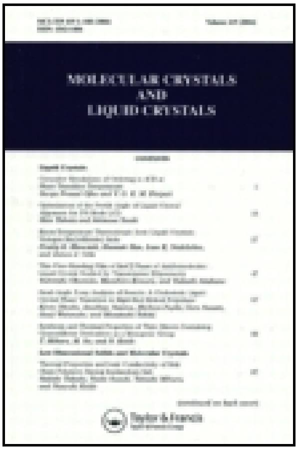

Molecular Crystals and Liquid Crystals

The Nematic Discotic Phase in Materials Containing a Siloxane Core

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THE NEMATIC DISCOTIC PHASE IN MATERIALS CONTAINING A SILOXANE CORE

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The synthesis of a series of novel multipodes based on disc-shaped mesogens with a siloxane core is described. Their phase behaviour is characterised and compared to the liquid crystalline properties of the discotic molecules without the siloxane moieties. We observed that incorporation of the siloxane group results in a strong decrease of all transition temperatures, resulting for one series in (close to) room temperature nematic mesophases. In a second series all liquid crystalline properties were suppressed. Introduction of nematic phases was accomplished via the formation of charge transfer complexes.

Keywords: charge transfer complexes; discotic; liquid crystals; mesomorphic properties; nematic; siloxane

INTRODUCTION

Discotic liquid crystalline materials were first discovered twenty-five years ago. Among the many architectural motifs that have been published since then, surprisingly few display the nematic (N or N_D) mesophase [1]. Disc-shaped mesogens that show a nematic phase, usually features this phase at high temperatures. These high temperatures have been reduced by means of asymmetrical substitution of the mesogen [2]. Attachment of the mesogen to a side chain polymer [3] and application of charge transfer complexes [4].

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Multipodes, wherein several mesogens are hold by one single core, offer the advantages of low molar mass systems (pure, monodisperse molecules) and polymers (suppression of crystallisation). The use of siloxanes as core material is appealing, since these materials show a substantial suppression of crystallisation [5a]. Moreover, they tend to (micro-)phase segregate, which could lead to new, fascinating mesophases [5b,c].

In this paper, we present the synthesis and liquid crystalline properties of the first discotic multi- and monopodes, based on a siloxane core. Two different mesogens were applied in this study, **A1** and **B1**, both showing nematic discotic mesophases. Charge transfer complexes, resulting from the non-covalent interactions between the mesogens and TNF are used to modify the phase behaviour of monomers and dimers.

RESULTS AND DISCUSSION

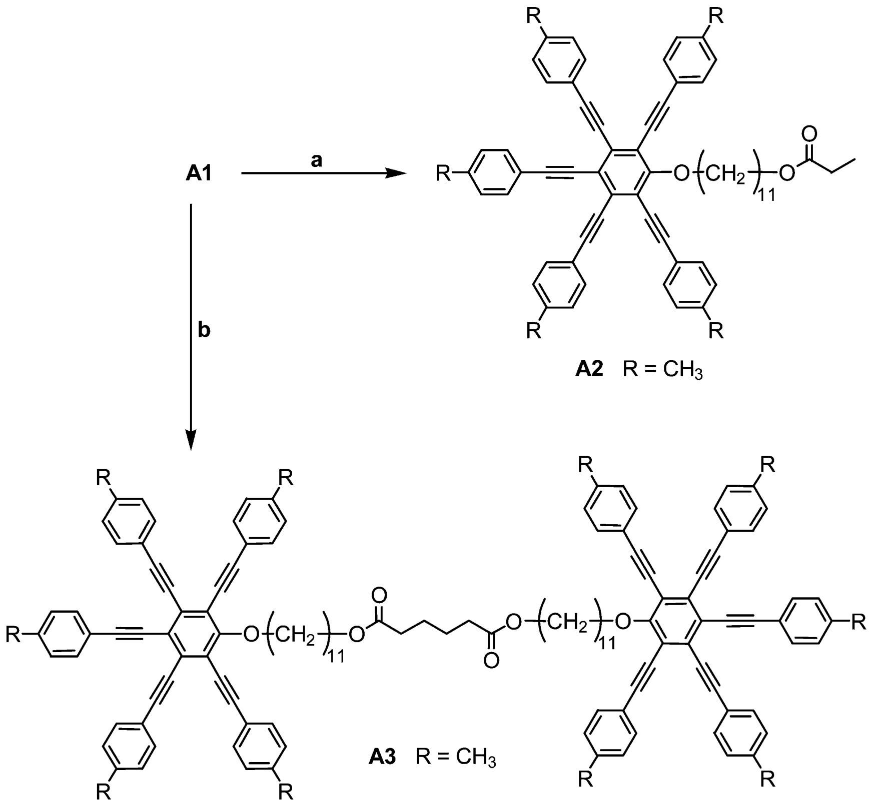
Synthesis

The synthesis of hydroxyl functionalised mesogen **A1** shown in Figure 1 and the corresponding propionate ester **A2** has been discussed before [3a]. The adipic ester dimer was prepared by a straightforward esterification reaction between the mesogen (small excess) and the adipoyl chloride, see Scheme 1. Subsequent purification by column chromatography yielded the dimer **A3** in a good yield.

Siloxane moieties incorporate into the spacer by means of high yielding hydrosilylation reactions, requiring a slight extension of the spacer, see Scheme 2. Pentenoic acid was protected with hexamethyldisilazane, preventing the acid to complex with the platinum in Karstedt's catalyst. The protected compound was then attached to the siloxane group via the hydrosilylation reaction. After deprotection of the acid under basic conditions, coupling reactions under standard esterification conditions with **A1** or **B1** yielded the siloxane multipodes. It is emphasised that the synthesis was performed in this order. Extensive testing showed that the internal triple bonds of the mesogens **A1** and **B1** are too susceptible to carry out the hydrosilylation reaction with the siloxane group.

Phase Behaviour

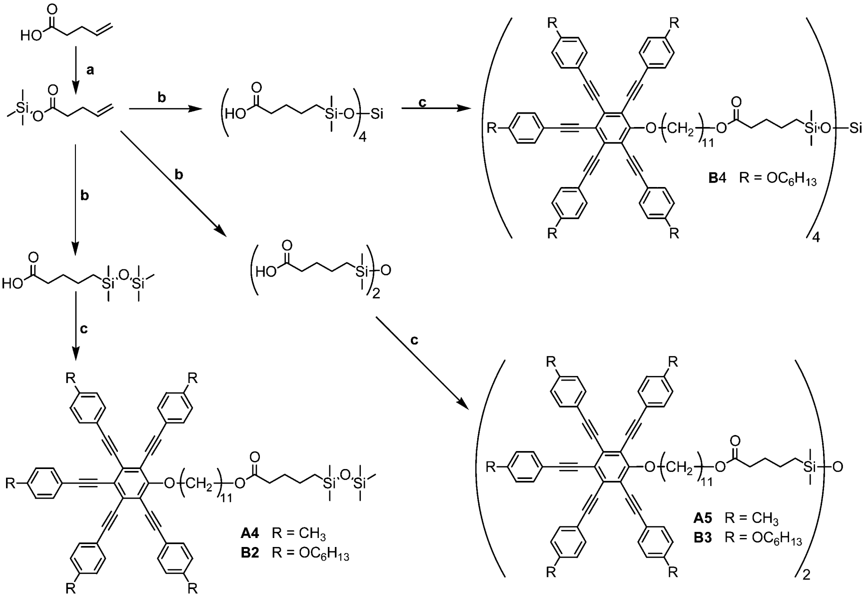
The phase behaviour of the methyl-substituted mesogens (series **A**) is summarised in Table 1. Mesogens **A1–A3** behave qualitatively as was expected: For **A2** the transition temperatures drop, due to the presence of the longer spacer and the absence of the stabilising hydrogen bonds, compared to **A1**. Linking two mesogens together as in **A3** results in a rise in the transition temperatures, because of the reduced mobility of the



SCHEME 1 Synthesis of the short-spacer dimer and the corresponding monomer. (a) Propionyl chloride, triethylamine, 4-(dimethylamino)pyridine, CH_2Cl_2. (b) Adipoyl chloride, 4-(dimethylamino)pyridine, triethylamine, CH_2Cl_2.

mesogens. The liquid crystalline properties of the mesogens with the siloxane groups are fully suppressed. Earlier, we described the nearly linear dependence of the clearing temperature T_{NI} with the fraction of rigid mesogen in the material. Obviously, this fraction in the siloxane compounds strongly reduced. The crystallisation temperature, however, is much less dependent on the rigid mesogen fraction, which resulted in loss of the liquid crystalline properties.

Similar characteristics are observed in the phase behaviour of the hexyloxy-substituted mesogens (series **B**), which are summarised in Table 2. The clearing temperatures of the mesogens with the siloxane groups are strongly reduced with respect to mesogen **B1**. However, in this series, the melting temperatures have decreased considerably as well, resulting in stable nematic phases at low temperatures. In fact, we believe



SCHEME 2 Synthesis of the multipodes with siloxane cores. (a) Hexamethylsilazane, THF. (b) Pentamethylsiloxane (monomer) or tetramethylsiloxane (dimer) or tetrakis(dimethylsiloxy)silane (tetramer), Karstedt's catalyst, toluene. (c) A1 or B1, diisopropylcarbodiimide, 4-(dimethylamino)pyridine, CH_2Cl_2.

that **B2** is the second material showing a nematic discotic phase at room temperature [6]. Again the dimer **B3** shows some stabilisation of the mesophase, compared to **B2**. The reduction of the clearing temperature of **B4** can be explained by realising that the central siloxane group is larger in the case of the tetramer.

TABLE 1 Phase Behaviour of the Methyl-Substituted Mesogens

Mesogen	Phase behaviour^{a,b}				
A1	K	174	N	226	I
A2	K	155	N	196	I
A3	K	169	N	209	I
A4	K	135			I
A5	K	142			I

^{a} K = Crystalline, N = Nematic discotic, I = Isotropic.
^{b} Phase transitions in °C.

TABLE 2 Phase Behaviour of the Hexyloxy-Substituted Mesogens

Mesogen	Phase behaviour[a,b]						
B1	K	71			N	117	I
B2	K	11			N	24	I
B3	K_1	34	K_2	38	N	55	I
B4	K_1	26	K_2	34	N	45	I

[a] K = Crystalline, N = Nematic discotic, I = Isotropic.

[b] Phase transitions in °C.

X-ray Diffraction

Various samples have been subjected to X-ray diffraction measurements. The results for **B3** are shown in Figure 2. At 50°C, a characteristic pattern for a nematic phase is observed: The diffuse reflection at small diffraction angles ($d = 22.5\,\text{Å}$), corresponds to the lateral disc-disc distance, while the diffuse reflection at larger angles ($d = 4$–$4.5\,\text{Å}$) matches sum of the π-π distance between two mesogens and the characteristic alkyl-alkyl distances. the reflection of the siloxane groups ($d = 7.8\,\text{Å}$) is observed as a shoulder in the latter reflection, indication that in the N_D phase microphase separation occurs at least to some extent.

Dimer **B3** shows an extra phase between the crystalline and the nematic discotic phase, which could not be identified by its optical texture. However, the presence of a large number of reflections in the small and wide angle region indicates that this phase can be identified as a second crystalline phase.

Charge Transfer Complexes

Specific interactions, such as charge transfer (CT) interactions [4a] have shown to introduce liquid crystalline properties in non-mesogenic materials

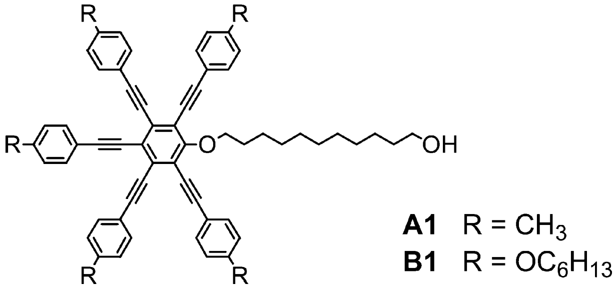


FIGURE 1 Structure of the investigated mesogens.

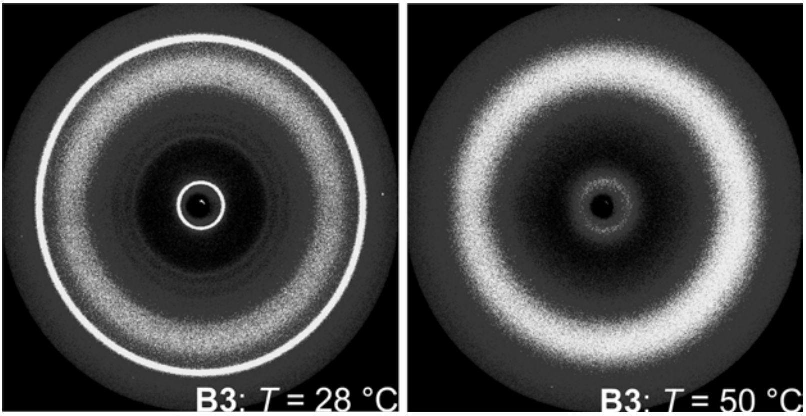


FIGURE 2 X-ray diffraction pattern of the siloxane dimer **B3**: (a) at 50°C (ND phase) and (b) at 28°C (Col_X/K_2 phase).

[4,7]. We have studied the results of these non-covalent interactions between the methyl-substituted mesogens (series A) and the electron deficient 2,4,7-trinitro-9-fluoreneone (TNF). At equimolar ratios, all CT complexes show a N_D mesophase, see Table 3. This result is particularly interesting for the complexes with siloxane mesogenics (in which all liquid crystalline properties have disappeared), since in these materials the mesophase is induced by mixing two crystalline compounds.

The combination of DSC studies of various complexes and carefully prepared contact samples between the methyl-substituted mesogens and TNF allowed us to construct schematic phase diagrams, see Figures 3 and 4. Addition up to 50 mol-% of TNF [8] to mesogens **A2** or **A3** hardly effects the clearing temperature of these materials. The melting temperature of the crystalline phase is slightly suppressed – resulting in wider

TABLE 3 Phase Behaviour of the Charge Transfer Complexes of **A2–A5** with TNF

Complex	Phase behaviour[a,b]				
TNF	K	176			I
A2:TNF	K	106	N	182	I
A3:TNF	K	135	N	193	I
A4:TNF	K	123	N	162	I
A5:TFN	K	127	N	163	I

[a] K = crystalline, N = nematic discotic, I = isotropic.
[b] Phase transitions in °C.

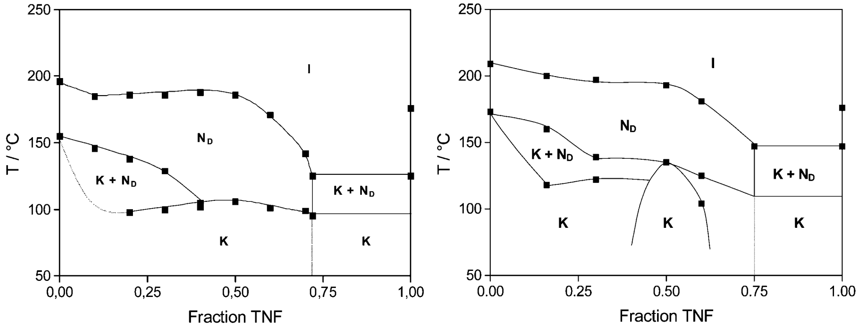


FIGURE 3 Schematic phase diagrams of TNF with the short-spacer dimer **A3** (right) and the corresponding monomer **A2** (left).

mesophase – and biphasic areas are observed at low TNF fractions. Complexes at exact equimolar concentrations do not show any phase separation during microscopy experiments and the transitions observed in DSC experiments are sharp and well defined. Addition of more TNF results in a strong destabilisation of the nematic phase and complexes with more than 75 mol-% TNF immediately macrophase seperate into fractions of pure TNF and complexes containing about 75 mol-% TNF.

The sketched phase diagrams of the siloxane multipodes with TNF look rather similar. However, in these complexes the nematic phase is only observed at TNF concentrations between 25 to 75 mol-%. Less than 25 mol-% or more than 75 mol-% of TNF again leads to macroscopic demixing, even in the isotropic phase. It is interesting to note that the maxima in the clearing temperatures of both complexes occur at equimolar

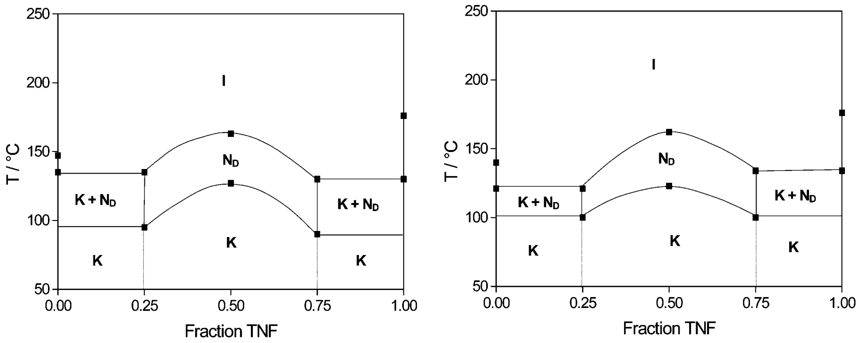


FIGURE 4 Schematic phase diagrams of TNF with the siloxane dimer **A5** (right) and the corresponding monomer **A4** (left).

ratios, indicating an optimal 1:1 interaction between the mesogenic moieties and the TNF molecules. Optimal properties at 1:1 ratios have been reported for other charge transfer complexes before, but remarkably, in other cases the best properties were obtained from deviating ratios [7b,c].

CONCLUSIONS

We have synthesised the first series of multipodes consisting of a siloxane core and discotic mesogens. The siloxane group lowers all transition temperatures, in particular the clearing temperatures. This resulted in a total shift of the nematic phase to lower temperatures for the hexyloxy-substituted mesogens (series B). To the best of our knowledge, mesogen **B2** is the second mesogen that displays a nematic discotic phase at room temperature. For the methyl-substituted mesogens (series A) introduction of the siloxane groups resulted in the loss of all liquid crystalline properties. Addition of TNF resulted in the formation of charge transfer complexes, which gave rise to reintroduction of liquid crystalline properties. The best properties were observed at 1:1 donor-acceptor complexes. We believe that the application of siloxanes is a step forward towards room temperature nematic discotic materials, provided that the melting temperature of the crystalline phase can be suppressed equally effective.

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[4] (a) Complexes of an electron-rich donor with an electron rich acceptor, showing an induced absorption band are often referred to as charge transfer complexes. However, it should be stressed that the attractive interaction between these molecules is rather a combination of Van der Waals, quadrupolar and charge transfer interactions. For the sake of clarity, in this contribution the name charge transfer complex is used to describe the total sum of interactions.
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[8] In all complexes the discussed ratios are the molar ratios of the *mesogenic groups* and TNF, rather than the actual molecular ratios.