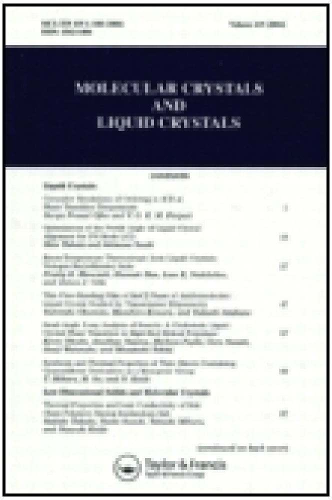

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: K. J. Shepperson , T. Meyer & G. H. Mehl (2004) Polyphilic Multicomponent Dimers with Perfluorinated Cores, Molecular Crystals and Liquid Crystals, 411:1, 185-191, DOI: 10.1080/15421400490435026

To link to this article: http://dx.doi.org/10.1080/15421400490435026

Mol. Cryst. Liq. Cryst., Vol. 411, pp. 185/[1227]–191/[1233], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490435026

POLYPHILIC MULTICOMPONENT DIMERS WITH PERFLUORINATED CORES

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The linking of segments, which have a tendency to phase separate at suitable temperatures, by covalent bonding has been employed in the synthesis of inorganic-organic hybrids. This approach can be utilised to tailor the stability range and the properties (eg viscosity) of liquid crystal materials. Research into such materials has focused strongly on the combination of calamitic moieties and silicones, however the introduction of a third phase separating segment, of which perfluorinated carbon chains are a good example, is an attractive area of research. In this paper we will report the synthesis and characterisation of materials incorporating a range of calamitic mesogens. These are attached either terminally or laterally to flexible linear chains containing alkyl and siloxane units fused to a central perfluorinated chain. The phase behaviour of the investigated materials is characterised by nematic and smectic phases with transition temperatures close to ambient. The size of the different linear units was varied systematically in order to investigate their contribution to the mesomorphic phase behaviour. The liquid-crystalline properties, investigated by optical polarising microscopy, differential scanning calorimetry and X-ray diffraction will be discussed.

Keywords: liquid crystal; micro-scgregation; perfluorinated; self-organisation; siloxane

INTRODUCTION

The influence of molecular geometry upon liquid crystalline phase behaviour is well understood and has been investigated thoroughly [1,2]. Less attention has been paid in the past to the question of miscibility between covalently bonded groups in systems that can lead to microphase separation [3]. In recent years this question has been addressed with studies of siloxane and perfluorinated groups linked to conventional mesogens

We thank Paul Kouwer for the XRD studies. We also thank Quinetiq and the EU for their financial support of this project.

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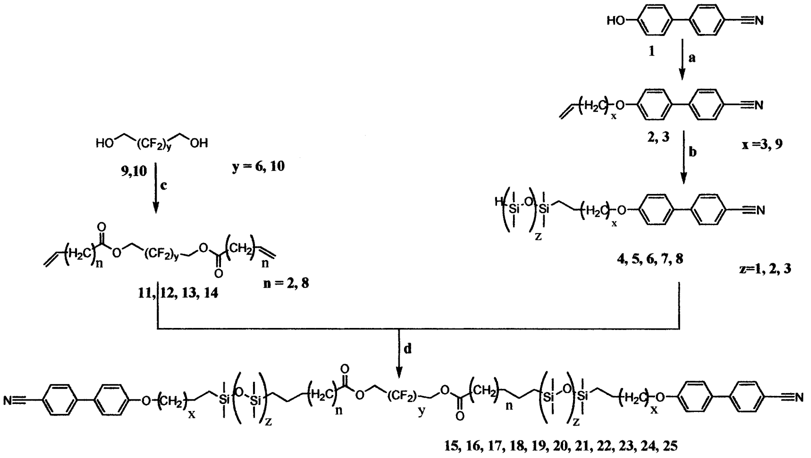
[4,5,6]. Research on polyphilic materials that combine both perfluorinated and siloxane moieties in the same system is thus attractive.

For the investigation of materials containing a range of microphase separating groups on the liquid crystalline phase behaviour; perfluorinated groups and siloxane moieties were selected in conjunction with conventional calamitic mesogens. In order to examine linear dimeric materials the cyanobiphenyl group **1** was selected, as it allows a comparison with a large number of related systems. The cyanobiphenyl group was attached to a hydrocarbon chain of five or eleven methylene units with an ether linkage as shown for molecules **2** and **3** depicted in Scheme 1.

The mesogens were bonded to a disiloxane, trisiloxane or tetrasiloxane moiety in a hydrosylilation reaction leading to materials **4**, **5**, **6**, **7** and **8** in a convergent synthesis. A perfluorinated diol containing either eight, compound **9**, or twelve difluoromethane units, material **10**, were chosen



a) 1-bromo pent-4-ene or 1-bromoundec-10-ene, K_2CO_3, KI, butanone.

b) 1,1,3,3- tetramethyldisloxane or

1,1,3,3,5,5-hexmethyltrisiloxane or 1,1,3,3,5,5,7,7- octamethyltetrasiloxane, Karstedt's catalyst, toluene or THF.

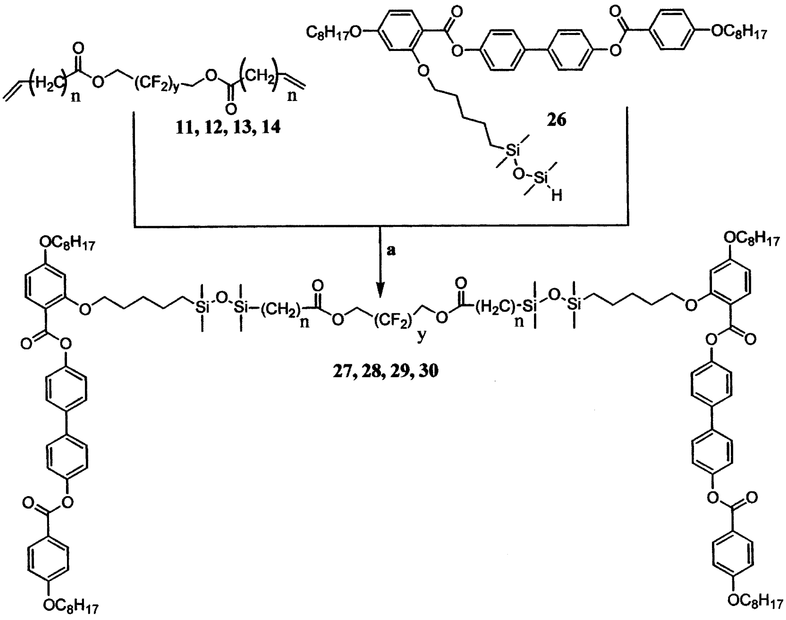
c) DIC, DMAP, PTSA, DCM, pentenoic acid or undecenoic acid.

d) Karstedt's catalyst, toluene or THF.

SCHEME 1 Synthesis of linear polyphilic systems.

and both alcohol functions were connected by an esterification reaction using either pentenoic or undecenoic acid to give the central perfluorinated cores **11**, **12**, **13**, and **14**. The mesogenic groups **4**, **5**, **6**, **7** and **8** were subsequently linked with the siloxane unit to the central perfluorinated core via a hydrosilylation reaction leading to the final products **15**, **16**, **17**, **18**, **19**, **20**, **21**, **22**, **23**, **24**, and **25**, whose properties are listed in Figures 1, 2, and 3.

In order to evaluate the influence of a modulation in the architecture of the mesogens a laterally functionalised mesogen **26** was connected to the perfluoralkyl cores **11**, **12**, **13** and **14** leading to the target compounds **27**, **28**, **29** and **30** shown in Scheme 2 and where the properties are listed (Fig. 4) [7,8]. The mesogen selected is characterised consisting of four aromatic rings in the central core with terminal alkoxy chains of eight methylene units, and a short spacer consisting of a tetramethyldisiloxane unit and five methylene groups linked to the aromatic core via an ether linkage. This compound was used previously for the investigation of nematic multipodes and dendrimers [8].



a) Karstedt's catalyst, toluene or THF.

SCHEME 2 Synthesis of laterally connected dimers.

RESULTS

The materials of an overall linear shape with a perfluoralkyl core where **x** = 10 CF_2 units showed a smectic A phase, which increases in stability as the alkyl spacer lengths **n** and **m** were increased from five to eleven units. A highly ordered smectic phase was observed for compounds **17** and **18**, which was dependent on the length of the spacer between the biphenyl and the siloxane moiety.

With a shorter perfluorinated core of six CF_2 units an increase of the transition temperatures of the smectic A phase can be observed, which is less stable than for the materials with a longer central perfluorinated linking group. Additionally the highly ordered smectic X phase is only observed for material **21**.

The size of the siloxane group, **z**, was increased in order to observe the effect on liquid crystalline behaviour in these materials. When comparing the effect of siloxane and perfluorinated groups on the liquid crystalline phase behaviour, it is noticeable that the enlargement of siloxane moiety is considerably more effective in lowering the transition temperatures than a decrease in the size of the perfluorinated unit. This is shown by material **23** (Figure 3).

Compound	**x**	**n**	**y**	**Transitions °C; ΔH (J/g)**
15	5	5	10	K 10.2 (9.82) SmA 12.3 (4.21) I
16	5	11	10	K 10.7 (15.45) SmA 23.7 (10.47) I
17	11	5	10	K 18.3 (13.87) SmX (2.31) 38.1 SmA 47.2 (4.18) I
18	11	11	10	K 22.0 (11.65) SmX 29.5 (4.51) SmA 55.4 (7.68) I

FIGURE 1 Linear materials with a central perfluorinated core of 10 CF_2 units.

Compound	**x**	**n**	**y**	**Transitions °C; ΔH (J/g)**
19	5	5	6	Melts below -50
20	11	5	6	K 31.0 (25.40) SmA 37.8 (5.11) I
21	11	11	6	K 39.0 (34.10) SmX 43.9 (2.31) SmA (0.66) 47.9 I

FIGURE 2 Linear materials with a central perfluorinated core of six CF_2 units.

Compound	x	n	Y	Z	Transitions °C; ΔH (J/g)
22	5	5	10	3	K –39 (12.61) SmA 10.3 (6.32) I
23	5	11	10	3	K 9.9 (26.20) SmA (5.47) 14.7 I
24	5	5	6	3	Melts below –50
25	5	5	10	4	K 6.9 (10.83) K 23.4 (23.04)

FIGURE 3 Linear materials with an enlarged siloxane unit.

Compound	y	n	Transitions °C; ΔH (J/g)
27	10	5	K 33.8 (10.79) N 102.0 (0.38) I
28	10	11	K 37.1 (10.94) N 88.4 (0.13) I
29	6	5	K 39.5 (11.17) N 94.2 (0.27) I
30	6	11	K 31.9 (11.34) N 88.2 (0.33) I

FIGURE 4 Lateral materials with a central perfluorinated core of six or ten CF_2 units.

The transition temperatures of the side-on mesogens was lowered by attachment to the perfluorinated siloxane core and increased by the lengthening of the alkyl spacer **m**. The effect on the liquid crystalline behaviour of altering the spacer and core in the lateral materials is less dramatic than observed in the linear materials.

CONCLUSIONS

A series of polyphilic dimeric materials were synthesised and their phase behaviour examined. The central perfluorinated chain proved to be a suitable tool for lowering the transition temperatures of smectic A and nematic phases of conventional mesogenic groups. With a suitable length of alkyl spacer in the appropriate position the materials also exhibited a highly ordered smectic X phase. The effect of this core on a number of architectures proved to be quite strong for the linear materials. For the laterally connected dimers the lowering of transition temperatures is much less noticeable. These results are in accordance with earlier research, where it was observed that for suitabley slecleted laterally attached systems there is little effect on the liquid crystalline behaviour when they are attached to central core units.

EXPERIMENTAL

The synthetic procedure for compound **15** is given as an example of the synthesis of the dimeric materials.

Preparation of 4′-Pent-4-enyloxy-biphenyl-4-carbonitrile (2)

5-bromo-1-pentene (7 g, 0.0469 mol) was added to **1** (9.16 g, 0.0469 mol) in butanone (150 ml), potassium iodide (1.00 g) and potassium carbonate (25.88 g, 0.187 mol). The reaction mixture was heated under reflux for 24 hours. The inorganic materials were removed by filtration and the solvent removed *in vacuo*. The crude product was recrystallised twice from methanol to yield yellow/white crystals. Yield: 83%, 10.27 g. Transition Temperatures: K 83.8 N 89.0 I. NMR ^{1}H: 1.95 (2H, qu), 2.3 (2H, q), 4.0 (2H, t), 5.05 (2H, m), 5.9 (1H, m). IR: 3414, 2932, 2227, 1641, 1603, 1531, 1470, 1184. Mass Spec: 69, 140, 151, 166, 195, 263.

Preparation 4′-[5-(1,1,3,3-Tetramethyl-disiloxanyl)-pentyloxy]-biphenyl-4-Carbonitrile (4)

2 (5 g, 0.0189 mol) was mixed with THF (20 ml) and Karstedt's catalyst (50 μl) added then this was added to 1,1,3,3-tetramethyl disiloxane (25 g, 0.189 mol) and THF (20 ml). The reaction mixture was left to stir overnight. The solvent was then removed *in vacuo*. The crude product was purified by column chromatography (silica, DCM, hexane 3:2) to yield a white room temperature liquid crystalline material. Yield: 41%, 3.09 g. Transitions: K -14.1 SmA 46.1 I. NMR ^{1}H: 0.0 (8H, m), 0.1 (4H, m), 0.5 (2H, t), 1.4 (4H, m), 1.8 (2H, qu), 4.0 (2H, t), 4.6 (1H, m), 6.9 (2H, d), 7.5 (2H, d), 7.6 (4H, q). NMR ^{13}C: 18, 23, 53 (5C), 59, 110, 117, 119, 124,125 147,155.

Preparation of Pent-4-enoic acid 1H, 1H, 12H, 12H perfluro-pent-4-enoyloxy-dodecyl ester (11)

9 (1 g, 0.00177 mol) was added to 4-pentenoic acid (0.45 g, 0.00453 mol) with DMAP (0.29 g, 0.00226 mol) and PTSA (0.43 g, 0.00226 mol), this was dissolved in DCM (50 ml). After stirring for 5 mins DIC (1.38 g, 0.0113 mol) was added to the solution and the reaction mixture left to stir

for 24 hrs. The reaction mixture was filtered to remove the DCU by-product and the solvent removed *in vacuo*. The crude product was purified by column chromatography (DCM, Silica) to yield a white crystalline solid. Yield: 0.90 g, 70%. Transition Temperatures: K 53.1 I
H NMR: 2.4 (2H, q), 2.55 (2H, t), 4.6 (2H, t), 5.05 (2H, t), 5.9 (1H, m).
Mass spec: 83, 94,164, 564, 601, 643, 684, 700, 726.

Preparation of (15)

11 (0.1 g, 0.190 mmol) was dissolved in THF (5 ml) and Karstedt's catalyst (20 µl) added. The solution had air bubbled through it for 30 secs then it was left to stir for 40 mins. **4** (0.22 g, 0.570 mmol) was added and the mixture left to stir overnight. The solvent was removed *in vacuo* and the crude product purified by column chromatography (silica, DCM/Hexane 2:3) to give a clear liquid.

Yield: 0.08 g, 29%. Transition Temperatures: K 10.2 SmA 12.3 I.

NMR ^{1}H: 0.0 (8H, m), 0.1 (4H, m), 0.5 (4H, t), 1.4 (8H, m), 1.8 (2H, qu), 4.0 (2H, t), 4.5 (2H, t), 6.9 (2H, d), 7.5 (2H, d), 7.6 (4H, q). IR (KBr) $^{\nu}$max: 2931, 2862, 2231, 1766, 1618, 1499, 1474, 1257.

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