Completely miscible disc and rod shaped molecules in the nematic phase†

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Disc and rod shaped molecules which are completely miscible in the nematic phase were synthesised and the miscibility behaviour was investigated and confirmed by POM, DSC and XRD studies.

Molecules which exhibit uniaxial nematic phase behaviour are the basis of the current LCD technology; their biaxial nematic relatives have so far proven to be rather elusive. The biaxial nematic phase (N_b) was first predicted in 1970, and is characterised by two directors (compared to only one in the uniaxial variant), which are orthogonal to each other. It has been investigated intensively in theoretical studies.[1,2] Experimental evidence for lyotropic systems and very recently for the first time several thermotropic systems has been reported.[3,4]

Great theoretical and computational effort has been concentrated on mixtures of nematic rod and disc shaped molecules, which are individually uniaxial nematic (N_u), where in a certain region in the phase diagram biaxial nematic phase behaviour should occur, as shown schematically in Fig. 1.[5–10] Common for all of these models, is the occurrence of the N_b phase in the minimum of the rod–disc phase diagram. Associated is a strong decrease of the latent heat of the N to I transition upon approaching the tricritical point. The nature of the N_u–N_b transition is however model dependent and hence still discussed. Experimentally research has been hampered by the lack of fully miscible rod and disc shaped molecules.[10–12] Only recently a combined system containing rods and discs in a molecule has been reported, which is miscible at all concentrations with rods and discs.[13]

In this report we present, to the best of our knowledge the first, systems where rod shaped molecules are completely miscible in the nematic phase with disc shaped molecules. As rod shaped mesogens the systems R_1, and R_2 were prepared, as they are known to exhibit nematic phase behaviour over a wide temperature range and additionally, as they contain a high hydrocarbon content, when compared to many other mesogens with similar transition temperatures.[13] The disc shaped mesogens D_2, D_3, and D_4 were synthesised by simple esterification of D_1 with undecyloxy benzoic acid, 10-undecenoic acid and octanoic acid and are shown in Scheme 1.[14,15]

The transition temperatures of R_1, R_2, D_2, D_3 and D_4 are summarised in Table 1. All materials exhibit a nematic mesophase, monotropic for D_2 and enantiotropic for R_1, R_2, D_3 and D_4.The mixing behavior was investigated by studying contact samples with optical microscopy and by preparation of discrete mixtures, which were studied by polarized optical microscopy (POM) and DSC and for selected examples by XRD.

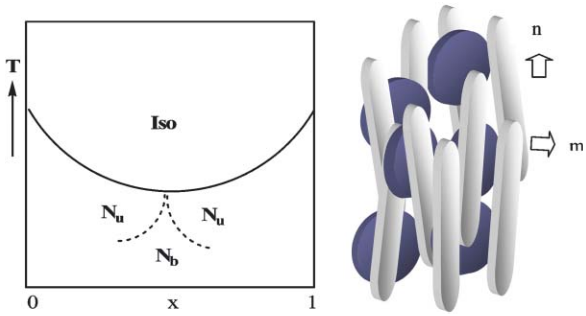
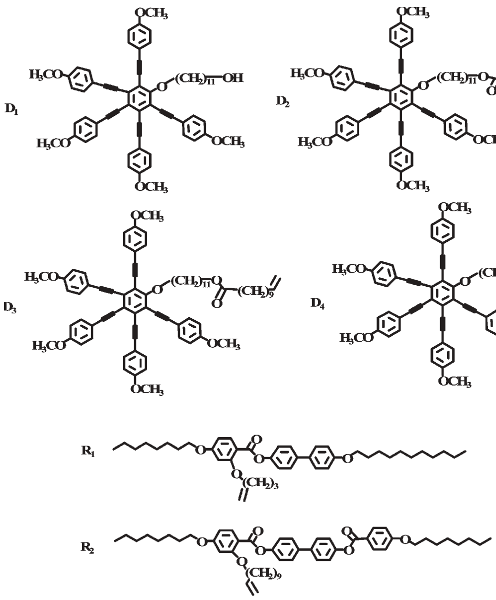


Fig. 1 Schematic phase diagram containing the N_b phase for mixtures of rods and discs. *x* represents the fraction of discs. The shape of the phase diagram, especially the transitions between the N_b and the N_u phases, is actually dependent on the model used. ***n*** and ***m*** refer to the two nematic directors in the biaxial phase.



Scheme 1 Structures of disc and rod shaped molecules used for mixtures.

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Table 1 Phase behaviour of discs and rods

Sample	Temperatures (°C) [enthalpies (ΔH) J g^{-1})]					
$\mathbf{D_2}^a$	Cr	92	(N	81	[−0.08])	I
$\mathbf{D_3}^b$	Cr	80	N	140	[0.12]	I
$\mathbf{D_4}^c$	Cr	95	N	157	[0.11]	I
$\mathbf{R_1}^d$	Cr	54	N	73	[1.75]	I
$\mathbf{R_2}^d$	Cr	93	N	141	[1.77]	I

[a] Monotropic phase transition. [b] Enantiotropic, crystallisation on cooling at 11 °C. [c] Enantiotropic, crystallisation on cooling at 49 °C. [d] On cooling both rods exhibit liquid crystal properties at room temperatures and crystallise slowly below 0 °C.

Contact studies of D_2 and R_1 and D_2 and R_2 showed complete miscibility over the whole composition range. Various attempts to detect regions with a miscibility gap have failed. A nematic phase, characterised by a typical schlieren and/or marbled texture, is observed over the full width of the phase diagrams of both D_2–R_1 and D_2–R_2. The POM micrographs are shown in Fig. 2. On cooling the samples, the nematic regions increase and meet at a minimum temperature, forming a continuous nematic phase, ranging from pure disc (left) to pure rod (right). Destabilisation of the nematic phase, due to mixing, causes a minimum in the clearing temperature at ~18 °C in the D_2–R_1 mixture at $D_2 \approx 80\%$ and at ~28 °C in the D_2–R_2 mixture at $D_2 \approx 84\%$. The shift in the minimum transition temperatures to a lower content of rods in the phase diagram for the D_2–R_2 mixture is likely to be associated with the larger aromatic ring system in R_2, when compared to R_1.

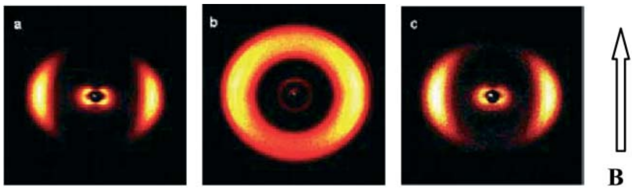

Fig. 3 X-Ray diffractograms of (a) R_2 at $T = 100$ °C, (b) D_2 at $T = 75$ °C (on cooling) and (c) D_2–R_2 mixture at the minimum of the transition temperature $c = 15.87\%$ (R_2) and at $T = 33$ °C (on cooling); direction of the magnetic field **B**.

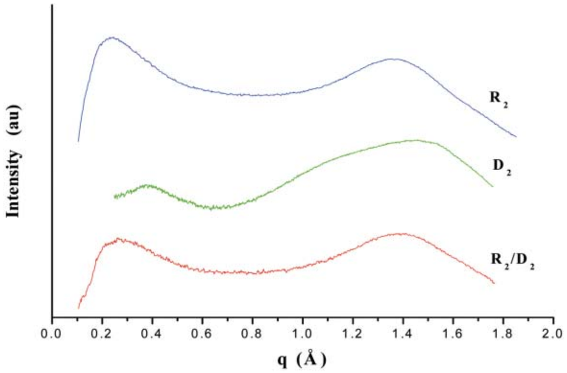

Fig. 4 Radially integrated XRD patterns of the pure disc (D_2), pure rod (R_2) and mixture D_2–R_2 at the minimum of the transition temperature ($c = 15.87\%$).

The phase structures of D_2, R_2 and the mixture D_2–R_2 at the minimum of the transition temperature were further investigated by X-ray diffraction (XRD) of samples in capillaries. Fig. 3 shows the diffractograms and Fig. 4 the radially integrated intensities. The diffraction pattern of R_2 is characterised by diffuse crescent shaped reflections (~4.63 Å, corresponding to the lateral distance of the hydrocarbon groups) and four small off-meridian intensities (~25.5 Å, corresponding approximately to the length of an aromatic mesogen), and attributed to the formation of cybotactic clusters, typical for such systems. However it should be noted that for bow-shaped molecules it was possible to assign such a pattern to the formation of the biaxial nematic phase.[4c] Fig. 3b shows the non-oriented pattern of D_2, typical for this class of molecule with intensities at ~16.78 Å (in line with the diameter of the aromatic disc), and 4.31 Å. The diffraction pattern of mixture D_2–R_2, containing only 15.87% of R_2 in the nematic phase, is characterised by four weak off-meridian intensities at 23.8 Å and wide angle reflections at 4.45 Å. The small angle reflections are very weak and the pattern is similar to that of R_2, thus excluding high ordered LC

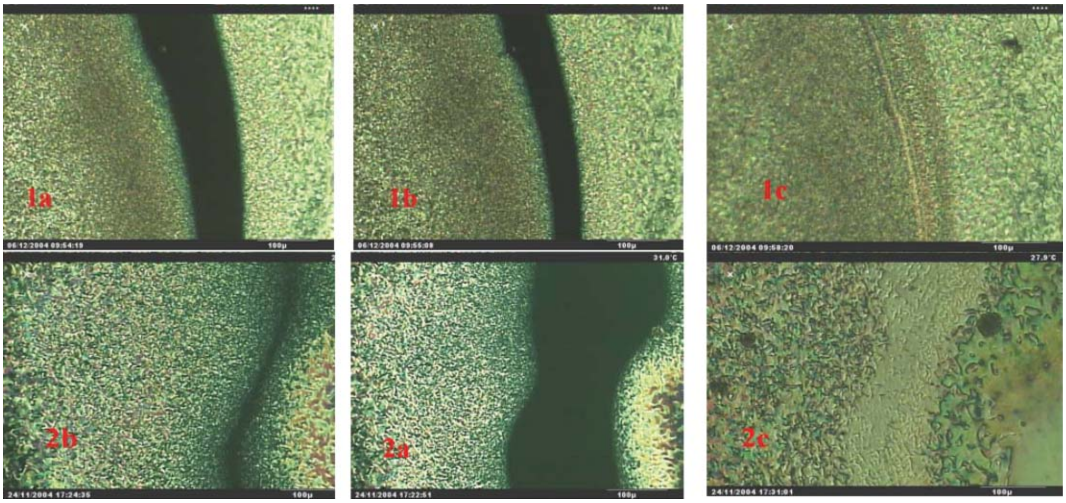

Fig. 2 Optical textures of contact samples of 1: D_2 and R_1 at (1a) $T = 25.5$ °C, (1b) $T = 22.8$ °C, (1c) $T = 18.0$ °C and 2: D_2 and R_2 at (2a) $T = 31.0$ °C, (2b) $T = 29.5$ °C, (2c) $T = 27.9$ °C. The isotropic area in between the nematic regions disappears on cooling and a continuous nematic phase is formed. All pictures taken with crossed polarisers.

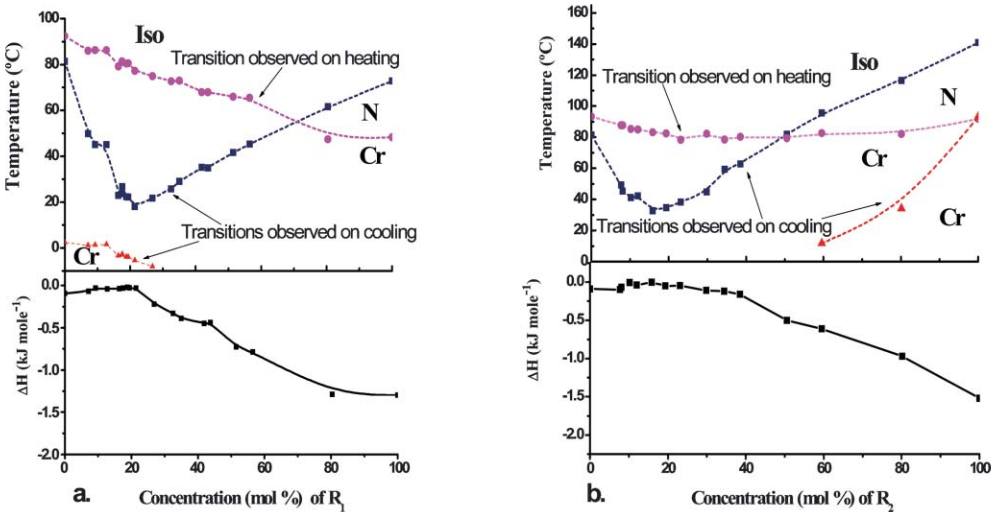

Fig. 5 Phase diagrams of (a) D_2–R_1, (b) D_2–R_2. The upper plots refer to the mixtures of discs and rods as determined by DSC measurements. The compositions are plotted as molar concentrations of the rods. Data shown in magenta refer to enantiotropic N–I transitions obtained on heating; data shown in blue refer to N–I transitions recorded on cooling. Data shown in red indicate crystallisation temperatures recorded on cooling. Glass transitions are omitted. The sketched lines are guides for the eyes only. The lower plots refer to the enthalpy changes associated with the N–I transitions recorded on cooling.

phases or crystalline structures. In other words, this supports the assignment of the phase structure as nematic. Notable is that this mixture can be easily aligned, differentiating this system from structurally related "rod–disc" materials.[13]

The results of detailed DSC investigations of the phase diagrams for the mixtures of D_2 and R_1 and D_2 and R_2 are summarised in Fig. 5 and details for the systems D_3–R_2 and D_4–R_2 are provided in the supporting information.[14] In all phase diagrams the latent heat of the nematic to isotropic transition decreases on approaching the transition minima, see Fig. 5.

Minima of $\sim$0.02 kJ mol^{-1} for both mixture systems are recorded at the detected minimum N–I temperatures, which are low compared to 0.09 kJ mol^{-1} for D_2, 1.30 kJ mol^{-1} for R_1 and 1.52 kJ mol^{-1} for R_2. In conclusion, the preparation of a phase diagram with a continuous phase consisting of mixtures of rod and disc shaped molecules in the nematic phase was shown. The position of the N–I minimum in the phase diagram is dependent on the size of the rod shaped mesogen and it is associated with the minimum of the transition enthalpy. This is in line with theoretical models for the formation of nematic biaxiality. For the nematic miscibility the size of the hydrocarbon chains plays a crucial role. This has so far not yet been recognised fully for theoretical and experimental studies. For further studies on nematic biaxiality the investigation of enantiotropic nematic rod–disc mixtures is required.

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