The Nematic Lateral Phase: A Novel Phase in Discotic Supramolecular Assemblies

**Paul H. J. Kouwer, Wolter F. Jager,
Wim J. Mijs, and Stephen J. Picken***

*Delft University of Technology, Polymer Materials
and Engineering, Julianalaan 136,
2628 BL Delft, The Netherlands*

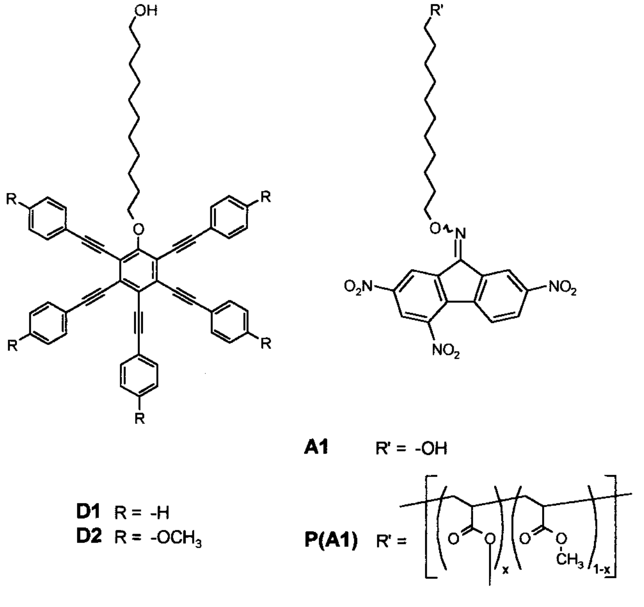
Received June 11, 2001
Revised Manuscript Received August 18, 2001

Introduction. Recently, discotic liquid crystals[1] (DLCs) have gained attention due to their various possible applications, e.g., as compensation layers in LCD technology and for one-dimensional conduction. However, before DLCs can be applied, knowledge and control over the mesomorphic properties, i.e., the phase behavior and transition temperatures, of such materials are crucial.

Columnar mesophases (Col_X) are obtained if the disk-shaped mesogens stack into columns and the columns possess a long-range 2D order. Besides the highly ordered columnar phases, two nematic phases are distinguished. In the nematic discotic (N_D) phase, the mesogens only possess orientational order. In the nematic columnar (N_{Col}) phase, the molecules stack into (short) columns, and the columns order in a nematic arrangement, analogous to the nematic phase in calamitic liquid crystals. Note that in this case it is the rod-shaped superstructure consisting of an array of disk-shaped molecules that forms the building blocks of the nematic arrangement.[2] This is an example of a nematic liquid mesophase that combines the required absence of long-range positional order with a high local degree of organization. Other examples of this phenomenon are well-known from for example wormlike micelles,[3a] chromonic liquid crystals,[3b] and the reentrant isotropic and nematic phases in occurring several truxene derivatives,[3c] which show nematic phases with a regular local molecular arrangement.

Specific supramolecular interactions, like charge transfer (CT) interactions,[4] can be used to modify liquid crystalline properties. Applying an electron-deficient *acceptor* to an electron-rich *donor* results in CT complexes with synergistic properties. We have prepared CT complexes of donors **D1**[5] and **D2** with acceptors **A1** and the macromolecular equivalent **P(A1)**[6] (see Figure 1). On the basis of our previous experience on similar liquid crystalline materials, we find that it is useful to prepare polymer analogues of the mesogens, since often they give rise to a much wider temperature range of mesophase formation. This in most cases is due to the effective suppression of crystallization and allows the formation of additional mesophases.[2c] Moreover, instead of obtaining a crystalline phase, the mesophase can be frozen in at low temperatures, where it is stable in time. Investigation of the liquid crystalline properties of these complexes reveals a novel nematic lateral (N_L) phase and demonstrates the pronounced effect of the polymer on the phase behavior.

Results and Discussion. Characterization of the materials was performed by differential scanning calorimetry (DSC), optical polarizing microscopy (OPM), and X-ray diffraction (XRD). Except for **D2**, the pure materials did not show any liquid crystalline properties. However, all the equimolar donor−acceptor complexes exhibited mesophases. The results are summarized in Figure 1.



D1:A1	: K	93	N_D	96	(1.2)	I						
D1:P(A1)	: G_N	33	N_L	101	(5)	I						
D2:A1	: K	80	N_D	146	(0.3)	I						
D2:P(A1)	: G_{Col}	45	Col_h	94	(1)	N_L	109	(5)	N_D	145	(0.3)	I

Figure 1. Investigated materials and thermal behavior of the equimolar CT complexes of **D1** and **D2** with **A1** and **P(A1)**, measured with OPM and DSC. Transition temperatures are given in [°C] and latent heat values (between the brackets) in [J g^{-1}]. K = crystalline; N_D = nematic discotic; N_L = nematic lateral; G = glass (N or Col phase frozen in); Col_h = columnar hexagonal; I = isotropic.

The **D1**:**A1** mixture shows a very narrow N_D phase, induced by mixing two nonmesomorphic materials. The complex with a high molar mass acceptor **D1**:**P(A1)** shows a nematic phase as well. However, the latent heat at the N → I transition has increased by a factor of 4, indicating an increased order in the nematic phase. Second, crystallization is suppressed, and hence, a nematic phase with much wider temperature range is obtained.

Just like the pure **D2**, the complexes **D2**:**A1** and **D2**:**P(A1)** exhibited a N_D phase. The clearing temperatures as well as the latent heat values at the clearing point are about equal for both complexes. However, where **D2**:**A1** crystallizes at low temperatures, **D2**:**P(A1)** shows a transition at 109 °C to another nematic phase, which we call the nematic lateral (N_L) phase. Interestingly, the optical texture did not change at the transition, despite the large latent heat (5 J g^{-1}) that was observed in the DSC experiments. Both the N_D and the N_L phase showed a typical *schlieren* texture (Figure 2a), which is characteristic for the nematic arrangement.[7a] Even after deformation, the schlieren texture returned rapidly. A uniform planar aligned nematic phase (Figure 2b,c) showed a large change in the polarization colors. Preliminary birefringence measurements indicate a 10%

---

* Corresponding author. E-mail: S.J.Picken@tnw.tudelft.nl.

10.1021/ma011007j CCC: $20.00

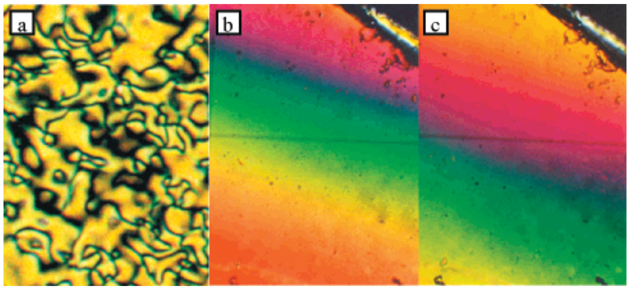


Figure 2. Photographs of optical textures of **D2**:**P(A1)** at (a) 100 °C (schlieren texture), (b) 100 °C (uniform planar aligned), and (c) 120 °C (same spot as b). All pictures are taken with crossed polarizers; magnification (a) 104×, (b, c) 52×.

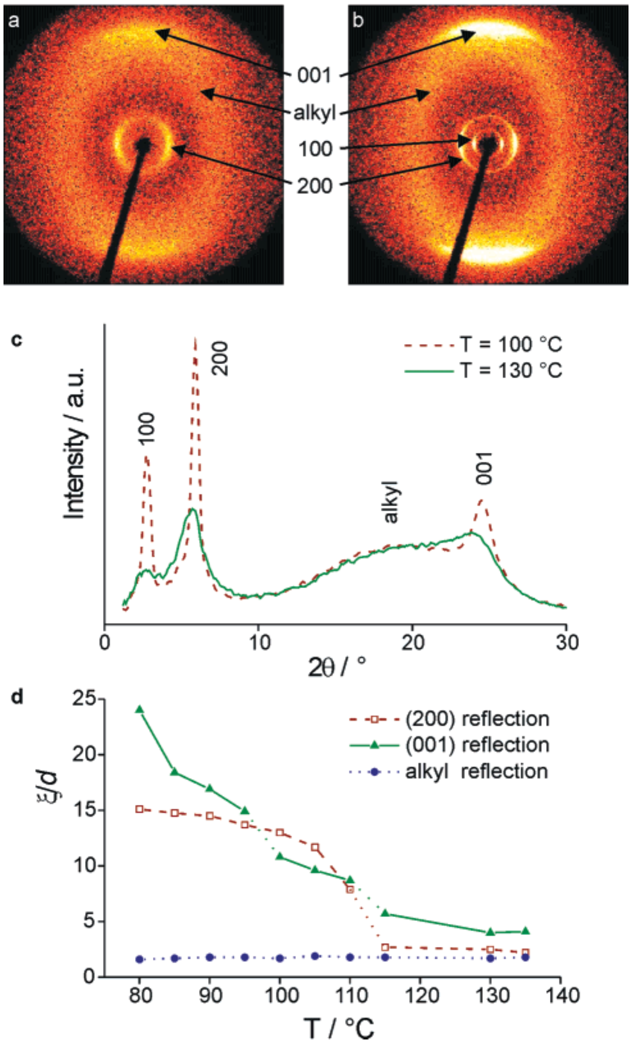


Figure 3. XRD results of complex **D2**:**A1**: (a) pattern at 130 °C (N_D phase); (b) pattern at 100 °C (N_L phase); (c) radial scan at 130 °C (solid) and 100 °C (broken); and (d) temperature dependence of the correlation length of the (200) reflection (lateral direction) (broken), (001) reflection (columnar direction) (solid), and the (alkyl) reflections (dotted).

change of the order parameter at the transition: $\langle P_2 \rangle$ decreasing from approximately 0.60 (at 105 °C) to 0.53 (at 110 °C).[8]

All complexes were subjected to XRD experiments. The N_D phases of **D1**:**A1** and **D2**:**A1** (Figure 3a) showed two diffuse reflections, attributed to the planar (001) and the lateral (200) disk–disk distance. The (100) reflection of the size of a donor plus an acceptor molecule (~26 Å) is only visible as a shoulder in the diagram.

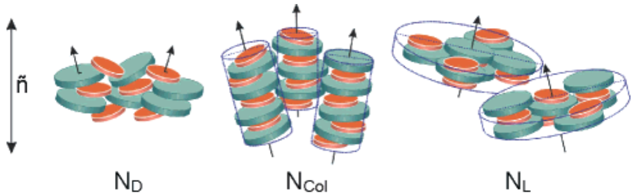


Figure 4. Schematic representation of the nematic phases of discotic mesogens: nematic discotic (N_D); nematic columnar (N_{Col}) and nematic lateral (N_L). **ñ** is the director, and the arrows indicate the orientation of the molecules/aggregates. Note that the sizes of the aggregates of the N_{Col} and the N_L phase are much larger than schematically depicted here!

Table 1. Typical Values of the Relative Correlation Lengths in the Various Nematic Phases in the Lateral (⊥) and the Columnar (||) Direction with Respect to the Director ñ

	Miller index	N_D	N_{Col}[9]	N_L
$(\xi/d)_{alkyl}$	alkyl	2.3	2.3	2.3
$(\xi/d)_{\perp}$	200	2.0	2.8	8.5
$(\xi/d)_{\parallel}$	001	4.2	8.5	8.5

Surprisingly, the N_L phases of **D1**:**P(A1)** and **D2**:**P(A1)** (Figure 3b) showed a tremendous sharpening of the reflections, including the (100) reflection as shown in Figure 3c.

These observations were quantified by calculating the spacing d and correlation length ξ of the various reflections, using the Bragg law: $2d \sin \theta = n\lambda$, where θ is the diffraction angle and the Scherrer equation: $\xi\omega_{1/2} \cos \theta = 0.89\lambda$, where $\omega_{1/2}$ is the full width at half-maximum of the reflection. To allow easy comparison, the correlation length was divided by the spacing, which results in a measure for the length scale of spatial order in terms of the dimensions of the molecular building blocks. The temperature dependence of ξ/d is shown in Figure 3d. The (001) reflection shows two pronounced steps at the $Col_h \rightarrow N_L$ and the $N_L \rightarrow N_D$ transitions. The (200) reflection shows only a step at the $N_L \rightarrow N_D$ transition.

Combining our experimental data (DSC, OPM, and XRD), we can conclude the following: Even after extensive annealing, the N_L phase shows all the required features to unambiguously identify it as a nematic phase, i.e., schlieren of $\pm^1/_2$ and ± 1 disclinations,[7a] occasional disclination lines, a smooth appearance, and due to a low viscosity spontaneous flow and fast texture coarsening.[7b] However, to our surprise, we found large latent heat values at the transitions (~5 J g^{-1}) in combination with a strong sharpening of the reflections in the XRD diagrams. The latter is a strong indication for a *locally* high ordered material. Seemingly, this is in contrast with the lack of positional order of the nematic phase. However, we propose that in the N_L phase the disk-shaped molecules assemble in disk-shaped superstructures. It is these supramolecular assemblies that exhibit a nematic arrangement. The transition from the N_L phase to the N_D phase coincides with a breakup of the nematic ordered aggregates and hence is rather a transition in the kind of building block than a phase transition in the true sense of the word. This is analogous to the well-established N_{Col} phase that forms a nematic phase from uniaxial assemblies including the occurrence of N_{Col} to N_D transitions in some materials.[2c,d]

Since all three nematic phases show the same optical textures in microscopy experiments, XRD analysis was used to investigate the different nematic phases. By calculating the (relative) correlation length ($=\xi/d$) from the various reflections, it is easy to establish the kind of local order and hence type of nematic phase (see Table 1). Typically, the N_{Col} phase[9] shows a high ξ/d value in the columnar (||) direction only, whereas the N_L phase shows high ξ/d values in the columnar and the lateral (⊥) direction.

Conclusions. In summary, we have prepared a series of equimolar CT complexes, wherein a nematic mesophase has been either induced or modified. Macromolecular complexes showed typical nematic schlieren textures, combined with a high local organization, as determined with XRD and large latent heat values. For this reason we suggest a novel nematic phase, the nematic lateral (N_L) phase. The N_L phase is characterized by high enthalpy changes at the transition as well as high relative correlation lengths in the parallel as well as in the perpendicular direction.

Acknowledgment. We thank Vanina Kleiman for the preparation of **D2**, Otto van den Berg for the preparation of **A1** and **P(A1)**, Ben Norder for technical assistance with the thermal analysis, and Enno Klop of the Akzo Nobel Chemicals Research Arnhem−Applied Physics department for assistance in performing the XRD analysis.

Supporting Information Available: Experimental details, OPM, DSC, and XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For a review on DLCs read: (a) Cammidge, A. N.; Bushby, R. J. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley VCH: New York, 1998; Vol. 2B, pp 693−748. (b) Chandrasekhar, S. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley VCH: New York, 1998; Vol. 2B, pp 749−780.

(2) (a) Ringsdorf, H.; Wüstefeld, R.; Zerta, E.; Ebert, M.; Wendorff, J. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 914−918. (b) Praefcke, K.; Singer, D.; Kohne, B.; Ebert, M.; Liebmann, A.; Wendorff, J. H. *Liq. Cryst.* **1991**, *10*, 147−159. (c) Kouwer, P. H. J.; Jager, W. F.; Mijs, W. J.; Picken, S. J. *Macromolecules* **2000**, *33*, 4336−4342. (d) Kouwer, P. H. J.; Gast, J.; Jager, W. F.; Mijs, W. J.; Picken, S. J. *Mol. Cryst. Liq. Cryst.*, in press.

(3) (a) Lawson, K. D.; Flautt, T. J. *J. Am. Chem. Soc.* **1967**, *89*, 5489. (b) Lydon, J. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley VCH: New York, 1998; Vol. 2B, pp 981−1007. (c) Warmerdam, T. W.; Nolte, R. J. M.; Drenth, W.; Miltenburg, J. C. van; Frenkel, D.; Zijlstra, R. J. J. *Liq. Cryst.* **1988**, *3*, 1087−1104.

(4) For a review in CT complexation in DLCs, see: (a) Praefcke, K.; Singer, D. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley VCH: New York, 1998; Vol. 2B, pp 945−967. (b) Praefcke, K.; Holbrey, J. D. *J. Inclusion Phenom.* **1996**, *24*, 19−41. (b) Ringsdorf, H.; Wüstefeld, R. *Philos. Trans. R. Soc. London* **1990**, *A 330*, 95−108.

(5) Janietz, D.; Hofmann, D.; Reiche, J. *Thin Solid Films* **1994**, *244*, 794−798. (b) Elaborate purification of **D1** leads to an increase in the melting temperature: $T_m = 123$ °C.

(6) For experimental details we refer to the Supporting Information.

(7) (a) Some more remarks on the nematic texture as observed for the N_L phase: Long-range smectic or columnar order is not compatible with a schlieren texture due to the incompressibility of the lamellae or 2D stacks. Defects in these materials results in typical focal conical textures (for lamellae) and "oak-leaf" or mosaic textures (for columns). A S_C phase, also exhibiting a schlieren texture in a homeotropic alignment, can be excluded due to the presence of clear $\pm ^1/_2$ disclinations in our texture. (b) If we would have been looking at a phase with long-range positional order, like a columnar phase, it would certainly have led to the formation of an elastic network due to the presence of the polymer backbone. This is contrary to our observations.

(8) The birefringence (or actually the optical retardation) versus temperature was measured using a variable compensator, and the results were fitted to a Maier−Saupe curve, which is appropriate to describe the order parameter $\langle P_2 \rangle$ as a function of temperature in a nematic phase. From this procedure we determined the retardation at $\langle P_2 \rangle = 1$ ($T = 0$ K), and we estimated the change in the order parameter near the transition.

(9) Values for the N_{Col} phase were calculated for a complex of **D1**:**TNF** at 150 °C.

MA011007J