolar interactions in these cases might offset the apparently unfavourable interaction between the spacers and terminal chains discussed earlier for symmetric dimers. It is noteworthy, however, that in these cases alternating intercalated smectic phases are only observed

This journal is © The Royal Society of Chemistry 2007

Chem. Soc. Rev., 2007, **36**, 2096–2124 | 2107

for bent dimers reinforcing the view that molecular shape plays an important role in driving the formation of the phase.

Frustrated smectic phases: bent dimers and unusual phase behaviour

Frustrated smectic phases are widely considered to arise from a competition between different characteristic length scales[73] and examples include re-entrant, incommensurate and modulated smectic phases. A common example of a compound showing such behaviour would contain a polar terminal group, such as a cyano group.[74] For such a system the competing periodicities are the molecular length and the length of the anti-parallel molecular pairs which form to minimize the dipolar energy. If we now pack these molecules into a layered arrangement in which the periodicity is approximately the molecular length we fill space most efficiently but introduce unfavourable dipolar interactions between neighbouring molecules. Alternatively, if instead we allow the molecules to form the anti-parallel molecular pairs and pack these into layers, we minimise the dipolar energy but fill space much less efficiently. To relieve this competition, structures can be adopted in which both periodicities can be accommodated and the modulated smectic Ã and smectic C̃ are examples of such arrangements.[74,75] Purely steric effects can also provide the packing frustration required to drive the formation of these phases. If, for example, the mesogenic unit has greater steric bulk than the terminal chains then this gives rise to a packing stress within a layer which may be relieved by the system adopting a modulated structure.[53]

Liquid crystal dimers have been found to exhibit a rich variety of frustrated smectic phases. If we first return to the $m.OnO.m$ series, a new modulated hexatic phase was identified for dimers having long odd-membered spacers (n = 9, 11) and long terminal chains (m = 10, 12, 14) in which the tilted hexatic smectic monolayers have a periodic modulation in their smectic structure analogous to the Sm C̃ ribbon phase.[53] This phase, termed the Sm1 phase, has been observed on cooling the isotropic, smectic A and smectic C phases. In the Sm1 phase the mesogenic groups are tilted symmetrically with respect to the layer normal and the modulation is purely displacive along the b-axis. Thus, this phase could be considered as the modulated SmF or SmI phase in which the tilt direction of the director with respect to the local hexagonal net has yet to be determined. Fig. 16 shows a sketch of the molecular arrangement within the Sm1 phase but it must be stressed that in reality the domain boundaries are much less well defined. The obvious question given the previous discussion of frustrated smectic phases is what are the two competing periodicities in this system? The molecules in Fig. 16 are represented as bananas reflecting the fact that all the dimers exhibiting this phase contain an odd-membered spacer and hence, presumably a bent molecular shape. By contrast, the corresponding even-membered dimers having a linear molecular structure form conventional monolayer smectic phases in which the layer spacing is approximately equal to the molecular length. It is clear, therefore, that molecular shape is again playing a critical role in determining phase behaviour and it was suggested that the bent odd-membered
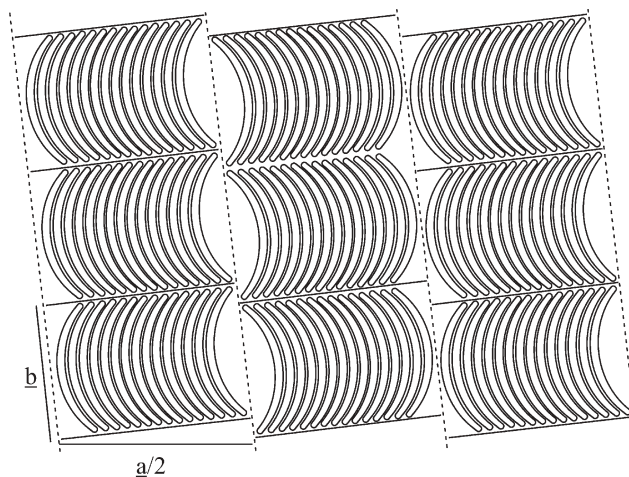

Fig. 16 A sketch of the molecular organisation in the Sm1 phase. The bananas represent bent odd-membered dimers.

dimers interlock giving rise to a periodicity l' which lies between the molecular length and twice the molecular length, i.e., $l < l' < 2l$. It is this length which then competes with that of the monolayer layer periodicity. A second new modulated hexatic phase was discovered on cooling the Sm1 phase shown by 10.O9O.10 and this has been termed the Sm2 phase.[53] The optical texture of this phase is indistinguishable from that of the preceding Sm1 phase and no enthalpy change could be detected accompanying the transition. The presence of the new phase could only be detected using X-ray diffraction. Rather surprisingly, the two phases appear to coexist over a broad temperature range although this is thought to be a kinetic effect. Unfortunately, the monotropic nature of the phase, which remains the only known example of the Sm2 phase, precludes the possibility of detailed structural investigations to elucidate the phase structure.

Further support for this suggestion that molecular shape plays a critical role in the formation of frustrated smectic phases can be found in the behaviour of the odd members of the chiral non-symmetric series,[76] **12**, which exhibit a smectic C̃ phase whereas the even members do not exhibit modulated phases. More recently, Takanishi et al. have reported frustrated smectic layer structures for a series of symmetric dimers but again these have only been observed for a bent odd-membered spacer.[77]

A rich source of frustrated smectic phases has been found to be non-symmetric dimers containing a cholesteryl-based unit.[78–83] These include examples of incommensurate smectic A phases in which the competing periodicities coexist along the layer normal. The first example of this type of phase was seen by Jin and co-workers for the non-symmetric dimer referred to as KI5,[78,79] **13**, with n = 5.

In this incommensurate smectic A phase the larger periodicity is thought to correspond to the molecular length while the shorter periodicity suggests a coexisting intercalated arrangement of the dimers. Jin and his colleagues extended these studies to consider the effect of the terminal chain length on the smectic behaviour in this series[80] and showed that for long terminal chain lengths the incommensurate smectic phase is not seen but instead two commensurate smectic phases are

observed with periodicities reflecting the molecular length. Replacing the Schiff's base unit with a tolane group results in the observation of incommensurate smectic packing in twist grain boundary (TGB) phases.[81] Similar materials have been studied by Marcelis *et al.*[84] and Yelamaggad *et al.*[85] **14**, and the cyano substituted dimers exhibited an interdigitated smectic A phase while for the alkoxy substituted compounds having short spacers, a monolayer smectic A phase was observed. By comparison, homologues having longer spacers exhibited an intercalated smectic A phase and the transition of this to the chiral nematic phase is accompanied by a TGB phase whereas the monolayer smectic A–chiral nematic phase transition is not. TGB phases have now been observed for a range of non-symmetric dimers containing a cholesteryl-based mesogen.[86–89] Yelamaggad *et al.* used such non-symmetric dimers exhibiting a range of phases including TGB phases to form Cu(II) and Pd(II) based complexes.[90] The resulting metallomesogens exhibited either a conventional smectic A phase or the chiral nematic phase depending on the length of the terminal chains in the structure.
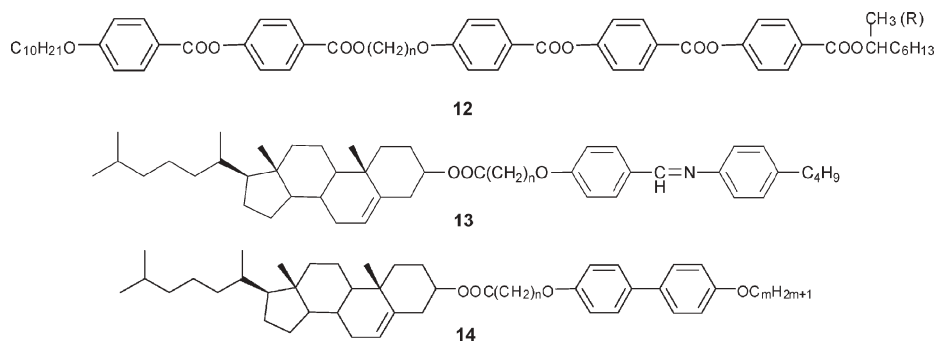
Chirality and liquid crystal dimers

Chirality in liquid crystalline systems has been a major area of considerable research interest for both technological and fundamental reasons[67,91] and a wide range of chiral dimers have now been reported in the literature. These have included symmetric[92–102] and non-symmetric dimers,[76,78,79,93,103–106] with the chiral centre being located either in the spacer or in the terminal chains. The majority of chiral dimers contain cholesteryl groups and these have shown a wide range of unusual frustrated smectic phases, some of which have been described in the preceding section.
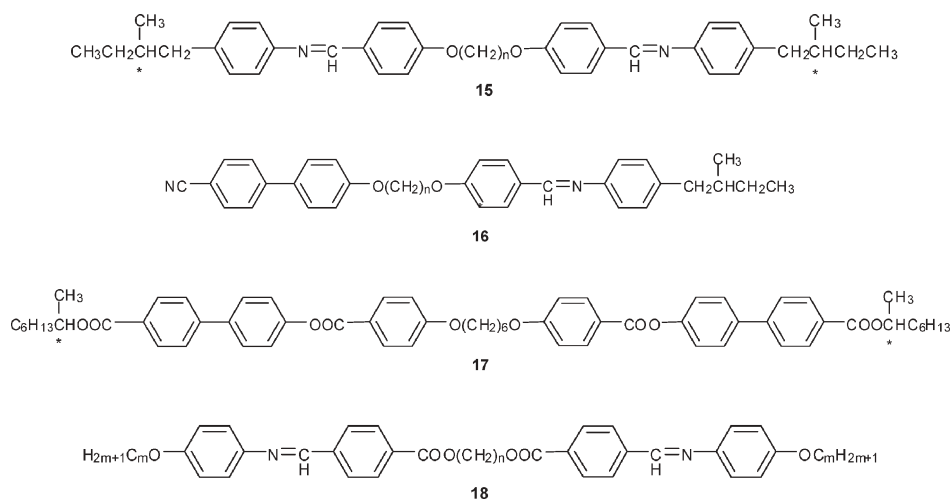
A central issue in the study of liquid crystal dimers has been to determine how the form chirality of the chiral phase depends on the parity of the spacer. The expectation was that given, as we have seen, the transitional behaviour of dimers depends strongly on the length and parity of the spacer then so would the form chirality of a chiral phase consisting of dimers. If we consider, for example, a specific property of the chiral smectic C phase such as the spontaneous polarisation, then for a conventional low molar mass liquid crystal this is considerably smaller than would be predicted, and this is often attributed to a weak coupling of both the molecular motion to the biaxial environment of the tilted phase, and of the chiral group to the dipole moment. To enhance the value of the spontaneous polarisation the liquid crystal should possess a high degree of orientational order and the chiral centre should be strongly coupled to both the core of the molecule and to the transverse dipole moment. These conditions would be met, in principle, in an even-membered liquid crystal dimer in which the chiral centre was located in the spacer. This intriguing possibility has still to be extensively investigated although the limited data available suggest that dimers having chiral spacers actually exhibit ferroelectric smectic phases with low values of the spontaneous polarisation.[103]

To test the more general hypothesis that the form chirality of the chiral phase should depend strongly on the length and parity of the spacer Luckhurst and co-workers[93] considered the transitional properties of two sets of chiral dimers, one symmetric, **15**, and the other non-symmetric, **16**. The symmetric compound with $n = 6$ showed both a smectic A phase and a chiral nematic phase while the octyl homologue exhibited only the chiral nematic phase. Four members of the non-symmetric series were prepared ($n = 6$–9) and each showed a smectic A and a chiral nematic phase. In addition, a chiral nematic–blue phase transition was observed for the heptyl and nonyl homologues but not for the hexyl and octyl members which instead exhibited chiral nematic–isotropic transitions. This general pattern of behaviour in which odd-membered chiral dimers show blue phases while even-membered dimers do not has now been repeated for a number of materials and it would appear, therefore, that as expected the form chirality does indeed exhibit a dependence on the parity of the spacer. This behaviour has been rationalised in terms of the smaller pitch for the odd- relative to the even-membered dimers which arises from the smaller twist elastic constant of odd dimers and is related to their lower orientational order. Surprisingly, the helical twisting powers of odd- and even-membered dimers in a common conventional low molar mass nematic solvent appear to depend solely on the nature of the chiral group and not on its environment.[93] Thus, similar helical twisting powers are observed for both odd- and even-membered dimers.

Nishiyama *et al.* described the properties of the chiral symmetric dimer,[107] **17**, which shows ferrielectric and anti-ferroelectric phases with high values of the tilt angle. Surprisingly, both enantiomers prepared show an endothermic event in their DSC traces at temperatures just above the clearing temperature which was not seen in the DSC trace of the racemic dimer. The authors extended their study to include a range of spacer lengths and these also showed ferrielectric and/or antiferroelectric phases.[108] The even members of the series ($n = 6, 8, 12$) all show the endothermic event in their DSC traces at temperatures just above their clearing temperatures.

12

13

14

This journal is © The Royal Society of Chemistry 2007

Chem. Soc. Rev., 2007, **36**, 2096–2124 | 2109

15

16

17

18

This peak becomes broader and weaker as the spacer length is increased. The molecular origin of this event remains unclear.

Watanabe and co-workers have described the properties of a series of bent shaped achiral odd-membered symmetric dimers,[109,110] **18**, and binary mixtures composed of homologues with differing terminal chain lengths. Surprisingly the butyl and hexyl homologues (m = 4 or 6, n = 5) both show an intercalated SmC phase with an anticlinic tilting of the mesogenic units between the layers and in which the spacers and terminal chains are randomly mixed. The longer homologue (m = 16) forms a chiral, anticlinic and antiferroelectric phase in which the terminal chains and spacers do not mix. As expected, on mixing m = 4 with m = 16 the intercalated phase is destabilised by the addition of the hexadecyl homologue because as we saw earlier the mismatch in length between the spacer (n = 5) and terminal chains (m = 4, 16) simply cannot be accommodated in the intercalated arrangement. Again it is important to note that the authors ascribe the phase behaviour of these molecules to the overall bent shape resulting from the odd-membered spacer.

Dimers containing siloxane spacers

Dimers consisting of two mesogenic units joined *via* a flexible spacer containing an organosiloxane group form an interesting subclass of materials. Siloxane containing liquid crystalline dimers have the tendency to form smectic phases due to the microsegregation of the siloxane groups,[35,111] while the mesogenic groups have a strong tendency to tilt resulting in the smectic C phase, for example, **19**. If siloxane containing dimers are compared to analogous dimers containing wholly alkyl chains it is observed that the nematic phase is suppressed and that tilted smectic phases are exhibited in preference to the orthogonal smectic A phase. The anticlinic structure of the SmC phase in siloxane containing dimers has been attributed to the V-shaped conformation of the dimers, rather than being driven by the correlations of dipoles between molecules as is seen in more conventional dimeric materials. The high tilt angles observed for these dimers is also relatively temperature independent. Cells and thin films made from these types of materials are also more mechanically rugged than alkyl linked dimers and the strong microphase separation aids in the

formation of aligned cells. The V-shaped conformation adopted by odd-membered dimers results in the formation of a smectic C_A phase with an alternation of the local tilt angle between the layers. Indeed, when ferroelectric mesogens are linked *via* a trisiloxane spacer the dimers have a tendency to form an antiferroelectric phase. Siloxane dimers have also been synthesised which exhibit a de Vries type smectic A phase. The electro-optical properties of the ferro- and antiferroelectric mesophases of organosiloxane dimers have attracted interest.[33–35,111–113] These include materials with a large molecular tilt in the antiferroelectric phase.[33–35] Molecules with a 45° tilt have a switching angle of 90°. Cells containing these materials which are aligned parallel to the confining substrates exhibit very high contrast ratios.

Achiral siloxane-based dimers have also been synthesised,[114–117] **20**. These dimers exhibit smectic A phases over broad temperature ranges. Polariser-free, bistable devices which have the potential to be fabricated on flexible substrates incorporating the smectic A phase have been proposed.[115,116] Siloxane-based dimers show promise in this application due to their ruggedness and faster electro-optic responses compared to polymers. The write mode of such a device is a highly birefringent texture induced by electrohydrodynamic instabilities caused by the movement of a charged dopant. To erase this state a higher ac frequency is applied which reorientates the smectic A domains to give an optically isotropic state. The write and erase modes show long term stability.

Liquid crystal dimers and the flexoelectric effect

Liquid crystal dimers have been used in devices utilising the flexoelectric effect.[118–123] Such devices which are based on short pitch chiral nematic materials have fast response times and a temperature-independent optical tilt angle which is linear with applied field amplitude. Dimers have application potential in these devices as their structure allows the possibility to design materials with favourable flexoelectric properties.[118,122] Thus, dimers and their mixtures exhibit flexoelectric coupling due to the strong dipole moments present while at the same time having low dielectric anisotropy due to the terminal dipole moments pointing in opposite directions at each end of the molecule. Examples of dimers

19

20
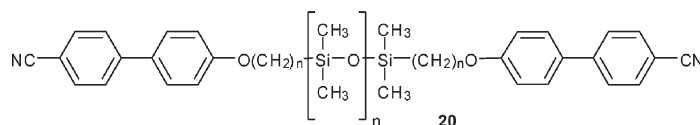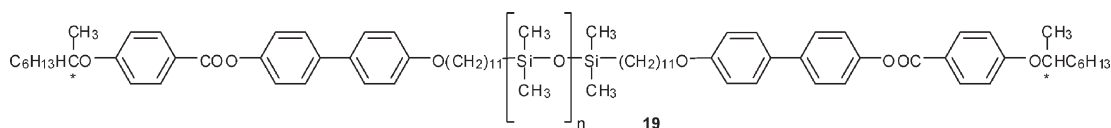
used in mixtures to study the flexoelectric effect are **21** and **22**.

21

23

22
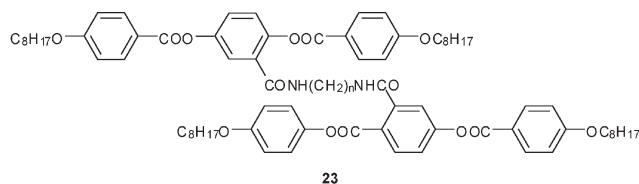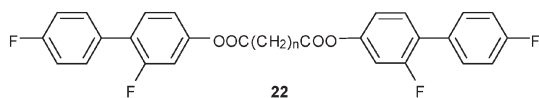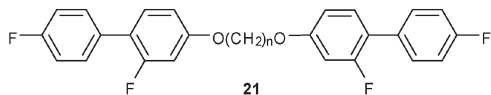
High twisting power chiral dopants are added to induce the chiral nematic phase. Selected mixtures of these dimers exhibited a blue phase over a very wide temperature range.[124] Normally blue phases exist over a short temperature range, around 0.5–2 °C[125,126] while these mixtures of a dimer with a chiral dopant exhibited BPI* over 40–50 °C. BPII* and BPIII* were also present. It is believed that the large values of the localised flexoelectric polarisation stabilises the blue phases. The pitch of the blue phase could be altered by varying the amount of chiral dopant added, to give red, green and blue reflections in BPI*. The reflected colour can be reversibly switched in an applied electric field, with a wide voltage-dependent colour range. Such materials could be used as tunable optical filters or in three-dimensional organic lasers.[124,126–128]

T- and H-shaped dimers

In all the liquid crystal dimers discussed so far the mesogenic units have been linked by the flexible spacer *via* terminal positions. There are, however, two other possible molecular architectures we should consider in which the mesogenic units are either linked by the spacer *via* lateral positions giving H-shaped molecules,[129–132] or in which one mesogenic unit is connected to the spacer in a terminal position while the other is linked at a lateral site giving T-shaped molecules.[129,131] Fig. 17 shows the dependence of the transition temperatures on the length of the flexible spacer for a series of H-shaped dimers, namely, the α,ω-bis[2,5-bis(4-*n*-octyloxybenzoyloxy)benzami-do]alkanes,[129] **23**.

All eight homologues (*n* = 3–10) of this series exhibited nematic behaviour with the shorter members (*n* = 3–5) also showing a smectic C phase. It is evident that the dependence of the nematic–isotropic transition temperature on the length and parity of the spacer is not as dramatic as seen for conventional dimers, but nonetheless there is initially a large odd–even effect

but which quickly attenuates. This odd–even effect presumably reflects the change in the average molecular shape on changing the parity of the spacer. Thus for even–membered H-shaped dimers the long axes of the two mesogenic units are essentially co-parallel for an even-membered spacer but are inclined at some angle with respect to each other for an odd-membered spacer. This difference in shape also accounts for the alternation seen for the melting points on increasing the spacer length and the respective ease at which the two shapes can pack efficiently into a crystal lattice. It is interesting to note that increasing the spacer length in these H-shaped dimers also promotes nematic over smectic behaviour as we saw earlier for conventional linearly linked dimers. An H-shaped dimer has been reported containing a spacer incorporating a siloxane moiety which shows nematic behaviour.[113]

Fewer examples of T-shaped dimers have been reported in the literature; for example, Weissflog *et al.*[129] synthesised, **24**, and this shows a smectic A and a nematic phase. More recently, Jin and co-workers[133] reported the first
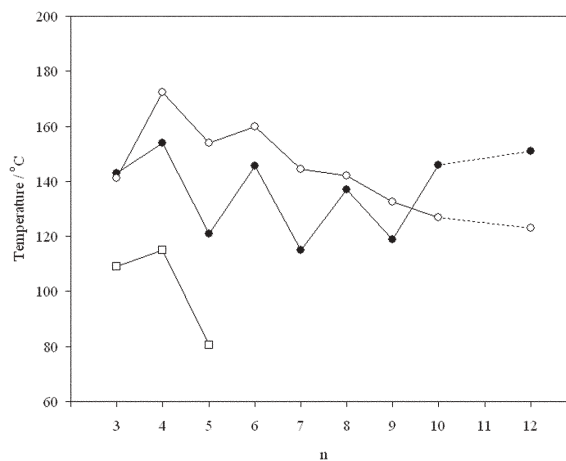
Fig. 17 The dependence of the transition temperatures on the number of methylene units, *n*, in the flexible spacer for the laterally linked or H-shaped dimers, the α,ω-bis[2,5-bis(4-*n*-octyloxybenzoyloxy)-benzamido]alkanes;[129] ○ denotes nematic–isotropic transitions and □ smectic C–nematic transitions. Melting points are indicated by ●.

This journal is © The Royal Society of Chemistry 2007

Chem. Soc. Rev., 2007, **36**, 2096–2124 | 2111

C$_8$H$_{17}$O—〈benzene〉—COO—〈benzene〉(OOC—〈benzene〉—OC$_8$H$_{17}$)(COOCH$_2$—〈benzene〉—OOC—〈benzene〉—OC$_n$H$_{2n+1}$)

24
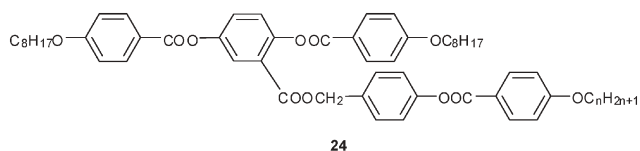
study comparing the properties of linear, H- and T-shaped dimers containing the same mesogenic units and the molecular structures of these are shown in Fig. 18. It should be noted, however, that this study was restricted to even-membered spacers (n = 4, 8, 12). The H-shaped dimers showed smectic behaviour while for the linear and T-shaped dimers only nematic behaviour was seen. The conventional linear dimers exhibited the highest liquid crystal–isotropic transition temperatures and the H-shaped dimers the lowest. For all three sets of compounds the clearing temperature decreased with increasing spacer length. It was suggested that the strong nematic tendencies of the T-shaped dimers indicated that the spacer adopts conformations for which the two mesogenic units are held more or less co-parallel, a view supported by the observation that there is a weaker dependence of the clearing temperature on the length of the flexible spacer for the T-shaped dimers than for the corresponding linear dimers. Indeed, the trend in the clearing temperatures strongly suggests that the molecular biaxiality must increase on passing from the linear to the T-shaped to the H-shaped dimers.

Dimers containing bent core mesogenic units

Bent core, or banana, liquid crystals have received much attention in recent years.[134] Despite consisting of achiral molecules these rigid core bent-shaped mesogens exhibit polar order and chiral superstructures. The majority of this research has concentrated on the fundamental structure–property relationships in conventional bent-core liquid crystals while there have been relatively few reports of dimers composed of two linked bent-core moieties.

The first reported 'banana dimer' consisted of two rigid bent-core mesogenic units linked *via* a flexible alkyl spacer containing dimethylsiloxane units in the centre,[135] **25**. The

siloxane spacer leads to microphase separation which decouples the layers. X-Ray diffraction studies revealed an intercalated structure with the molecules also tilted within the layers. The dimer containing an odd number of dimethylsiloxane units exhibits an optical texture with chiral domains whereas the dimer with an even number of units does not. The odd-membered dimers show ferroelectric switching and the even-membered dimers show antiferroelectric switching, indicating a strong dependence of phase structure upon the length and parity of the flexible spacer; this is due to the geometry of the siloxane spacer and the bent shape of the mesogenic units. Similar behaviour has been reported for other bent-core mesogenic dimers.[136] Marcelis and co-workers extended this series of compounds by varying the terminal chain and also the two alkyl spacers linking the mesogenic units to the central siloxane core.[137] It was found that the layer spacing was only weakly dependent on the length of the terminal chains. All the homologues exhibited a SmCP$_F$ phase and thus no odd–even effect was observed on phase type on varying the parity of the alkyl spacers. The authors also reported the corresponding materials containing wholly alkyl chain spacers. These did not exhibit polar phases, but instead showed a more conventional tilted smectic phase. Other bent-core dimers containing wholly alkyl-spacers have been reported which exhibited a columnar phase with an oblique lattice.[138,139] The materials exhibited ferroelectric switching and thus the phase was assigned as Col$_{ob}$P$_F$. Again, the parity of the flexible spacer had no effect on the phase behaviour, although increasing the length of the terminal chain increased the temperature range of the mesophase. Weissflog and co-workers compared dimers containing either alkyl, tetraethylene glycol or siloxane containing spacers.[140] Those containing wholly alkyl spacers were not mesogenic, while those with tetraethylene glycol spacers exhibited columnar mesophases and those with siloxane containing spacers exhibited a SmCP$_F$ mesophase.

If we compare this rather small group of bent-core containing dimers we can see that the composition of the flexible spacer plays an important role in determining the phase behaviour of the dimers. Dimers linked *via* alkyl chains or
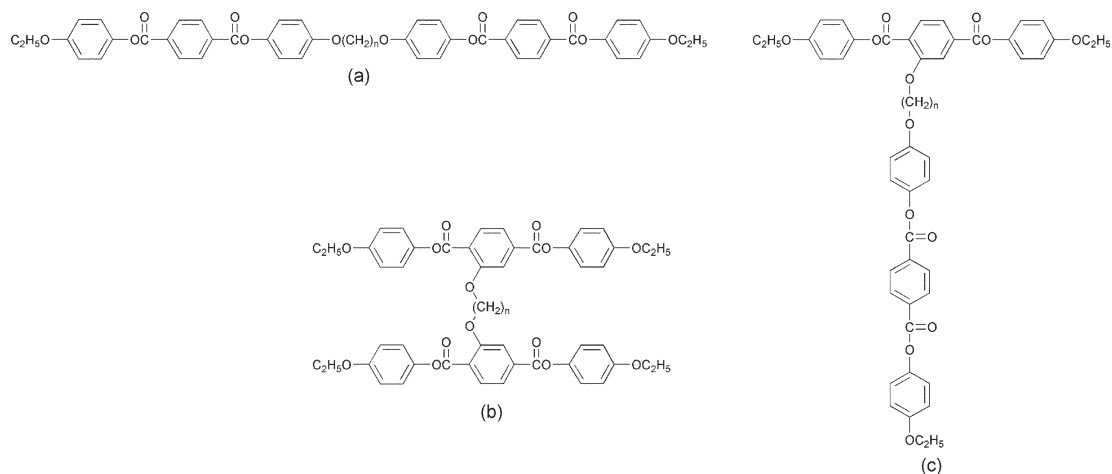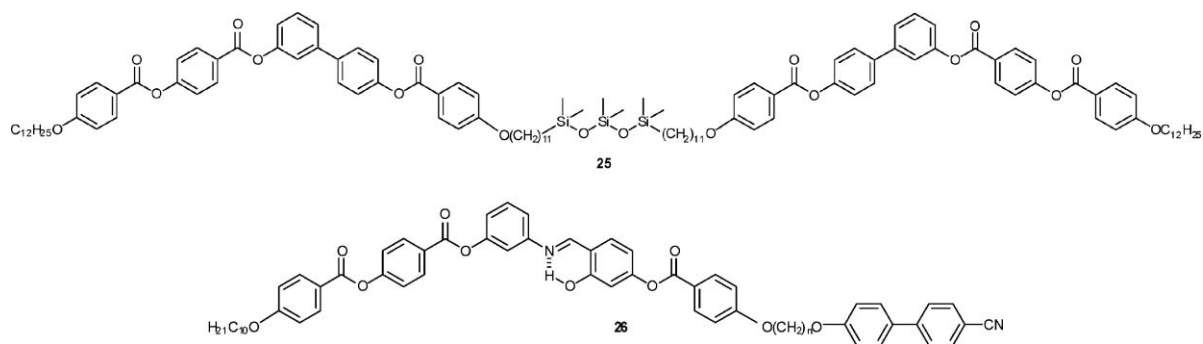
(a)

(b)

(c)

Fig. 18 Molecular structures of (a) a conventional linear dimer, (b) a laterally linked H-shaped dimer and (c) a T-shaped dimer containing terminally and laterally linked mesogenic units.[133]

25

26

ethylene glycol exhibit either tilted smectic or columnar mesophases rather than 'banana' phases with polar ordering. The addition of a siloxane group into the central spacer leads to microphase separation and the emergence of polar tilted smectic phases. The phase behaviour shows a strong dependence on the parity of the central siloxane group, although this effect is not observed on varying the alkyl chains on either side of it. It should be noted that the length of the flexible spacer here is longer than that in the corresponding dimers linked solely by an alkyl spacer, including as it does both the siloxane group and two alkyl spacers either side of it.

Non-symmetric dimers containing both a bent-core and calamitic mesogenic units have recently been reported by Yelamaggad et al.[141] **26**. The dimer containing a pentamethylene spacer was not mesogenic while the member with a hexamethylene spacer exhibited a nematic, smectic A and a further unidentified mesophase. On the basis of optical studies the first two phases were identified as biaxial nematic, N_b, and biaxial smectic A, SmA_b, although it should be noted that these are rather tentative assignments. This group has also studied bent-core/rod dimers containing a chiral group, specifically the cyanobiphenyl group of **26** is replaced by a cholesteryl moiety.[142,143] Even-membered dimers exhibited blue phases over a long temperature range, chiral nematic and then either columnar or tilted smectic phases. The odd-membered dimers exhibited only a columnar phase, indicating a strong dependence of packing on the parity of the flexible spacer for such dimers. Weissflog and co-workers have reported dimers containing a bent-core mesogenic unit connected to an achiral calamitic moiety.[144] The dimers exhibited a nematic and columnar phase, and the authors suggest that there is a microsegregation of the calamitic and bent-core units within the columnar phase.

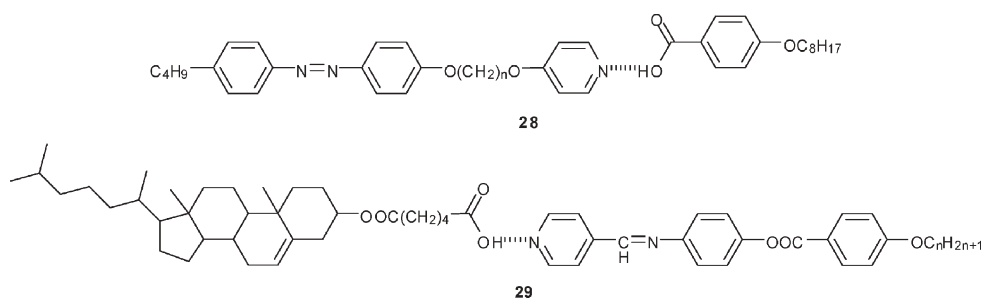## Liquid crystal dimers containing disc-like units

The overwhelming majority of symmetric liquid crystal dimers consist of molecules containing two identical rod-like or calimitic mesogenic units. By comparison, the numbers of symmetric dimers containing two disc-like mesogenic units are relatively few. This situation has arisen to a large extent due to the significant synthetic challenges in preparing monofunctionalised discotic precursors, without which the preparation of symmetric discotic dimers normally involves laborious separation procedures involving several isomers of the discotic core. Advances in the synthetic methodologies used to prepare, in particular, triphenylene-based compounds, however, have

made discotic dimers more readily accessible.[17,145–147] Kumar[17] and Laschat et al.[147] have recently reviewed structure–property relationships in discotic dimers, oligomers and polymers and so here we will restrict ourselves to a high level discussion of the general properties of discotic dimers.

Boden et al.[148] have reported the most complete series of discotic liquid crystal dimers which contained two identical triphenylene-based mesogenic groups attached via a flexible spacer, **27**.

27
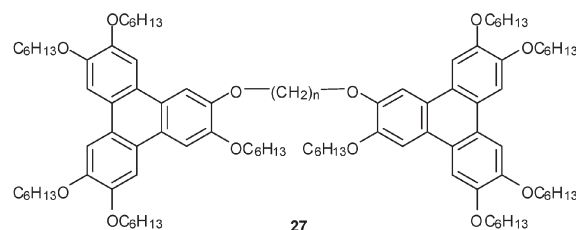
Liquid crystallinity was not observed for the short spacer lengths (n = 3, 5, 7). This was attributed to steric crowding within the molecule resulting in the two triphenylene units not being co-planar. This in turn inhibits the formation of a columnar structure. For the remaining homologues a hexagonal columnar phase was observed which could be supercooled to form a glassy columnar phase. In these compounds the spacer is sufficiently long to avoid steric crowding within the molecule and the discs can now pack efficiently into columns which are bridged by the spacers. Interestingly, the clearing temperatures of these dimers are very similar to those of the corresponding compounds containing just a single triphenylene unit suggesting that the stability of the columnar phase can be attributed largely to the interactions between the aromatic cores while the alkyl chains, including the spacers, simply fill spacer providing, of course, that the spacers are sufficiently long to bridge the columns. This view is supported by the observation that the highest clearing temperatures are observed for the decyl and dodecyl homologues which most closely match to twice the length of the peripheral alkyl chains attached to the triphenylene cores which would be the expected intercolumn distance within the mesophase. This interpretation of the behaviour of discotic dimers would also predict that the pronounced alternations observed for dimers containing rod-like mesogenic units should not be observed and indeed this is the case. For this series there is just 1 °C difference between the clearing temperatures of the octyl and nonyl homologues. It appears, therefore, that in discotic

This journal is © The Royal Society of Chemistry 2007

Chem. Soc. Rev., 2007, **36**, 2096–2124 | 2113

C₄H₉ ... O(CH₂)ₙO ... HO ... OC₈H₁₇

28

... OOC(CH₂)₄ ... OH ... N ... C=H ... N ... OOC ... OCₙH₂ₙ₊₁

29

dimers the spacer has little effect on the mesophase behaviour providing it is sufficiently long to span the inter-column distance.

Recent computer simulations of a model for discotic liquid crystal dimers gave good agreement with experimental results.[149] Specifically, when compared to monomers the dimers have a broader temperature range columnar nematic phase and the crystalline phase is suppressed in favour of a broader temperature range columnar phase. Short spacer lengths prevented the formation of columns whereas longer spacers lead to the formation of columns and to an increase in orientational order.

Discotic dimers have a very strong tendency to exhibit columnar phases but an example of one showing nematic behaviour was reported by Praefcke et al.[150] which consisted of two multialkynyl units attached via a flexible spacer. This particular dimer attracted considerable interest because conoscopic studies suggested that it exhibited the biaxial nematic phase (see later section) although this was shown not to be the case by NMR spectroscopy using selectively deuterated materials.

Hydrogen bonding and dimers

Liquid crystal dimers have been assembled using non-covalent bonds; for example, binary equimolar mixtures of 1-(4-pyridyloxy)-5-[4-(4-butylphenylazo)phenoxy]pentane or 1-(4-pyridyloxy)-6-[4-(4-butylphenylazo)phenoxy]hexane with 4-octyloxybenzoic acid show smectic A behaviour even though both pyridyl-based compounds are not liquid crystalline.[151] The observation of liquid crystallinity for the mixture is attributed to the formation of a hydrogen bond between the unlike species giving an extended complex, **28**. It is interesting to note that both the clearing temperature and associated entropy change for the complex containing the even-membered spacer are considerably higher than those observed for the odd-membered complex. This strongly suggests the formation of an extended supramolecular liquid crystal dimer, and it is apparent that the specific interaction between the pyridyl and acid fragments has not only enhanced the clearing temperature but also increased the degree of molecular ordering within the mesophase.

Other examples of such supramolecular dimers were reported by Lee et al.[152] which included a cholesteryl-based mesogen attached via a flexible spacer to a hydrogen-bond acceptor, **29**. These hydrogen-bonded dimers exhibited frustrated phase behaviour similar to that seen for the corresponding conventional dimers described in earlier. Specifically, the periodicity in the smectic phase exhibited by these mixtures

depended on the lengths of the terminal chain attached to the pyridyl-based hydrogen bond acceptor. Thus for long terminal chains a layer periodicity corresponding to the estimated length of the complex was observed while for short chain lengths the layer spacing falls to a value of about half the length of the complex. The competition between these two length scales gives rise to the formation of an incommensurate smectic phase in which over long range the two periodicities coexist.

Liquid crystal dimers and the search for the biaxial nematic phase

In the uniaxial nematic, N_u, phase the molecules are arranged such that there are no positional correlations between their centres of mass but the unique axes of the molecules are arranged about a common direction known as the director, n, see Fig. 19(a). By comparison in the biaxial nematic, N_b, phase there is also a correlation of the molecules in a direction perpendicular to n and the phase is often schematically represented as consisting of lozenge-shaped molecules, see Fig. 19(b). Thus, in the N_u phase the physical properties in the plane perpendicular to n are angle independent whereas in the N_b phase they are not.

The existence of the N_b phase was predicted over 30 years ago by Freiser[153] and this triggered considerable research world-wide focussed on the search for a N_b phase exhibited by a low molar mass thermotropic liquid crystal. There have been a number of claims for such behaviour but the validity of many of these has been questioned.[154,155] It is worth noting here that the identification of the biaxial nematic phase is not a trivial task[156] although macroscopic biaxiality may be demonstrated using conoscopy. This requires a well-aligned sample, however, the production of such a sample may induce the observed
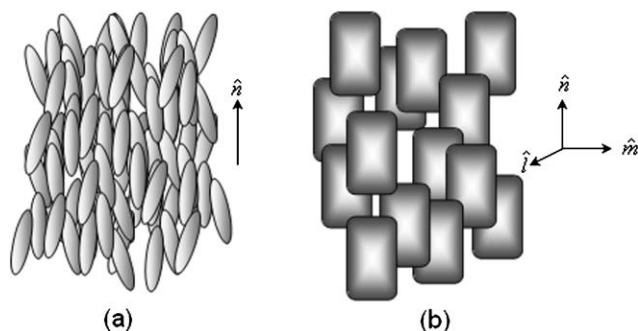
Fig. 19 Schematic representations of (a) the uniaxial nematic phase and (b) the biaxial nematic phase.

biaxiality. For many years it was believed that the observation of a Schlieren texture containing only two-brush defects could be used to assign the N_b phase. This view is now in doubt and furthermore the same texture has been observed for the biaxial smectic A phase.[157] Evidence for the presence of the N_b phase can be found in the magnitude of the entropy change associated with the nematic–isotropic transition which is predicted to be second order in nature if the phase is biaxial.[158] The preferred identification method however, is deuterium NMR spectroscopy.[159,160]

Theoretical studies have shown that mixtures of rods and discs can exhibit the N_b phase.[161,162] In such a mixture the optimum packing arrangement has the long axes of the rods arranged perpendicularly to the short axes of the discs and hence, the system has two directors. In these simulations an attractive interaction is required between the rods and discs to prevent phase separation into two N_u phases. In real systems, however, this phase separation does occur. To overcome this difficulty Fletcher and Luckhurst[163] joined the disc-shaped [pentakis(4-pentylphenyl-ethynyl)]benzene and the rod-shaped cyanobiphenyl units via a flexible alkyl spacer ranging in length from 6 to 12 methylene units, **30**.

30
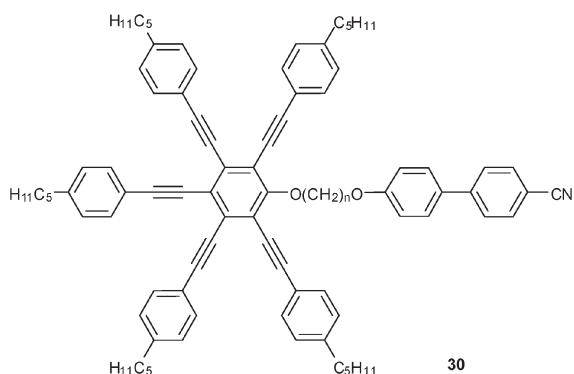
Only one of these compounds exhibited liquid crystalline behaviour; the hexyl homologue which showed a strongly monotropic nematic phase. Indeed, the clearing temperatures of these non-symmetric dimers are considerably lower than the average values of those of the discotic[164] and calamitic[20] parent symmetric dimers. This observation was attributed to the extreme difficulty in simultaneously packing the rod-like and disc-like units which may, at least in part, be relieved by increasing the spacer length. Equimolar mixtures of these non-symmetric dimers with 2,4,7-trinitro-9-fluorenone (TNF) do exhibit monotropic nematic behaviour. The formation of the nematic phase in these mixtures is presumably driven by the specific interaction between the electron-rich disc units and the electron-accepting TNF molecules. The monotropic nature of these phases, however, precluded the detailed experimental investigations required to establish whether these molecules do exhibit the biaxial nematic phase.

This approach was developed by Hunt et al.[165] who synthesised and characterised a compound in which the rod-like unit was attached laterally to the disc-like group via a flexible spacer, **31**.

31
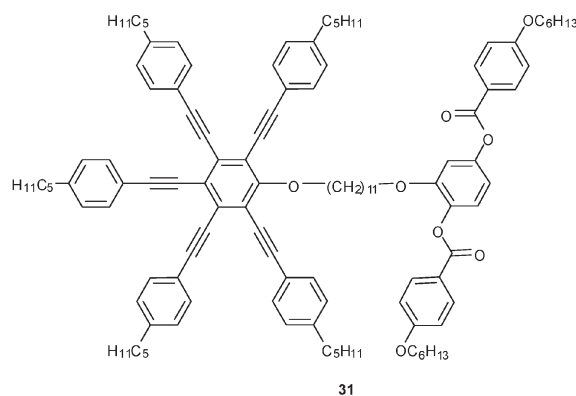
This material also exhibited a monotropic nematic phase but which did not readily crystallise and hence could be studied. The nematic–isotropic entropy change was very small and given that theory predicts the biaxial nematic–isotropic phase transition to be second order in nature, this was an encouraging result. Attempts to determine the symmetry of the phase were not successful but deuterium NMR spectroscopy did show that the combination of the rod and disc units in a single structure does give rise to a highly biaxial molecule. This strongly suggests that this approach could result in the discovery of a low molar mass thermotropic biaxial nematogen. Subsequently, Date and Bruce used this rod–disc dimer to successfully stabilize mixtures of rods and discs although the symmetry of the nematic phase exhibited by the mixture has yet to be reported.[166]

Another recent claim for the biaxial nematic phase has involved a non-symmetric liquid crystal dimer consisting of rod-like and banana-shaped mesogenic units, reported by Yelamaggad et al. and described earlier.[141] Again this assignment is a rather preliminary one which now requires verification.

Mehl and co-workers[167–169] have reported the phase behaviour of a number of oligomeric compounds containing disc-like and rod-like units interconnected by flexible spacers, but given their non-linear connectivity these fall outwith the scope of this review.

We have already discussed the properties of methylene-linked dimers and seen how geometrical factors alone could be used to account for the difference in transitional behaviour between these and the corresponding ether-linked dimers.[25,27] Luckhurst and co-workers developed a more transparent model to understand how geometrical factors influence the transitional properties of dimers in which the dimers can adopt just two conformations, one linear and one bent.[26,170] This model predicts that dimers containing short odd-membered methylene-linked spacers which would show high concentrations of bent conformers in the isotropic phase should exhibit a nematic–nematic transition. Experimentally, the nematic–isotropic entropy exhibited by 1,5-bis(4-cyanobiphenyl-4′-yl)pentane is very small suggesting that the transition is approaching second order in nature.[10] Theory predicts that following such a second order transition a biaxial nematic phase should be observed. Unfortunately, for this particular dimer the formation of a smectic phase precludes the possibility of observing a nematic–nematic phase transition. Indeed, the short odd-membered methylene linked dimers

This journal is © The Royal Society of Chemistry 2007

Chem. Soc. Rev., 2007, **36**, 2096–2124 | 2115

studied to date have either shown monotropic nematic behaviour or a tendency to exhibit smectic phases presumably arising form their bent molecular shape.[22–24]

Liquid crystal trimers

Liquid crystal trimers consist of molecules containing three mesogenic units joined by two flexible spacers. A number of differing molecular architectures are possible for liquid crystal trimers including linear,[10,171–184] terminally/laterally connected,[185–187] cyclic,[188–193] tribranched/starshaped[194–200] and mixed calamitic/discotic trimers.[185,201,202]

Our focus here will be the linear trimers, and interest in these arises not only from their possible role as model compounds for semi-flexible main-chain liquid crystal polymers, but also because like dimers, they exhibit quite different properties to conventional low molar mass mesogens. Like dimers, trimers may be classed as being symmetric, or non-symmetric. Non-symmetry may be introduced into the trimeric structure in a variety of ways; for example, non-symmetric trimers may consist of different mesogenic units (either two or all three may differ),[174,175,177,185,201,202] contain different flexible spacers or terminal chain lengths,[10,203] have different terminal groups, or indeed have some combination of all these structural features.[179,180,182,183]

There are relatively few examples of linear liquid crystal trimers in the literature and even fewer complete homologous series.[10,176,177,204–206] The first reported trimer[171] was synthesised by 'step-wise polymerisation' as part of an oligomer series to obtain model compounds for polyesters. These oligomers were not mesogenic and at the time is was predicted that for a stable nematic phase to be observed in oligomers approximately six mesogenic repeating units were required, which turned out not to be the case. The first homologous series of liquid crystal trimers reported contained two cyanobiphenyl moieties and a central biphenyl core, these trimers are refered to as TCBOn, **32**, and may be considered as the trimeric analogues of the dimeric BCBOn series, **2**.[10,21,177] All members of the series exhibited a nematic phase and in addition those with $n = 4–11$ exhibited a monotropic smectic A phase.

More recently a homologous series of symmetric trimers containing an azobenzene mesogenic unit have been reported, and its transitional properties compared to those of the
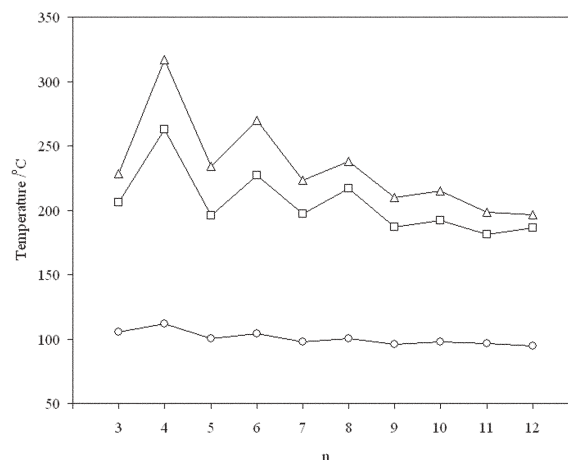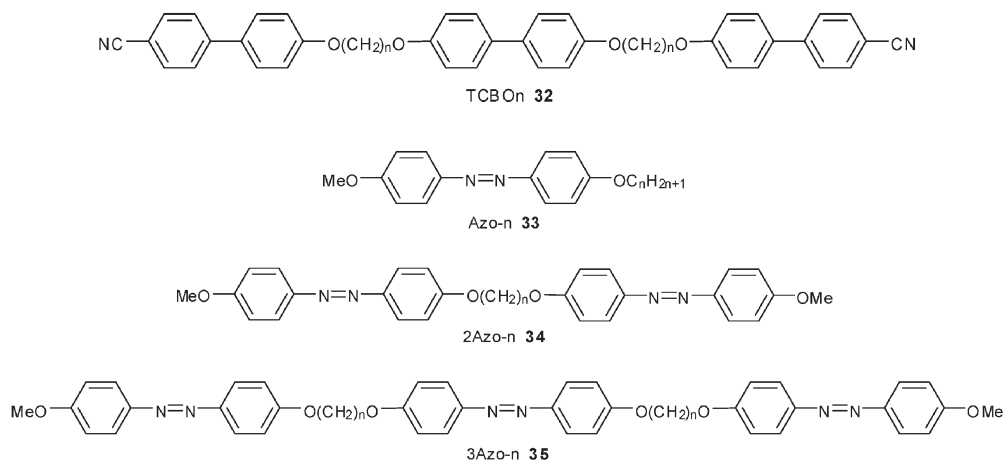

Fig. 20 Dependence of the nematic-isotropic transition temperatures of the 3Azo-n ($\triangle$), 2Azo-n ($\square$) and Azo-n ($\bigcirc$) series on the length of the alkyl chains in each series.

corresponding dimers and conventional low molar mass materials (monomers).[204] The acronyms used to describe the monomers, dimers and trimers are Azo-n (**33**), 2Azo-n (**34**) and 3Azo-n (**35**), respectively, where n refers to the number of carbon atoms in the terminal chain of the Azo-n series and to the number to methylene units in the flexible spacers of the 2Azo-n and 3Azo-n series.

The trimers exhibit a nematic mesophase for all values of n and both the melting and clearing temperatures depend strongly on the length and parity of the flexible spacers. Specifically, the transition temperatures exhibit a strong odd–even effect on increasing n in which even members show the higher values. The alternation in the melting points do not appear to attenuate on increasing n. By contrast the nematic–isotropic transition temperatures exhibit a pronounced odd–even effect which does attenuate quickly on increasing n, see Fig. 20. This behaviour is similar to that observed for dimers and semi-flexible main-chain polymers.[207] The clearing entropy change also shows a strong odd–even effect in which the even–membered trimers have the higher values, and which is not attenuated on increasing n, see Fig. 21. In general the values of $\Delta S_{NI}/R$ for the even members are approximately twice that of the adjacent odd members. The value for $n = 4$ is unexpectedly low due to decomposition of the material.
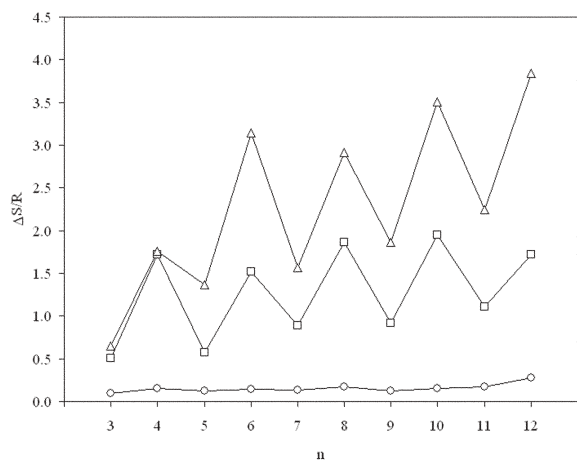

TCBOn **32**

Azo-n **33**

2Azo-n **34**

3Azo-n **35**

Fig. 21 The dependence of the nematic-isotropic entropy change on the length of the flexible spacers for the 2Azo-*n* (□) and 3Azo-*n* (△) series. Also shown are the nematic-isotropic entropy changes for the Azo-*n* (○) series.

The observation of pronounced odd–even effects in both the transition temperatures and entropy changes as the length of the spacers are varied for the trimers can be explained in the same manner as for the behaviour of dimers and semi-flexible main-chain polymers.[10,12,177,207] Thus, if a trimer is considered in its most extended all-*trans* conformation two distinct molecular shapes are possible depending on the parity of the spacers. Odd-membered trimers have the two outer mesogenic units inclined with respect to the central unit giving a stretched 'S' shape, see Fig. 22(a). By comparison even-membered trimers have all three mesogenic units co-parallel, resulting in an extended rod-like molecular structure, Fig. 22(b). The even-membered trimers therefore have an enhanced shape anisotropy which allows the molecules to pack more efficiently in the liquid crystal phase, resulting in higher transition temperatures and entropy changes. This interpretation does not take into account the flexibility of the alkyl spacers and a more realistic argument includes a wider range of conformations.[12,13] The approach developed by Luckhurst and co-workers[10,12] to describe the behaviour of dimers has also been successful in modelling the behaviour of trimers.[208]

Comparisons of the clearing temperatures and entropies exhibited by the trimers with those shown by the corresponding dimers and monomers are shown in Fig. 20 and Fig. 21.
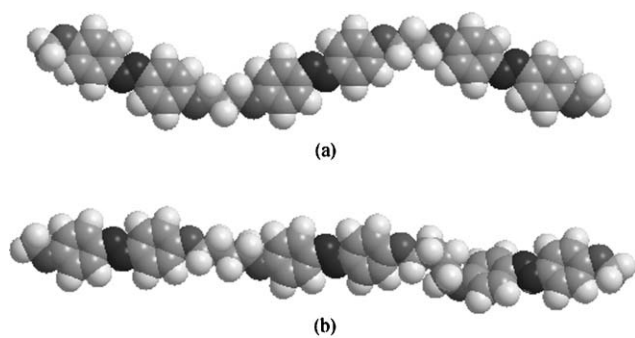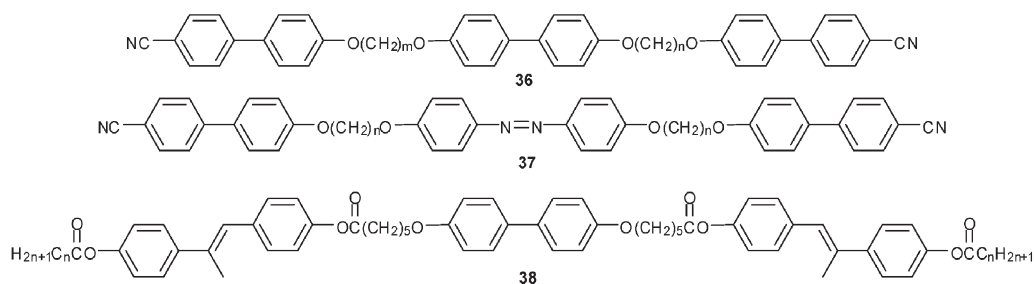

Fig. 22 Molecular shapes of the all-*trans* conformation of trimers containing (a) odd- (*n* = 3) and (b) even- (*n* = 4) membered flexible spacers.

The trimers have the highest clearing temperatures and entropies, followed by the dimers and then the monomers. This is expected as adding mesogenic units increases the shape anisotropy of the molecule. Pronounced odd–even effects are seen for the clearing temperatures and entropies of both the dimers and trimers on increasing *n*, but for the monomers much weaker alternations in these quantities are observed as the length of the terminal alkyl chain is varied. It is interesting to note that as *n* is increased the transition temperatures of the dimers and trimers become more similar. This raises the question as to whether the clearing temperatures of the dimers would actually be greater than those of the trimers for much longer spacers but this has yet to be investigated. The difference in clearing temperatures between the trimers and dimers is much smaller than the difference between the dimers and monomers. The values of $\Delta S_{NI}/R$ are highest for the trimers, and in general twice those of the corresponding dimers, Fig. 21. The values of $\Delta S_{NI}/R$ for the monomers are appreciably lower than either those of the dimers or trimers. The $\Delta S_{NI}/R$ values of the odd-membered trimers are similar to those observed for the even-membered dimers. There is a greater increase in $\Delta S_{NI}/R$ on going from an even-membered dimer to an even-membered trimer than is seen for the odd-members, and hence the magnitude of the odd–even effect for the trimers is greater than that seen for the dimers. The small increase in T_{NI} suggests that the mesogenic units in the trimers are correlated to the same extent as in the dimers whereas the larger increase in $\Delta S_{NI}/R$ suggests a significant increase in the orientational order of the mesogenic groups on passing from the dimer to trimer.

Of the two complete trimer series reported only the TCBO*n* series exhibited smectic behaviour in adition to the nematic phase. The phase was assigned as a smectic A phase on the basis of its optical texture. The monotropic nature of the phase precluded the possibility of X-ray studies to confirm this assignment. Barnes and Luckhurst reported non-symmetric analogues of the TCBO*n* series in which the two flexible spacers were of different lengths,[10] **36**. These also exhibited monotropic phases which were assigned as smectic A on the basis of their optical textures. Ikeda *et al.*[175] prepared trimers with an even number of carbon atoms in the flexible spacers, **37**, which exhibited an enantiotropic phase, assigned as a smectic C phase, again on the basis of the optical textures. For all these compounds no X-ray diffraction data were obtained to determine the structure of the smectic phase. Centore *et al.*[174] synthesised trimers with a variable terminal alkyl chain, **38**. These materials exhibited both a smectic A and smectic C phase. X-Ray diffraction studies of the smectic C phase gave a layer spacing indicative of a conventional monolayer smectic C phase.

Non-symmetric trimers have been reported in which the terminal groups, linking groups and two flexible spacers were varied to give four related homologous series,[206] **39**. In the MeO6E.*n*OMe and CN6E.*n*CN series the length of one of the flexible spacers is held constant at six methylene units while the second spacer is varied from *n* = 3 to 12 methylene units. In these series the mesogenic units differ, with the two outer moieties being identical azobenzene-based groups while the central one is a Schiff's base unit. In the second two series the

This journal is © The Royal Society of Chemistry 2007

Chem. Soc. Rev., 2007, **36**, 2096–2124 | 2117

NC⟨⟩⟨⟩O(CH₂)ₘO⟨⟩⟨⟩O(CH₂)ₙO⟨⟩⟨⟩CN

36

NC⟨⟩⟨⟩O(CH₂)ₙO⟨⟩N=N⟨⟩O(CH₂)ₙO⟨⟩⟨⟩CN

37

H₂ₙ₊₁CₙCO⟨⟩OC(CH₂)₅O⟨⟩⟨⟩O(CH₂)₅CO⟨⟩OCCₙH₂ₙ₊₁

38

terminal mesogenic units differ: one is an electron rich methoxyazobenzene group and the other an electron deficient cyanoazobenzene group. Again one spacer is held at six methylene units while the other is varied from $n = 3$ to 12 methylene units. It should be noted that the linking units to the central mesogenic unit also differ in each series: specifically, one spacer is attached *via* an ester linkage and the other by an ether linkage.

The MeO6E.*n*CN and CN6E.*n*OMe series were designed to contain both electron rich and electron deficient liquid crystal units to exploit specific electrostatic interactions which play an important role in the self-organization of a range of systems including binary mixtures,[150,209] liquid crystal dimers[13] and copolymers.[210,211]

All four series exhibited an enantiotropic nematic phase for all values of *n*. Both the clearing temperatures and transition entropies showed an odd–even effect, see Fig. 23. The magnitude of the odd–even effect observed in the clearing temperature for any one of the four series is not as large as that seen for symmetric trimers such as the 3Azo-*n* series because in these non-symmetric trimers one of the spacers always contains an odd number of connecting atoms. Thus, the change in the average molecular shape on varying the length of the other spacer is not so pronounced. Similar results were seen in the non-symmetric trimers reported by Barnes and Luckhurst, **36**.[10]

Although there are many examples in the literature of non-symmetric dimers exhibiting smectic behaviour, of the four non-symmetric trimer series only two homologues, MeO6E.11CN and CN6E.11OMe, were smectogenic. It is also interesting to note that a 1 : 1 binary mixture of MeO6E.11OMe and CN6E.11CN also exhibited a monotropic smectic phase, the texture of which was similar to that of MeO6E.11CN. The X-ray diffraction pattern of the smectic mesophase of CN6E.11OMe showed one diffraction peak in the low-angle region and a diffuse band in the wide-angle region. The low-angle peak gave a *d*-spacing of just 19.0 Å. This is surprising given the calculated molecular length of 60.4 Å. This strongly suggests that this trimer is forming a triply-intercalated phase, see Fig. 24. In this micro-phase
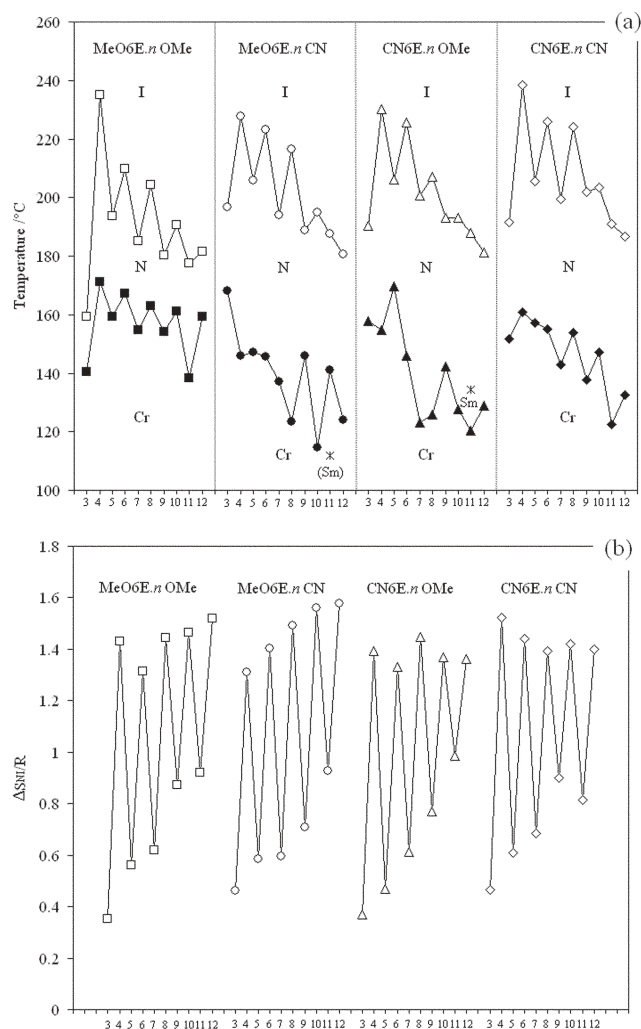
Fig. 23 (a) Dependence of the transition temperatures on the number of methylene units, *n*, in the variable flexible spacer, for the four trimer series **39**. Closed symbols represent crystal-nematic and open symbols nematic–isotropic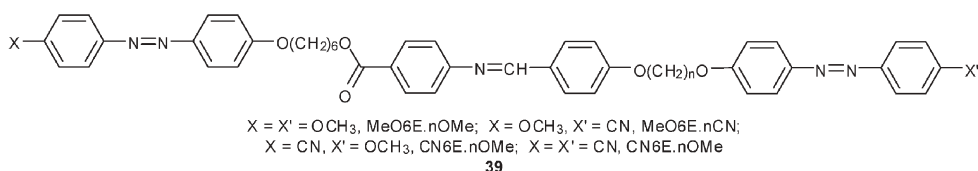 transition temperatures. * Denotes Sm–N transition temperatures. (b) Dependence of the nematic–isotropic entropy on the number of methylene units, *n*, in the variable flexible spacer for the four trimer series **39**.

X⟨⟩N=N⟨⟩O(CH₂)₆O⟨⟩C(=O)⟨⟩N=CH⟨⟩O(CH₂)ₙO⟨⟩⟨⟩N=N⟨⟩X'

X = X' = OCH₃, MeO6E.nOMe; X = OCH₃, X' = CN, MeO6E.nCN;
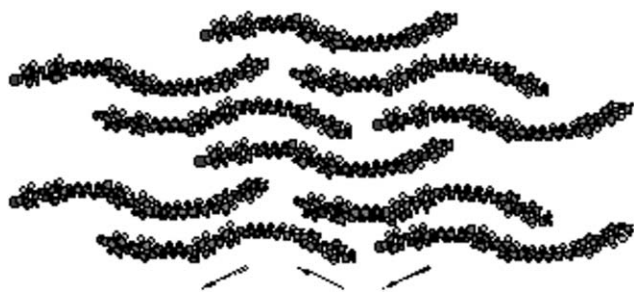X = CN, X' = OCH₃, CN6E.nOMe; X = X' = CN, CN6E.nOMe

39

Fig. 24 Schematic representation of the triply-intercalated alternating smectic C phase exhibited by CN6E.11OMe.

separated arrangement the mesogenic units and the flexible spacers each constitute a domain. The three different mesogenic units are contained in one domain while the two spacers are mixed in the other. Within a layer all the mesogenic units tilt in one direction and in the next layer tilt in the opposite direction such that the global tilt angle is zero. It was proposed that the driving force for this biasing of rotation about the molecular long-axis may arise from a dipolar interaction involving the linking ester groups. This organisation is reminiscent of that seen in semi-flexible main-chain liquid crystal polymers[212,213] and dimers[69,70,214] containing odd-membered spacers. Only the odd-membered trimers show this behaviour, suggesting that the formation of the smectic phase is somehow related to the parity of the flexible spacer. Given that the principle difference between trimers on varying the spacer parity is their average shapes it seems reasonable to assume that this plays an important role in smectic phase formation. Specifically, it appears that only trimers having a bent structure exhibit this smectic phase. The triply-intercalated structure proposed can efficiently accommodate bent molecules and ensures optimal space filling within the structure whilst allowing microphase separation between chains and mesogenic cores. In addition each domain contains an equal number of the three different mesogenic groups, which is presumably entropically favourable. The absence of smectic phase behaviour for the undecyl homologues of the trimer series containing identical terminal mesogenic units, however, shows that the specific interaction between the unlike mesogenic units is also important in phase formation.

Several other non-symmetric trimers have been reported. Marcelis *et al.* reported trimers with the central mesogenic unit based on optically active estradiol and in which the two spacers are of differing lengths, **40**.[180] The trimers exhibit a chiral nematic phase with only a weak odd–even effect in the clearing temperatures. In this case due to the molecular shape of the central unit the mesogenic units are not co-parallel. A further set of compounds had a central biphenyl unit and two outer cholesteryl-based groups.[179] For these compounds a strong odd–even effect was observed in the clearing temperatures. As well as a chiral nematic phase, a smectic A phase was also observed for a number of homologues.

Yelamaggad *et al.* have reported trimers with differing mesogenic groups and flexible spacers, **41**.[182,183,215] Homologues with spacers of equal parity exhibit an undulating twist grain boundary phase (UTGBC*) over a wide temperature range. Where the spacers are mis-matched there is a fleeting TGB phase observed between the chiral nematic and smectic A phases.[183]

Chiral trimers have been reported which exhibit stable antiferroelectric smectic C and I phases.[216] Transition temperatures are essentially identical for the *S,S* and *R,R* compounds while a racemic mixture exhibited the anticlinic versions of the smectic C and I phases. Only compounds with an even number of atoms in the spacers, resulting in the more linear molecular structure, were liquid crystalline. Micro-phase segregation of the aromatic rigid cores and flexible aliphatic spacers was proposed as the driving force behind smectic phase formation. Tamaoki and co-workers reported examples of what may be described as trimers assembled *via* hydrogen bonding in which the central core was a pyridyl unit.[217] These cholesteryl esters exhibited a chiral nematic phase and on rapid cooling glassy liquid crystalline films were obtained.

Trimers containing non-calamitic units, or units joined in a non-linear fashion have also been reported. Griffin and co-workers reported four trimers in which the central calamitic mesogenic unit had the two outer units laterally attached to it, resulting in a molecule where the two outer units were parallel, with the central one perpendicular to them.[187] All the compounds were nematogenic and it was assumed that the central mesogenic unit adopted a position such as to be parallel to the terminal spacers, lying along the nematic field director.

Three rod-like mesogenic units have been attached around a central point *via* flexible spacers to give tribranched Y-shaped trimers.[199] These exhibited a phase assigned as smectic C. A branched trimer has also been reported where chiral mesogenic units were attached around a cyclohexane

40

41
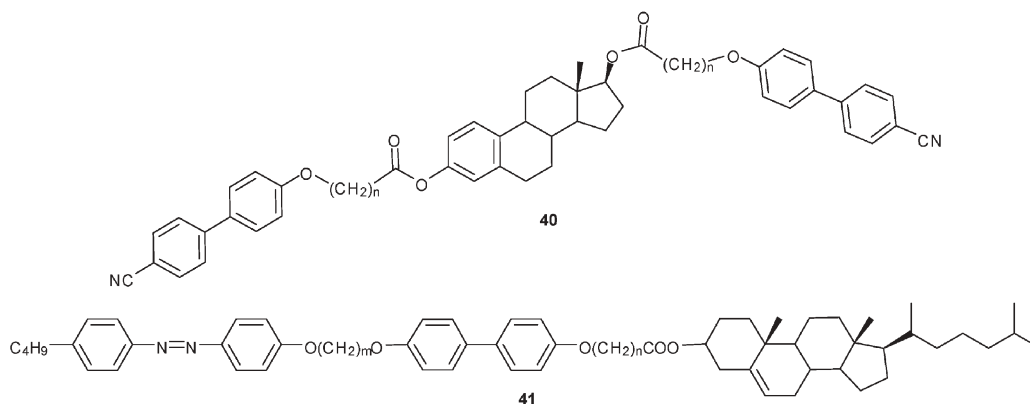
ring in the *cis*-1-, 3-, 5-positions.[197] This material exhibited a rich chiral smectic polymorphism. Other non-linear trimers such as tribranched[198] and laterally attached[187] have also been reported.

Non-linear oligomers have been synthesised in which the two outer mesogenic units are linked *via* flexible spacers to a central phenyl ring with either 3,4- or 3,5-substitution giving rise to V- and U-shaped oligomers respectively.[218,219] Only the *meta*-substituted 3,5- derivative shows a stable smectic phase. The same authors have also reported Y- and λ-shaped oligomers.[220,221]

Discotic trimers with three triphenylene-based mesogenic units attached around a benzene ring have been reported, which exhibit a monotropic columnar phase which did not crystallise even after being stored at room temperature for five months.[200] Linear trimers consisting of three discotic triphenylene units attached *via* two flexible spacers have been reported[222] as have mixed trimers containing both rods and discs.[185,202] Such materials tend to exhibit columnar phases. For recent reviews of rod/disc oligomers see refs. 17, 145 and 147.

Liquid crystal tetramers

Liquid crystal tetramers consist of molecules containing four interconnected mesogenic units. Relatively few series of linear liquid crystal tetramers have been reported to date. The first tetramers were reported by Griffin *et al.*[223] in which the central flexible spacer was varied, **42**. All four tetramers exhibited an enantiotropic nematic phase.

The first complete homologous series of linear liquid crystalline tetramers was reported by Imrie *et al.*[224] In this work the central spacer was held constant and the two outer spacers were varied from $n = 3$–12 methylene units in length, **43**. This series exhibited nematic and smectic phases. All members of the series except $n = 10$ and 12 exhibited a nematic phase, with $n = 6$–12 also having a smectic A phase, and $n = 10$ and 12 being solely smectic. It was suggested that the formation of the smectic A phase was due to an interaction between the differing mesogenic groups.

Two further series of tetramers have since been reported from which comparisons of the effects of varying the central spacer and outer spacers can be made.[225–227] The n–$p5p$–n series has an odd-membered central spacer whereas for the n–$p6p$–n series it is even-membered, **44**. The outer spacers were varied for $n = 3$–12 and both series were solely nematogenic. A large odd–even effect is seen for the clearing temperature which attenuated quickly on increasing n, Fig. 25. The transition temperatures are higher than those observed for
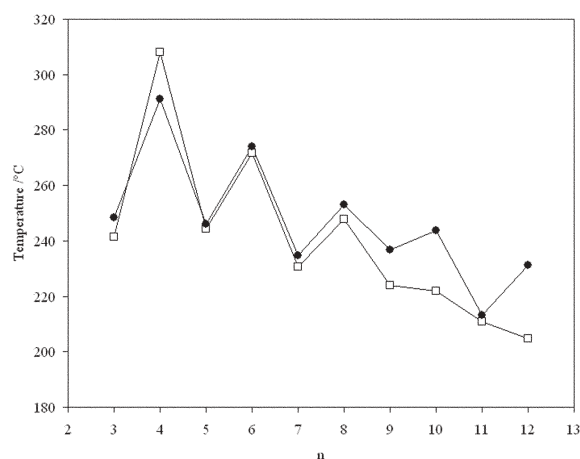

Fig. 25 The dependence of clearing temperature on n, the number of methylene units in the two outer spacers, for all liquid crystalline tetramer series; ● denotes the n–$p6p$–n series and □ the n–$p5p$–n series.

trimers, but the increase on adding an extra mesogenic unit is less than that observed on moving from dimers to trimers and from monomers to dimers. The clearing entropies also show an odd–even effect, Fig. 26. The tetramers' values are larger than those observed in trimer series and again, the increase is smaller than that observed on moving from dimers to trimers. The n–$p6p$–n series has higher values than the corresponding n–$p5p$–n series, presumably reflecting the more linear nature and efficient molecular packing of the even-membered trimers. The odd–even effect appears to attenuate slightly on increasing n. A similar result has been observed for other tetramer series.[224] This suggests that for odd-members on increasing n a greater proportion of the molecules are able to adopt a more linear conformation.

It is interesting to note the difference observed in the transition temperatures between these tetramers is surprisingly small. Indeed, several members of the n–$p5p$–n and n–$p6p$–n series have very similar clearing temperatures for corresponding values of n. This implies that whereas a large odd–even effect is observed on varying the outer spacers the effect is greatly diminished on varying the central spacer. Thus, the outer spacers play a far larger role in the odd–even effect than the central spacer does, implying that the mesogenic units are not strongly correlated along the molecule. The molecular significance of there results is not yet understood.

Yelamaggad *et al.* reported the first example of a liquid crystal consisting of molecules containing four differing mesogenic units, **45**.[228] These materials contain groups which
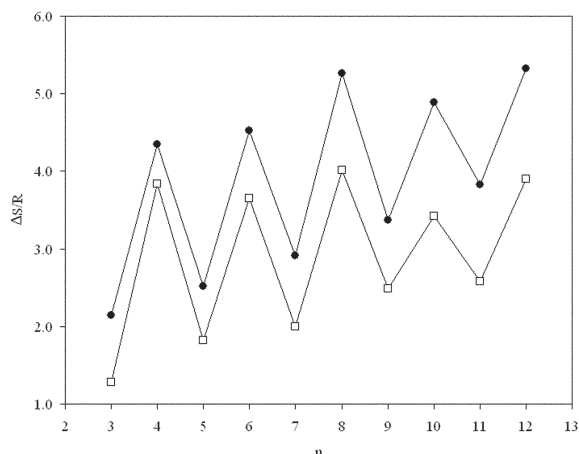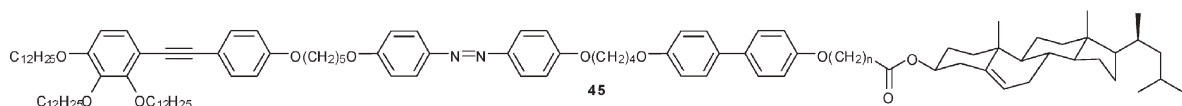
42

43

m = 5, n-p5p-n; m = 6, n-p6p-n
44

45
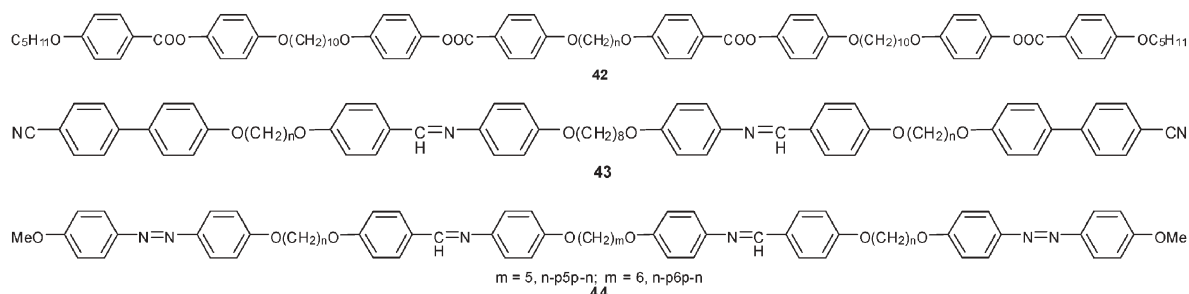
Fig. 26 Entropy change associated with the nematic–isotropic transition for the n–$p6p$–n series (●) and the n–$p5p$–n series (□).

are optically active, photochromic and half-disc shaped, and these linear tetramers exhibited a columnar mesophase.[229]

Where next?

The field of liquid crystal oligomers is an extremely buoyant one attracting considerable research interest for both fundamental and technological reasons. Fundamentally, highlights include non-symmetric liquid crystal dimers containing rod-like and disc-like units which are potential candidates to exhibit the much sought after but elusive biaxial nematic phase. Attaching these units *via* a spacer prevents their phase separation which would otherwise occur and opens up the wider and largely unexplored issue of interconnecting incompatible mesogenic groups. To date the focus has been very much to combine mesogenic units exhibiting a specific favourable interaction which led to the discovery of new smectic modifications. Moving forward, it is highly likely that the study of non-symmetric dimers containing incompatible mesogenic groups will lead to the discovery of an equally rich and new smectic polymorphism. Bent core liquid crystals have been one of the most intensively studied class of materials in recent years and again this has resulted in the discovery of new phase behaviour including the fascinating observation of chiral superstructures assembled from achiral molecules. By comparison and as we have seen, there are very few examples of dimers, or higher oligomers, containing bent core mesogens and this area promises to be a rich seam of new phase behaviour. While the study of liquid crystal dimers can be traced back to the early eighties, that of trimers and tetramers is very much newer and few examples of these classes of compounds have been reported. Even so, their study has already resulted in the discovery of new smectic phases and has shed light on the behaviour of liquid crystal semi-flexible main chain polymers. Most recently, Yelamaggad *et al.* reported the first example of a monodisperse liquid crystal pentamer consisting of five mesogenic units linked by four spacers.[231] These higher oligomers can be constructed using mesogenic units having differing properties giving truly multi-functional liquid crystals. In order to effect control over the properties of these materials and realize this multi-functional potential, however, it is not sufficient only to simply attach units together having the desired range of properties but we must also understand how these units self-organize in liquid crystal phases. Technologically, the use of liquid crystal dimers as dopants for liquid crystal display mixtures with faster relaxation times has recently been reported,[230] and we have seen that dimers have been found to exhibit a strong flexoelectric coupling. It is clear therefore that the area of liquid crystal oligomers will remain highly active for the foreseeable future!

References

1 C. K. Ober, J. Jin and R. W. Lenz, *Adv. Polym. Sci.*, 1984, **59**, 103.
2 G. S. Attard, *Trends Polym. Sci.*, 1993, **1**, 79.
3 A. Blumstein and O. Thomas, *Macromolecules*, 1982, **15**, 1264–1267.
4 G. W. Gray, in *The Molecular Physics of Liquid Crystals*, ed. G. R. Luckhurst and G. W. Gray, Academic Press, London, 1979, pp. 1–29.
5 G. Ungar, V. Percec and M. Zuber, *Macromolecules*, 1992, **25**, 75–80.
6 M. Tokita, K. Osada and J. Watanabe, *Liq. Cryst.*, 1998, **24**, 477.
7 A. C. Griffin and T. R. Britt, *J. Am. Chem. Soc.*, 1981, **103**, 4957–4959.
8 D. Vorländer, *Z. Phys. Chem.*, 1927, **126**, 449.
9 J. Rault, L. Liebert and L. Strzelecki, *Bull. Soc. Chim. Fr.*, 1975, 1175–1178.
10 G. R. Luckhurst, *Macromol. Symp.*, 1995, **96**, 1–26.
11 C. T. Imrie, F. E. Karasz and G. S. Attard, *Macromolecules*, 1993, **26**, 3803–3810.
12 C. T. Imrie and G. R. Luckhurst, in *Handbook of Liquid Crystals*, ed. D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, pp. 801–833.
13 C. T. Imrie, *Struct. Bonding*, 1999, **95**, 149–192.
14 C. T. Imrie and P. A. Henderson, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 298–311.
15 C. Tschierske, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 69–80.
16 I. M. Saez and J. W. Goodby, *J. Mater. Chem.*, 2005, **15**, 26–40.
17 S. Kumar, *Liq. Cryst.*, 2005, **32**, 1089–1113.
18 C. T. Imrie, Z. B. Lu, S. J. Picken and Z. Yildirim, *Chem. Commun.*, 2007, 1245–1247.
19 D. Demus, *Liq. Cryst.*, 1989, **5**, 75–110.
20 J. W. Emsley, G. R. Luckhurst, G. N. Shilstone and I. Sage, *Mol. Cryst. Liq. Cryst.*, 1984, **102**, 223.
21 G. R. Luckhurst, *Liq. Cryst.*, 2005, **32**, 1335–1364.
22 P. Barnes, A. G. Douglass, S. K. Heeks and G. R. Luckhurst, *Liq. Cryst.*, 1993, **13**, 603–613.
23 P. A. Henderson, O. Niemeyer and C. T. Imrie, *Liq. Cryst.*, 2001, **28**, 463–472.
24 P. A. Henderson, J. M. Seddon and C. T. Imrie, *Liq. Cryst.*, 2005, **32**, 1499–1513.
25 A. P. J. Emerson and G. R. Luckhurst, *Liq. Cryst.*, 1991, **10**, 861–868.
26 A. Ferrarini, G. R. Luckhurst, P. L. Nordio and S. J. Roskilly, *Chem. Phys. Lett.*, 1993, **214**, 409–417.
27 A. Ferrarini, G. R. Luckhurst, P. L. Nordio and S. J. Roskilly, *J. Chem. Phys.*, 1994, **100**, 1460–1469.

28 A. T. M. Marcelis, A. Koudijs and E. J. R. Sudhölter, *Liq. Cryst.*, 2000, **27**, 1515–1523.

29 D. Creed, J. R. D. Gross, S. L. Sullivan, A. C. Griffin and C. E. Hoyle, *Mol. Cryst. Liq. Cryst.*, 1987, **149**, 185–193.

30 T. Ohtake, K. Kanie, M. Yoshizawa, T. Mukai, K. Ito-Akita, H. Ohno and T. Kato, *Mol. Cryst. Liq. Cryst.*, 2001, **364**, 589–596.

31 C. T. Imrie, M. D. Ingram and G. S. McHattie, *Adv. Mater.*, 1999, **11**, 832.

32 W. K. Robinson, C. Carboni, P. Kloess, S. P. Perkins and H. J. Coles, *Liq. Cryst.*, 1998, **25**, 301–307.

33 M. N. Pivnenko, P. Lehmann, L. Komitov and H. J. Coles, *Liq. Cryst.*, 2005, **32**, 173.

34 N. Olsson, G. Andersson, B. Helgee and L. Komitov, *Liq. Cryst.*, 2005, **32**, 1125–1138.

35 N. Olsson, B. Helgee, G. Andersson and L. Komitov, *Liq. Cryst.*, 2005, **32**, 1139–1150.

36 X. T. Yang, S. Takeshita and S. Yano, *Mol. Cryst. Liq. Cryst.*, 2001, **365**, 1095–1102.

37 V. Prasad, K. H. Lee, Y. S. Park, J. W. Lee, D. K. Oh, D. Y. Han and J. I. Jin, *Liq. Cryst.*, 2002, **29**, 1113–1119.

38 Y. S. Park, K. H. Lee, J. W. Lee and J. L. Jin, *Liq. Cryst.*, 2003, **30**, 173–179.

39 A. Yoshizawa and T. Kawaguchi, *Liq. Cryst.*, 2007, **34**, 177–181.

40 G. W. Gray and K. J. Harrison, *Mol. Cryst. Liq. Cryst.*, 1971, **13**, 37.

41 G. W. Gray and K. J. Harrison, *Symp. Faraday Soc.*, 1971, **5**, 54.

42 G. W. Gray, *J. Phys. (Paris)*, 1975, **36**, 337.

43 D. Coates and G. W. Gray, *J. Phys. (Paris)*, 1975, **36**, 365.

44 R. D. Ennulat and A. J. Brown, *Mol. Cryst. Liq. Cryst.*, 1971, **12**, 367.

45 T. Itahara, *Liq. Cryst.*, 2005, **32**, 115.

46 R. Berardi, L. Muccioli and C. Zannoni, *ChemPhysChem*, 2004, **5**, 104–111.

47 S. J. Cowling, A. W. Hall and J. W. Goodby, *Liq. Cryst.*, 2005, **32**, 1483–1498.

48 S. J. Cowling, A. W. Hall and J. W. Goodby, *Chem. Commun.*, 2005, 1546–1548.

49 S. J. Cowling, A. W. Hall and J. W. Goodby, *Adv. Mater.*, 2005, **17**, 1077.

50 S. J. Cowling and J. W. Goodby, *Chem. Commun.*, 2006, 4107–4109.

51 M. R. Dodge, J. K. Vij, S. J. Cowling, A. W. Hall and J. W. Goodby, *Liq. Cryst.*, 2005, **32**, 1045.

52 R. W. Date, C. T. Imrie, G. R. Luckhurst and J. M. Seddon, *Liq. Cryst.*, 1992, **12**, 203–238.

53 R. W. Date, G. R. Luckhurst, M. Shuman and J. M. Seddon, *J. Phys. II*, 1995, **5**, 587–605.

54 C. C. Wu, *Mater. Lett.*, 2007, **61**, 1380–1383.

55 E. D. Do, K. N. Kim, Y. W. Kwon and J. I. Jin, *Liq. Cryst.*, 2006, **33**, 511–519.

56 J. L. Hogan, C. T. Imrie and G. R. Luckhurst, *Liq. Cryst.*, 1988, **3**, 645–650.

57 G. S. Attard, R. W. Date, C. T. Imrie, G. R. Luckhurst, S. J. Roskilly, J. M. Seddon and L. Taylor, *Liq. Cryst.*, 1994, **16**, 529–581.

58 G. S. Attard, R. W. Date, C. T. Imrie, G. R. Luckhurst, S. J. Roskilly, J. M. Seddon and L. Taylor, *Liq. Cryst.*, 2006, **33**, 1455–1485.

59 C. T. Imrie, *Liq. Cryst.*, 2006, **33**, 1449–1454.

60 J. W. Park, C. S. Bak and M. M. Labes, *J. Am. Chem. Soc.*, 1975, **97**, 4398–4400.

61 M. Domon and J. Billard, *J. Phys. (Paris)*, 1979, **40**, C3–413.

62 P. E. Cladis, *Mol. Cryst. Liq. Cryst.*, 1981, **67**, 177.

63 C. T. Imrie and L. Taylor, *Liq. Cryst.*, 1989, **6**, 1–10.

64 A. E. Blatch, I. D. Fletcher and G. R. Luckhurst, *Liq. Cryst.*, 1995, **18**, 801–809.

65 A. E. Blatch and G. R. Luckhurst, *Liq. Cryst.*, 2000, **27**, 775–787.

66 P. J. Le Masurier and G. R. Luckhurst, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 1593–1601.

67 J. W. Goodby, *J. Mater. Chem.*, 1991, **1**, 307–318.

68 A. T. M. Marcelis, A. Koudijs, Z. Karczmarzyk and E. J. R. Sudhölter, *Liq. Cryst.*, 2003, **30**, 1357–1364.

69 J. Watanabe, H. Komura and T. Niori, *Liq. Cryst.*, 1993, **13**, 455–465.

70 J. Watanabe, T. Izumi, T. Niori, M. Zennyoji, Y. Takanishi and H. Takezoe, *Mol. Cryst. Liq. Cryst.*, 2000, **346**, 77–86.

71 W. Weissflog, C. Lischka, S. Diele, I. Wirth and G. Pelzl, *Liq. Cryst.*, 2000, **27**, 43–50.

72 M. Sepelj, A. Lesac, U. Baumeister, S. Diele, H. L. Nguyen and D. W. Bruce, *J. Mater. Chem.*, 2007, **17**, 1154–1165.

73 J. Prost and P. Barois, *J. Chim. Phys. Phys.-Chim. Biol.*, 1983, **80**, 65–81.

74 F. Hardouin, A. M. Levelut, M. F. Achard and G. Sigaud, *J. Chim. Phys. Phys.-Chim. Biol.*, 1983, **80**, 53–64.

75 F. Hardouin, *Physica A*, 1986, **140**, 359–367.

76 V. Faye, A. Babeau, F. Placin, H. T. Nguyen, P. Barois, V. Laux and N. Isaert, *Liq. Cryst.*, 1996, **21**, 485–503.

77 Y. Takanishi, M. Toshimitsu, M. Nakata, N. Takada, T. Izumi, K. Ishikawa, H. Takezoe, J. Watanabe, Y. Takahashi and A. Iida, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2006, **74**, 051703.

78 F. Hardouin, M. F. Achard, J. I. Jin and Y. K. Yun, *J. Phys. II*, 1995, **5**, 927–935.

79 F. Hardouin, M. F. Achard, J. L. Jin, J. W. Shin and Y. K. Yun, *J. Phys. II*, 1994, **4**, 627–643.

80 F. Hardouin, M. F. Achard, M. Laguerre, J. Jin and D. Ko, *Liq. Cryst.*, 1999, **26**, 589–599.

81 S. W. Cha, J. I. Jin, M. F. Achard and F. Hardouin, *Liq. Cryst.*, 2002, **29**, 755–763.

82 S. W. Cha, J. Jin, M. Laguerre, M. F. Achard and F. Hardouin, *Liq. Cryst.*, 1999, **26**, 1325–1337.

83 D. W. Lee, J. I. Jin, M. Laguerre, M. F. Achard and F. Hardouin, *Liq. Cryst.*, 2000, **27**, 145–152.

84 A. T. M. Marcelis, A. Koudijs, E. A. Klop and E. J. R. Sudhölter, *Liq. Cryst.*, 2001, **28**, 881–887.

85 C. V. Yelamaggad, S. A. Nagamani, U. S. Hiremath and G. G. Nair, *Liq. Cryst.*, 2001, **28**, 1009–1015.

86 C. V. Yelamaggad and M. Mathews, *Liq. Cryst.*, 2003, **30**, 125–133.

87 C. V. Yelamaggad, M. Mathews, T. Fujita and N. Iyi, *Liq. Cryst.*, 2003, **30**, 1079–1087.

88 C. V. Yelamaggad, I. S. Shashikala, U. S. Hiremath, D. S. S. Rao and S. K. Prasad, *Liq. Cryst.*, 2007, **34**, 153–167.

89 W. K. Lee, K. N. Kim, M. F. Achard and J. I. Jin, *J. Mater. Chem.*, 2006, **16**, 2289–2297.

90 C. V. Yelamaggad, U. S. Hiremath, S. A. Nagamani, D. S. S. Rao and S. K. Prasad, *Liq. Cryst.*, 2003, **30**, 681–690.

91 V. A. Mallia and N. Tamaoki, *Chem. Soc. Rev.*, 2004, **33**, 76–84.

92 H. Poths, E. Wischerhoff, R. Zentel, A. Schonfeld, G. Henn and F. Kremer, *Liq. Cryst.*, 1995, **18**, 811–818.

93 A. E. Blatch, I. D. Fletcher and G. R. Luckhurst, *J. Mater. Chem.*, 1997, **7**, 9–17.

94 K. Shiraishi, K. Kato and K. Sugiyama, *Chem. Lett.*, 1990, 971–974.

95 J. Barbera, A. Omenat and J. L. Serrano, *Mol. Cryst. Liq. Cryst.*, 1989, **166**, 167–171.

96 J. Barbera, A. Omenat, J. L. Serrano and T. Sierra, *Liq. Cryst.*, 1989, **5**, 1775–1782.

97 Y. Suzuki, T. Isozaki, T. Kusumoto and T. Hiyama, *Chem. Lett.*, 1995, 719–720.

98 A. Yoshizawa, K. Matsuzawa and I. Nishiyama, *J. Mater. Chem.*, 1995, **5**, 2131–2137.

99 A. Yoshizawa, Y. Soeda and I. Nishiyama, *J. Mater. Chem.*, 1995, **5**, 675–681.

100 A. Yoshizawa and I. Nishiyama, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A.*, 1995, **260**, 403–422.

101 Y. I. Suzuki, T. Isozaki, S. Hashimoto, T. Kusumoto, T. Hiyama, Y. Takanishi, H. Takezoe and A. Fukuda, *J. Mater. Chem.*, 1996, **6**, 753–760.

102 A. T. M. Marcelis, A. Koudijs and E. J. R. Sudhölter, *J. Mater. Chem.*, 1996, **6**, 1469–1472.

103 M. Marcos, A. Omenat and J. L. Serrano, *Liq. Cryst.*, 1993, **13**, 843–850.

104 G. R. Luckhurst, R. A. Stephens and R. W. Phippen, *Liq. Cryst.*, 1990, **8**, 451–464.

105 A. T. M. Marcelis, A. Koudijs and E. J. R. Sudhölter, *Liq. Cryst.*, 1995, **18**, 843–850.

106 V. A. Mallia and N. Tamaoki, *J. Mater. Chem.*, 2003, **13**, 219–224.

107 I. Nishiyama, J. Yamamoto, J. W. Goodby and H. Yokoyama, *J. Mater. Chem.*, 2001, **11**, 2690–2693.
108 I. Nishiyama, J. Yamamoto, J. W. Goodby and H. Yokoyama, *Liq. Cryst.*, 2002, **29**, 1409–1423.
109 T. Izumi, S. Kang, T. Niori, Y. Takanishi, H. Takezoe and J. Watanabe, *Jpn. J. Appl. Phys.*, 2006, **45**, 1506–1514.
110 T. Izumi, Y. Naitou, Y. Shimbo, Y. Takanishi, H. Takezoe and J. Watanabe, *J. Phys. Chem. B*, 2006, **110**, 23911–23919.
111 D. Guillon, M. A. Osipov, S. Mery, M. Siffert, J. F. Nicoud, C. Bourgogne and P. Sebastiao, *J. Mater. Chem.*, 2001, **11**, 2700–2708.
112 L. Komitov, N. Olsson and B. Helgee, *Appl. Phys. Lett.*, 2006, **89**, 121919.
113 S. Diez, D. A. Dunmur, M. R. De la Fuente, P. K. Karahaliou, G. Mehl, T. Meyer, M. A. P. Jubindo and D. J. Photinos, *Liq. Cryst.*, 2003, **30**, 1021–1030.
114 D. J. Gardiner and H. J. Coles, *J. Appl. Phys.*, 2006, **100**, 124903.
115 D. J. Gardiner, C. J. Davenport, J. Newton and H. J. Coles, *J. Appl. Phys.*, 2006, **99**, 113517.
116 D. J. Gardiner and H. J. Coles, *J. Phys. D: Appl. Phys.*, 2007, **40**, 977–981.
117 J. R. Willmott, C. J. Davenport, J. Newton and H. J. Coles, *Mol. Cryst. Liq. Cryst.*, 2005, **434**, 537–545.
118 B. Musgrave, P. Lehmann and H. J. Coles, *Liq. Cryst.*, 1999, **26**, 1235–1249.
119 A. E. Blatch, M. J. Coles, B. Musgrave and H. J. Coles, *Mol. Cryst. Liq. Cryst.*, 2003, **401**, 161–169.
120 M. J. Clarke, A. E. Blatch and H. J. Coles, *Mol. Cryst. Liq. Cryst.*, 2005, **434**, 367–375.
121 B. J. Broughton, M. J. Clarke, A. E. Blatch and H. J. Coles, *J. Appl. Phys.*, 2005, **98**, 134109.
122 H. J. Coles, M. J. Clarke, S. M. Morris, B. J. Broughton and A. E. Blatch, *J. Appl. Phys.*, 2006, **99**, 034104.
123 A. Ferrarini, C. Greco and G. R. Luckhurst, *J. Mater. Chem.*, 2007, **17**, 1039–1042.
124 H. J. Coles and M. N. Pivnenko, *Nature*, 2005, **436**, 997–1000.
125 R. Miller, *Liq. Cryst. Today*, 1999, **9**, 7.
126 H. S. Kitzerow, *ChemPhysChem*, 2006, **7**, 63–66.
127 P. Palffy-Muhoay, W. Y. Cao, M. Moreira, B. Taheri and A. Munoz, *Philos. Trans. R. Soc. London, Ser. A*, 2006, **364**, 2747–2761.
128 A. D. Ford, S. M. Morris and H. J. Coles, *Mater. Today*, 2006, **9**, 36–42.
129 W. Weissflog, D. Demus, S. Diele, P. Nitschke and W. Wedler, *Liq. Cryst.*, 1989, **5**, 111–122.
130 J. Andersch and C. Tschierske, *Liq. Cryst.*, 1996, **21**, 51–63.
131 J. Andersch, C. Tschierske, S. Diele and D. Lose, *J. Mater. Chem.*, 1996, **6**, 1297–1307.
132 V. Surendranath, N. K. Lokanath, M. A. Sridhar and S. K. Prasad, *Liq. Cryst.*, 1998, **24**, 361–369.
133 W. S. Bae, J. W. Lee and J. I. Jin, *Liq. Cryst.*, 2001, **28**, 59–67.
134 R. A. Reddy and C. Tschierske, *J. Mater. Chem.*, 2006, **16**, 907–961.
135 G. Dantlgraber, S. Diele and C. Tschierske, *Chem. Commun.*, 2002, 2768–2769.
136 C. Keith, R. A. Reddy, U. Baumeister, H. Hahn, H. Lang and C. Tschierske, *J. Mater. Chem.*, 2006, **16**, 3444–3447.
137 R. Achten, A. Koudijs, M. Giesbers, A. T. M. Marcelis, E. J. R. Sudhölter, M. W. Schroeder and W. Weissflog, *Liq. Cryst.*, 2007, **34**, 59–64.
138 S. Umadevi, B. K. Sadashiva, H. N. S. Murthy and V. A. Raghunathan, *Soft Matter*, 2006, **2**, 210–214.
139 S. Umadevi and B. K. Sadashiva, *Liq. Cryst.*, 2007, **34**, 673–681.
140 B. Kosata, G. M. Tamba, U. Baumeister, K. Pelz, S. Diele, G. Pelzl, G. Galli, S. Samaritani, E. V. Agina, N. I. Boiko, V. P. Shibaev and W. Weissflog, *Chem. Mater.*, 2006, **18**, 691–701.
141 C. V. Yelamaggad, S. K. Prasad, G. G. Nair, I. S. Shashikala, D. S. S. Rao, C. V. Lobo and S. Chandrasekhar, *Angew. Chem., Int. Ed.*, 2004, **43**, 3429–3432.
142 C. V. Yelamaggad, I. S. Shashikala, G. X. Liao, D. S. S. Rao, S. K. Prasad, Q. Li and A. Jakli, *Chem. Mater.*, 2006, **18**, 6100–6102.
143 A. Jakli, G. Liao, I. Shashikala, U. S. Hiremath and C. V. Yelamaggad, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2006, **74**, 041706.
144 M. G. Tamba, B. Kosata, K. Pelz, S. Diele, G. Pelzl, Z. Vakhovskaya, H. Kresse and W. Weissflog, *Soft Matter*, 2006, **2**, 60–65.
145 S. Kumar, *Liq. Cryst.*, 2004, **31**, 1037–1059.
146 S. Kumar, *Chem. Soc. Rev.*, 2006, **35**, 83–109.
147 S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hagele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel and M. Tosoni, *Angew. Chem., Int. Ed.*, 2007, **46**, 4832–4887.
148 N. Boden, R. J. Bushby, A. N. Cammidge, A. El-Mansoury, P. S. Martin and Z. B. Lu, *J. Mater. Chem.*, 1999, **9**, 1391–1402.
149 I. Miglioli, L. Muccioli, S. Orlandi, M. Ricci, R. Berardi and C. Zannoni, *Theor. Chem. Acc.*, 2007, **118**, 203–210.
150 K. Praefcke, B. Kohne, D. Singer, D. Demus, G. Pelzl and S. Diele, *Liq. Cryst.*, 1990, **7**, 589–594.
151 M. J. Wallage and C. T. Imrie, *J. Mater. Chem.*, 1997, **7**, 1163–1167.
152 J. W. Lee, J. I. Jin, M. F. Achard and F. Hardouin, *Liq. Cryst.*, 2001, **28**, 663–671.
153 M. J. Freiser, *Phys. Rev. Lett.*, 1970, **24**, 1041.
154 G. R. Luckhurst, *Nature*, 2004, **430**, 413–414.
155 D. W. Bruce, *Chem. Rec.*, 2004, **4**, 10–22.
156 Y. Galerne, *Mol. Cryst. Liq. Cryst.*, 1998, **323**, 211.
157 T. Hegmann, J. Kain, S. Diele, G. Pelzl and C. Tschierske, *Angew. Chem., Int. Ed.*, 2001, **40**, 887–890.
158 N. Boccara, R. Mejdaniand and L. De Seze, *J. Phys.*, 1997, **38**, 149.
159 G. R. Luckhurst, *Thin Solid Films*, 2001, **393**, 40–52.
160 J. R. Hughes, G. Kothe, G. R. Luckhurst, J. Malthete, M. E. Neubert, I. Shenouda, B. A. Timimi and M. Tittelbach, *J. Chem. Phys.*, 1997, **107**, 9252–9263.
161 S. R. Sharma, P. Palffymuhoray, B. Bergersen and D. A. Dunmur, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1985, **32**, 3752–3755.
162 A. G. Vanakaras, S. C. Mcgrother, G. Jackson and D. J. Photinos, *Mol. Cryst. Liq. Cryst.*, 1998, **323**, 199.
163 I. D. Fletcher and G. R. Luckhurst, *Liq. Cryst.*, 1995, **18**, 175–183.
164 K. Praefcke, B. Kohne, B. Gundogan, D. Singer, D. Demus, S. Diele, G. Pelzl and U. Bakowsky, *Mol. Cryst. Liq. Cryst.*, 1991, **198**, 393–405.
165 J. J. Hunt, R. W. Date, B. A. Timimi, G. R. Luckhurst and D. W. Bruce, *J. Am. Chem. Soc.*, 2001, **123**, 10115–10116.
166 R. W. Date and D. W. Bruce, *J. Am. Chem. Soc.*, 2003, **125**, 9012–9013.
167 P. H. J. Kouwer and G. H. Mehl, *J. Am. Chem. Soc.*, 2003, **125**, 11172–11173.
168 P. H. J. Kouwer and G. H. Mehl, *Angew. Chem., Int. Ed.*, 2003, **42**, 6015–6018.
169 P. H. J. Kouwer, J. Pourzand and G. H. Mehl, *Chem. Commun.*, 2004, 66–67.
170 A. Ferrarini, G. R. Luckhurst, P. L. Nordio and S. J. Roskilly, *Liq. Cryst.*, 1996, **21**, 373–382.
171 P. Keller, *Mol. Cryst. Liq. Cryst.*, 1985, **123**, 247–256.
172 H. Furuya, K. Asahi and A. Abe, *Polym. J. (Tokyo, Jpn.)*, 1986, **18**, 779–782.
173 G. S. Attard and C. T. Imrie, *Liq. Cryst.*, 1989, **6**, 387–390.
174 R. Centore, A. Roviello and A. Sirigu, *Mol. Cryst. Liq. Cryst.*, 1990, **182B**, 233–244.
175 T. Ikeda, T. Miyamoto, S. Kurihara, M. Tsukada and S. Tazuke, *Mol. Cryst. Liq. Cryst.*, 1990, **182B**, 357–371.
176 N. V. Tsvetkov, V. V. Zuev and V. N. Tsvetkov, *Liq. Cryst.*, 1997, **22**, 245–253.
177 C. T. Imrie and G. R. Luckhurst, *J. Mater. Chem.*, 1998, **8**, 1339–1343.
178 B. Chen, A. Kameyama and T. Nishikubo, *Macromolecules*, 1999, **32**, 6485–6492.
179 A. T. M. Marcelis, A. Koudijs and E. J. R. Sudhölter, *Liq. Cryst.*, 1995, **18**, 851–855.
180 A. T. M. Marcelis, A. Koudijs and E. J. R. Sudhölter, *Liq. Cryst.*, 1996, **21**, 87–93.
181 N. Tamaoki, H. Matsuda and A. Takahashi, *Liq. Cryst.*, 2001, **28**, 1823–1829.

182 C. V. Yelamaggad, U. S. Hiremath, D. S. Shankar Rao and S. Krishna Prasad, *Chem. Commun.*, 2000, 57–58.

183 C. V. Yelamaggad, S. Anitha Nagamani, U. S. Hiremath, D. S. Shankar Rao and S. Krishna Prasad, *Liq. Cryst.*, 2001, **28**, 1581–1583.

184 A. C. Sentman and D. L. Gin, *Adv. Mater.*, 2001, **13**, 1398–1401.

185 W. Kreuder, H. Ringsdorf, O. Herrmann-Schonherr and J. H. Wendorff, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1249–1252.

186 J. Andersch, S. Diele, D. Lose and C. Tschierske, *Liq. Cryst.*, 1996, **21**, 103–113.

187 P. Liu, C. He, C. J. Booth and A. C. Griffin, *Mol. Cryst. Liq. Cryst.*, 1999, **332**, 243.

188 V. Percec and M. Kawasumi, *Liq. Cryst.*, 1993, **13**, 83–94.

189 V. Percec and M. Kawasumi, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1319.

190 J. F. Li, V. Percec and C. Rosenblatt, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 1993, **48**, R1–R4.

191 J. F. Li, V. Percec, C. Rosenblatt and O. D. Lavrentovich, *Europhys. Lett.*, 1994, **25**, 199–204.

192 V. Percec, A. D. Asandei and M. Zhao, *Chem. Mater.*, 1996, **8**, 301–308.

193 I. M. Syed, V. Percec, R. G. Petschek and C. Rosenblatt, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2003, **67**, 011704.

194 G. S. Attard, A. G. Douglass, C. T. Imrie and L. Taylor, *Liq. Cryst.*, 1992, **11**, 779–784.

195 K. Zab, D. Joachimi, O. Agert, B. Neumann and C. Tschierske, *Liq. Cryst.*, 1995, **18**, 489–494.

196 K. Zab, D. Joachimi, E. Novotna, S. Diele and C. Tschierske, *Liq. Cryst.*, 1995, **18**, 631–637.

197 M. Li, L. Detre, P. Cluzeau, N. Isaert and H. Nguyen, *Liq. Cryst.*, 1998, **24**, 347–359.

198 D. Goldmann, D. Janietz, C. Schmidt and J. H. Wendorff, *Liq. Cryst.*, 1998, **25**, 711–719.

199 K. Lee, J. Lee and J. Jin, *Liq. Cryst.*, 2001, **28**, 1519–1525.

200 S. Kumar and M. Manickam, *Liq. Cryst.*, 1999, **26**, 939–941.

201 S. Mahlstedt, D. Janietz, C. Schmidt, A. Stracke and J. H. Wendorff, *Liq. Cryst.*, 1999, **26**, 1359–1369.

202 S. Mahlstedt, D. Janietz, A. Stracke and J. H. Wendorff, *Chem. Commun.*, 2000, 15–16.

203 P. J. Barnes, *PhD Thesis*, University of Southampton, Chemistry, 1994.

204 P. A. Henderson, A. G. Cook and C. T. Imrie, *Liq. Cryst.*, 2004, **31**, 1427–1434.

205 C. T. Imrie, P. A. Henderson and J. M. Seddon, *J. Mater. Chem.*, 2004, **14**, 2486–2488.

206 P. A. Henderson and C. T. Imrie, *Liq. Cryst.*, 2005, **32**, 673–682.

207 E. Chiellini and M. Laus, in *Handbook of Liquid Crystals*, ed. D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, pp. 26–51.

208 M. Vacatello, *Macromol. Theory Simul.*, 2002, **11**, 501–512.

209 M. M. Naoum, R. I. Nessim, G. R. Saad and T. Y. Labeeb, *Liq. Cryst.*, 2002, **29**, 929–943.

210 A. A. Craig and C. T. Imrie, *Polymer*, 1997, **38**, 4951–4957.

211 C. T. Imrie, *Trends Polym. Sci.*, 1995, **3**, 22.

212 J. Watanabe and M. Hayashi, *Macromolecules*, 1988, **21**, 278–280.

213 J. Watanabe and M. Hayashi, *Macromolecules*, 1989, **22**, 4083–4088.

214 J. Watanabe, T. Niori, S. Choi, Y. Takanishi and H. Takezoe, *Jpn. J. Appl. Phys.*, 1998, **37**, L401–403.

215 C. V. Yelamaggad, S. A. Nagamani, D. S. S. Rao and S. K. Prasad, *J. Chem. Res., Synop.*, 2001, 493–495.

216 I. Nishiyama, J. Yamamoto, J. W. Goodby and H. Yokoyama, *J. Mater. Chem.*, 2003, **13**, 2429–2435.

217 A. Takahashi, V. A. Mallia and N. Tamaoki, *J. Mater. Chem.*, 2003, **13**, 1582–1587.

218 A. Yoshizawa, H. Kinbara, T. Narumi, A. Yamaguchi and H. Dewa, *Liq. Cryst.*, 2005, **32**, 1175–1181.

219 T. Narumi, M. Miyamoto and A. Yoshizawa, *Liq. Cryst.*, 2007, **34**, 585–590.

220 A. Yamaguchi, I. Nishiyama, J. Yamamoto, H. Yokoyama and A. Yoshizawa, *J. Mater. Chem.*, 2005, **15**, 280–288.

221 A. Yoshizawa, M. Nakata and A. Yamaguchi, *Liq. Cryst.*, 2006, **33**, 605–609.

222 N. Boden, R. J. Bushby, A. N. Cammidge and P. S. Martin, *J. Mater. Chem.*, 1995, **5**, 1857–1860.

223 A. C. Griffin, S. L. Sullivan and W. E. Hughes, *Liq. Cryst.*, 1989, **4**, 677–684.

224 C. T. Imrie, D. Stewart, C. Remy, D. W. Christie, I. W. Hamley and R. Harding, *J. Mater. Chem.*, 1999, **9**, 2321–2325.

225 P. A. Henderson, R. T. Inkster, J. M. Seddon and C. T. Imrie, *J. Mater. Chem.*, 2001, **11**, 2722–2731.

226 P. A. Henderson and C. T. Imrie, *Macromolecules*, 2005, **38**, 3307–3311.

227 P. A. Henderson and C. T. Imrie, *Liq. Cryst.*, 2005, **32**, 1531–1541.

228 C. V. Yelamaggad, S. Anitha Nagamani, U. S. Hiremath, D. S. Shankar Rao and S. Krishna Prasad, *Liq. Cryst.*, 2002, **29**, 231–236.

229 C. V. Yelamaggad, S. A. Nagamani, U. S. Hiremath, D. S. S. Rao and S. K. Prasad, *Mol. Cryst. Liq. Cryst.*, 2003, **397**, 507–529.

230 K. Araya, D. A. Dunmur, M. C. Grossel, G. R. Luckhurst, S. E. Marchant-Lane and A. Sugimura, *J. Mater. Chem.*, 2006, **16**, 4675–4689.

231 C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao and S. K. Prasad, *Org. Lett.*, 2007, **9**, 2641–2644.

2124 | *Chem. Soc. Rev.*, 2007, **36**, 2096–2124

This journal is © The Royal Society of Chemistry 2007