Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A Plastic Columnar Discotic Phase

B. Glüsen [a], A. Kettner [a] & J. H. Wendorff [a]

[a] Fachbereich Physikalische Chemie und Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität, D-35032, Marburg, Germany

To cite this article: B. Glüsen, A. Kettner & J. H. Wendorff (1997): A Plastic Columnar Discotic Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 303:1, 115-120

To link to this article: http://dx.doi.org/10.1080/10587259708039414

Mol. Cryst. Liq. Cryst., 1997, Vol. 303, pp. 115–120
Reprints available directly from the publisher
Photocopying permitted by license only

A PLASTIC COLUMNAR DISCOTIC PHASE

B. GLÜSEN, A. KETTNER, J.H. WENDORFF
Fachbereich Physikalische Chemie und Wissenschaftliches Zentrum für
Materialwissenschaften, Philipps-Universität, D-35032 Marburg, Germany

Abstract A plastic columnar discotic phase is reported for several triphenylene derivatives. It is characterized by a three-dimensional positional order of the molecules, as in a crystalline state, while maintaining the rotational mobility of the molecules. Only very minute changes in structure and dynamics occur at the phase transition from the normal discotic hexagonal phase to the discotic plastic phase.

INTRODUCTION

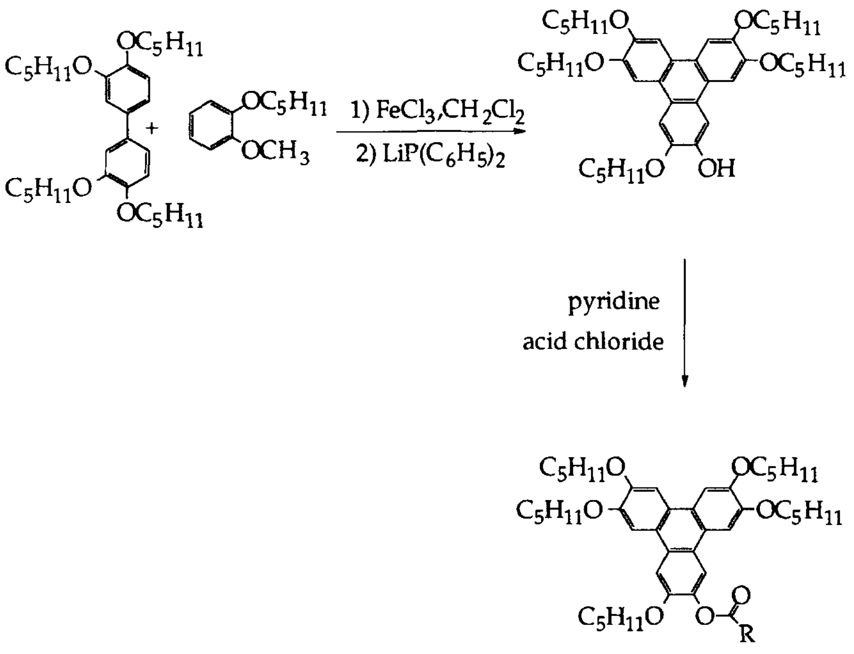
The general observation for ordered discotic columnar phases is that the one-dimensional intracolumnar order and the two-dimensional positional order defined by the packing of the columns are not correlated.[1, 2] This is obvious from the absence of mixed X-ray reflections (hkl) characteristic of the crystalline state.

While calamitic mesogens are known to form several smectic mesophases with three-dimensional positional order[3], corresponding phases for discotic mesogens are rare. Certain hexathiotriphenylenes[4] and tribenzylenes[5] form phases with a three-dimensional positional order of the centers of the molecules and a helical order within the columns. The phases still exhibit a typical LC-structure with well-ordered rigid cores and disordered flexible side-chains, while rotational mobility is absent.

This contribution is concerned with a novel discotic columnar phase which fills the gap between ordered columnar phases and the crystalline state. In contrast to the known helical phases it is very closely related to the liquid-crystalline phase. A three-dimensional positional order occurs, while the rotational mobility of the molecules on their sites around the column normal continues in the new phase, as in a plastic crystal. For this reason we have proposed to call it the discotic plastic phase.[6]

SYNTHESIS

The discotic plastic phase has so far been observed on one symmetrically substituted triphenylene, the 2,3,6,7,10,11-Hexabutyloxytriphenylene (H4T), and on asymmetrically substituted triphenylene esters, which were prepared via the corresponding biphenyl compound as shown in scheme 1.[7] The esters of pivalic acid (pivaloate), 1-adamantane carboxylic acid (adamantanoate) and trifluor-methane sulfonic acid (triflate)[8] exhibit the new phase.



SCHEME 1 Synthesis of asymmetrically substituted triphenylene derivatives

PHASE BEHAVIOR

The phase behavior of the compounds was characterized by differential scanning calorimetry (DSC). The phase transition temperatures are summarized in TABLE I.

TABLE I: Transition Temperatures

compound	c	T/°C	D_{hp}	T/°C	D_{ho}	T/°C	i
H4T	•	89	•			146	•
adamantanoate			•	135	•	186	•
pivaloate			•	65	•	178	•
triflate			•	87	•	181	•

The pivaloate exhibits an additional low temperature phase below -5°C, which has not yet been characterized. The enthalpy of the D_{hp} to D_{ho} transition was between 0.1 and 1.0 kJ/mole in all cases. Additionally, also several esters and monovinylethers with five butyloxy side chains instead of the pentyloxy ones show the D_{hp}-phase (e.g. the ethyloxy vinylether[9] from 81°C to 126°C).

STRUCTURE

The structures of the mesophases were examined by wide angle X-ray diffraction. FIGURE 1 shows the X-ray diffraction diagram of the adamantanoate. The D_{ho}-phase shows several Bragg peaks at smaller scattering angles, which can be attributed to a two-dimensional hexagonal lattice and an asymmetric peak, which can be assigned to the intracolumnar order.

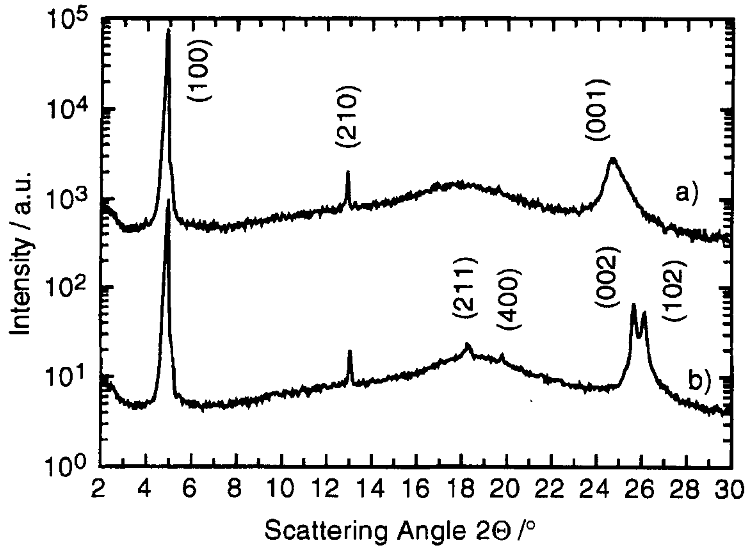


FIGURE 1 X-ray diffraction diagram for the adamantanoate
a) T=150°C, D_{ho}-phase; b) T=21°C, D_{hp}-phase.

TABLE II Lattice constant a_{hex}, (hkl) indices and d-spacings (in Å) for the X-ray reflections in the D_{ho} and in the D_{hp}-phase compared with values calculated from the a_{hex} values

T/°C	a_{hex}	(100)	(210)			(001)	
150	21.0	18.27	6.87			3.61	
calc'd		18.18	6.87				
				(211)	(400)	(002)	(102)
21	20.7	18.03	6.79	4.85	4.48	3.46	3.41
calc'd		17.96	6.79	4.85	4.49		3.40

The reflections attributed to the hexagonal lattice remain unchanged in the D_{hp}-phase. The broad reflection of the intracolumnar order, however, splits into two sharp reflections and a new reflection occurs at intermediate scattering angles (see TABLE II). Flat camera investigations on oriented samples show that the wide angle doublet corresponds to (002) and (102) reflections and the intermediate reflection (at 4.85Å) to the mixed reflection (211): it displays four maxima with respect to the azimuthal intensity distribution, i.e. a three-dimensional long range order is found.

In order to get more detailed information on the nature of the phase transition we performed X-ray measurements of selected reflections over a wide temperature range. In the D_{hp}-phase, the intercolumnar distance increases with increasing temperature but after the phase transition, in the D_{ho}-phase, it remains constant. The intracolumnar distance however shows a stepwise increase by about 0.5% at the transition from the D_{hp} to the D_{ho}-phase. Aditionally, the temperature dependence of the intracolumnar distance is stronger in the D_{ho}-phase than in the D_{hp}-phase.

DYNAMIC BEHAVIOR

The occurrence of the mixed reflections in the X-ray measurements indicates that the lower temperature phase could, in fact, be crystalline. The dielectric relaxation behavior proves this assumption to be wrong. FIGURE 2 shows the variation of the relaxation behavior around the transition from the D_{hp} to the D_{ho}-phase.

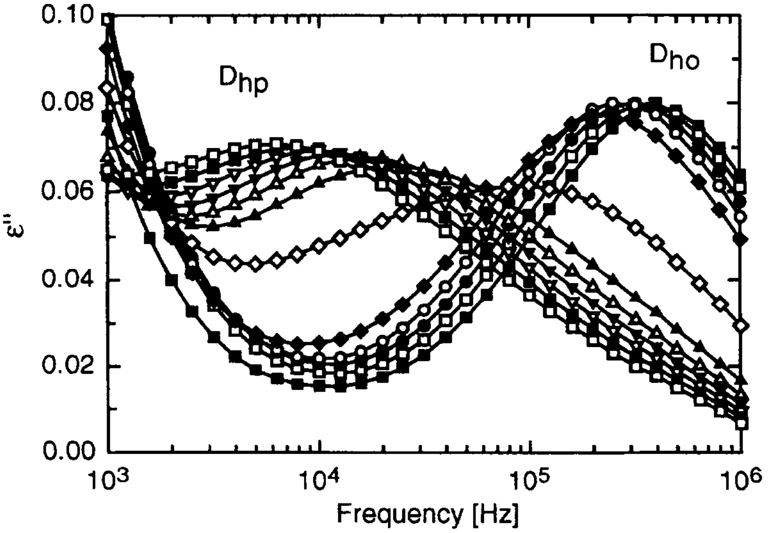


FIGURE 2 Imaginary part ε" of the dielectric function versus frequency from 112°C (D_{hp}) to 134°C (D_{ho}) in 2°C steps

A main relaxation is observed for both phases. Such a relaxation has been attributed to rotations of the molecules in similar compounds[10] showing the D_{ho}-phase. The additional increase of ε" in the low frequency region is due to DC-conductivity. Note that this measurement is made with decreasing temperature where the D_{ho}-phase can be supercooled and the phase transition occurs at about 124°C.

To learn more about the nature of the relaxation we analyzed the relaxation time distribution. It turned out to be asymmetric and could therefore be represented by the Havriliak-Negami equation[11]. We found that the character of the relaxation changes only slightly at the phase transition from the D_{hp} to the D_{ho}-phase. The relaxation strength $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ decreases slightly, the relaxation time distribution gets sharper and the mean relaxation time τ_0 increases by one decade. This means that the same relaxation process takes place in both phases and is only slightly influenced by the different environment. The molecules are as mobile in the discotic plastic phase as in the D_{ho} phase.

CONCLUSION

The new phase is characterized by a three-dimensional positional order of the centers of the molecules and rotational mobility of the molecules around the column axis. It has features in common with plastic crystals. The discotic plastic phase displays a set of interesting properties, among them charge carrier mobilities exceeding 10^{-2} cm²/Vs.[12] This makes it a prime candidat for applications as organic photoconductors and light emitting diodes.[13]

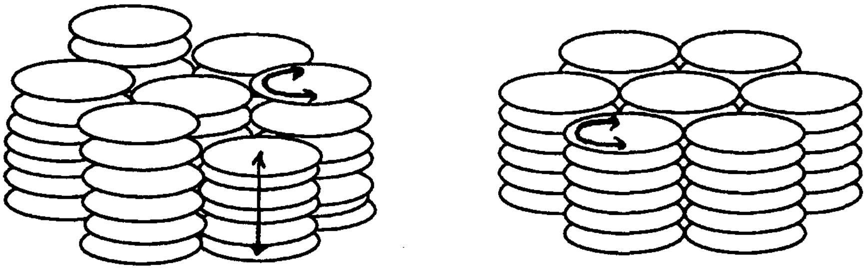


FIGURE 3 Schematic representation of the D_{ho}-phase (left) and the D_{hp}-phase (right)

We would like to acknowledge the financial support by the Deutsche Forschungsgemeinschaft (SFB 383). B.G. also gratefully acknowledges the support by the Fonds der Chemischen Industrie.

REFERENCES

1. S. Chandrasekhar, B.K. Sadashiva, K.A. Suresh, Pramana, 9, 471 (1977).
2. A.M. Levelut, J. Chim. Phys., 80, 149 (1983).
3 S. Chandrasekhar, Liquid Crystals 2. ed. (Cambridge University Press, 1992), pp 300 and references therein.
4. a) P.A. Heiney, E. Fontes, W.H. de Jeu, A. Riera, P. Carrol, A.B. Smith, J. Phys. France, 50, 461 (1989).
   b) E. Fontes, P.A. Heiney, W.H. de Jeu, Phys. Rev. Lett., 61, 1202 (1988).
5. A.M. Levelut, J. Malthete, A. Collet, J. Phys. France, 47, 351 (1986).
6. B. Glüsen, W. Heitz, A. Kettner, J.H. Wendorff, Liq. Cryst. 20, 627 (1996)
7. P. Henderson, H. Ringsdorf, P. Schuhmacher, Liq. Cryst., 18, 191 (1995)
8. P. Henderson, S. Kumar, J.A. Rego, H. Ringsdorf, P. Schuhmacher, J. Chem. Soc., Chem. Commun., 1059 (1995)
9. I. Bleyl, Ch. Erdelen, K.-H. Etzbach, D. Haarer, W. Paulus, H.-W. Schmidt, Proceedings of the 25. Freiburger Arbeitstagung Flüssigkristalle (Freiburg, 1996)
10. M. Möller, J.H.Wendorff, M. Werth, H.W.Spiess, J. Non-Cryst. Solids, 170, 295 (1994)
11. S. Havriliak, S. Negami, J. Polym. Sci., Polym. Symp., 14, 99 (1966)
12. J. Simmerer, B. Glüsen, W. Paulus, A. Kettner, P. Schuhmacher, D. Adam, K.H. Etzbach, K. Siemensmeyer, J.H. Wendorff, H. Ringsdorf, D. Haarer, accepted by Advanced Materials (1996)
13. T. Christ, B. Glüsen, A. Greiner, A. Kettner, R. Sander, V. Stümplen, V. Tsukruk, J.H. Wendorff, submitted to Advanced Materials (1996)