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SUBSTITUENT EFFECTS IN DISCOTIC LIQUID CRYSTALS

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A series of novel mesogens have been prepared by a five-fold Sonogashira reaction of terminal acetylenes with a functionalized pentabromophenol. The corresponding side chain polymers were prepared by a polymer analogous substitution reaction. The mesogens differ in the nature of the substituents, linking five hexyl tails to the aromatic core, i.e. CH₃, O, S, SO₂ and CONH groups. A wide range of mesophases and corresponding transition temperatures has been detected, ranging from low melting nematic phases to highly stable columnar phases. The widely variable phase behavior is described in terms of specific intermolecular interactions.

Keywords: discotic; liquid crystals; mesomorphic properties; nematic; substituent; supramolecular chemistry

INTRODUCTION

Supramolecular chemistry – “the chemistry beyond the molecule” – has a large number of non-covalent interactions at its disposal [1]. These secondary interactions include forces like (i) electrostatic interactions (ion-dipole, dipole-dipole), (ii) hydrogen bonding, (iii) π - π stacking, (iv) Van der Waals forces (dispersion and induction forces) and (v) hydrophobic or, more general, solvophobic effects. A combination of these non-covalent interactions is used in nature to build complex structures that can show multiple levels of organisation. The interest in the self-organisation and self-assembly in synthetic systems has grown considerably. This is displayed in numerous contributions in the literature, discussing the effects of the wide range of secondary interactions available [2]. Liquid crystals

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are self-assembling by nature. The interactions mentioned above, can improve or, oppositely, diminish the extent of organisation (i.e. the extent of order) in the liquid crystalline phases. This makes liquid crystals ideal models to study the effects of various interactions on the molecular organisation.

Disc-shaped liquid crystals self-organise into nematic (N) or columnar (Col_X) mesophases, see Figure 1. In disc-shaped molecules specific interactions can be conveniently introduced via the substituent that links the flexible tail to the aromatic core. Here, we present the synthesis and the liquid crystalline properties of a novel series of disc-shaped mesogens. The mesogens vary in the substituents that links the aliphatic tail to the aromatic core. The resulting differences in phase behaviour are explained in terms of specific interactions.

RESULTS AND DISCUSSION

Synthesis of the Mesogens

The synthesis of the disc-shaped liquid crystals is outlined in Scheme 1. Instead of more conventional numbering of the prepared mesogens, we have chosen to include the functional groups into the numbering: In the numbering $n\mathbf{X}\text{-D}$, n represents the length of the tails (number of carbon atoms); \mathbf{X} represents the linking group and \mathbf{D} stands for disc. Analogously, the corresponding polymers are shown as: $\mathbf{P}(n\mathbf{X}\text{-D})$. Mesogens **6CH₂-D**, **6O-D**, **6S-D** and **6Am-D** were prepared by a five-fold palladium catalysed cross-coupling reaction (Sonogashira reaction) between a terminal acetylene and a pentabromo-phenol derivative [3]. The crude products were obtained in reasonable yields, however, purification is tedious and is costly in yield of final product. It is emphasised that acetylenes with electron

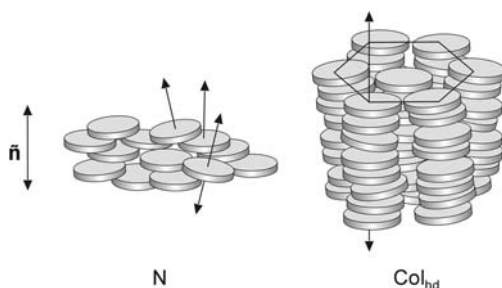
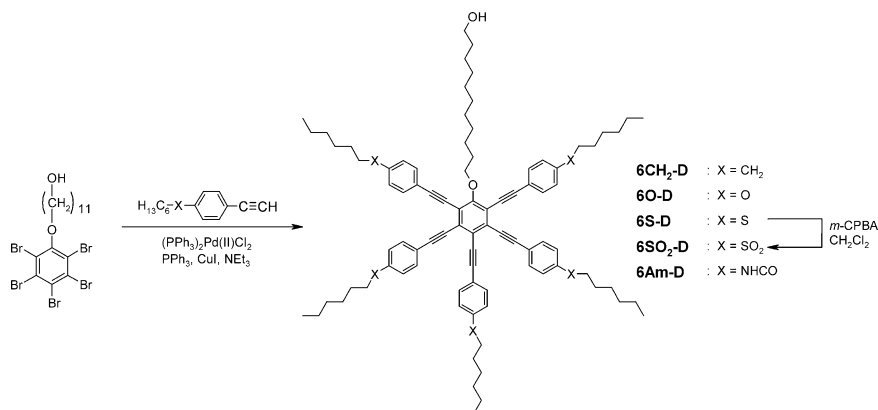


FIGURE 1 Commonly observed mesophases for disc-shaped liquid crystals: the nematic (N) and an example of a columnar phase; here the columnar hexagonal (Col_h) phase is presented.

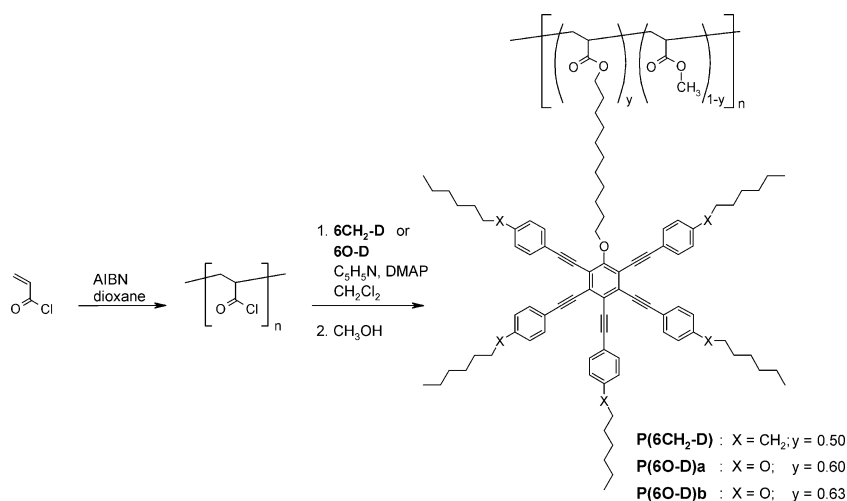


SCHEME 1 Synthesis of the mesogens.

withdrawing groups (SO₂, NO₂, etc.) can not be coupled to the central core in a satisfactory way. Hence, **6SO₂-D** was prepared by selective oxidation of **6S-D** using 3-chloroperoxybenzoic acid (*m*-CPBA), giving the final product in high yields.

Synthesis of the Polymers

Mesogens **6CH₂-D** and **6O-D** were incorporated in a polymer backbone. The polymers were synthesised by a polymer analogous reaction (see



SCHEME 2 Synthesis of the polymers **P(6CH₂-D)** and **P(6O-D)**.

Scheme 2) between the mesogens and the reactive poly(acryloyl chloride) [3b]. At the final stages of the reaction, the remaining acyl groups were converted to methyl esters by addition of an excess of dry methanol. This prevents the formation of (crosslinking) anhydride groups or carboxylic acid groups, which are expected to have a major influence on the phase behaviour, in particular the glass transition temperature. The clear advantage of this approach is that polymers with a sufficient chain length can be prepared relatively easily, taking into account that the triple bonds of the mesogens are expected to hinder a (free-radical) polymerisation reaction.

Liquid Crystalline Properties

The mesophase behaviour of the low molar mass mesogens as well as the polymers of **6CH₂-D** and **6O-D** is summarised in Table 1. Mesogen **6CH₂-D** shows a monotropic N phase at low temperatures. In the corresponding polymer, all mesogenic properties disappear and **P(6CH₂-D)** is characterised as an amorphous material with a low glass transition temperature. Changing the linking group from methylene to oxygen results in a stabilisation of the nematic phase. The nematic phase of compound **6O-D** shows the characteristics of a nematic texture during microscopy experiments, see Figure 2a. Moreover, at elevated temperature, the phase aligns rapidly in an homeotropic organisation between two unprepared microscope slides. The photograph, shown in Figure 2a is taken at 80°C after only 30 seconds annealing, resulting already in a very low birefringence. Further annealing (~5 minutes at 80°C) resulted in almost complete homeotropic alignment. The corresponding polymer **P(6O-D)**

TABLE 1 Thermal Behaviour of the Mesogens, Measured with OPM and DSC

Material	Thermal behaviour ^{a, b}					
6CH₂-D	Cr	[39 (34)	N	52 (1.2)] ^b	57 (36)	I
6O-D	Cr	71 (33)	N		118 (0.15)	I
6S-D	Cr	56 (65)	Col_{hd}		167 (0.21)	I
6SO₂-D	G_{Col}	115	Col_{hd}		>260	d
6Am-D	Cr				215 (16)	I/d
P(6CH₂-D)	G_I	-15				I
P(6O-D)	G_N	24	N		113 (0.18)	I

^aTransition temperatures are shown in [°C] and latent heat values (between the brackets) in [kJ mol⁻¹].

^bCr = Crystalline; G_{Col/N/I} = Glassy (Columnar/Nematic/Isotropic) phase frozen in); N = Nematic; Columnar hexagonal, disordered; I = Isotropic; d = decomposition. ^bMonotropic phase transition.

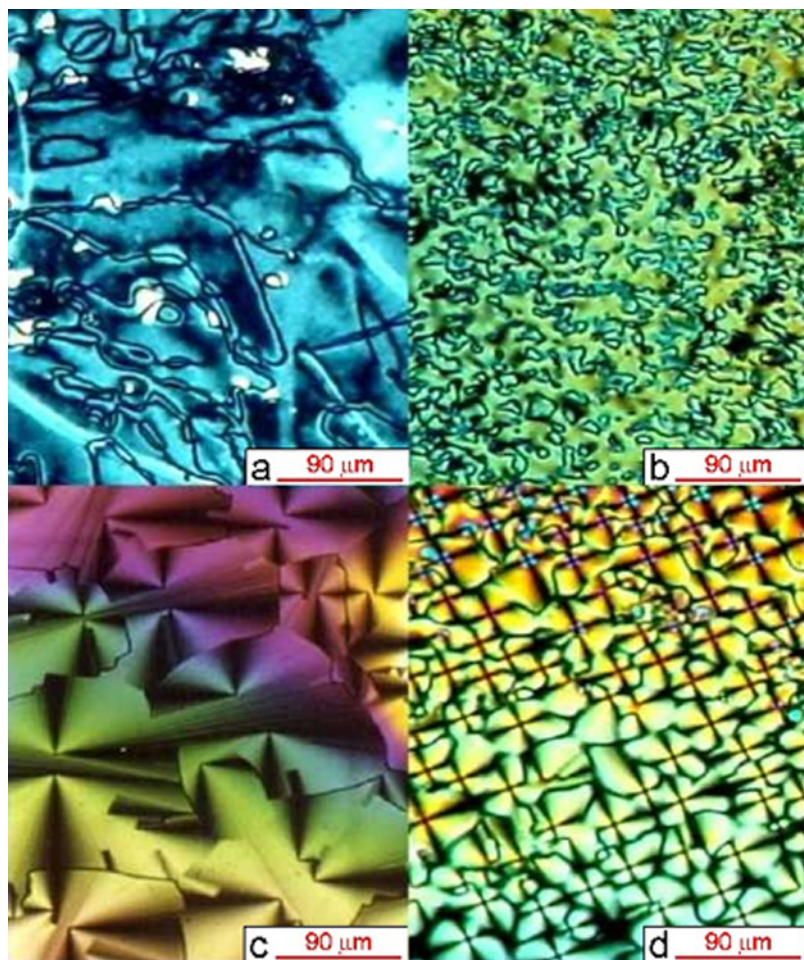


FIGURE 2 Optical textures of (a) low birefringent homeotropic N phase of **60-D** at 80°C; (b) N phase of **P(60-D)** at 100°C; (c) Col_{hd} phase of **6S-D** at 100°C; (d) Col_{hd} phase of **6SO₂-D** at 255°C (freshly formed columnar phase from the isotropic phase). All pictures were taken with crossed polarizers. (See COLOR PLATE VI)

shows a N_D phase as well, with a clearing temperature roughly equal to that of the monomer. The presence of the polymer backbone prevents crystallisation and a glass transition at 24°C is observed, resulting in a material with a nematic discotic phase close to room temperature. Only recently, the first example of a room temperature nematic phase obtained from disk-shaped liquid crystals was reported. Contrary to the monomer,

the N_D phase hardly aligns between microscope slides, see Figure 2b. The approach of suppression of crystallisation by chemically linking mesogens proves to be successful in obtaining low temperature nematic discotic phases. It is anticipated that the use of an even more flexible backbone (such as polyether or polysiloxane) could lower the glass transition temperature even further, opening up the way towards real room temperature nematic discotic mesophases.

The fan-shaped optical texture of **6S-D** (see Figure 2c) is characteristic of a columnar phase. At high temperatures, a transition with a small latent heat to the isotropic phase is observed. The mesophase of **6SO₂-D** could be characterised by fast cooling from the isotropic phase at elevated temperatures, although the optical textures remained rather difficult to interpret, see Figure 2d. The growing hexagons and six-leafed "oak-leaf" textures are characteristic for a Col_h mesophase. Compound **6SO₂-D** did not show any melting or crystallisation phenomena, but rather showed a second order transition at lower temperatures, attributed to the formation of a columnar plastic (Col_p) phase. Due to degradation at elevated temperatures ($> 250^\circ\text{C}$), no clearing temperature (and obviously no latent heat) could be determined. The penta-amide **6Am-D** cleared at high temperatures and neither microscopy experiments nor DSC analysis could distinguish between a highly ordered columnar or a ill-defined crystalline phase at lower temperatures.

Substituent Effects

A wide range of liquid crystalline properties is observed for the series of mesophases. The (monotropic) nematic phase of **6CH₂-D** can be well understood by taking the fraction of rigid mesogen into account. A series of methyl substituted mesogens, both molar mass and high molecular weight, has been described in literature. It was shown that the clearing temperature T_{NI} was strongly dependent on the rigid mesogen fraction [M]. Both the heptyl-substituted materials as well as the pentyl substituted material (and a corresponding side chain polymer) fit perfectly on the same line, see Figure 3. In other words, regardless of the length and the position (attached to the mesogen or to the polymer backbone) of any alkyl group, the N_D to isotropic transition temperature can simply be predicted, just by calculating its fraction of rigid mesogens [M]. It is striking to see that this relation holds for such a variety of materials and over a wide temperature range.

The mesophases of **6S-D**, **6SO₂-D** and **6Am-D** are strongly stabilised, resulting in columnar mesophases or even a crystalline phase for **6Am-D** which remain stable up to high temperatures. It still is unclear why the thio-ether **6S-D** shows such stabilisation with respect to ether **6O-D**. This

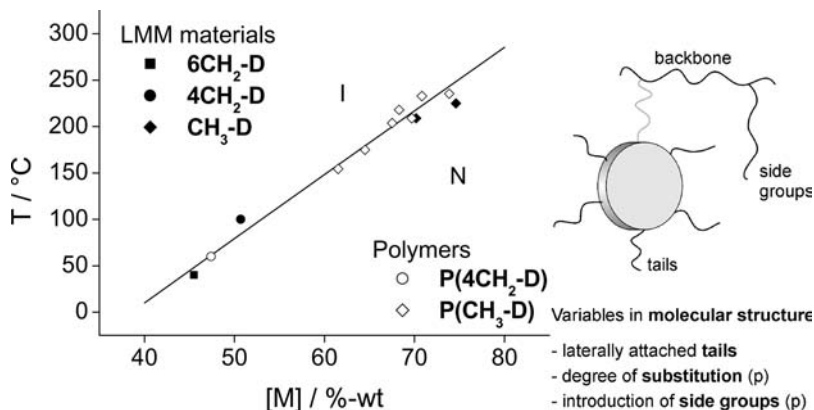


FIGURE 3 Clearing temperature T_{NI} as a function of the rigid mesogen fraction $[M]$ for various alkyl-substituted mesogens: LLM (low molar mass) materials and polymers. In the schematic picture (right) all the variables in the molecular structure for this series of materials are illustrated. The materials differ in size of the laterally attached tails and whether a polymer backbone is present or not. The polymers also show differences in the degree of substitution and the presence (type and concentration) of any side groups attached to the backbone. The solid line represents the power-law equation: $T_{NI} = 695 \cdot [M]^{0.98}$ which was determined before [6].

is opposite to the commonly observed effect. The strong additional stabilisation of the **6SO₂-D** can be explained by the five sulphon groups introducing multiple dipole-dipole interactions, resulting in a columnar mesophase up to 280°C. A further increase in the intracolumnar order is found in the penta-amide, where the formation of attractive hydrogen bonds completely prevent any mesophase formation.

CONCLUSIONS

We have synthesised a novel series of disc-shaped mesogens with different substituents linking the five hexyl tails to the aromatic core. The liquid crystalline behaviour was investigated with DSC and OPM and it was observed that the stability of the mesophase was strongly dependent on the linking group, ranging from a monotropic N_D at low temperatures (**6CH₂-D**) to a columnar phase, stable to 280°C (**6SO₂-D**). By attaching **6O-D** to a polyacrylate backbone, crystallisation was suppressed, making room temperature nematic discotic liquid crystals within arms reach. Further modification of the mesophase behaviour is possible using non-covalent charge transfer interactions, which will be investigated in the near future.

REFERENCES AND NOTES

- [1] Lehn, J. M. (1995). *Supramolecular Chemistry*, VCH, Weinheim: New York.
- [2] For example, read: (a) Lawrence, D. S., Jiang, T., & Levett, M. (1995). *Chem. Rev.*, *95*, 2229. (b) Philip, D. & Stoddart, J. F. (1996). *Angew. Chem. Int. ed. Engl.*, *35*, 1154.
- [3] (a) Janietz, D., Praefcke, K., & Singer, D. (1993). *Liq. Cryst.*, *13*, 247–253. (b) Kouwer, P. H. J., Jager, W. F., Mijs, W. J., & Picken, S. J. (2000). *Macromolecules*, *33*, 4336.
- [4] (a) The room temperature nematic phase was observed in a discotic liquid crystal based on a hexakis(phenylethynyl)benzene core and substituted with a *rac*-4-methylnonyl tails, resulting in a broad distribution of stereo isomers. (b) Kumar, S. & Varhney, S. K. (2000). *Angew. Chem. Int. Ed. Engl.*, *39*, 3140.
- [5] By fast heating in an OPM experiment a clearing temperature of $\sim 280^{\circ}\text{C}$ could be estimated.
- [6] Kouwer, P. H. J., Mijs, W. J., Jager, W. F., & Picken, S. J. (2001). *J. Am. Chem. Soc.*, *123*, 4645.