

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Triphenylene-based discotic liquid crystal dimers, oligomers and polymers

Sandeep Kumar^a

^a Raman Research Institute, Bangalore - 560 080, India

To cite this Article Kumar, Sandeep(2005) 'Triphenylene-based discotic liquid crystal dimers, oligomers and polymers', *Liquid Crystals*, 32: 9, 1089 – 1113

To link to this Article: DOI: 10.1080/02678290500117415

URL: <http://dx.doi.org/10.1080/02678290500117415>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Invited Article

Triphenylene-based discotic liquid crystal dimers, oligomers and polymers

SANDEEP KUMAR

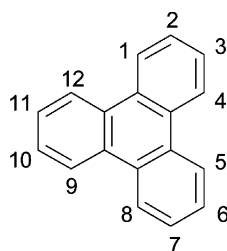
Raman Research Institute, C.V. Raman Avenue, Bangalore - 560 080, India

(Received 30 September 2005; in final form 4 February 2005; accepted 11 February 2005)

Discotic liquid crystals are unique nanostructures with remarkable electronic and optoelectronic properties. Triphenylene derivatives play a major role in the research on discotic liquid crystals. Following recent reviews of the chemistry of triphenylene-based monomeric liquid crystals, this article now reviews the chemistry and physical properties of triphenylene-based discotic dimeric, oligomeric and polymeric liquid crystals.

1. Introduction

This article follows recent reviews of the chemistry of triphenylene-based monomeric liquid crystals [1, 2]. The symmetrical aromatic hydrocarbon 'triphenylene' (1) in which three benzene rings fuse to form a common fourth ring, has been known in the chemical literature for more than a century. It was first isolated from the pyrolytic products of benzene by Schmidt and Schultz [3]. Triphenylene is a ubiquitous combustion effluent that pollutes the environment, into which it is released from various sources such as, for example, coal burning electric power plants, refineries and internal combustion engines. This tris-annulated benzene system was first synthesized by the aldol trimerization of cyclohexanone in the early twentieth century [4]. Later several other methods for its synthesis were developed and it has been the subject of various chemical and physical studies [5, 6].



1: Triphenylene

Triphenylene received the considerable attention of researchers after the discovery of discotic liquid crystals

(DLCs) in 1977 [7]. Billard *et al.* in 1978 introduced this tetracyclic aromatic hydrocarbon as a novel core for DLCs [8]. Triphenylene as a core for DLCs is attractive for many reasons: (i) it possess C_3 symmetry, (ii) its chemistry is relatively accessible, (iii) its derivatives are thermally as well as chemically stable and (iv) they show a variety of mesophases. The electron-rich nature of triphenylene-based discotics makes them suitable for doping with electron acceptors and, leading to p-type organic semiconductors. Triphenylene-based DLCs have been extensively studied for their various physical properties including one-dimensional charge migration [9], one-dimensional energy migration [10], electroluminescence [11], ferroelectric switching [12] and alignment and self-assembling behaviour on surfaces [13]. At present about 500 discotic LCs based on a triphenylene core are known in the literature. Chemistry of triphenylene-based monomeric LCs has recently been reviewed [1, 2]. Although the chemistry of selected triphenylene-based liquid crystal dimers and oligomers has recently been discussed by Imrie and co-workers [14], no separate review on the chemistry of triphenylene-based discotic liquid crystal dimers, oligomers and polymers is available in the literature. In order to remedy this situation, this article aims to cover the chemistry and physical properties of these non-conventional triphenylene-based DLCs. In the tables that follow, as well as in the text, transition temperatures are given in °C, Cr=crystal, Col=columnar phase, Col_h=hexagonal columnar phase, Col_{hd}=hexagonal disordered columnar phase, Col_p=columnar plastic phase, N_D=nematic discotic phase, g=glass transition, Lm=lamellar phase, LC=unknown mesophase and I=isotropic phase.

Corresponding author. Email: skumar@rri.res.in

2. Triphenylene-based discotic liquid crystal dimers

A liquid crystal dimer is composed of molecules containing two mesogenic groups linked, often, via a flexible spacer or, more rarely, through a rigid spacer. The physical properties of liquid crystalline dimers are significantly different from those of conventional low molar mass LCs. Dimers serve as ideal model compounds for polymers or networks, due to the striking similarities in their transitional behaviour coupled with their ease of purification and characterization and, like polymers, some dimers form glassy mesophases. The various structural possibilities for dimers are shown schematically in figure 1. Dimers in which two identical mesogens are connected via a flexible spacer, figure 1(a), are the most widely synthesized and studied. However, several examples are known in which two non-symmetric mesogens are connected, figure 1(b). Figures 1(c) and 1(d) show laterally linked symmetrical and non-symmetrical calamitic dimers. Similar to calamitic systems, symmetric, figure 1(g), and non-symmetric, figure 1(h), discotic dimers are also possible; see figures 1(g) and 1(h), respectively. Linear and lateral calamatic-discotic dimers are shown in figures 1(e) and 1(f). Dimers in which two discogens are connected laterally or linearly to a calamitic molecule are depicted in figures 1(i) and 1(j), respectively. In addition to these possibilities, several other combinations, such as banana-rod, banana-disk, metal-bridged dimers (metallomesogens) and cyclic dimers in which two mesogenic units are connected to each other via more than one spacer are also possible. These structures have not been shown in

figure 1. In addition, all these structures are also possible but with a rigid spacer instead of a flexible spacer.

In comparison with the large number of LC dimers consisting of two rod-like mesogens, the number of discotic dimers is very small [14]. The first discotic dimer was based on a benzene core and prepared by Lillya and Murthy [15]. Later, several other benzene-based dimers were reported by Zamir *et al.* [16]. Praefcke and co-worker prepared a discotic nematic dimer based on two multiyne units. The biaxial nature of this nematic phase was reported on the basis of microscopic studies [17]. They also reported discotic dimers based on scylloinositol [18]. Examples of other discotic dimers include derivatives of phthalocyanine [19], cyclotetraveratrylene [20], anthraquinone [21], hexabenzocoronene [22] and combinations of disk- and rod-like units [23–25].

2.1. Symmetrical triphenylene discotic liquid crystal dimers

The pioneering work of Ringsdorf's group on the synthesis of triphenylene-based polymeric side chain and main chain DLCs [26, 27] also opened routes to triphenylene-based discotic dimers and oligomers. They prepared mono- and di-functionalized triphenylenes using a statistical approach and converted them into side chain and main chain polymers. The potential utility of discotic dimers, oligomers and polymers had not yet been fully explored, primarily due to the difficulties in preparing appropriately functionalized discotic precursors. In recent years, however, there have been many advances in the synthesis of

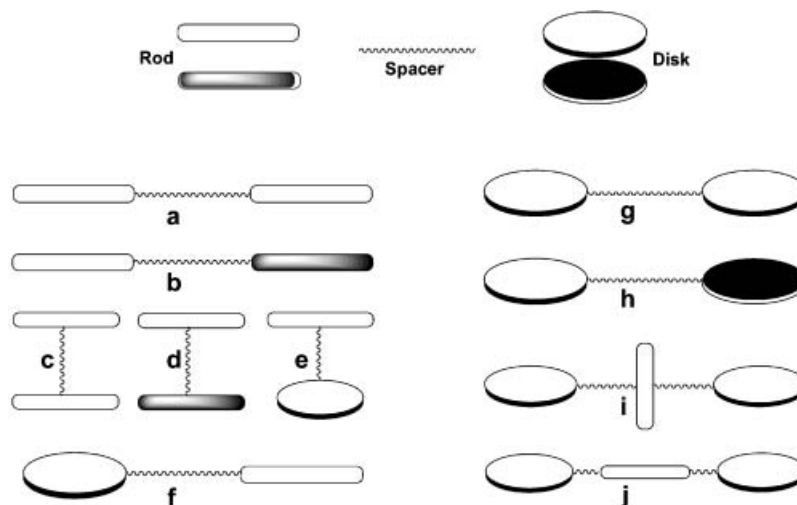


Figure 1. Sketches of some possible molecular architectures for liquid crystal dimers: (a) symmetric calamitic dimer; (b) non-symmetric calamitic dimer; (c) laterally linked symmetric calamitic dimer; (d) laterally linked non-symmetric calamitic dimer; (e) lateral discotic-calamitic dimer; (f) linear discotic-calamitic dimer; (g) symmetric discotic dimer; (h) non-symmetric discotic dimer; (i) two discogens laterally linked to a calamitic molecule; (j) two discogens terminally linked to a calamitic molecule.

mono-functionalized triphenylenes. These methods have been briefly discussed in a previous review article [1].

Given a readily available supply of monohydroxypentaalkoxytriphenylenes, it is straightforward to prepare various triphenylene dimers. Although the simplest way to prepare a dimer is by attaching the two monomers via a flexible spacer, the chemistry of triphenylene dimers actually began with a rather complicated molecule in which the two triphenylene units were connected through a calamitic molecule. Thus, to prepare the chemical equivalent of the 'Wheel of Mainz', Ringsdorf and co-worker linked two triphenylene units laterally to a calamitic mesogen, **2** [28]. Compound **2** was found to be a spherulitic

crystalline compound melting at 167°C. Attaching the two triphenylene molecules linearly to an azobenzene moiety results in only an amorphous material **3**, but replacing the azobenzene by a mesogenic azobiphenyl moiety gave a liquid crystalline material **4**. It melts at 72°C to a highly viscous mesophase and clears at 120°C. The optical texture of this mesophase resembles that of SmB mesophase. X-ray studies on this compound indicate a layered structure typical for smectic phases but in which the molecular disks are regularly stacked as observed for columnar phases [28]. As two discotic and one calamitic mesogens are contained in these molecules, they have also been described as trimesogens in some literature.

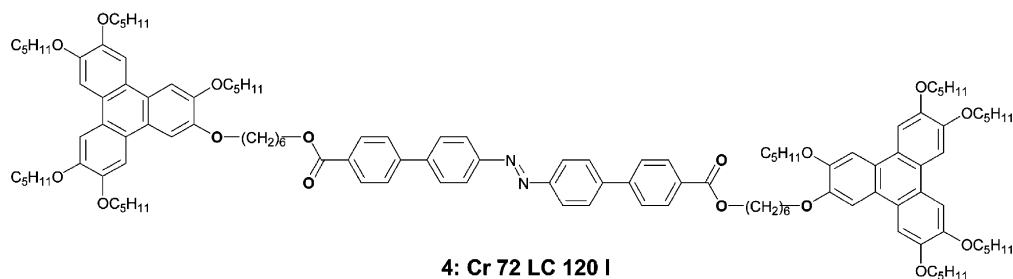
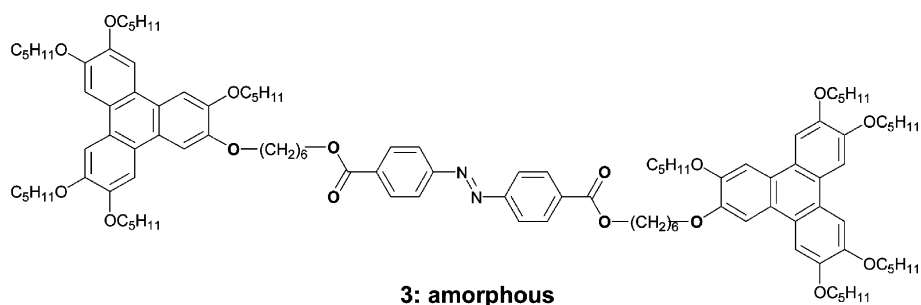
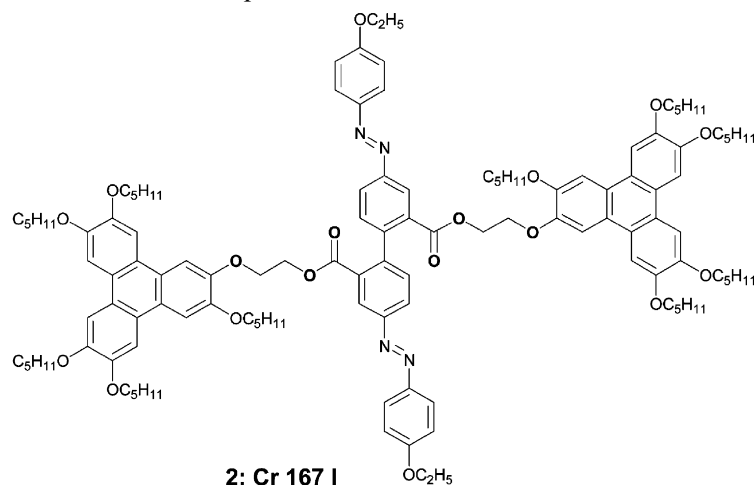


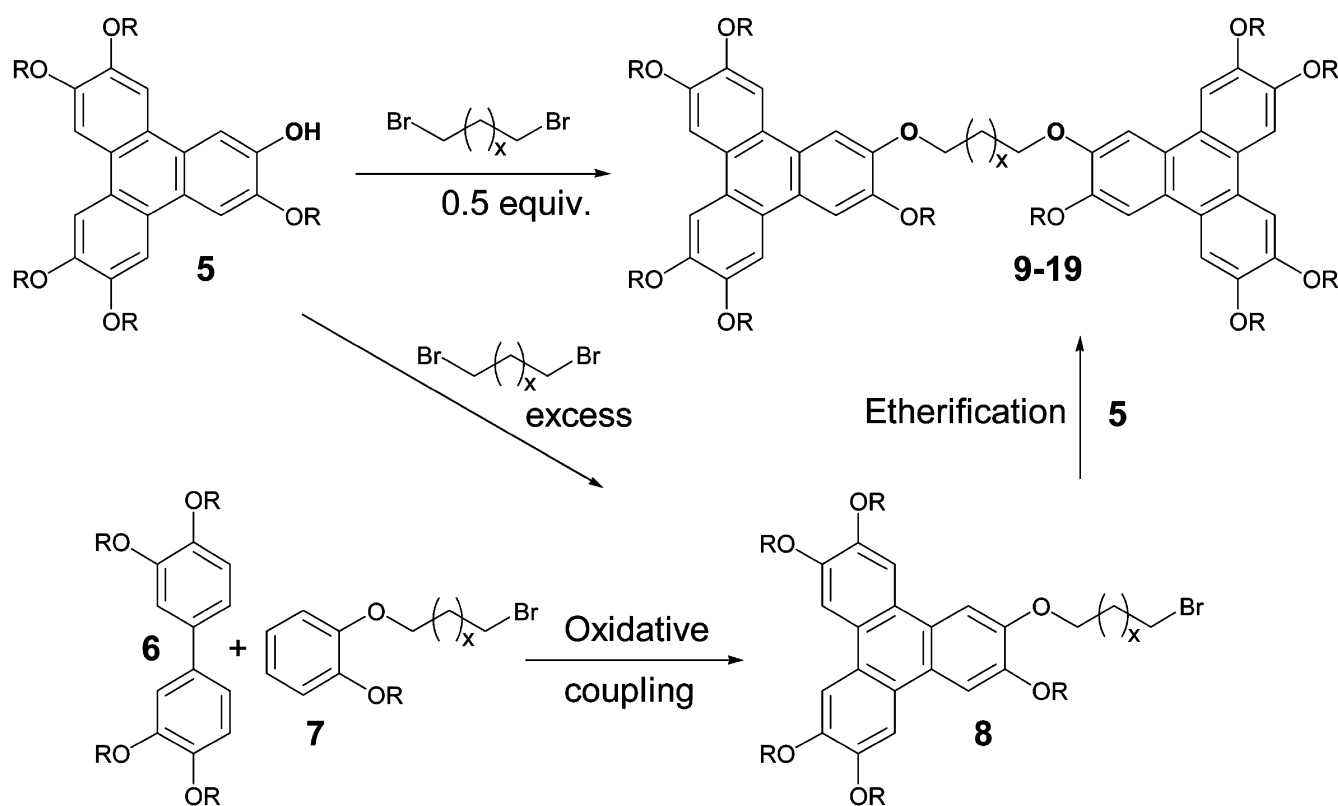
Table 1. Thermal behaviour (°C) of symmetrical triphenylene-based dimers.

Compound	R	x	Phase transition	Ref.
9	C ₄ H ₉	6	Col _p 154 I	[35]
10	C ₄ H ₉	8	Col _p 148.5 I	[33]
			Col _p 149 I	[34]
			Col _p 147 I	[35]
11	C ₅ H ₁₁	8	Cr 67.0 Col _h 135.6 I	[29]
			Cr 64 (g -59) Col _h 135 I	[30]
12	C ₆ H ₁₃	1	Cr 81 I	[35]
13	C ₆ H ₁₃	3	Cr 98 I	[35]
14	C ₆ H ₁₃	5	Cr 69 I	[35]
15	C ₆ H ₁₃	6	Cr 58 (g 35) Col _h 91 I	[35]
16	C ₆ H ₁₃	7	Cr 72 (g 35) Col _h 92 I	[35]
17	C ₆ H ₁₃	8	Cr 50 (g 35) Col _h 104 I	[35]
18	C ₆ H ₁₃	10	Cr 68 (g 35) Col _h 107 I	[35]
19	C ₆ H ₁₃	14	Cr 41 (g 35) Col _h 84 I	[35]

The most commonly prepared triphenylene-based dimers contain two identical triphenylene moieties connected via a spacer. Often the spacer is a polymethylene, O(CH₂)_nO, chain [29–35], but in some cases ester or amide linkages in the middle of the spacer or at its terminal positions have also been used [35–38]. The thermal behaviour of symmetrical triphenylene-based

dimers with polymethylene spacers is summarized in table 1. These symmetrical dimers may be synthesized either in a single step by reacting a monohydroxytriphenylene with 0.5 mol equivalent of the appropriate α , ω -dibromoalkane under classical etherification reaction conditions or in two steps. In the two-step procedure, the monohydroxypentaalkoxytriphenylene is first reacted with an excess of the appropriate α , ω -dibromoalkane to obtain the ω -brominated product **8** (see scheme 1) which may be reacted further with monohydroxytriphenylene to obtain the desired dimer. This two-step process is particularly important for preparing non-symmetrical dimers. The intermediate ω -brominated product **8** can also be prepared using the biphenyl-phenyl oxidative coupling route [39–42].

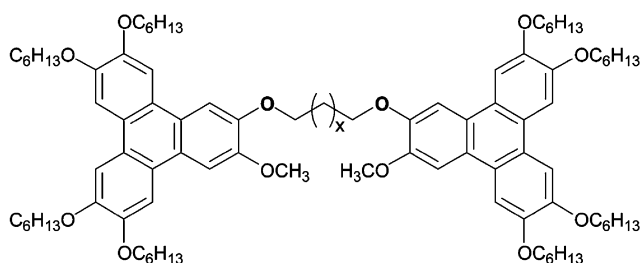
The length of the spacer has a dramatic influence on the thermal behaviour of the dimers. Symmetrical triphenylene-based dimers with short spacers are not liquid crystalline. Modelling studies suggest that the two triphenylene units are not coplanar due to steric crowding. Only those dimers in which the spacer is more than seven methylene units form columnar mesophases. In most of these dimers the columnar phase freezes into a glassy state on cooling. The stability of the glassy state depends on the spacer length as well as on the symmetry



Scheme 1. Synthetic routes to symmetrical triphenylene dimers.

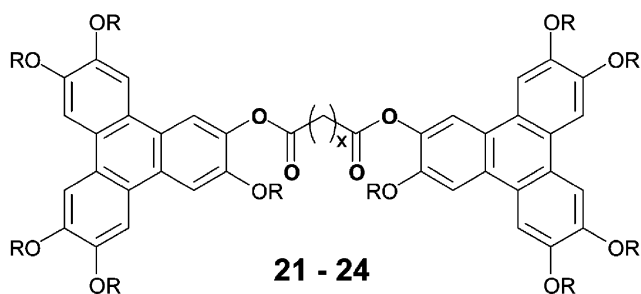
of the molecule. The non-symmetrical dimers usually give longer-lived glasses. As the length of the spacer increases, in general the lifetime of the glassy state decreases [35].

Boden and co-workers have reported another symmetrical dimer, **20**, which differs from those described already in the sense that instead of five long alkoxy chains on each disc, one chain is replaced by a methoxy group. On heating, this compound shows a crystals to isotropic transition at 112°C, but on cooling exhibits a monotropic columnar phase at 98°C that persists down to a glass transition at 33°C [31, 35].



20: x = 8, Cr (98 Col_h 33 g) 112 I

Four symmetrical triphenylene-based dimers, **21–24**, in which two pentaalkoxytriphenylene units are connected via ester linkages instead of ether linkages were reported by Kranig *et al.* in 1990 [38]. All four compounds were reported to be liquid crystalline at room temperature (see table 2). These dimers exhibit much broader mesophase ranges compared with the dimers linked via ether groups. This behaviour is in accord with that observed for the non-symmetrical monomeric compounds. Thus, monoalkanoyloxypentaalkoxytriphenylenes (having one ester-bonded and five ether-bonded peripheral chains) show broader mesophase ranges than the parent hexaalkoxy- or hexaalkanoyloxy-triphenylenes. The mesophase stabilization in such compounds due to the steric hindrance of the ester group has been discussed by Spiess and co-workers [43].



21 - 24

Table 2. Thermal behaviour (°C) of symmetrical triphenylene-based dimers linked via an ester-attached chain. All data from ref. [38].

Compound	R	x	Phase transition
21	C ₅ H ₁₁	10	Col _h 180 I
22	C ₅ H ₁₁	12	Col _h 168 I
23	C ₅ H ₁₁	14	Col _h 147 I
24	C ₇ H ₁₅	14	Col _h 147 I

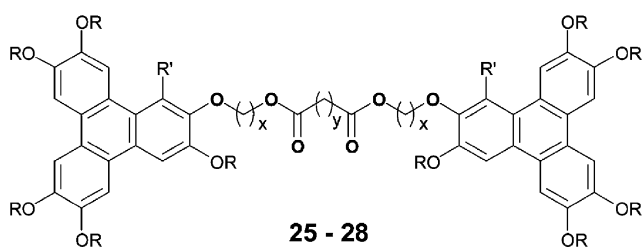
While the hydroxy-functional group has often been utilized to prepare dimers, in order to tune the electronic properties of the molecule, core functionalization is also necessary. Most triphenylene-based DLCs are colourless, low fluorescence materials and thus their use in many applications is limited. In an effort to enhance the fluorescence as well as the liquid crystallinity of triphenylene-based dimers, a number of monofunctionalized triphenylene-based discotics bearing conjugative electron-withdrawing or electron-donating groups attached directly to the core were prepared [44]. Nitration of hexaalkoxytriphenylenes at the α -position not only induces a molecular dipole and colour in the molecule, but also enhances the mesomorphic properties [45–47]. Thus, two types of functional groups, (i) hydroxy to allow the manipulation of mechanical properties via conversion into oligomers or polymers and nitro, cyano, halogens, etc., to modify the electronic properties of the molecule, have been incorporated separately in triphenylene-based molecules. The combination of these two types of functionalized triphenylene molecules leads to novel bifunctional derivatives, in which one type of functional group may be used to tune the electronic nature of the molecule, while at the same time the other may be utilized to convert them into a processable oligomer or polymer.

Three such nitro-functionalized triphenylene dimers, **25–27**, have recently been prepared starting from 2-hydroxy-3,6,7,10,11-pentaalkoxytriphenylene [36]. Unfortunately, the synthesis of the precursor mononitromonohydroxypentaalkoxytriphenylene is difficult, and often the nitration of the monohydroxypentaalkoxytriphenylene results only in the oxidized products 3,6,7,10,11-pentaalkoxytriphenylene-1,2-diones. Under highly controlled and careful reaction conditions, the 3,6,7,10,11-pentaalkoxy-1-nitro-2-triphenylenol can be isolated and this has to be alkylated immediately with a ω -hydroxybromoalkane. The resulting alcohol can be coupled with various diacid chlorides or diacides to obtain the dimers. Thus, these dimers have an ester group in the middle of the spacer. A similar dimer, **28**, but without the nitro group in the triphenylene unit,

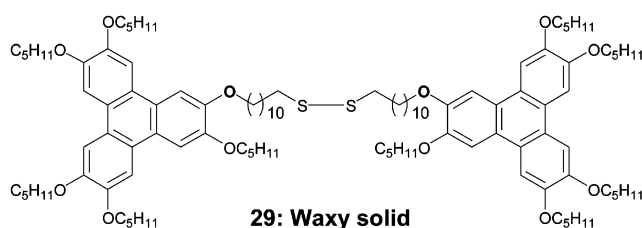
Table 3. Thermal behaviour ($^{\circ}\text{C}$) of symmetrical triphenylene-based dimers linked via an ether spacer having an ester group at its centre.

Compound	R	R'	x	y	Phase transition	Ref.
25	C_4H_9	NO_2	2	0	Cr [169.1 Col] 198.8 I	[36]
26	C_4H_9	NO_2	2	2	Col_h 163.0 I	[36]
27	C_4H_9	NO_2	2	4	Col_h 144.9 I	[36]
28	C_5H_{11}	H	7	1	Cr 33.5 I	[37]

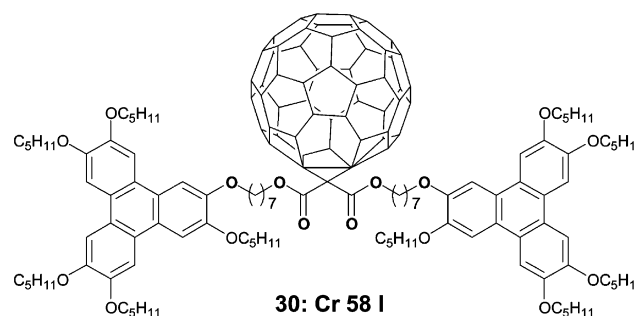
was reported by Manickam *et al.* [37]. The thermal behaviour of these dimers is summarized in table 3, and the spacer length of the diacid plays a critical role in determining the phase behaviour of the dimers. The presence of two or more methylene units in the spacer gives a liquid crystal dimer with a very broad mesophase range, while spacers with less than two methylene units result in a monotropic mesophase (compound **25**) or a crystalline phase (compound **28**). This may be attributed to the steric hindrance of the two carbonyl groups, which is less pronounced if they are separated by two or more methylene units. The presence of the nitro group makes these materials yellow-coloured. Although, these nitro-substituted dimers have very interesting properties, for example, stability of the mesophase at ambient temperature, very broad mesophase range, and yellow colour and contain the highly polar nitro group, because of synthetic difficulties they could not be prepared in sufficient amounts for suitable physical studies.



The formation of highly ordered self-assembled monolayers (SAMs) by mesogenic thiols, disulphides and thioethers on gold-covered substrates is well known [48]. Schonherr *et al.* studied the SAMs formation of the disulphide-bridged triphenylene-based dimer **29**. This waxy solid dimer shows an edge-on orientation on the gold surface [49].

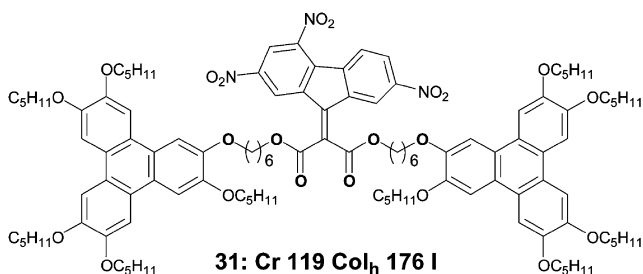


Fullerene (C_{60}) and its derivatives have received considerable interest since the discovery of C_{60} in 1985 [50]. A number of chemical and physical properties of this carbon allotrope have been explored by many researchers throughout the world. Several studies have been devoted to the incorporation of calamitic mesogens into the C_{60} framework [51]. To explore the possibility that the insertion of C_{60} into a columnar mesophase may result in novel materials useful in device applications, Preece and co-worker synthesized the C_{60} Bingel cyclopropanation-bistriphenylene adduct **30** [37]; but as expected, the fullerene-bridged triphenylene-based dimer shows no liquid crystalline behaviour.

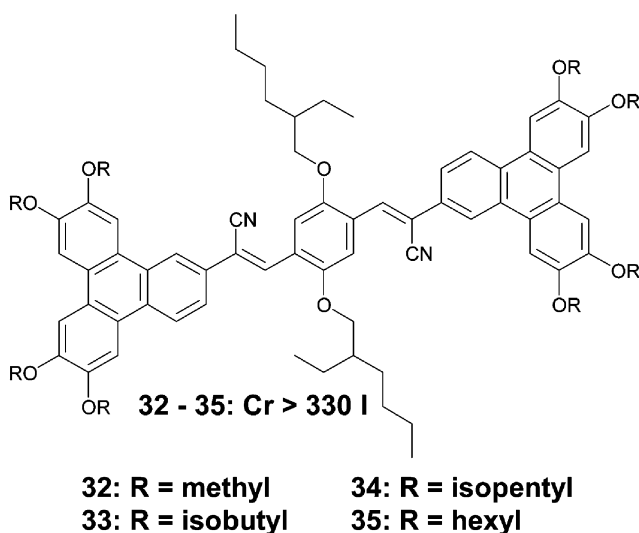


The stabilization and induction of mesophases due to charge-transfer interactions between donor and acceptor molecules have been well documented [52]. In most cases, trinitrofluorenone (TNF) has been used as the electron-acceptor. In order to understand the nature of the molecular stacking in liquid crystalline donor-acceptor dimers, TNF has been covalently connected to the mesogenic moiety [52–54]. In a novel triphenylene-based discotic donor-acceptor-donor type dimer, two triphenylene fragments were chemically connected to a TNF-based unit. The dimer **31**, a condensation product of the corresponding acceptor diethyl ester and the free alcohol derivative of the triphenylene-based monomer, forms a columnar mesophase in the temperature range 119–176 $^{\circ}\text{C}$. The Langmuir–Blodgett film formed by this compound shows an edge-on orientation of the

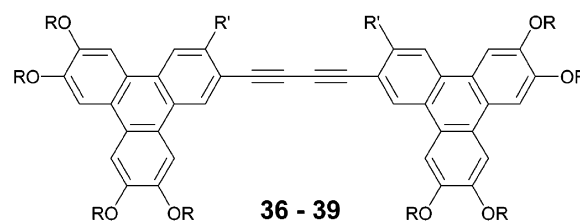
molecules (the columns lie parallel to a solid substrate) [54].



Hanack and co-workers have recently designed and synthesized four novel conjugated-bridged triphenylene-based dimers **32–35** for the construction of organic light emitting diodes (OLEDs) [55]. In these compounds an electron-withdrawing cyano-substituted *p*-phenylene-vinylene unit was linked to two triphenylene units. These dimers were prepared by a double Knoevenagel reaction of the mono-functionalized cyanomethyltriphenylene derivatives and a terephthalaldehyde derivative. All four dimers were found not to be liquid crystalline and melted above 330°C. They exhibit orange to red photoluminescence and a strong bathochromic shift of more than 250 nm when compared with a monomeric triphenylene-based system.



Discotic dimers, in which the two units are connected to each other via a long flexible alkyl spacer, generally form columnar phases as the molecules have sufficient flexibility to stack in adjacent columns. Linking two discotic units via a short rigid spacer would be expected to give rise to steric hindrance arising from the overlapping or interdigitation of the aliphatic side chains, while the weak distortion in the planarity of the core would reduce the strong π - π interactions between the discs. Thus, the rigid molecules may adopt more or less parallel orientations but lose their long range translational order and, therefore, are likely to form discotic nematic phases. This concept has recently been realized by the synthesis of the four triphenylene dimers **36–39** in which two identical triphenylene units were connected via a rigid π -conjugated diacetylene spacer [56–58]. These dimers form discotic nematic mesophases over a wide temperature range. The thermal behaviour of these compounds is summarized in table 4. These dimers were prepared by the dimerization of triphenylene-based derivatives having a free monoacetylene group; these in turn can be prepared from monobromopentaalkoxytriphenylene. Compound **39** differs from the other three in that one of the five alkoxy chains has been replaced by an alkylsulphonyl chain. This unusual triphenylene derivative, having three different types of peripheral chain, was prepared using a complicated multi-step synthesis [58]. As can be seen from the thermal data, this change destabilizes the nematic phase.

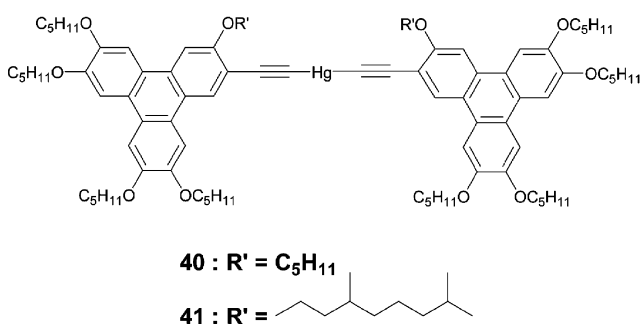


Another π -conjugated discotic dimeric system comprises the metal-bridged triphenylene dimers. Although mercury-bridged linear calamitic dimers were described by Vorlander in 1923 [59], similar discotic structures

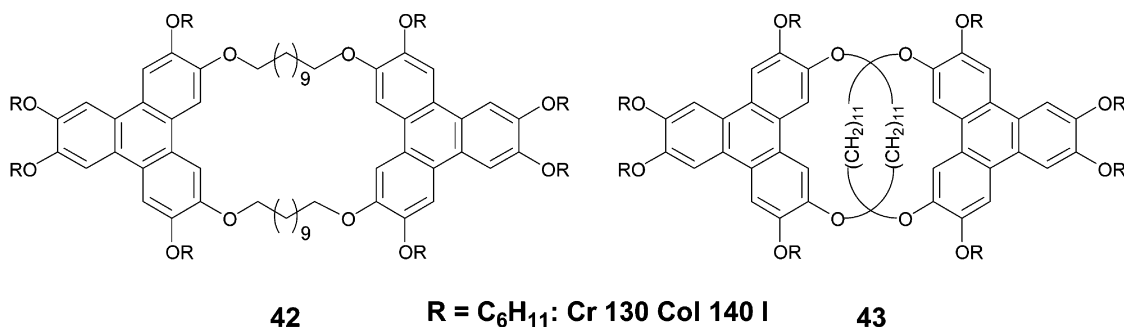
Table 4. Thermal behaviour (°C) of diacetylene-bridged triphenylene-based dimers.

Compound	R	R'	Phase transition	Ref.
36	C ₄ H ₉	OC ₄ H ₉	Cr 188.6 N _D 243.5 I	[56]
37	C ₅ H ₁₁	OC ₅ H ₁₁	Cr 161.0 N _D 215.9 I	[56]
38	C ₆ H ₁₃	OC ₆ H ₁₃	Cr 135.3 N _D 172.8 I	[56]
39	C ₅ H ₁₁	SC ₅ H ₁₁	Cr 182.5 N _D 196.3 I	[58]

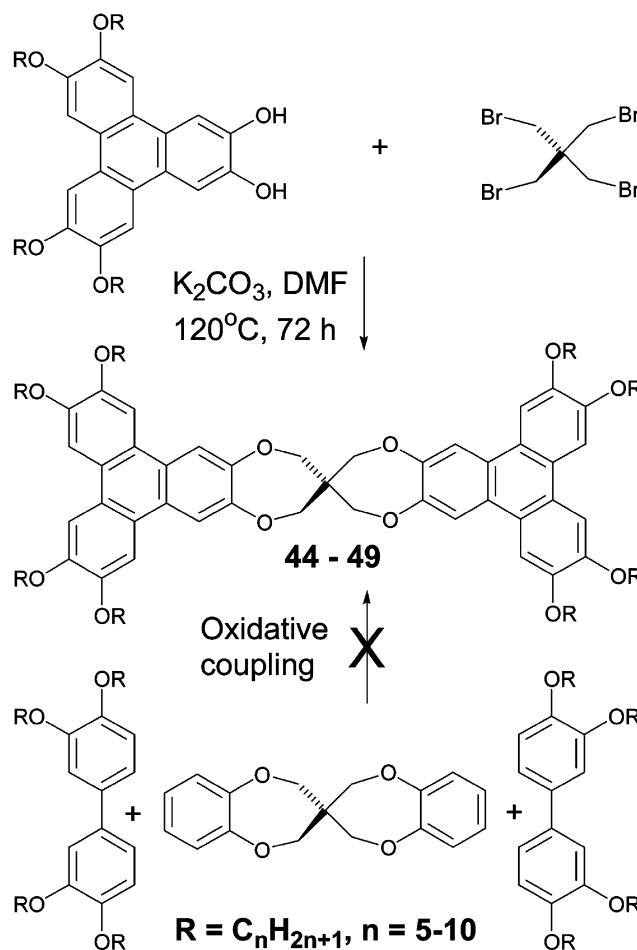
appeared only in 2001 [60]. Two organometallic DLCs in which a mercury atom is located at the centre of two substituted triphenylene molecules were prepared by Kumar and Varshney [60]. The crystalline compound **40** transforms into a highly viscous but shearable fluid phase at about 150°C. On further heating, this mesophase changes to an isotropic phase at about 210°C but with decomposition. In order to reduce the clearing temperature, one of the normal alkyl chains was replaced by a branched chain (compound **41**). This material on first heating shows a solid to solid transition at about 110°C and this soft solid transforms into the isotropic phase at 186°C. On cooling the isotropic phase, a metastable nematic discotic phase appears at 185°C. This monotropic mesophase has a strong tendency to crystallize which begins in the mesophase and is complete by 180°C. On subsequent heating, the first transition at 110°C is not observed and the crystal melts to the isotropic liquid at 186°C.



During the preparation of main chain triphenylene-based polymers, Boden and co-workers isolated a low molar mass compound that was identified as a cyclic dimer having structure **42** or **43**. The similarity of the ¹H NMR spectrum of the dimer with that of the polymer supports structure **42** over **43**. The dimer shows a mesophase range of 130–140°C [39].



Schulte *et al.* prepared six novel triphenylene-based spiro-twins **44–49** by condensing 1,2-dihydroxytriphenylenes with a tetrabromide [61]. Although the phenyl–biphenyl coupling route to prepare a variety of symmetrical and non-symmetrical triphenylenes is well established [39–42], efforts to prepare these spiro-twins by this technique failed (see scheme 2) [61]. Whereas compounds **44** and **45** containing pentyloxy and



Scheme 2. Synthesis of triphenylene-based spiro-twins.

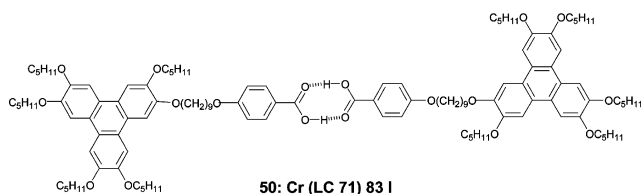
Table 5. Thermal behaviour ($^{\circ}\text{C}$) of triphenylene-based spiro-twins. All data from ref. [61].

Compound	R	Phase transition
44	C_5H_{11}	Cr 222 I
45	C_6H_{13}	Cr 155 I
46	C_7H_{15}	Cr 70 Col 103 I
47	C_8H_{17}	Cr 65 Col 109 I
48	C_9H_{19}	Cr 60 Col 121 I
49	$\text{C}_{10}\text{H}_{21}$	Cr 56 Col 106 I

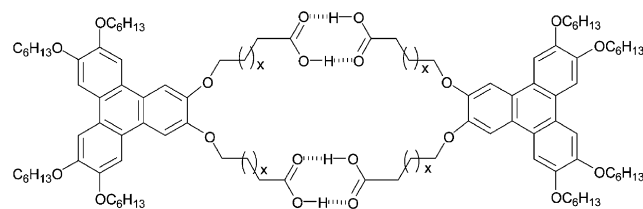
hexyloxy chains, respectively, showed only crystal to isotropic phase transitions, the higher homologues **46–49** displayed columnar mesophases. Their thermal behaviour is summarized in table 5.

2.2. Hydrogen-bonded symmetrical triphenylene discotic dimers

The role of hydrogen bonding in the formation and stabilization of LCs has now been well established, and several classes of liquid crystalline compounds involving intramolecular or intermolecular hydrogen bonding have been described [62]. The first compounds found to exhibit liquid crystalline behaviour due to hydrogen bonding were the 4-alkyl- and 4-alkoxybenzoic acids [63]. The terminally carboxylic acid-functionalized triphenylene derivative **50** was reported by Maliszewskij *et al.* [64] and this shows a monotropic mesophase. X-ray studies indicate the possibility of dimer formation due to hydrogen bonding.



Six homologues of the triphenylene-based series, **51–56**, containing two terminal carboxylic acids were prepared by Shimizu and co-workers [65, 66]. Using temperature dependent IR spectroscopy, it was observed that the band intensity of the hydrogen-bonded carbonyl, in the carboxylic acid dimer, increases at the isotropic to columnar phase transition on cooling. The mesomorphic behaviour of these materials depends significantly on the spacer length connecting the triphenylene core and carboxylic acid groups. The transition temperatures of these compounds are given in table 6.



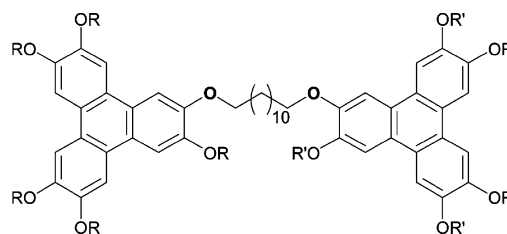
51–56: x = 3–7, 10

Table 6. Thermal behaviour ($^{\circ}\text{C}$) of hydrogen-bonded triphenylene-based dimers. All data from ref. [65].

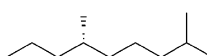
Compound	n	Phase transition
51	3	Cr (117 Col _h) 130 I
52	4	Cr 94 Col _h 105.3 I
53	5	Cr (80.6 Col _h) 103.8 I
54	6	Cr (68 Col _h) 106.1 I
55	7	Cr 95.4 I
56	10	Cr 69.1 I

2.3. Non-symmetric triphenylene-based discotic dimers

The concept of reducing the molecular symmetry in order to reduce the melting point in monomeric discotic liquid crystals has been adopted by several workers [1]. It is also known that the crystallization of glassy columnar phases shown by monomeric DLCs is retarded by reducing the symmetry of the disc [35]. Non-symmetric discotic dimers can be easily prepared by linking two different triphenylene units using a two-step synthesis procedure as shown in scheme 1. Two such non-symmetric triphenylene-based dimers, **57** and **58**, have been reported. In **57** a pentahexyloxytriphenylene unit was connected to a pentabutyloxytriphenylene unit via a $\text{O}(\text{CH}_2)_{10}\text{O}$ spacer. This compound shows a Col_h phase to isotropic phase transition at 98°C . On cooling, the columnar phase freezes into a glassy state at 30°C [35].

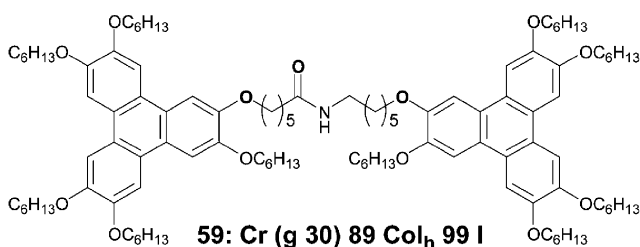


57: R = n-C₆H₁₃, R' = n-C₄H₉: Col_h (g 30) 98 I

58: R =  R' = n-C₁₀H₂₁: Cr 34 Col_h 45 I

In compound **58** a pentadecyloxytriphenylene subunit was tethered to a chiral pentakis(3,7-dimethyloctyloxy)triphenylene via a decyl spacer. This compound shows a crystal to columnar phase transition at 34°C and clears at 45°C in the first heating run in the DSC. On cooling, the columnar phase appears at 44°C and is stable to 0°C. Despite the presence of a chiral triphenylene unit, no chiral mesophase was observed in this dimer [67].

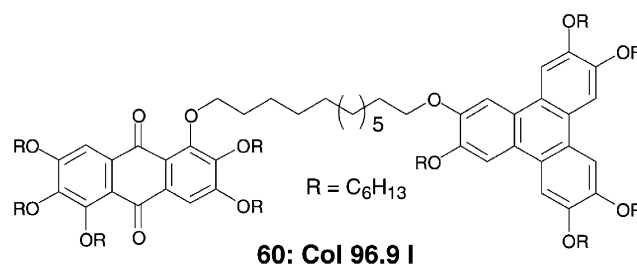
The synthesis of dimer **59**, in which there is an amide linking in the linking chain, was reported by Boden *et al.* [35]. The compound was obtained by condensing an amine-terminated triphenylene-based derivative with an acid chloride-functionalized triphenylene-based unit. It exhibits an enantiotropic columnar phase and forms a glass on cooling at about 30°C. The glassy columnar state is stable for several months at room temperature [35].



Several examples of non-symmetrical charge-transfer dimers in which a triphenylene-based unit is connected to an electron-deficient non-liquid crystalline TNF or anthraquinone moiety have been reported. Strictly speaking, these are not discotic dimers, as only one discotic fragment is involved. The second semirigid unit is either a non-liquid crystalline or a calamitic group. These compounds can be best described as monofunctional triphenylenes and their physical properties have been discussed in the previous review [1].

An interesting example of a non-symmetric discotic donor- σ -acceptor dimer is compound **60** in which a triphenylene-based derivative was linked to an electron-deficient discotic liquid crystalline anthraquinone-based moiety [68]. Compound **60** displays a columnar mesophase over a wide temperature range. On first heating, it shows a weak broad peak, probably a glass transition, at about 40°C and the mesophase to isotropic phase transition at 96.9°C. On cooling, the isotropic to columnar phase transition appears at 94.3°C. The DSC trace does not show either crystallization or a glass transition on cooling to room temperature. On subsequent reheating, the DSC shows only a mesophase to isotropic transition while the weak transition at 40°C is not seen. The UV spectrum of

dimer **60** shows no additional absorption bands when compared with the individual spectra of the donor and acceptor. Therefore, it is unlikely that dimer **60** forms either an intermolecular or intramolecular charge-transfer complex. In this dimer, the discotic liquid crystalline donor and acceptor subunits may segregate into different columns. However, further studies are needed to confirm the detailed structure of the mesophase.

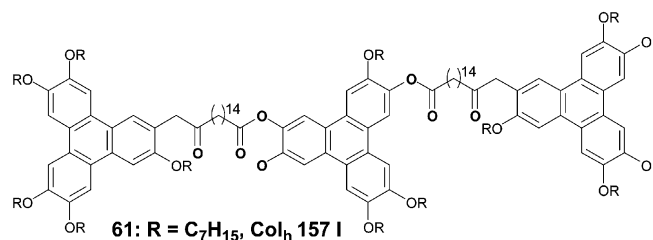


3. Triphenylene-based discotic oligomers

This section presents the chemistry and physical properties of triphenylene-based discotic trimers, tetramers, pentamers, hexamers and star-shaped oligomers.

In contrast to the range of calamitic trimers described in the literature [14, 69], only a few discotic trimers are known. Triphenylene-based trimers may be grouped into essentially two types, linear trimers in which three triphenylene units are connected with two flexible spacers, figure 2(a), and star-shaped trimers in which three triphenylene fragments are linked to a central core, figure 2(b).

Ringsdorf and co-workers prepared the linear triphenylene trimer **61** by reacting a monofunctionalized triphenylene-based derivative, 3,6,7,10,11-pentakis(heptyloxy)-2-triphenylenyl acetate, with an excess of hexadecanoic diacid and then condensing the resultant acid-functionalized triphenylene-based derivative with a difunctionalized triphenylene-based molecule [38]. The trimer is liquid crystalline at room temperature and shows a mesophase to isotropic phase transition at 157°C. It is possible that it forms a glass at lower temperatures but the glass transition could not be detected by DSC.



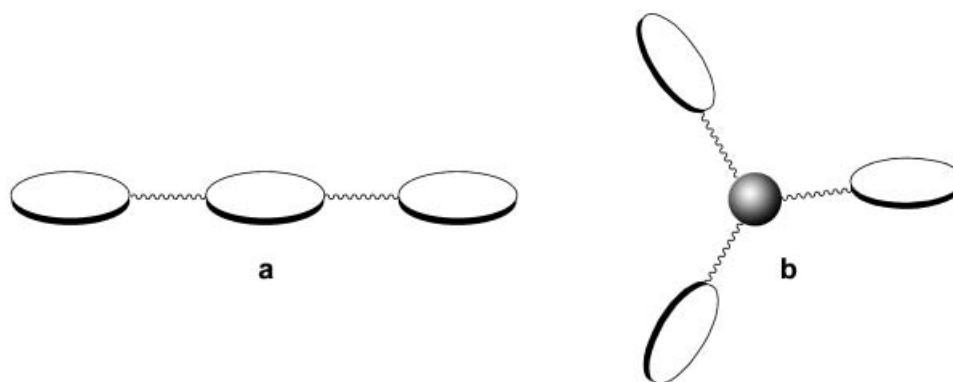
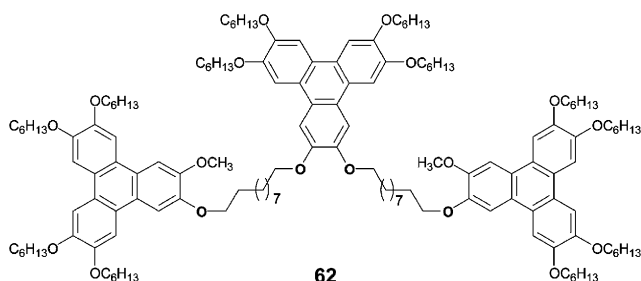


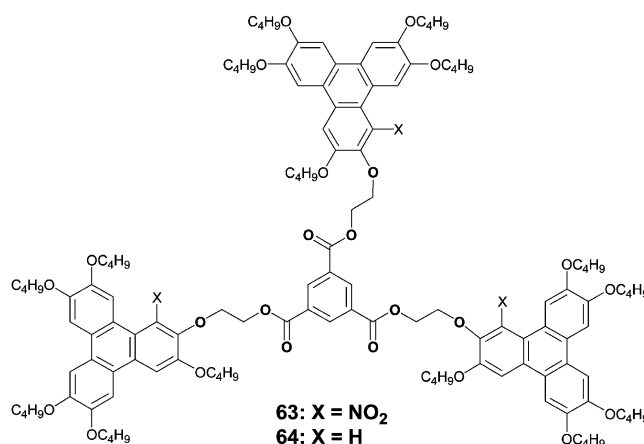
Figure 2. Sketches of (a) a linear trimer and (b) a star-shaped trimer.

The linear trimer **62**, in which three triphenylene units were connected via two spacers linked by ether groups, was reported by Boden and co-workers [31]. The compound was prepared by reacting the ω -brominated product **8** (scheme 1) with 1,2-dihydroxytriphenylene. Like the dimer **56**, it also shows complicated thermal behaviour. On first heating, it exhibits a crystal to mesophase transition at 60°C, a mesophase to mesophase transition at 92°C and clears at 109°C. On cooling, the columnar mesophase appears at 105°C, transforming into a glassy state at 32°C. The glass crystallizes slowly over a period of months.

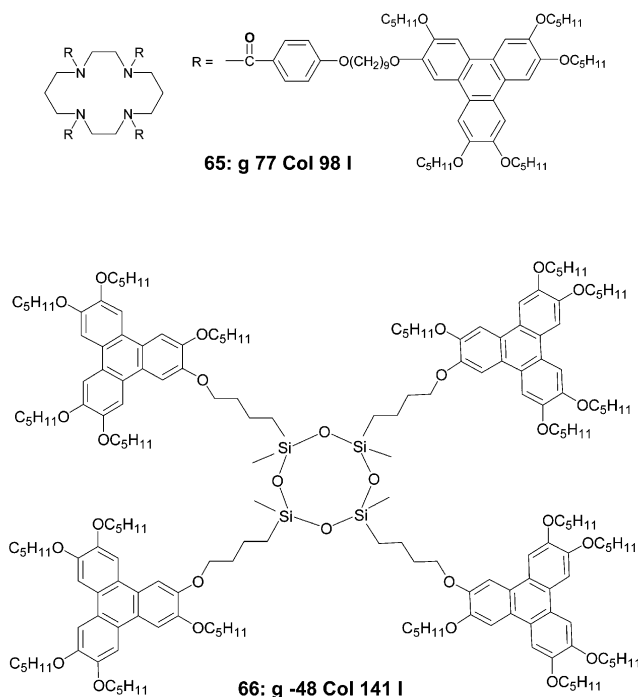


The synthesis of star-shaped trimers is relatively straightforward as it involves the preparation of just monofunctionalized triphenylenes which may be attached to a trifunctional central nucleus to obtain the trimer. Two such trimers have recently been reported by Kumar and Manickam [70]. These molecular architectures consist of a trisubstituted benzene as the central core and three triphenylene-based or nitro-functionalized triphenylene-based units as the outer cores. These outer cores are linked to the central core via ester-ether linkages through an alkyl chain spacer. While the nitro-functionalized trimer **63** exhibits a monotropic columnar mesophase, the unfunctionalized trimer **64** was found not to be liquid crystalline. Trimer **63** shows two peaks in the first DSC heating run, one weak transition at

161.1°C and a broad peak at 181.3°C. On cooling, the columnar phase appears at 158.7°C and this remains stable to room temperature. By comparison trimer **64** melts at 185°C and crystallizes at 166°C on cooling. Selected molecular parameters of these trimers have recently been calculated by Akopova *et al.* [71].



Although linear calamitic tetramers were reported in 1999 [72], a linear discotic tetramer has not yet been prepared (probably because of synthetic difficulties). However, a few star-like triphenylene-based tetramers have been reported [32, 64, 73], in which four monofunctionalized triphenylene-based units were connected to a central tetrafunctionalized core. Ringsdorf and co-workers prepared triphenylene tetramers **65** and **66** by attaching the monofunctionalized triphenylene-based unit to an azacrown or siloxane core, and studied their various physical properties [10, 32, 64, 74]. The tetramer **65** shows a glass transition at 77°C and a mesophase to isotropic transition at 98°C, while tetramer **66** exhibits a very broad columnar phase between the glass transition at -48°C and the clearing temperature at 141°C.



Contrary to the general belief that a flat or nearly flat core is essential to form columnar mesophases, it has recently been shown that molecules with a tetrahedral core unit can also organize into columnar mesophases [75]. The tetrafunctional alcohol pentaerythritol unit is a widely used core in dendrimer chemistry and has been incorporated into triphenylene-based tetramers by Schulte *et al.* [61]. The tetramers **67** and **68** with pentyloxy and hexyloxy chains, respectively, are not liquid crystalline but the higher homologues **69–72** displayed a columnar mesophase. Their thermal behaviour is summarized in table 7.

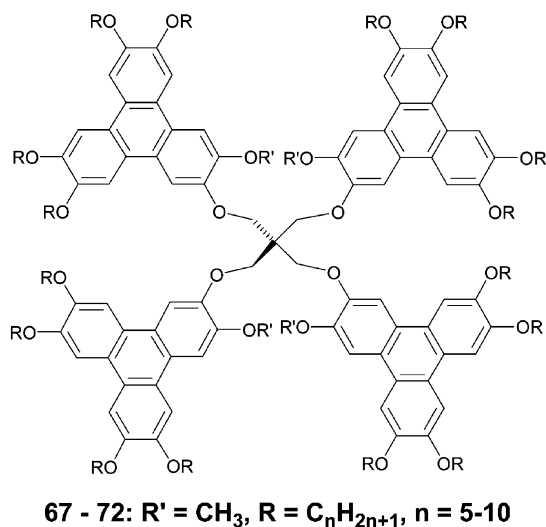
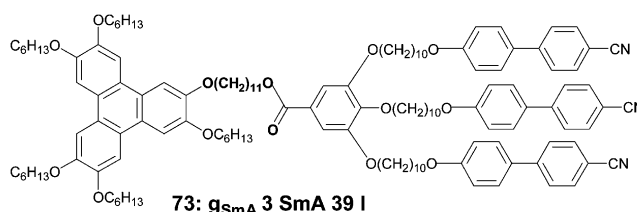


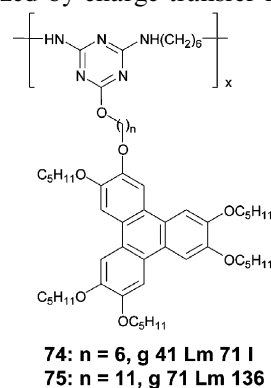
Table 7. Thermal behaviour (°C) of triphenylene-based carbon-centred tetramers. All data from ref. [61].

Compound	R	Phase transition
67	C ₅ H ₁₁	Cr 142 I
68	C ₆ H ₁₃	Cr 116 I
69	C ₇ H ₁₅	g -40 Col _h 80 I
70	C ₈ H ₁₇	g -59 Col _h 79 I
71	C ₉ H ₁₉	g -69 Col _h 59 I
72	C ₁₀ H ₂₁	g -61 Col _h 58 I

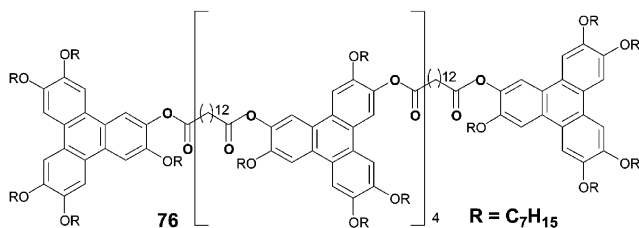
Compound **73**, which may be described as a mixed tetramer in which three well known calamitic cyanobiphenyls are linked to a monofunctionalized triphenylene-based unit, has been reported by Kouwer *et al.* As expected, this compound displays a smectic mesophase [76].



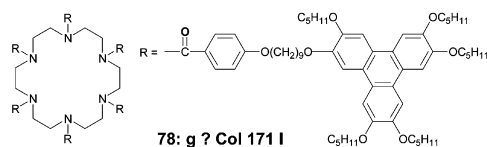
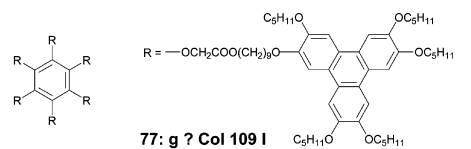
Two triphenylene-based side chain oligomers **74**, **75**, in which pentapentyloxytriphenylene side groups were attached to amino-substituted 1,3,5-triazine moieties forming part of the main chain, were reported by Janietz *et al.* [77]. GPC analysis indicates co-existence of up to pentameric structures in these triazine oligomers. Oligomer **74** shows a glass transition at 41°C and a mesophase to isotropic phase transition at 121°C. These transitions occur at 71 and 136°C, respectively, in the case of oligomer **75**. A lamellar SmA-like arrangement of the molecules was reported for these oligomers [77]. Doping of **74** and **75** with TNF results in an increase of the clearing temperature of the binary system and the mesogenic layer structure of the oligomeric triphenylene changes to a rectangular columnar arrangement, presumably stabilized by charge transfer interactions [77].



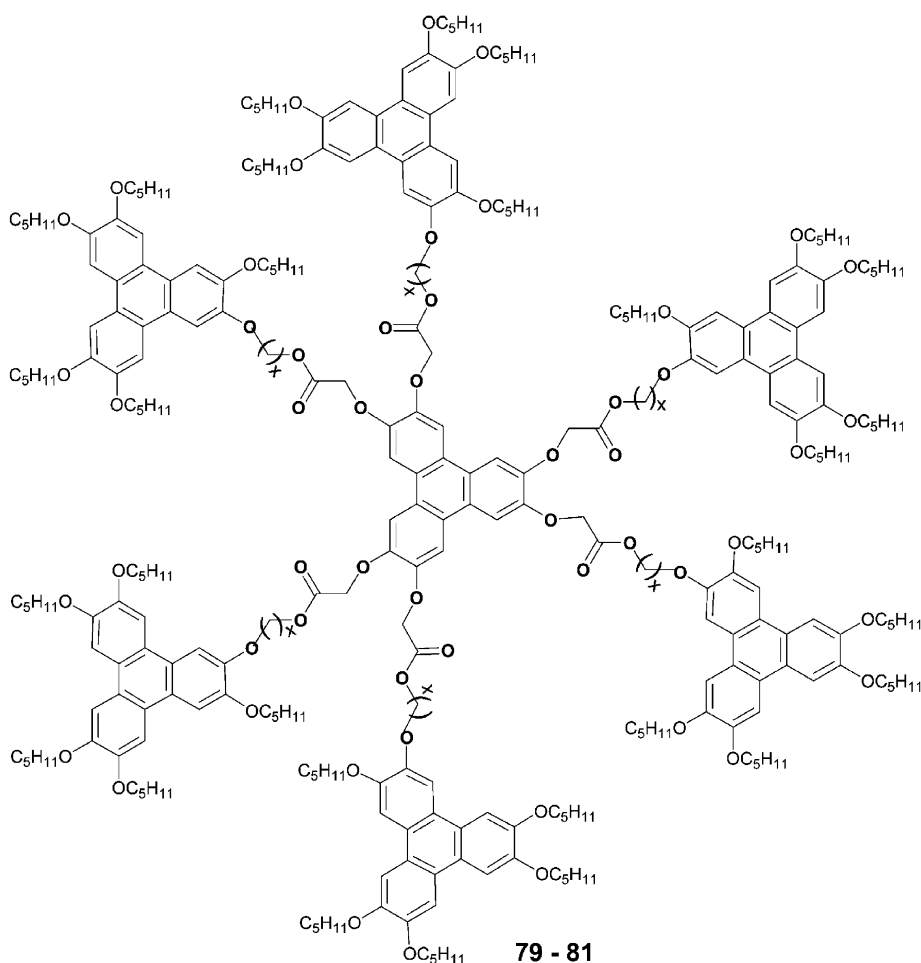
The linear hexamer **76** was obtained as one of the products from the condensation reaction of the difunctional triphenylene-based derivative with a diacid. It shows a glass transition at 35°C and a columnar mesophase to isotropic phase transition at 195°C [38].



Two star-shaped triphenylene-based hexamers are known in which six triphenylene units were linked either to a central benzene core **77** or to a central aza-crown core **78**. Compound **77** shows a columnar mesophase to isotropic phase transition at 109°C while **78** exhibits this transition at 171°C [64].



The attachment of six peripheral triphenylene units via flexible spacers generated the novel triphenylene-based heptamers **79–81** [78]. Atomic force microscopy and X-ray diffraction studies on ultrathin films of these molecules formed at the air-water interface indicate that the central core sits parallel to the interface, while the peripheral triphenylene substituents sit perpendicular to it [64]. The transition temperatures of these heptamers are listed in table 8.



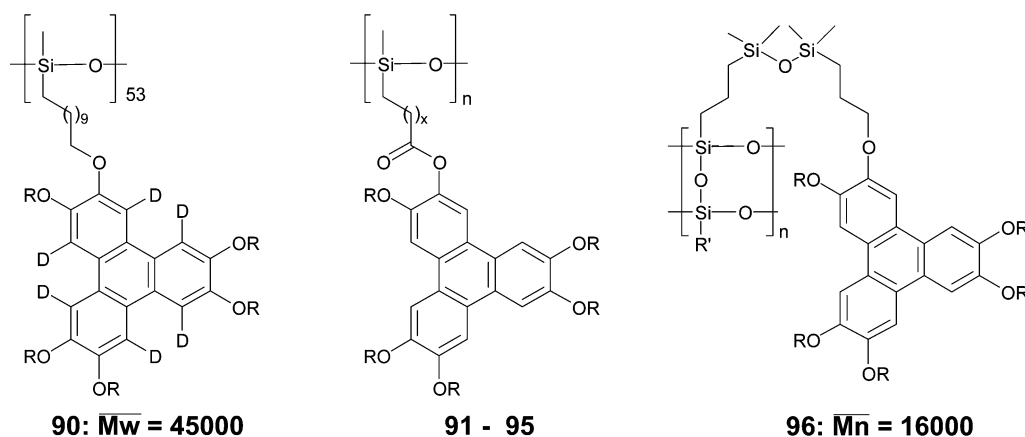


Figure 3. Structures of triphenylene-containing polysiloxanes.

average molecular weight of $45\,000\text{ g mol}^{-1}$, was prepared for use in NMR studies [83]. It shows a glass transition at -35°C and a columnar phase to isotropic phase transition at 75°C ; a columnar to columnar phase transition at 45°C was also observed [83]. The corresponding undeuteriated polymer **86c** ($\overline{DP} = 50$, $\overline{M}_w = 45\,000\text{ g mol}^{-1}$) shows the same phase behaviour [84] but the columnar phase to columnar phase transition at 45°C is seen only in the first heating run. In polymers **86–90** and in the ladder-like polysiloxane **96**, the spacer is linked to the discs via ether groups, while in polymers **91–95** it is joined via ester linkages [98]. As expected, the polymers with ester linkages exhibit higher clearing temperatures than those with ether links. The ladder-like polymer **96** ($\overline{M}_n = 16\,000\text{ g mol}^{-1}$) shows a glass transition at 20.6°C and a columnar to isotropic phase transition at 62.1°C . The formation of a board-like columnar

structure in this polymer was revealed using XRD and AFM [127].

The monofunctionalized triphenylene-based derivatives having a terminal acrylate or methacrylate group may be polymerized readily by the free radical polymerization technique. The general structures of the polymers obtained are shown in figure 4 and their thermal behaviour is summarized in table 10.

The polyacrylate **97** and the polymethacrylate **101** prepared by Ringsdorf and co-workers were found not to be liquid crystalline; GPC indicates the relative molecular weights, $380\,000\text{ g mol}^{-1}$ (polystyrene standard, THF, RI detection) for **97** and $3\,800\,000\text{ g mol}^{-1}$ for **101**. The polymethacrylate **101** showed a glass transition at 30°C and the polyacrylate **97** at -6°C . On doping with trinitrofluorenone, an electron acceptor, a nematic columnar phase (N_c) was induced in these amorphous polymers [85]. At a doping

Table 9. Transition temperatures ($^\circ\text{C}$) of triphenylene-containing polysiloxanes.

Compound	<i>R</i>	<i>x</i>	Phase transition	Ref.
86a	C_5H_{11}	9	g -19 Col 39 I	[26]
86b	C_5H_{11}	9	g -41 Col _h 75 I	[98]
86c	C_5H_{11}	9	g -35 Col 75 I	[84]
87	C_5H_{11}	3	g -53 Col _h 141 I	[98]
88	C_5H_{11}	6	g -52 Col _h 131 I	[98]
89	C_5H_{11}	9	g -29 Col 36 I	[26]
90	C_5H_{11}	9	g -35 Col 75 I	[83]
91	C_5H_{11}	3	g -54 Col _h 171 I	[98]
92	C_5H_{11}	6	g -51 Col _h 186 I	[98]
93	C_5H_{11}	9	g -37 Col _h 112 I	[98]
94	C_7H_{15}	9	g -62 Col _h 112 I	[98]
95	CH_2CH_2 $\text{CH}(\text{CH}_3)_2$	9	Col _h 81 I	[98]
96	C_5H_{11}		g 20.6 Col 62.1 I	[127]

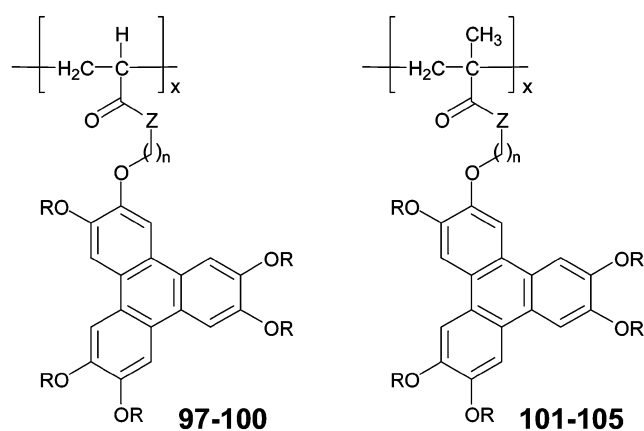


Figure 4. Structures of triphenylene-based polyacrylates and polymethacrylates.

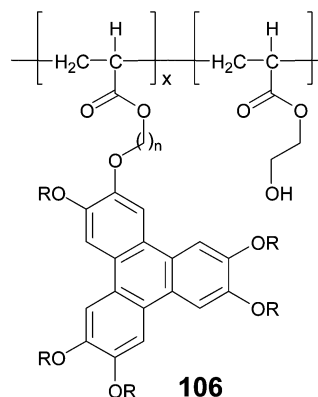
Table 10. Transition temperatures ($^{\circ}\text{C}$) of triphenylene-containing polyacrylates and polymethacrylates.

Compound	R	n	Z	$\overline{M}_w/\text{g mol}^{-1}$	Phase transition	Ref.
97	$(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_3$	0	$(\text{CH}_2\text{CH}_2\text{O})_3$	380000	g -6 I	[85]
98	C_5H_{11}	11	O		g -8 Col _h 39 I	[98]
99	C_6H_{13}	6	O	7350	g 5 Col 84 I	[112]
100	C_6H_{13}	0	$(\text{CH}_2\text{CH}_2\text{O})_2$	8960	Col 117 I	[112]
101	C_5H_{11}	6	O	3800000	g 30 I	[85]
102	C_5H_{11}	11	O		g -16 amorphous	[98]
103	C_6H_{13}	11	O	61000	g 2 Col 45 I	[111]
104	C_6H_{13}	6	O	148000	no transition	[112]
105	C_6H_{13}	0	$(\text{CH}_2\text{CH}_2\text{O})_2$	8890	Col 110 I	[112]

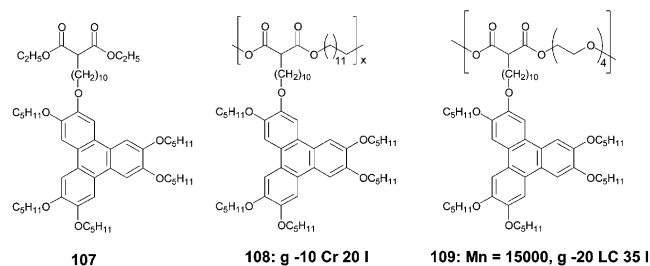
of 3:1 (polymer:TNF), the phase behaviour, g 10 N_c 88 I for **97** and g 50 N_c 170 I for **101** was observed [85].

Of the polyacrylates and polymethacrylates having both identical triphenylene-based units and spacers (**98** and **102**), only the polyacrylate shows a mesophase [98]. The non-mesomorphic nature of the polymethacrylate was attributed to the rigidity of the methacrylate-based polymer backbone. In contrast to this observation, however, the Imrie and Boden groups have recently shown that appropriately substituted triphenylene-containing polymethacrylates can form columnar phases [111, 112]. Polymer **103** having a weight average molar mass of $61\,000\text{ g mol}^{-1}$ but a number average molar mass of only $9\,000\text{ g mol}^{-1}$, due to a high polydispersity, exhibits a glass transition at 2°C and a mesophase to isotropic phase transition at 45°C [111]. Similarly, polymethacrylate **105** displays a columnar phase at room temperature and clears at 110°C [112]. Bleyl *et al.* prepared a number of polyacrylates by the photopolymerization of acrylate-functionalized triphenylene-based monomers to study their charge transport properties, but only partial polymerization was achieved [109]. The thermal behaviour of these polymers was not described. The polymerization of a nitro-functionalized triphenylene-based acrylate was reported to give polyacrylates with molar masses up to $8\,000\text{ g mol}^{-1}$, but the thermal behaviour of those polyacrylates was not reported [122].

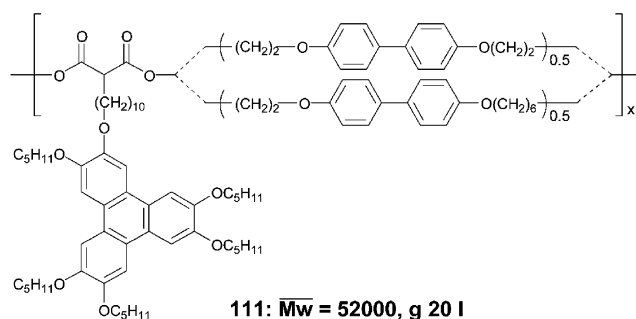
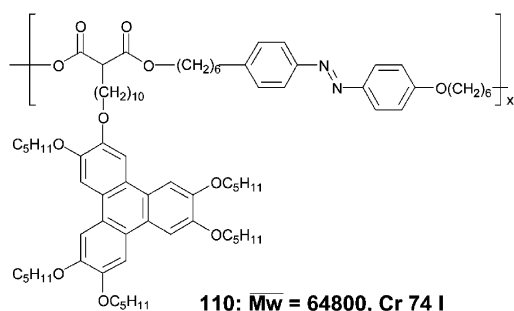
The free radical copolymerization of an acrylate-terminated triphenylene-based monomer with 2-hydroxyethyl acrylate leads to the formation of copolymers of the general structure **106**. These copolymers exhibit mesophase to isotropic transitions between 104°C and 165°C depending upon their composition. The average molecular weight of these polymers ranges from $51\,000$ to $1\,000\,000\text{ g mol}^{-1}$. The formation of networks having columnar order in these polymers was reported [117]; copolymerization of a triphenylene-based acrylate with methyl acrylate is reported to give a copolymer which does not show liquid crystallinity [112].



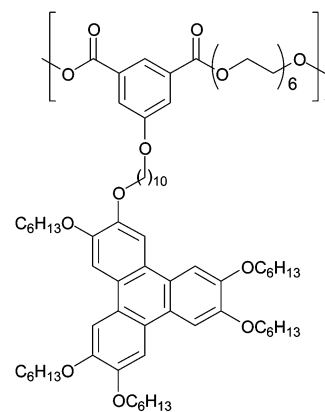
The condensation of the malonate-terminated triphenylene-based monomer **107** with α , ω -diols resulted in the synthesis of the triphenylene-based side chain polyesters **108** and **109**. Polymer **108** showed a glass transition at -10°C and a crystal to isotropic phase transition at 20°C [85]. By comparison, the polyester **109** exhibits a transition at -20°C from a glassy phase to a liquid crystalline phase, a liquid crystal-liquid crystal phase transition at 20°C and a mesophase to isotropic phase transition at 35°C [102].



The polycondensation of malonate **107** with dihydroxy-functionalized calamitic mesogens furnished polymers **110** and **111** having a triphenylene derivative as a side group discotic mesogen and azobenzene or biphenyl derivatives as rod-like mesogens in the main chain. Unfortunately, neither polymer exhibits liquid crystalline behaviour. The homopolymer **110** with an average molecular weight of $64\,800\text{ g mol}^{-1}$ showed a crystals to crystal transition at 50°C and crystal to isotropic transition at 74°C . The copolymer **111** having an average molecular weight of $52\,000\text{ g mol}^{-1}$ was found to be amorphous with a glass transition temperature of 20°C [96].



Very recently, Imrie and co-workers prepared a triphenylene-based side chain polymer by melt polycondensation of the triphenylene-substituted isophthalate with polyethylene glycol (PEG 300) [128]. The polymer **112** exhibits a weak glass transition at -17°C and a mesophase to isotropic transition at 47°C . An enhancement in the mesophase range was observed upon complexation of the polymer with lithium perchlorate. The 14:1 (**112**: LiClO_4) complex displays a glass transition at -11°C and a clearing transition at 57°C [128].



112: g -17 Col? 47 I

Ring-opening metathesis polymerization of discotic liquid crystalline monomers has been reported, leading to polynorbornenes **113**, **114** and polybutadienes **115**, **116** bearing pentyloxy- or decyloxy-substituted triphenylene-based units in the side chain [108]. While decyloxytriphenylene-based polymers exhibit columnar mesophases, pentyloxytriphenylene derivatives were found not to be liquid crystalline. Reduction of the polybutadiene backbone gives triphenylene-substituted polybutane derivatives **117** and **118**. Again, only the decyloxytriphenylene-substituted polybutane **118** shows mesomorphism. The thermal behaviour of these side chain polymers is summarized in table 11.

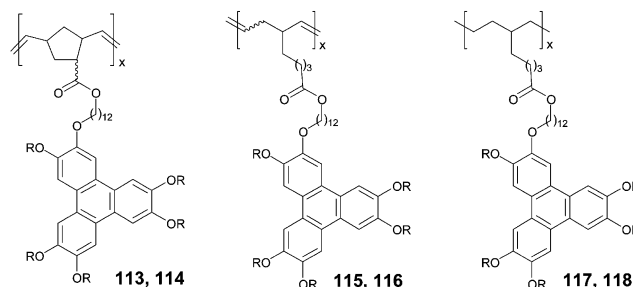


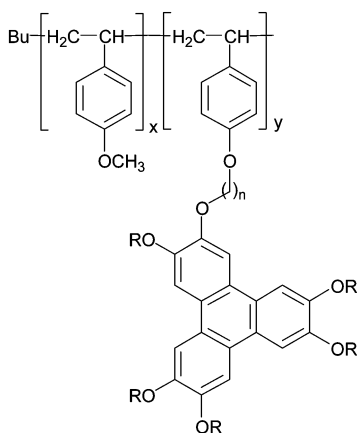
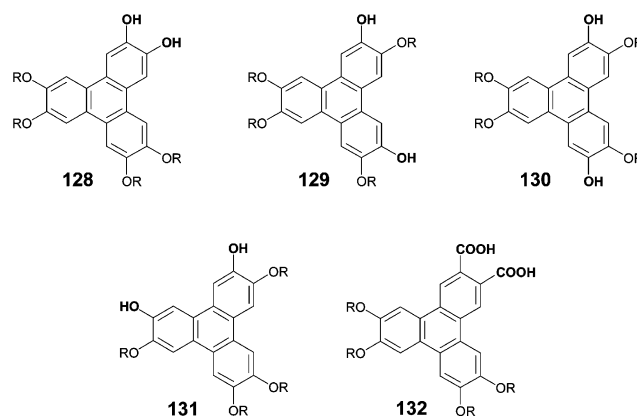
Table 11. Thermal behaviour ($^\circ\text{C}$) of polynorbornenes, polybutadienes and polybutanes containing alkoxytriphenylenes. All data from ref. [108].

Compound	R	$M_n/\text{g mol}^{-1}$	Phase transition
113	C_5H_{11}	48500	g -4 I
114	$\text{C}_{10}\text{H}_{21}$	46500	g -3 Col _{hd} 36 Col _{hd} 42 I
115	C_5H_{11}	157000	g -12 I
116	$\text{C}_{10}\text{H}_{21}$	33000	g -17 Col _{hd} 37 Col _{hd} 45 I
117	C_5H_{11}	125000	g -17 I
118	$\text{C}_{10}\text{H}_{21}$	50000	g -18 Col _{hd} 34 Col _{hd} 43 I

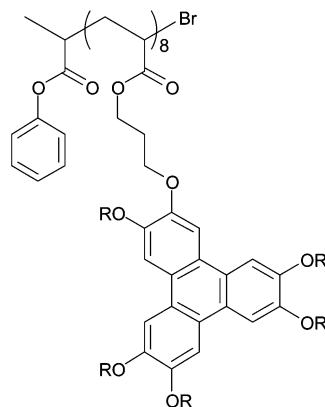
The side chain diblock polymers **119–121** containing a side group triphenylene-based block and a *p*-methoxystyrene block were prepared by Boden and co-workers by alkylating the diblock copolymer, poly[*p*-methoxystyrene)-*b*-(*p*-hydroxystyrene)] with ω -bromo-terminated alkoxytriphenylenes [114]. *p*-Methoxystyrene and *p*-*tert*-butoxystyrene were used in 18:1 and 18:3 ratios, respectively, to prepare the diblock copolymers. No indication of columnar phase formation was observed in these polymers. All the three polymers (**119**: $R=C_6H_{13}$, $x:y=18:1$, $n=6$, $\overline{M}_n=24\,000\text{ g mol}^{-1}$; **120**: $R=C_6H_{13}$, $x:y=18:3$, $n=6$; and **121**: $R=C_4H_9$, $x:y=18:3$, $n=10$, $\overline{M}_n=21\,000\text{ g mol}^{-1}$) show birefringent streaks in the range 85–95°C and a very broad clearing range above 140°C. Although microphase separation in these copolymers was not apparent, block copolymers prepared from a triphenylene-based macroinitiator **122** and *tert*-butylacrylate, using atom transfer radical polymerization, show clear microphase segregation. The five copolymers **123–127** with poly-*tert*-butylacrylate blocks of lengths ranging from $\overline{DP}=6$ to $\overline{DP}=101$ were prepared using the triphenylene macroinitiator **122** which was prepared from 2,6,7,10,11-pentapentyloxy-3-(3-acryloylpropyloxy)triphenylene using the atom transfer radical polymerization technique [126]. Thermal transitions (g 36 Col 163 I) consistent with separate phases of poly-*tert*-butylacrylate (T_g 40–45°C) and polytriphenylene acrylate (g 83 Col 163 I) were observed in the DSC traces of these block copolymers. The formation of a columnar phase in the polytriphenylene acrylate block was confirmed by X-ray studies [126].

4.2. Triphenylene-based main chain polymers

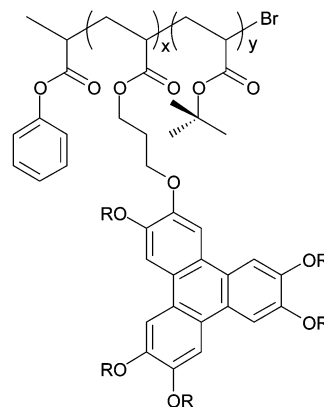
Difunctional triphenylene derivatives are the precursor molecules for the preparation of main chain polymers. The functional groups are often hydroxyl moieties which may be converted easily to ethers or esters. The two hydroxy groups in a dihydroxytetraalkoxytriphenylene may give rise to four different isomers, as shown in structures **128** (2,3-dihydroxy), **129** (2,6-dihydroxy), **130** (2,7-dihydroxy) and **131** (2,11-dihydroxy) [39, 40]. In addition to these dihydroxy-functionalized triphenylenes, a 2,3-dicarboxylic acid-functionalized triphenylene **132** has also been reported [80]. The two most common methods for the preparation of tetraalkoxydihydroxy-triphenylenes are shown in scheme 4.



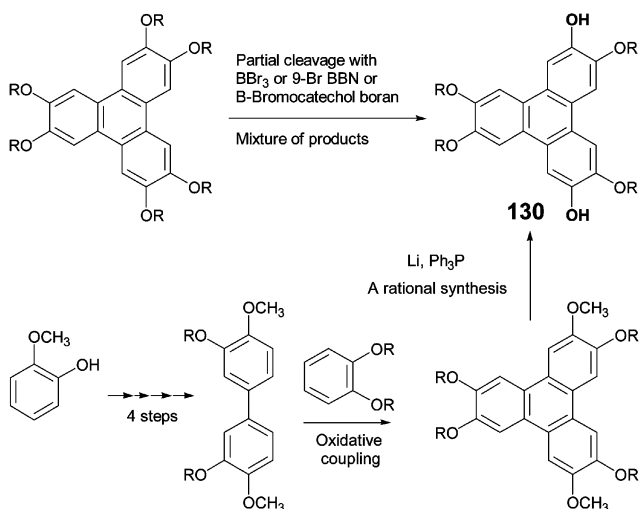
119: $R = C_6H_{13}$, $x:y = 18:1$,
 $n = 6$, $\overline{M}_n = 24000$
120: $R = C_6H_{13}$, $x:y = 18:3$,
 $n = 6$
121: $R = C_4H_9$, $x:y = 18:3$,
 $n = 10$, $\overline{M}_n = 21000$



122: $R = C_5H_{11}$,
 $\overline{M}_n = 6560$,
g 83 Col 163 I



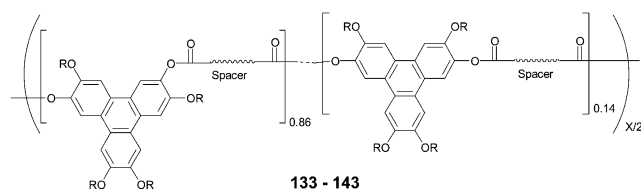
123 - 127: $R = C_5H_{11}$,
 $\overline{M}_n = 9990$,
g 36 Col 163 I



Scheme 4. Synthetic routes to 2,7-dihydroxytetraalkoxytriphenylenes. Other isomers can be prepared in a similar fashion.

Following their synthesis of triphenylene-based side chain polymers, the Ringsdorf group reported the synthesis of triphenylene-based main chain discotic liquid crystal polymers in 1985 [27]. The melt polycondensation of bifunctionalized triphenylene derivatives (a mixture of 2,6- and 2,7-functionalized isomers) with various α,ω -diacids yielded polymers **133–143**. Their thermal data are listed in table 12. The polymers having 10 or 14 methylene units in the spacer, except for **142** with chiral peripheral chains and a tetradecyl spacer, show mesomorphism. The mesophase range of all these alkoxytriphenylene-containing polyesters was higher than that of the monomeric triphenylene hexaethers or esters. A similar mesophase stabilization was observed in triphenylene-based mixed ether–ester monomers and side chain polymers. Polymers with

very long spacers containing 20 methylene units (**137** and **143**) were found not to be liquid crystalline. Deuteriation of the side chain or aromatic groups does not significantly change the thermal behaviour of these polymers. Polymer **141**, having chiral peripheral chains and a short spacer, shows mesomorphism while those with longer spacers, **142** and **143**, were found to be amorphous in nature [85]. Compound **143** on doping with TNF exhibits a nematic columnar (N_c) phase. The formation of a helical superstructure in these chiral discotic polymers has been reported [85]. Subsequently, what were assumed to be 2,6- and 2,7-isomeric mixtures have been shown to be derivatives of only the 2,6-isomer [38, 80–85, 92, 104].



The main chain discotic-calamitic polymer **144** derived from a mixture of 2,6- and 2,7-functionalized triphenylene isomers and an azobiphenyl-based calamitic mesogen was found to be amorphous in nature, exhibiting only a glass transition at 130°C [95].

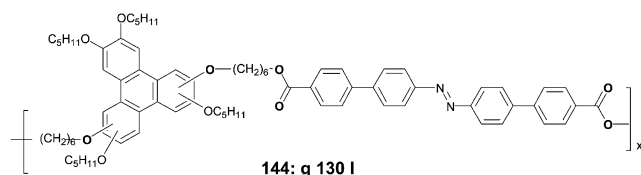
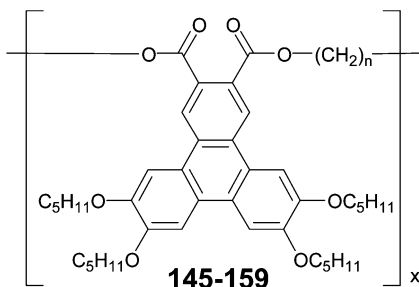


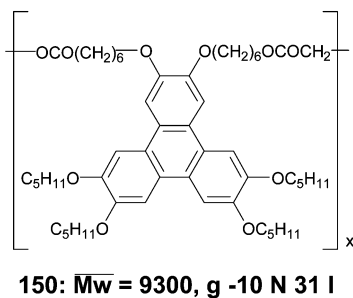
Table 12. Transition temperatures (°C) of isomeric mixtures of 2,6- and 2,7-linked triphenylene main chain polymers.

Compound	R	Spacer	$\overline{M}_w/\text{g mol}^{-1}$	Phase transition	Ref.
133	C ₅ H ₁₁	–(CH ₂) ₁₀ –		g 35 Col 195 I	[27]
134	C ₅ H ₁₁	–CD ₂ (CH ₂) ₈ CD ₂ –		g 50 Col 220 I	[27]
135	C ₅ H ₁₁	–(CH ₂) ₁₂ –	20000	g 50 Col 220 I	[38]
136a	C ₅ H ₁₁	–(CH ₂) ₁₄ –		g 60 Col 150 I	[27]
136b	C ₅ H ₁₁	–(CH ₂) ₁₄ –	19000	g 57 Col 143 I	[38]
136c	C ₅ H ₁₁	–(CH ₂) ₁₄ –	51000	g 57 Col 143 I	[83]
137	C ₅ H ₁₁	–(CH ₂) ₂₀ –		g 35 I	[27, 38]
138	CD ₂ C ₄ H ₉	–(CH ₂) ₁₄ –	28000	g 58 Col 140 I	[82]
139a	C ₇ H ₁₅	–(CH ₂) ₁₄ –		g 47 Col 182 I	[92]
139b	C ₇ H ₁₅	–(CH ₂) ₁₄ –	17000	g 50 Col 182 I	[38]
140	C ₂ H ₄ CD ₂ C ₄ H ₉	–(CH ₂) ₁₄ –		g 50 Col 180 I	[104]
141	CH ₂ C*H(CH ₃)C ₂ H ₅	–(CH ₂) ₁₀ –	19000	g 140 Col 192 I	[85]
142	CH ₂ C*H(CH ₃)C ₂ H ₅	–(CH ₂) ₁₄ –	16000	g 108 I	[85]
143	CH ₂ C*H(CH ₃)C ₂ H ₅	–(CH ₂) ₂₀ –	18000	g 79 I	[85]

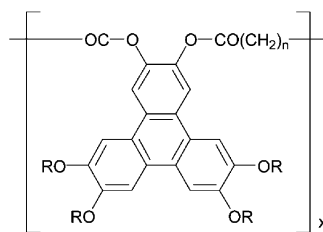
Wenz's rational synthesis of a 2,3-difunctionalized triphenylene derivative **132** followed by its polycondensation with various α,ω -diols having 8, 10, 12, 14 and 16 methylene units furnished polyesters **145–149**. All these polymers melt at about 93°C and clear between 100 and 200°C [80].



The polycondensation of malonic acid diethyl ester with the 2,3-difunctionalized triphenylene derivative 2,3-bis(6-hydroxyhexyl)oxy-6,7,10,11-tetrakis(pentyloxy)triphenylene afforded polymer **150** [93]. In contrast to the majority of triphenylene-based polymers, it shows a discotic nematic phase between the glass transition at -10°C and isotropic transition at 31°C . The nematic phase transforms into a columnar phase on doping with the electron-acceptor TNF. The complex exhibits the thermal behaviour, Col_h 130 I [99].

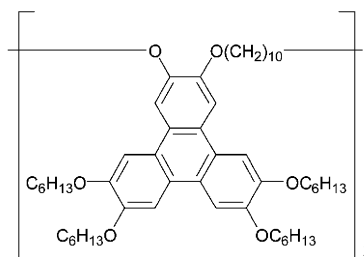


In polymers **151** ($n=14$) and **152** ($n=20$), triphenylene-based units with chiral peripheral chains ($\text{CH}_2\text{C}^*\text{H}(\text{CH}_3)\text{C}_2\text{H}_5$) were linked together via ester linkages. Both the polymers, having relative molecular weights 17000 and 15000 g mol^{-1} , respectively, were amorphous in nature. Polymer **151** shows a glass transition temperature at 105°C and polymer **152** at 75°C [85].



151: $\overline{M}_w = 17000$, g 105 I
152: $\overline{M}_w = 15000$, g 75 I

Polyetherification of 2,3-dihydroxy-6,7,10,11-tetrahexyloxytriphenylene with 1,10-dibromodecane yielded the polymer **153** with an average molecular weight of $\sim 7000 \text{ g mol}^{-1}$. This polymer showed a columnar phase to isotropic transition at 115°C [39].



153: $\overline{M}_w = 7000$, Cr 100 Col 115 I

The polyetherification of 2,7-dihydroxytetrahexyloxytriphenylene and 2,11-dihydroxytetrahexyloxytriphenylene (also referred to as 3,6-dihydroxytetrahexyloxytriphenylene) with α,ω -dibromoalkanes furnished polymers **154** and **155** [39]. Polyesterification of 2,11-dihydroxytetrahexyloxytriphenylene with α,ω -diacids produced polymers **156–158**. These polymers form an ordered columnar mesophase between the glass transition and clearing temperatures [125]. The thermal data of these polymers are listed in table 13.

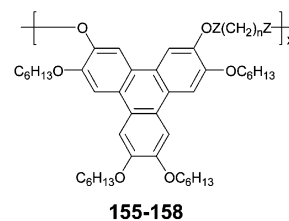
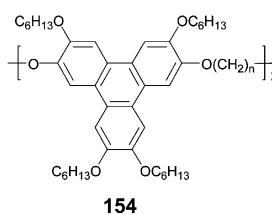


Table 13. Transition temperatures ($^{\circ}\text{C}$) of 2,7- and 2,11- (also referred to as 3,6-) linked triphenylene-based main chain polymers.

Compound	Z	n	M_w	Phase transition	Ref
154		11	24000	Cr 98 Col 118 I	[39]
155	CH_2	9	9000	Cr 93 Col 120 I	[39]
156	CO	8	39797	g 56 Col _h 211 I	[125]
157	CO	10	9656	g 40 Col _h 198 I	[125]
158	CO	12	8818	g 56 Col _h 211 I	[125]

Discotic main chain diblock and triblock copolymers containing one triphenylene block and either one or two polyethyleneoxy blocks, respectively, were prepared by the Leeds group [115]. Polyetherification of 2,7-dihydroxytetrahexyloxytriphenylene was carried out using 0.8 equivalent of 1,12-dibromododecane to ensure the termination of the polymerization with hydroxy-functionalized triphenylene moieties. The product, having an average of 11 triphenylene units in the discotic main chain block, was reacted *in situ* with 2-methoxypoly(ethyleneoxy)ethyl tosylate (PEG750). Chromatographic separation of the products furnished the diblock copolymer **159** and the triblock copolymer **160**. Both polymers were found to be liquid crystalline at room temperature. The columnar phase of copolymer **159** clears at 86°C , and that of **160** at 66°C . The triblock copolymers **161–163**, having polyethyleneoxide (PEO2000) blocks at both ends of the triphenylene block and linked via ester linkages, were also prepared by the Leeds group [121, 124]. The thermal behaviour of all these main chain block polymers is summarized in table 14.

4.3. Triphenylene-based discotic elastomers

Elastomers are loosely bound polymers. Liquid crystalline elastomers exhibit many entirely new properties which are not associated with monomeric or polymeric liquid crystals and, therefore, there are many potential applications of these materials to be explored [129]. While the field of calamitic elastomers has been well studied, only Ringsdorf and co-workers have reported discotic elastomers, [102, 105]. Elastomers are usually prepared in one or two steps from monomers having one terminal reactive functional group and a small amount of a difunctional reactive crosslinker. The first discotic elastomer was prepared using an olefin-terminated monofunctionalized triphenylene derivative and two crosslinkers with different reactive groups [102]. One of the crosslinkers contained two olefinic groups and the other possessed an olefinic group and a methacryloyl group. The critical feature of this reaction is the difference in the reactivity of the functional double bonds. During the first step of this reaction, the methacryloyl group remains essentially unreacted while

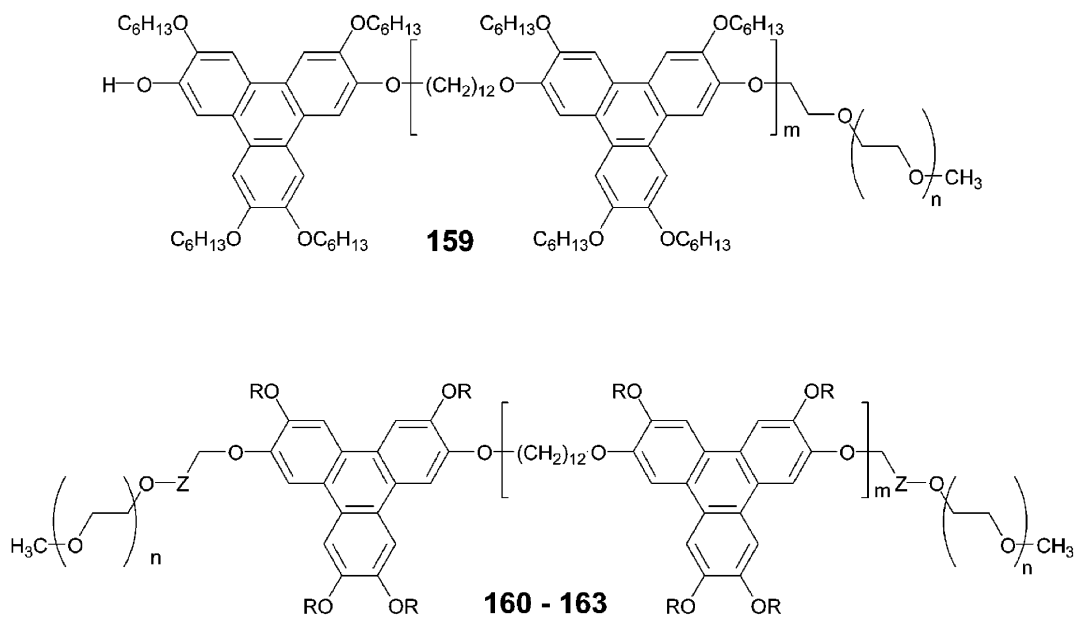


Table 14. Transition temperatures ($^{\circ}\text{C}$) of triphenylene-containing main chain block copolymers.

Compound	n	m	Z	$\overline{M}_w/\text{g mol}^{-1}$	Phase transition	Ref.
159	16	10–12		~ 10000	<20 LC 86 I	[115]
160	16	10–12	CH_2	~ 10000	<20 LC 66 I	[115]
161	~ 4 –13	~ 12	CO		Cr 43.9 Col _h 72.1 I	[121]
162	~ 4 –13	~ 33	CO		Cr 38–48 Col _h 85.7 I	[121]
[163a]	~ 12	~ 45	CO	18700	Cr 39.2 Col _h 81.4 I	[124]
[163b]	~ 12	~ 45	CO	18500	Cr 38.4 Col _h 85.7 I	[124]

the addition of the vinyl groups is almost complete. After this first crosslinking step, the weakly crosslinked network is mechanically deformed to obtain a macroscopic alignment of the liquid crystalline phase. In the second slow crosslinking step, additional bonds are introduced chemically to lock-in this anisotropic network. The formation of these elastomers is shown schematically in figure 5. Elastomer **164** was prepared using this methodology, while elastomer **165** was prepared without applying the mechanical field, to understand the effect of mechanical strain prior to the second crosslinking process. Both elastomers show very low clearing temperatures (g -50 Col 28 I) compared with the un-crosslinked triphenylene polymer (g -51 Col_{ro} 131 I). This is attributed to the disturbed

columnar packing due to the bifunctional calamitic crosslinker [102]. To compensate for this, the bifunctional calamitic crosslinker was replaced by a bifunctional triphenylene-based crosslinker. Five triphenylene-based elastomers, **166–170**, with different concentrations of discotic crosslinker and load applied during the synthesis were prepared [105]. The thermal behaviour of these elastomers is summarized in table 15.

4.4. Triphenylene-based discotic compensation films

The negative birefringence film formed by polymerized nematic discotic liquid crystals is their first successful commercial application. The Fuji Photo Film Company

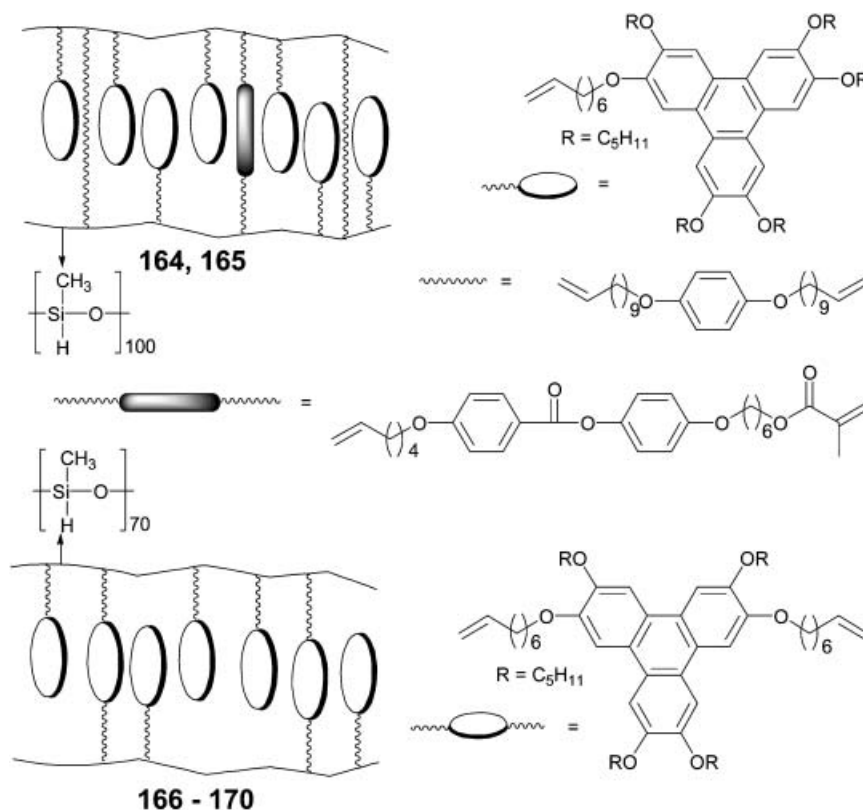


Figure 5. Schematic representation of triphenylene-based discotic elastomers.

Table 15. Transition temperatures (°C) of triphenylene-based discotic elastomers.

Compound	Phase transition	Ref.
164	g-50 Col 28 I	[102]
165	g-50 Col 28 I	[102]
166	g-50 Col 106 I	[105]
167	g-49 Col 94 I	[105]
168	g-50 Col 94 I	[105]
169	g-45 Col 78 I	[105]
170	g-44 Col 76 I	[105]

of Japan recently developed phase compensation films from polymerized triphenylene-based discotic nematic liquid crystals to improve the viewing angle of commonly used LCDs [130]. Twisted nematic and supertwisted nematic display devices have dominated the commercial display market since their invention. The liquid crystal layer in these devices consists exclusively of calamitic liquid crystals (composed of rod-shaped molecules). The major disadvantage of these types of devices is the narrow viewing cone and image inversion due to the positive birefringence of the liquid crystal layer. These effects can be suppressed by the use of compensation films, which should ideally have negative birefringence. The most promising materials for negative birefringence films are discotic liquid crystals. The films are usually prepared by aligning the reactive monomer homeotropically in the nematic phase followed by photopolymerization. Triphenylene benzoate derivatives with one to six acrylate end groups or epoxide groups have been used to prepare anisotropic networks. All these crosslinked polymers showed no thermal transition up to 200°C [107, 110, 112, 116, 118–120].

References

- [1] S. Kumar. *Liq. Cryst.*, **31**, 1037 (2004).
- [2] A.N. Cammidge, R.J. Bushby. *Hand Book of Liquid Crystals*, Vol. 2B. D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), Chap. VII, Wiley-VCH (1998).
- [3] H. Schmidt, G. Schultz. *Ann.*, **203**, 118 (1880).
- [4] C. Mannich. *Ber.*, **40**, 159 (1907).
- [5] C.M. Buess, D.D. Lawson. *Chem. Rev.*, **60**, 313 (1960).
- [6] D. Perez, E. Guitian. *Chem. Soc. Rev.*, **33**, 274 (2004).
- [7] S. Chandrasekhar, B.K. Sadashiva, K.A. Suresh. *Pramana*, **9**, 471 (1977).
- [8] J. Billard, J.C. Dubois, N.H. Tinh, A. Zann. *Nouv. J. Chimie*, **2**, 535 (1978). C. Destrade, M.C. Mondon and J. Malthete. *J. Phys. Suppl. C3*, **40**, 17 (1979).
- [9] A large number of papers have appeared on the physical properties of discotic liquid crystals. It is difficult to cover all these and, therefore, only a few selected recent references are given here: A. Bayer, S. Zimmermann, J.H. Wendorff. *Mol. Cryst. liq. Cryst.*, **396**, 1 (2003). E.I. Kats. *Mol. Cryst. liq. Cryst.*, **396**, 23 (2003); J.M. Warman and A.M. Van de Craats. *Mol. Cryst. liq. Cryst.*, **396**, 41 (2003); K.J. Donovan, T. Kreouzis, K. Scott, J.C. Bunning, R.J. Bushby, N. Boden, O.R. Lozman and B. Movaghar. *Mol. Cryst. liq. Cryst.*, **396**, 91 (2003); K. Scott, K.J. Donovan, T. Kreouzis, J.C. Bunning, R.J. Bushby, N. Boden and O.R. Lozman. *Mol. Cryst. liq. Cryst.*, **397**, 253 (2003) and references therein.
- [10] S. Marguet, D. Markovitsi, P. Millie, H. Sigal, S. Kumar. *J. Phys. Chem. B*, **102**, 4697 (1998). D. Markovitsi, S. Marguet, L. Gallos, H. Sigal, P. Millie, P. Argyrakis, S. Kumar and H. Ringsdorf. *Chem. Phys. Lett.*, **306**, 163 (1999).
- [11] I. Seguy, P. Destruel, H. Bock. *Synth. Met.*, **111–112**, 15 (2000). I.H. Stapff, V. Stumpflen, J.H. Wendorff, D.B. Spohn and D. Mobius. *Liq. Cryst.*, **23**, 613 (1997); T. Christ, B. Glusen, A. Greiner, A. Kettner, R. Sander, V. Stumpflen, V. Tsukruk and J.H. Wendorff. *Adv. Mater.*, **9**, 48 (1997).
- [12] G. Heppke, D. Kruerke, C. Lohning, D. Lotzsch, D. Moro, M. Muller, H. Sawade. *J. mater. Chem.*, **10**, 2657 (2000).
- [13] S.E. Tsvetkov, T.S. Perova, J.K. Vij, D. Simpson, S. Kumar, F. Vladimirov. *Mol. Cryst. liq. Cryst. C*, **11**, 267 (1999). T. Perova, S. Tsvetkov, J.K. Vij and S. Kumar. *Mol. Cryst. liq. Cryst.*, **351**, 95 (2000); K. Ichimura, S. Furumi, S. Morino, M. Kidowaki, M. Nakagawa, M. Ogawa and Y. Nishiura. *Adv. Mater.*, **12**, 950 (2000); H. Monobe, K. Kiyohara, M. Heya, K. Awazu and Y. Shimizu. *Mol. Cryst. liq. Cryst.*, **397**, 59 (2003); N. Katsonis, A. Marchenko and D. Fichou. *J. Am. chem. Soc.*, **125**, 13682 (2003) and references therein.
- [14] C.T. Imrie, P.A. Henderson. *Curr. Opin. colloid interface Sci.*, **7**, 298 (2002). C.T. Imrie. *Physical Properties of Liquid Crystals: Nematics*, D. Dunmur, A. Fukuda and G. Luckhurst (Eds), p. 36, INSPEC, London (2001); C.T. Imrie. *Structure and Bonding*, D. M. P. Mingos (Ed.), p. 149 Springer-Verlag, Berlin (2001); C.T. Imrie and Luckhurst. *Hand Book of Liquid Crystals*, Vol. 2B, D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess and V. Vill (Eds), Chap. X, Wiley-VCH (1998).
- [15] C.P. Lillya, Y.L.N. Murthy. *Mol. Cryst. liq. Cryst.*, **2**, 121 (1985).
- [16] S. Zamir, E.J. Wachtel, H. Zimmermann, S. Dai, N. Spielberg, R. Poupko, Z. Luz. *Liq. Cryst.*, **23**, 689 (1997).
- [17] K. Praefcke, B. Kohne, D. Singer. *Liq. Cryst.*, **7**, 589 (1990).
- [18] B. Kohne, P. Marquardt, K. Praefcke, P. Psaras, W. Stephan, K. Turgay. *Chimia*, **40**, 360 (1986).
- [19] G.C. Bryant, M.J. Cook, S.D. Haslam, R.M. Richardson, T.G. Ryan, A.J. Thorne. *J. mater. Chem.*, **4**, 209 (1994).
- [20] V. Percec, C.G. Cho, C. Pugh, D. Tomazos. *Macromolecules*, **25**, 1164 (1992).
- [21] K. Krishnan, V.S.K. Balagurusamy. *Liq. Cryst.*, **28**, 321 (2001).
- [22] S. Ito, P.T. Herwig, T. Bohme, J.P. Rabe, W. Rettig, K. Mullen. *J. Am. chem. Soc.*, **122**, 7698 (2000).
- [23] I.D. Fletcher, G.R. Luckhurst. *Liq. Cryst.*, **18**, 175 (1995).
- [24] S. Mahlstedt, D. Janietz, C. Schmidt, A. Stracke, J.H. Wendorff. *Liq. Cryst.*, **26**, 1359 (1999).
- [25] P.H.J. Kouwer, C.J. Welch, G. McRobbie, B.J. Dodds, L. Priest, G.H. Mehl. *J. mater. Chem.*, **14**, 1798 (2004).

- [26] W. Kreuder, H. Ringsdorf. *Makromol. Chem. rapid Commun.*, **4**, 807 (1983).
- [27] W. Kreuder, H. Ringsdorf, P. Tschirner. *Makromol. Chem. rapid Commun.*, **6**, 367 (1985).
- [28] W. Kreuder, H. Ringsdorf, O.H. Schonherr, J.H. Wendorff. *Angew. Chem. int. Ed.*, **26**, 1249 (1987).
- [29] S. Zamir, R. Poupko, Z. Luz, B. Huser, C. Boeffel, H. Zimmermann. *J. Am. chem. Soc.*, **116**, 1973 (1994).
- [30] D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, W. Paulus, K. Siemensmeyer, K.H. Etzbach, H. Ringsdorf, D. Haarer. *Adv. Mater.*, **7**, 276 (1995).
- [31] N. Boden, R.J. Bushby, A.N. Cammidge, P.S. Martin. *J. mater. Chem.*, **5**, 1857 (1995).
- [32] S. Kumar, P. Schuhmacher, P. Henderson, J. Rego, H. Ringsdorf. *Mol. Cryst. liq. Cryst.*, **288**, 211 (1996).
- [33] A. Bacher, I. Bleyl, C.H. Erdelen, D. Haarer, W. Paulus, H.-W. Schmidt. *Adv. Mater.*, **9**, 1031 (1997).
- [34] A.M. Van de Craats, L.D.A. Siebbeles, I. Bleyl, D. Haarer, Y.A. Berlin, A.A. Zharikov, J.M. Warman. *J. phys. Chem. B*, **102**, 9625 (1998).
- [35] N. Boden, R.J. Bushby, A.N. Cammidge, A. El-Mansoury, P.S. Martin, Z. Lu. *J. mater. Chem.*, **9**, 1391 (1999).
- [36] S. Kumar, M. Manickam, H. Schonherr. *Liq. Cryst.*, **26**, 1567 (1999).
- [37] M. Manickam, A. Smith, M. Belloni, E.J. Shelley, P. Ashton, N. Spencer, J.A. Preece. *Liq. Cryst.*, **29**, 497 (2002).
- [38] W. Kranig, B. Huser, H.W. Spiess, W. Kreuder, H. Ringsdorf, H. Zimmermann. *Adv. Mater.*, **2**, 36 (1990).
- [39] N. Boden, R.J. Bushby, A.N. Cammidge. *J. Am. chem. Soc.*, **117**, 924 (1995).
- [40] P. Henderson, H. Ringsdorf, P. Schuhmacher. *Liq. Cryst.*, **18**, 191 (1995).
- [41] S. Kumar, M. Manickam. *Chem. Commun.*, 1615 (1997).
- [42] S. Kumar, S.K. Varshney. *Liq. Cryst.*, **26**, 1841 (1999); S. Kumar and S.K. Varshney. *Synthesis*, 305 (2001).
- [43] M. Werth, S.U. Vallerien, H.W. Spiess. *Liq. Cryst.*, **10**, 759 (1991).
- [44] J.A. Rego, S. Kumar, H. Ringsdorf. *Chem. Mater.*, **8**, 1402 (1996).
- [45] N. Boden, R.J. Bushby, A.N. Cammidge, S. Duckworth, G. Headdock. *J. mater. Chem.*, **7**, 601 (1997).
- [46] K. Praefcke, A. Eckert, D. Blunk. *Liq. Cryst.*, **22**, 113 (1997).
- [47] S. Kumar, M. Manickam, V.S.K. Balagurusamy, H. Schonherr. *Liq. Cryst.*, **26**, 1455 (1999).
- [48] A. Ulman. *Introduction to Ultrathin Films: From Langmuir-Blodgett Films to Self-Assembly*. Academic Press, Boston (1991).
- [49] H. Schonherr, F.J.B. Kremer, S. Kumar, J.A. Rego, H. Wolf, H. Ringsdorf, M. Jaschke, H. Butt, E. Bamberg. *J. Am. chem. Soc.*, **118**, 13051 (1996).
- [50] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley. *Nature*, **318**, 162 (1985).
- [51] T. Chuard, R. Deschenaux. *Helv. Chim. Acta*, **79**, 736 (1996). R. Deschenaux, M. Even and D. Guillon. *Chem. Commun.*, 537 (1998); T. Chuard and R. Deschenaux. *Chimia*, **52**, 547 (1998); N. Tirelli, F. Cardullo, T. Habicher, U.W. Suter and F. Diederich. *J. chem. Soc. Perkin Trans. 2*, 193 (2000); D. Felder, B. Heinrich, D. Guillon, J.F. Nicoud and J.F. Nierengarten. *Chem. Eur. J.*, **6**, 3501 (2000); S. Campidellei and R. Deschenaux. *Helv. Chim. Acta*, **84**, 589 (2001); S. Campidellei, C. Eng, I.M. Saez, J.W. Goodby and R. Deschenaux. *Chem. Commun.*, 1520 (2003).
- [52] K. Praefcke, D. Singer. *Hand Book of Liquid Crystals*, Vol. 2B, D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), Chap. XVI, Wiley-VCH, (1998).
- [53] S. Mahlstedt, D. Janietz, A. Stracke, J.H. Wendorff. *Chem. Commun.*, 15 (2000).
- [54] V.V. Tsukruk, H. Bengs, H. Ringsdorf. *Langmuir*, **12**, 754 (1996).
- [55] R. Freudenmann, B. Behnisch, M. Hanack. *J. mater. Chem.*, **11**, 1618 (2001).
- [56] S. Kumar, S.K. Varshney. *Org. Lett.*, **4**, 157 (2002).
- [57] S. Kumar. *Pramana*, **61**, 199 (2003).
- [58] S. Kumar, J.J. Naidu. *Liq. Cryst.*, **29**, 899 (2002).
- [59] D. Vorlander. *Z. phys. Chem.*, **105**, 211 (1923).
- [60] S. Kumar, S.K. Varshney. *Liq. Cryst.*, **28**, 161 (2001).
- [61] J.L. Schulte, S. Laschat, V. Vill, E. Nishikawa, H. Finkelmann, M. Nimtz. *Eur. J. org. Chem.*, 2499 (1998).
- [62] See, for example, T. Kato. *Hand Book of Liquid Crystals*, Vol. 2B, D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), Chap. XVII, Wiley-VCH (1998) C.M. Paleos and D. Tsiourvas. *Angew. Chem. int. Ed.*, **34**, 1696 (1995); D. Stewart, B.J. Paterson and C.T. Imrie. *Eur. Poly. J.*, **33**, 285 (1997); V. Percec, C.H. Ahn, T.K. Bera, G. Ungar and D.J.P. Yearley. *Chem. Eur. J.*, **5**, 1070 (1999); J. Barbera, L. Puig, J.L. Serrano and T. Sierra. *Chem. Mater.*, **16**, 3308 (2004).
- [63] G.W. Gray. *Molecular Structure and Liquid Crystals*, p. 161 (London: Academic Press) (1967) and references therein.
- [64] N.C. Maliszewskyj, P.A. Heiney, J.Y. Josefowicz, T. Plesniviy, H. Ringsdorf, P. Schuhmacher. *Langmuir*, **11**, 1666 (1995).
- [65] W. Wan, H. Monobe, T. Sugino, Y. Tanaka, Y. Shimizu. *Mol. Cryst. liq. Cryst.*, **364**, 597 (2001).
- [66] Y. Setoguchi, H. Monobe, W. Wan, N. Terasawa, K. Kiyohara, N. Nakamura, Y. Shimizu. *Thin solid Films*, **438-439**, 407 (2003).
- [67] D. Hirst, S. Diele, S. Laschat, M. Nimtz. *Helv. Chim. Acta.*, **84**, 1190 (2001).
- [68] S. Kumar, J.J. Naidu, S.K. Varshney. *Mol. Cryst. liq. Cryst.*, **411**, 355 (2004).
- [69] See, for example: C.T. Imrie, P.A. Henderson, J.M. Seddon. *J. mater. Chem.*, **14**, 2486 (2004). C.T. Imrie and G. Luckhurst. *J. mater. Chem.*, **14**, 2486 (2004) and references therein.
- [70] S. Kumar, M. Manickam. *Liq. Cryst.*, **26**, 939 (1999).
- [71] O. Akopova, N. Usoltseva, N. Zharnikova. *Mol. Cryst. liq. Cryst.*, **411**, 319 (2004).
- [72] C.T. Imrie, D. Stewart, C. Remy, D.W. Christie, I.W. Hamley, R. Harding. *J. mater. Chem.*, **9**, 2321 (1999).
- [73] D. Markovitsi, S. Marguet, J. Bondkowski, S. Kumar. *J. phys. Chem. B*, **105**, 1299 (2001).
- [74] D. Haarer, J. Simmerer, D. Adam, P. Schuhmacher, W. Paulus, K. Etzbach, K. Siemensmeyer, H. Ringsdorf. *Mol. Cryst. Liq. Cryst.*, **283**, 63 (1996).
- [75] C. Tschierske. *J. mater. Chem.*, **8**, 1485 (1998).
- [76] P.H.J. Kouwer, J. Pourzand, G.H. Mehl. *Chem. Commun.*, 66 (2004).
- [77] D. Janietz, R. Festag, C. Schmidt, J.H. Wendorff. *Liq. Cryst.*, **20**, 459 (1996).
- [78] T. Plesniviy, H. Ringsdorf, P. Schuhmacher, U. Nutz, S. Diele. *Liq. Cryst.*, **18**, 185 (1995).

- [79] See, for example: D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), *Hand Book of Liquid Crystals*, Vol. 3, Wiley-VCH, Weinheim (1998). V.P. Shibaev and L. Lam (eds). *Liquid Crystalline and Mesomorphic Polymers*, Springer-Verlag (1994); C.B. McArdle (ed.). *Side-chain Liquid Crystal Polymers*, Blackie (1989); A. Ciferri, W.R. Krigbaum and R.B. Meyer (eds). *Polymer Liquid Crystals*, Academic press (1982); A. Blumstein (eds). *Liquid Crystalline Order in Polymers*, Academic press (1978).
- [80] G. Wenz. *Makromol. Chem. rapid. Commun.*, **6**, 577 (1985).
- [81] M. Engel, B. Hisgen, R. Keller, W. Kreuder, B. Reck, H. Ringsdorf, H.-W. Schmidt, P. Tschirner. *Pure appl. Chem.*, **57**, 1009 (1985).
- [82] O. Herrmann-Schönherr, J.H. Wendorff. *Makromol. Chem. rapid. Commun.*, **7**, 97 (1986).
- [83] B. Huser, H.W. Spiess. *Makromol. Chem. rapid. Commun.*, **9**, 337 (1988).
- [84] B. Huser, T. Pakula, H.W. Spiess. *Macromolecules*, **22**, 1960 (1989).
- [85] H. Ringsdorf, R. Wustefeld, E. Zerta, M. Ebert, J.H. Wendorff. *Angew. Chem. int. Ed.*, **28**, 914 (1989).
- [86] M.M. Green, H. Ringsdorf, J. Wagner, R. Wustefeld. *Angew. Chem. int. Ed.*, **29**, 1478 (1990).
- [87] T.-C. Hsu, B. Huser, T. Pakula, H.W. Spiess, M. Stamm. *Makromol. Chem.*, **191**, 1597 (1990).
- [88] W. Kranig, C. Boeffel, H.W. Spiess. *Macromolecules*, **23**, 4061 (1990).
- [89] W. Kranig, C. Boeffel, H.W. Spiess, O. Karthaus, H. Ringsdorf, R. Wustefeld. *Liq. Cryst.*, **8**, 357 (1990).
- [90] H. Ringsdorf, R. Wustefeld. *Phil. Trans. r. Soc. London.*, **A 330**, 95 (1990).
- [91] O. Karthaus, H. Ringsdorf, C. Urban. *Makromol. Chem. macromol. Symp.*, **46**, 347 (1991).
- [92] S. Bauer, T. Plesnivý, H. Ringsdorf, P. Schuhmacher. *Makromol. Chem. macromol. Symp.*, **64**, 19 (1992).
- [93] I.G. Voigt-Martin, R.W. Garbella, P. Schuhmacher. *Macromolecules*, **25**, 961 (1992).
- [94] O. Karthaus, H. Ringsdorf, V.V. Tsurkruk, J.H. Wendorff. *Langmuir*, **8**, 2279 (1992).
- [95] M. Ebert, G. Frick, C. Baehr, J.H. Wendorff, R. Wustefeld, H. Ringsdorf. *Liq. Cryst.*, **11**, 293 (1992).
- [96] O. Karthaus, H. Ringsdorf, M. Ebert, J.H. Wendorff. *Makromol. Chem.*, **193**, 507 (1992).
- [97] M.V.d. Auweraer, C. Catry, L. Feng Chi, O. Karthaus, W. Knoll, H. Ringsdorf, M. Sawodny, C. Urban. *Thin solid Films*, **210/211**, 39 (1992).
- [98] M. Werth, H.W. Spiess. *Makromol. Chem. rapid. Commun.*, **14**, 329 (1993).
- [99] M. Vandevyver, P.-A. Albouy, J.P. Mingotaud, A. Barraud, O. Karthaus, H. Ringsdorf. *Langmuir*, **9**, 1561 (1993).
- [100] V.V. Tsurkruk, J.H. Wendorff, O. Karthaus, H. Ringsdorf. *Langmuir*, **9**, 614 (1993).
- [101] H.W. Spiess. *Ber. Bunsenges. Phys. Chem.*, **97**, 1294 (1993).
- [102] C. Catry, M.V.d. Auweraer, F.C. de Schryver, H. Bengs, L. Haussling, O. Karthaus, H. Ringsdorf. *Makromol. Chem.*, **194**, 2985 (1993).
- [103] H. Bengs, H. Finkelmann, J. Kupfer, H. Ringsdorf, P. Schuhmacher. *Makromol. Chem. rapid. Commun.*, **14**, 445 (1993).
- [104] I.G. Voigt-Martin, M. Schumacher, M. Honig, P. Simon, R.W. Garbella. *Mol. Cryst. liq. Cryst.*, **254**, 299 (1994).
- [105] G. Kruk, J.K. Vij, O. Karthaus, H. Ringsdorf. *Supramol. Sci.*, **3**, 51 (1995).
- [106] S. Disch, H. Finkelmann, H. Ringsdorf, P. Schuhmacher. *Macromolecules*, **28**, 2424 (1995).
- [107] C.D. Favre-Nicolin, J. Lub. *Macromolecules*, **29**, 6143 (1996).
- [108] M. Weck, B. Mohr, B.R. Maughon, R.H. Grubbs. *Macromolecules*, **30**, 6430 (1997).
- [109] I. Bleyl, C.H. Erdelen, K.-H. Etzbach, W. Paulus, H.-W. Schmidt, K. Siemensmeyer, D. Haarer. *Mol. Cryst. liq. Cryst.*, **299**, 149 (1997).
- [110] D. Christine, C.D. Favre-Nicolin, J. Lub, P. van der Sluis. *Mol. Cryst. liq. Cryst.*, **299**, 157 (1997).
- [111] D. Stewart, G.S. McHattie, C.T. Imrie. *J. mater. Chem.*, **8**, 47 (1998).
- [112] N. Boden, R.J. Bushby, Z.B. Lu. *Liq. Cryst.*, **25**, 47 (1998).
- [113] T. Wang, D. Yan, E. Zhou, O. Karthaus, H. Ringsdorf. *Polymer*, **39**, 4509 (1998).
- [114] N. Boden, R.J. Bushby, Z.B. Lu, H. Eichhorn. *Mol. Cryst. liq. Cryst.*, **332**, 281 (1999).
- [115] N. Boden, R.J. Bushby, H. Eichhorn, Z.B. Lu, R. Abeysekera, A.W. Robardes. *Mol. Cryst. liq. Cryst.*, **332**, 293 (1999).
- [116] C.D. Braun, J. Lub. *Liq. Cryst.*, **26**, 1501 (1999).
- [117] R.V. Talroze, O.A. Otmakhova, M.A. Koval, S.A. Kuptsov, N.A. Plate, H. Finkelmann. *Macromol. Chem. Phys.*, **201**, 877 (2000).
- [118] L.-H. Wu, W.-C. Lee, C.-S. Hsu, S.-T. Wu. *Liq. Cryst.*, **28**, 317 (2001).
- [119] M. Inoue, M. Ukon, H. Monobe, T. Sugino, Y. Shimizu. *Mol. Cryst. liq. Cryst.*, **365**, 439 (2001).
- [120] T. Sergan, M. Sonpatki, J. Kelly, L.-C. Chien. *Mol. Cryst. liq. Cryst.*, **359**, 245 (2001).
- [121] N. Boden, R.J. Bushby, G. Cooke, O.R. Lozman, Z. Lu. *J. Am. chem. Soc.*, **123**, 7915 (2001).
- [122] H. Schönherr, M. Manickam, S. Kumar. *Langmuir*, **18**, 7082 (2002).
- [123] N. Boden, R.J. Bushby, O.R. Lozman. *Mol. Cryst. liq. Cryst.*, **400**, 105 (2003).
- [124] R. Abeysekera, R.J. Bushby, C. Caillet, I.W. Hamley, O.R. Lozman, Z. Lu, A.W. Robardes. *Macromolecules*, **36**, 1526 (2003).
- [125] W. Wan, H. Monobe, Y. Tanaka, Y. Shimizu. *Liq. Cryst.*, **30**, 571 (2003).
- [126] O.A. Otmakhova, S.A. Kuptsov, R.V. Talroze, T.E. Patten. *Macromolecules*, **36**, 3432 (2003).
- [127] C.-Y. Ba, Z.-R. Shen, H.-W. Gu, G.-Q. Guo, P. Xie, R.-B. Zhang, C.-F. Zhu, L.-J. Wan, F.-Y. Li, C.-H. Huang. *Liq. Cryst.*, **30**, 391 (2003).
- [128] C.T. Imrie, R.T. Inkster, Z. Lu, M.D. Ingram. *Mol. Cryst. liq. Cryst.*, **408**, 33 (2004).
- [129] See, for example: M. Warner, E.M. Terentjev. *Liquid Crystal Elastomers*. Clarendon Press, Oxford (2003), S.M. Kelly. *Liq. Cryst.*, **24**, 71 (1998); R. Zentel. *Angew. Chem. int. Ed. adv. Mater.*, **28**, 1407 (1989); H. Finkelmann. *Adv. polym. Sci.*, **60/61**, 99 (1984).
- [130] K. Kawata. *The Chemical Record*, **2**, p 59 (2002), H. Mori, Y. Itoh, Y. Nishuira, T. Nakamura and Y. Shinagawa. *Jpn. J. appl. Phys.*, **36**, 143 (1997).