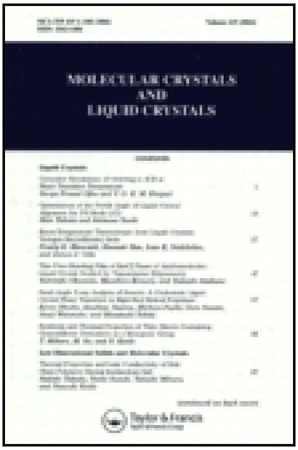


Molecular Crystals and Liquid Crystals

# Investigation of the Complete Miscibility of Disc-rod Mesogens in the Nematic Phase

Daniela Apreutesei [a] [b] & Georg Mehl [a]

[a] Department of Chemistry, University of Hull, Hull, UK

[b] Faculty of Industrial Chemistry, Gh. Asachi Technical University, Iasi, RO

Version of record first published: 31 Aug 2006

To cite this article: Daniela Apreutesei & Georg Mehl (2006): Investigation of the Complete Miscibility of Disc-rod Mesogens in the Nematic Phase, Molecular Crystals and Liquid Crystals, 449:1, 107-115

To link to this article: http://dx.doi.org/10.1080/15421400600582523

*Mol. Cryst. Liq. Cryst.*, Vol. 449, pp. 107–115, 2006

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600582523

# Investigation of the Complete Miscibility of Disc-rod Mesogens in the Nematic Phase

**Daniela Apreutesei**
Department of Chemistry, University of Hull, Hull, UK and Faculty of Industrial Chemistry, Gh. Asachi Technical University, Iasi, RO

**Georg Mehl**
Department of Chemistry, University of Hull, Hull, UK

*The synthesis and the phase behaviour of nematic dimers, built up from rod and disc shaped mesogens, separated by extended spacers is described. Miscibility studies with the rod as well as disc shaped mesogens were performed and OPM data of contact samples and the results of detailed DSC experiments of mixtures are presented. Full miscibility in the nematic phase was observed.*

**Keywords:** biaxial nematic; disc-rod mixtures; liquid crystal; nematic

## INTRODUCTION

The interest in the thermotropic biaxial nematic phase has intensified recently [1], with the focus of research either concentrated on side-chain polymers, bent core mesogens or soft supermolecular multipodes. All of these systems are based on the concept that below a certain temperature the rotation about a molecular long axis, the primary nematic director is hindered and a second ordering is formed [1–4]. The alternative approach of achieving a biaxial nematic by the mixing of rods and discs has attracted considerable theoretical interest [5–8]. Common in all of the theoretical models is that full miscibility of rod and discs is required and that biaxiality is associated with a minimum at the latent heat of the nematic-isotropic phase transition positioned at the lowest point in nematic-isotropic phase transition temperature in the phase diagram. A large range of disc and rod shaped systems have been investigated [9–11]. Of particular

Address correspondence to Georg Mehl, Department of Chemistry, University of Hull, Hull, HU6 7RX, UK. E-mail: g.h.mehl@hull.ac.uk

interest have been rod-disc amphiphiles, materials, which contain rod and disc shaped mesogens in one molecule. For such a system full miscibility of rods and discs could be observed in the nematic phase. The miscibility of these systems has been attributed mainly to a similar aspect ratio of rods and the disc. In this presentation we report our result of the investigation of a system containing one rod and one disc, mixed with rods and disc. Crucially different to previously reported systems is, that the length of the alkyl chain connecting the rod and disc has been extended significantly, when compared to previous systems.

## RESULTS AND DISCUSSION

Following the previous investigations, we synthesized new systems miscible in the nematic phase containing disc-rod structures connected directly. Compared to previously synthesised systems the length of the hydrocarbon chain linking rods and disc has been increased [13]. The structures of the disc **D**, the rod, **R**, and the rod-disc system **DR**, are shown in Figure 1. Contact microscopy studies of the disc-rod system **DR** with the rod, **R**, and the disc, **D**, show a complete miscibility over the whole composition range. Various attempts to detect regions with a miscibility gap have failed. A nematic phase, characterized by a typical *schlieren* and/or marbled texture, is observed over the full width of the phase diagram of either **DR**/**D** and or **DR**/**R**. The OPM micrographs are shown in Figure 2. The pure materials were placed on the sides of the microscopy slides and flowed at high temperature

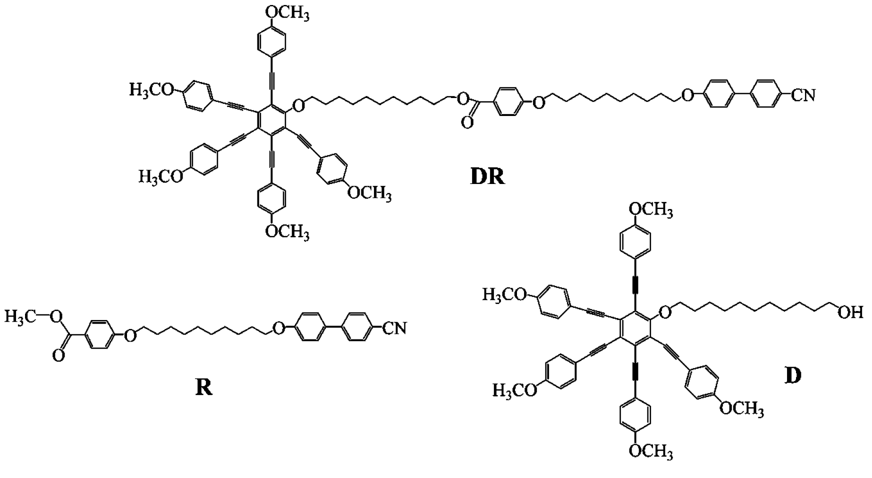
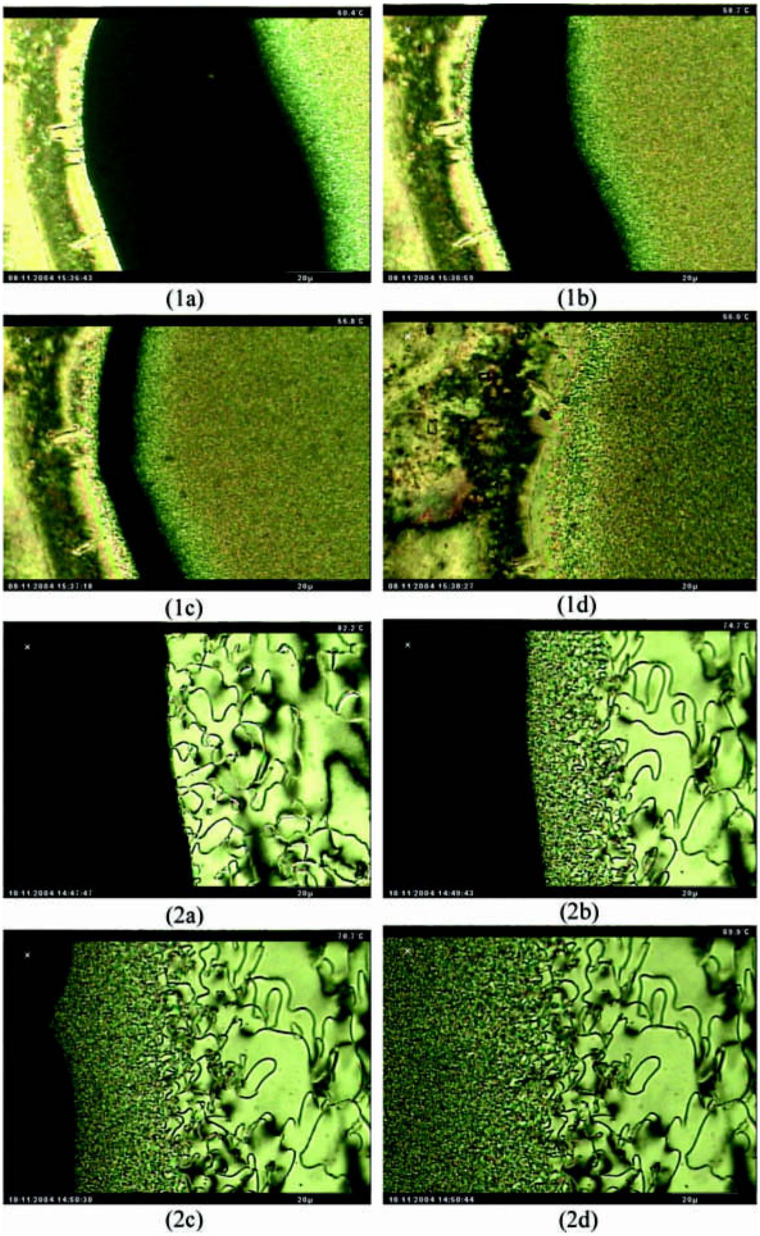


**FIGURE 1** The structure of the investigated compounds.



(1a) (1b)

(1c) (1d)

(2a) (2b)

(2c) (2d)

**FIGURE 2** Optical textures of contact samples of 1. **DR** and **D** at a) T = 60.4°C, b) T = 58.7°C, c) T = 56.8°C d) T = 56°C and 2. **DR** and **R** at a) T = 82.2°C, b) T = 74.5°C, c) T = 70.7°C d) T = 69.9°C; The isotropic area in between disappears on cooling and a continuous nematic phase is formed. All pictures taken with crossed polarisers.

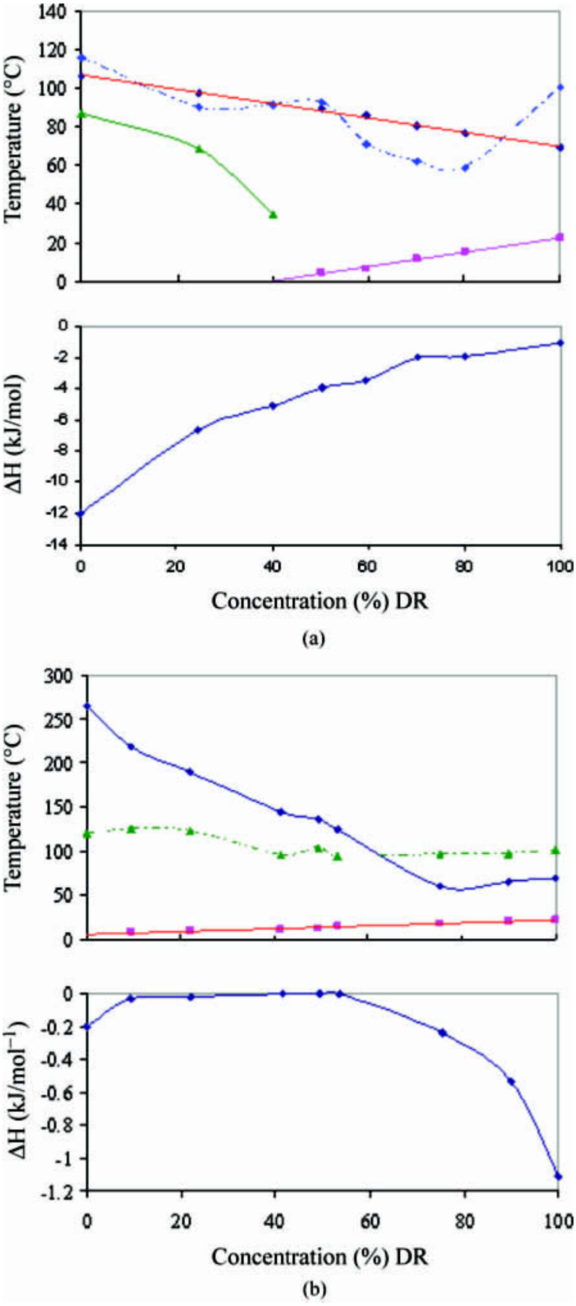
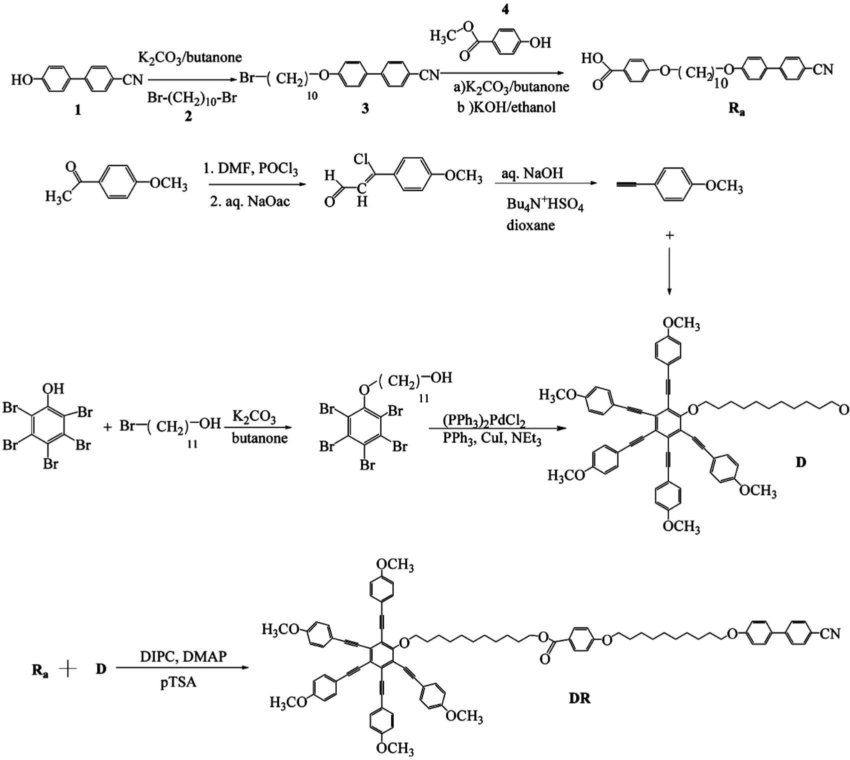


**FIGURE 3** Phase diagrams of a) **DR**/**R** (● Iso-N (cooling) ■ Tg —▲— N-Cr (cooling) –·◆·– Cr-l (heating)) and b) **DR**/**D** (—◆—Iso-N (cooling) ■ Tg ▲ Cr-l (heating)) as measured by DSC (cooling 10°C/min).



**SCHEME 1** Synthesis of disc-rod compounds.

together and mixed. On cooling the nematic regions increase and meet at a minimum temperature, forming a continuous nematic phase.

The phase diagrams of both mixtures are presented in Figure 3. The transitions temperatures of mixtures between **DR** and **R** show a linear dependence of the clearing temperature with concentration of the rod. The phase diagram of **DR**/**D** mixtures has a minimum of the

**TABLE 1** Phase Behaviour of Disc and Rods

| Sample | Transition temperatures (°C) | | | ΔH (kJ mol$^{-1}$) | |
|---|---|---|---|---|---|
| **DR**[a] | $C_N$ | 22.5 | N | 69.1(–1.11) | I |
| **R**[a] | $C_r$ | 87.1 | N | 105.9(–11.9) | I |
| **D**[b] | $C_r$ | 137 | N | 246 (0.2) | I |

[a] monotropic phase transition.

[b] enantiotropic phase transition.

transition temperatures at $\sim$20% disc due to the destabilisation of the nematic phase on mixing.

The synthesis of the investigated compounds is presented in Scheme 1. The disc $\mathbf{D_1}$ has been prepared according to the literature reports [12]. The rod **R** has been prepared by etherification of 4-hydroxy-4′-cyanobiphenyl and 1,10-dibromodecane under Williamson conditions and a further etherification with methyl 4-hydroxybenzoate. Ester deprotection and esterification with **D** provided the disc-rod mesogen **DR**. The phase behaviour of the pure compounds is summarized in Table 1.

## CONCLUSIONS

The presented results confirm that complete miscibility in the nematic phase of molecules which contain one rod and one disc with either rod or disc shaped molecules can be achieved. The length of the alkyl spacer linking rod and disc shaped groups is crucial in enhancing the miscibility of the system, when compared to related materials. The construction of such a phase diagram is a significant step forward in the design and development of future materials exhibiting a nematic biaxial phase. As theory for the $N_B$ phase predicts, the mixtures exhibit a minimum in the transition enthalpies when approaching the minimum nematic to isotropic transition.

## EXPERIMENTAL

### Materials

All materials were used as purchased unless mentioned otherwise. The synthesis and properties of the discotic mesogen **D** has been published before [12].

## INSTRUMENTATION

Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol JNM-ECP 400 M Hz FT-NMR spectrometer. Chemical shifts are reported in ppm relative to TMS. Thermal properties were investigated using a a Mettler Toledo differential calorimeter (DSC 822$^e$) in nitrogen against an indium standard. Transition temperatures were determined as the onset of the maximum in the endotherm or exotherm. The mesophases were studied on an Olympus BH-2 optical polarising microscope, equipped with a Mettler FP82 HT hot stage and a Mettler FP90 central processor. Pictures of the mesophases were taken using a JVC digital video camera connected to a PC. Software *Studio Capture*, supplied by Studio86 Designs was used for image capturing.

### Synthesis of 4′-(10-bromodecyloxy) biphenyl-4-carbonitrile (3)

A mixture of **1** (1eq), dibromoalcane **2** (5eq), $K_2CO_3$ (2eq), KI (0.2 eq) and butanone was refluxed overnight. The mixture was allowed to cool to room temperature, the solids were filtered off and the solvent was evaporated under reduced pressure. The oily residue was precipitated in methanol (five times the volume) and the crude product was filtered. Purification was carried out by crystallisation from acetone: MeOH and $CH_2Cl_2$:hexane. 79% Yield of a white powder. $^1$H-NMR $\delta_H$ ($CDCl_3$):7.66, 7.61, 7.51, 6.97 (8H, Ar), 3.99 (t, 2H, $-CH_2-O-$), 3.40 (t, 2H, $-CH_2-Br$), 1.92-1.78, 1.66-1.57 (m, $-CH_2-$). $^{13}$C-NMR $\delta_C$ ($CDCl_3$):159.64; 145.18; 132.51; 131.28; 128.28; 127.02; 127.02; 119.06; 115.01; 109.99; 67.83; 32.60; 33.75; 28.98; 27.85; 25.23.

### Synthesis of 4-methyl-[10-(4′-cyanobiphenyl-4-yloxi)decyloxi]benzoate(R)

A mixture of 3 (1eq), methyl 4-hydroxybenzoate (1.1eq), $K_2CO_3$ (1.5 eq), KI (0.5 eq) and butanone was refluxed overnight. The mixture was allowed to cool to room temperature, the solids were filtered off, washed thoroughly with warm acetone and the solvent was evaporated under reduced pressure. Purification was achieved using column cromatography column using a mixture of DCM/hexane 3:1 as eluent. Recristalization from methanol gives a white powder (87% yield). $^1$H-NMR $\delta_H$ ($CDCl_3$):7.07 (d, 2H, Ar), 7.69 (d, 2H, Ar), 7.63 (d, 2H, Ar), 7.52 (d, 2H, Ar), 6.99 (d, 2H, Ar), 6.90 (d, 2H, Ar), 4.00 (t, 4H, $-CH_2-$), 3.88 (s, 3H, $-CH_3$), 1.81 (m, 4H, $-CH_2-$), 1.34–1.47 (m, 12H, $-CH_2-$); $^{13}$C-NMR $\delta_C$ ($CDCl_3$):167.02; 163.02, 159.88; 145.37; 132.67; 131.66; 128.42; 127.16; 122.41; 119.24; 115.15; 114.14; 110.11; 68.25; 51.95; 29.56; 29.44; 29.30; 29.19; 26.11; 26.07.

### Synthesis of 4-[10-(4′-cyanobiphenyl-4-yloxi)decyloxi]benzoic acid 11-[pentakis(4-metoxyphenyletynyl)phenoxy]undecyl ester (DR)

The free carboxylic acid R1a was obtained by refluxing R1 in ethanol and aqueous KOH (4 N) until the TLC plates indicate complete consumption of the starting material (30 min). The reaction mixture was neutralised with con HCl, cooled and the precipitated product was filtered from the mixture. The products were used directly for the esterification with D1. A mixture of D1 (1 eq) and $R_{1a}$ (1.2 eq), DIPC (1.5 eq), DMAP (0.5 eq) and pTSA (0.5 eq) in $CH_2Cl_2$ was stirred for 6 days at room temperature under inert atmosphere. Subsequently the solvent was removed under reduced pressure and the residue was applied to a column for chromatography (silicagel, DCM). Recristalization from acetone. Yield 34%, pale yellow powder. $^1$H-NMR $\delta_H$ ($CDCl_3$):7.97 (d, 2H, Ar); 7.68 (d, 2H, Ar); 7.63 (d, 2H, Ar); 7.53 (m, 10H, Ar); 6.98 (d, 2H, Ar); 6.89 (m, 10H, Ar); 4.33 (t, 2H, $-CH_2-$); 4.26 (t, 2H, $-CH_2-$); 3.99 (t, 4H, $-CH_2-$), 3.84 (s, 3H, $-CH_3$), 1.25-1.93 (m, 34 H, $-CH_2-$); $^{13}$C-NMR $\delta_C$ ($CDCl_3$): 166.61; 164.72; 162.94; 160.12; 152.91; 145.36; 133.46; 133.38: 133.22; 132.66; 131.59; 131.31; 128.48; 128.41; 127.15; 123.94; 122.77; 119.99; 119.24; 115.64; 115.59; 115.4; 114.21; 114.16; 114.09; 110.07; 99.26; 99.13; 97.02, 86.73; 86.21; 83.65; 77.44; 77.12; 76.80; 68.22; 55.45; 31.05; 30.69; 29.73; 29.66; 29.57; 29.43; 29.30; 29.19; 28.86; 26.47; 26.18; 26.11; 26.07.

## REFERENCES

[1] Freiser, M. (1970). *J. Phys. Rev. Lett.*, *24*, 1041.

[2] (a) Straley, J. P. (1973). *Phys. Rev. A*, *10*, 1881.
(b) Alben, R. (1973). *J. Chem. Phys.*, *59*, 4299.
(c) De Gennes, P. G. & Prost, J. (1993). *The Physics of Liquid Crystals*, 2nd Ed., Clarendon Press: Oxford.

[3] (a) Yu, L. J. & Saupe, A. (1980). *Phys. Rev. Lett.*, *45*, 1000.
(b) Berjnov, V., Cabuil, V., Perzynski, R., & Raikher, Y. (1998). *J. Phys. Chem. B*, *102*, 7132.
(c) De Melo Filho, A. A., Laverde, A., & Fujiwara, F. Y. (2003). *Langmuir*, *19*, 1127.

[4] (a) Saalwaechter, K. & Severing, K. (2004). *Phys. Rev. Lett. 92*, 125501.
(b) Madsen, L. A., Dingemans, T. J., Nakata, M., & Samulski, E. T. (2004). *Phys. Rev. Lett.*, *92*(14), 145505.
(c) Acharya, B. R., Primak, A., & Kumar, S. (2004). *Phys. Rev. Lett.*, *92*(14), 145506.
(d) Yelamaggad, C. V., Prasad, S. K., Nair, G. G., Shashikala, I. S., Rao, S. S., Lobo, C. V., & Chandrasekhar, S. (2004). *Angew. Chem. Int. Ed.*, *26*, 3429–3432.
(e) Merkel, K., Kocot, A., Vij, J. K., Korlacki, R., Meyer, T., & Mehl, G. H. (2004). *Phys. Rev. Lett.*, *93*, 237801.
(f) Figueirinhas, J. L., Cruz, C., Filip, D., Feio, G., Ribeiro, A. C., Frere, Y., Meyer, T., & Mehl, G. H. (2005). *Phys. Rev. Lett.*, *94*, 107802.

[5] Stroobants, A. & Lekkerkerker, H. N. W. (1984). *J. Phys. Chem.*, *88*, 3669.

[6] Vanakaras, A. G. & Photinos, D. J. (1997). *Mol. Cryst. Liq. Cryst.*, *299*, 65.

[7] Palffy-Muhoray, P., Du Bruyn, J. R., & Dunmur, D. A. (1985). *J. Chem. Phys.*, 82.

[8] Galindo, A., Haslam, A. J., Varga, S., Jackson, G., Vanakaras, A .G., Photinos, D. J., & Dunmur, D. A. (2003). *J. Chem. Phys.*, *10*(8), 5216.

[9] (a) Fletcher, I. D. & Luckhurst, G. R. (1995). *Liq. Cryst.*, *18*, 175.
(b) Luckhurst, G. R. (2001). *Thin Solid Films*, *393*, 40.
(c) Praefcke, K. (2001). *Mol. Cryst. Liq. Cryst.*, *364*, 15.

[10] (a) Hunt, J. J., Date, R. W., Timini, B. A., Luckhurst, G. R., & Bruce, D. W. (2001). *J. Am. Chem. Soc.*, *123*, 10115.
(b) Date, R. W. & Bruce, D. W. (2003). *J. Am. Chem. Soc.*, *125*, 9012.

[11] (a) Kouwer, P. H. J. & Mehl, G. H. (2003). *J. Am. Chem. Soc.*, *125*, 11172.
  (b) Kouwer, P. H. J. & Mehl, G. H. (2003). *Mol. Cryst. Liq. Cryst.*, *397*, 301.
  (c) Apreutesei, D. & Mehl, G. H. (2006). *Chem. Commun.*, 609.
[12] Kouwer, P. H. J., Jager, W. F., Mijs, W. J., & Picken, S. J. (2002). *Macromolecules*, *35*, 4322.
[13] Fletcher, I. D. & Luckhurst, G. R. (1995). *Liq. Cryst.*, *18*, 175.