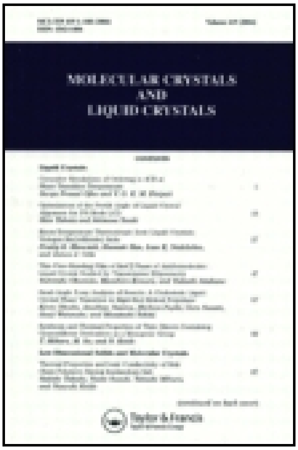

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Binary Phase Diagram of Triphenylene Derivatives: The Role of Hydrogen Bonds

Z. Yildirim [a], E. Mendes [a], S. J. Picken [a], I. Paraschiv [b], H. Zuilhof [b], W. M. de Vos [b] & E. J. R. Sudhölter [b]

[a] Delft University of Technology, Department of Materials Science and Technology, Delft, The Netherlands

[b] Laboratory of Organic Chemistry, Wageningen University, Wageningen, The Netherlands

Version of record first published: 31 Aug 2006

To cite this article: Z. Yildirim, E. Mendes, S. J. Picken, I. Paraschiv, H. Zuilhof, W. M. de Vos & E. J. R. Sudhölter (2005): Binary Phase Diagram of Triphenylene Derivatives: The Role of Hydrogen Bonds, Molecular Crystals and Liquid Crystals, 439:1, 237/[2103]-243/[2109]

To link to this article: http://dx.doi.org/10.1080/15421400590955190

Mol. Cryst. Liq. Cryst., Vol. 439, pp. 237/[2103]–243/[2109], 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590955190

Binary Phase Diagram of Triphenylene Derivatives: The Role of Hydrogen Bonds

Z. Yildirim
E. Mendes
S. J. Picken
Delft University of Technology, Department of Materials Science and Technology, Delft, The Netherlands

I. Paraschiv
H. Zuilhof
W. M. de Vos
E. J. R. Sudhölter
Laboratory of Organic Chemistry, Wageningen University, Wageningen, The Netherlands

In this study, the binary phase diagram of two triphenylene derivatives is investigated by using differential scanning calorimetry (DSC), optical polarizing microscopy (OPM), and wide-angle x-ray scattering (WAXS). The triphenylene derivatives studied are based on hexa-alklyoxy-triphenylene. One compound in the binary mixture HAT6 has six symmetrical hexyloxy tails each containing six carbon atoms. The other compound, HAT6-C10UC6, has one asymmetrical tail bearing a urea functionality at a specific distance from the aromatic core. The introduction of this asymmetrical H-bonding unit into the structure results in a complete disruption of liquid crystallinity while a "pseudo re-entrant" phenomenon is observed in the binary mixture phase diagram.

Keywords: binary phase diagram; columnar; discotic liquid crystal; re-entrant

INTRODUCTION

Since late '70s, there has been a great interest in the field of discotic liquid crystals (DLC), following the discovery of Chandrasekhar [1]. Discotic liquid crystals belong to the class of thermotropic liquid

Address correspondence to S. J. Picken, Delft university of Technology, Department of Materials Science and Technology, Julianalaan 136, 2628 BL Delft, The Netherlands. E-mail: s.j.picken@tnw.tudelft.nl

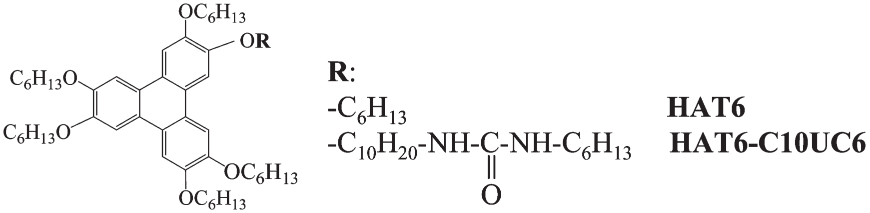

FIGURE 1 Molecular structure of triphenylene derivatives.

crystals and they are especially known for their self-assembling property into columnar structures. Discotic molecules can form a variety of mesophases. In addition to the columnar phase, which can exhibit various types of order within the columns (ordered, disordered, tilted) and between the columns (hexagonal, rectangular and oblique), several nematic phases are also encountered (nematic discotic, nematic columnar and nematic lateral [2]). Moreover, a helical columnar phase was reported for hexakis(hexylthio)triphenylene [3].

Due to π-π interaction between aromatic cores, discotic liquid crystals serve as one-dimensional pathways for charge transport. This enables DLC's to be attractive in many applications such as, photovoltaic devices, field effect transistors and molecular electronics. The conduction is enhanced as the distance between the aromatic cores decreases and also when the core motion is restricted. One of the ways of achieving this is to make use of intermolecular H-bonding [8–10]. The last one deserves special attention since it reports the smallest π-π distance in such systems, being 3.18 Å.

Liquid crystal mixtures are also employed in order to widen the mesophase range, to identify unknown compounds via mixing with mesogens with a known phase behaviour, and also to create new mesophases.

In this context, we studied a triphenylene derivative, which is able to form H-bonds. This compound is a derivative of well-known discotic liquid crystal, HAT6 (Fig. 1). HAT6 is known to exhibit a hexagonal columnar liquid crystalline phase between 68–97°C [11]; K 68 $\mathrm{Col_{hex}}$ 97 I. In the case of HAT6-C10UC6, liquid crystallinity is totally lost. To investigate this in more detail we have studied the binary mixture of HAT6-C10UC6 with HAT6. This will provide additional insight on the role of H-bonding on the stability of the columnar phase.

EXPERIMENTAL

The binary phase diagram was determined by visual inspection in OPM between crossed polarizers, using the contact sample method

[12] and by preparing several individual mixtures. The individual mixtures were prepared from CH_2Cl_2 solution. The contact sample method gives a rapid overview of the binary phase diagram; preparation of individual mixtures in the interesting regions can then be used to study the structures in more detail.

Pure compounds, individual mixtures and contact samples were all analysed using a Nikon Eclipse E600 polarizing optical microscope, equipped with a Mettler FP 82HT hot stage connected to the Mettler FP 80 central processor. The used heating/cooling rate was 5°C/min.

In addition we used DSC (Perkin-Elmer) and X-ray diffraction using a Bruker Nonius D8-Discover equipped with a home-built capillary heating oven.

RESULTS AND DISCUSSION

Individual mixtures of HAT6 and its derivative up to 0.3 mole fractions (HAT6-C10UC6) were prepared from solution. The binary phase diagram of HAT6 and HAT6-C10UC6 is displayed in Figure 2.

The points on this diagram were obtained by using optical polarizing microscopy (OPM) and DSC. In the binary phase diagram, up to 0.3 mole fraction (HAT6-C10UC6), three one-phase and three two-phase regions were observed. In the region near 0.15 mole fraction, the columnar phase completely disappears and re-appears again at higher concentration. However, in this case the mesophase range is considerably reduced.

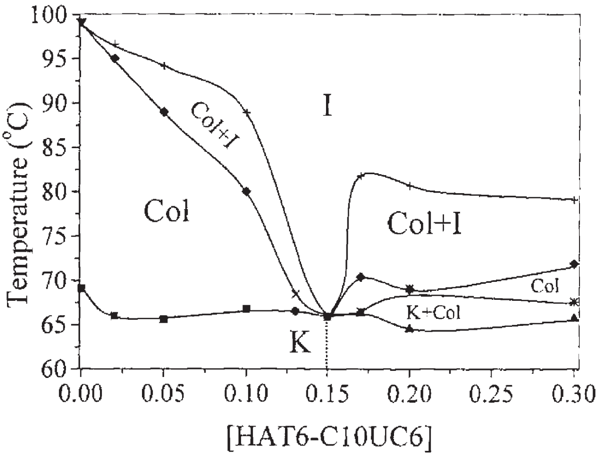

FIGURE 2 Binary phase diagram of HAT6/HAT6-C10UC6 (the curves are for guidance of the eye).

Re-entrant phase behavior is well known in liquid crystals. In this phenomenon, the same type of phase is found at different temperatures in the phase diagram. Some of the observed re-entrant phases are smectic C (SmC-SmA-SmC) [4], isotropic (K-N_D-I-Col_{ho}-I) [5], (SmA-I-Col_{ho}-I) [6], and hexagonal columnar (Col_{ho}) (Col_{ho}-Col_{hp}-Col_{ho}) [7]. In the present case, since the same phase is observed at different compositions of the binary mixture, we call this a *pseudo re-entrant* columnar phase. The point (0.15, 65.9) acts as a eutectic point. Also, starting from 0.13 mole fraction, a biphasic crystal and isotropic region is observed, which then turns into a two-phase crystal and columnar region at 0.17 mole fraction. The clearing temperature starts levelling off around 0.17 mole fraction and we expect approximately the same values for the rest of the diagram.

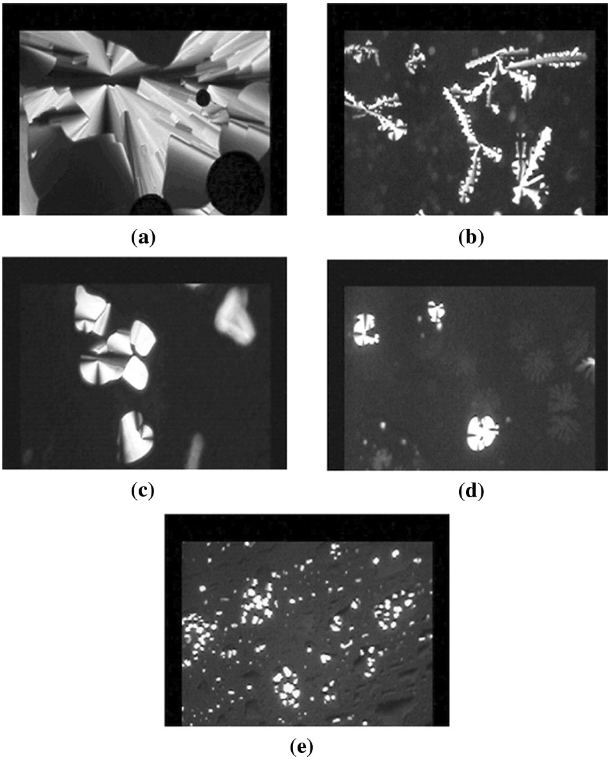

FIGURE 3 Optical textures of the Col phases at different compositions, cooling from I, at 70°C (a) 0% HAT6-C10UC6, (b) 2% HAT6-C10UC6, (c) 5% HAT6-C10UC6, (d) 17% HAT6-C10UC6, and (e) 30% HAT6-C10UC6.

Optical textures of the individual mixtures were investigated in detail and they are compared in Figure 3. All pictures were taken at the same temperature, namely 70°C and with the same magnification.

We see that a 2% mixture has a somewhat different structure, being dendrimer-like where the size of the growing dendrimers is rather small. The 5, 17, and 30% mixtures have all similar morphologies. Furthermore, we observe that with increasing HAT6-C10UC6 concentration the domain size noticeably decreases. In a study on interdigitated derivatives of triphenylene, it was found that as the tail size increased from C3 to C5 in hexapentyloxy triphenylenes, smaller domains are formed [13]. For this reason and to investigate the structure of the various phases in the binary phase diagram we have studied several binary mixtures using WAXS.

To explain the observed results we propose that they are related to distortions of the columnar structure via H-bonding. Distortions of the columnar phase, sketched in Figure 4 visualises the proposed mechanism for the pseudo re-entrant phase.

In this figure, three sets of two neighbouring columns are shown. In the first set, due to the absence of any imperfections, columns pack safely in hexagonal order. However, as HAT6-C10UC6 is added to pure HAT6, the second set, the presence of long functional tails begin to introduce strain in the columns, resulting in the destabilization of the hexagonal columnar packing. At positions where the longer tails bearing urea functionality meet each other, it is assumed that the intercolumnar distance is locally increased. This phenomenon might be used to explain the depression of the columnar phase as HAT6-C10UC6 is added into pure HAT6 and finally its total disappearance around 0.15 mole percent. Nonetheless, this situation is immediately compensated for, as soon as the probability of having these functional tails in the same column increases. In this case, intracolumnar

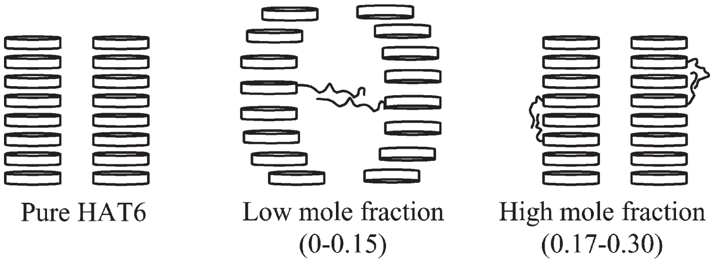

FIGURE 4 Proposed mechanism for the pseudo re-entrant phenomenon showing the columnar distortion as a function of HAT6-C10UC6 concentration.

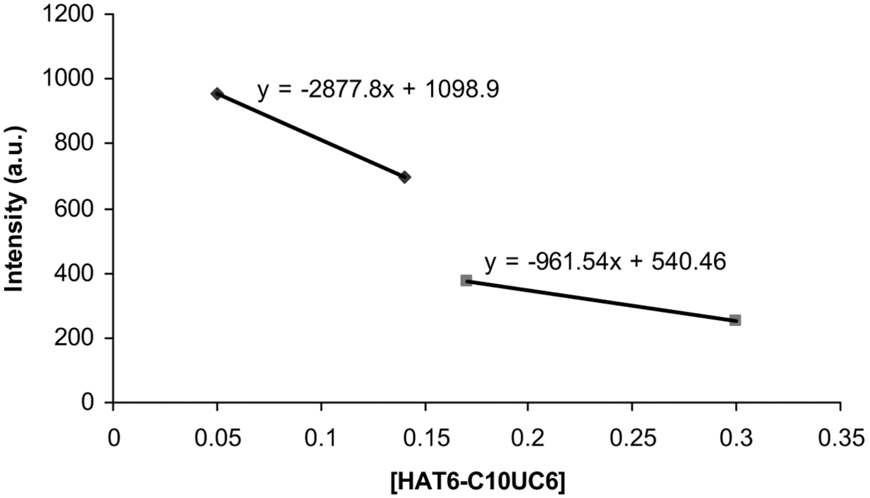

FIGURE 5 Variation of the intercolumnar intensity from WAXS with changing composition of the mixture. All data were recorded at 71°C.

H-bonding between these tails allows more or less the same intercolumnar spacing to be resumed and the columnar phase reappears.

To check this hypothesis, detailed WAXS measurements were carried out on different compositions at same temperature. Figure 5 represents the changes in the intensity of the intercolumnar peak as a function of HAT6-C10UC6 mole fraction, at 71°C.

As can be seen from the figure, the data corresponding to columnar phases before and after 0.15 mole fraction lie in two different lines, implying a difference between two Col phases in the binary phase diagram.

CONCLUSIONS

In order to investigate the effect of hydrogen bonding on the mesophases of discotic liquid crystals, we studied triphenylene derivatives based on hexa-alklyoxy-triphenylene. One of the compounds for the binary mixtures, HAT6, posses six symmetrical hexyloxy tails containing six carbon atoms each while the other compound, HAT6-C10UC6, posses one asymmetrical tail bearing an urea functionality at a specific distance from the aromatic core. Instead of increasing the stability of the columnar phase, the introduction of this asymmetrical H-bonding unit into the structure results in disruption of liquid crystallinity. The binary mixture of these two triphenylene derivatives, however, exhibits a rich phase diagram. The most striking characteristic observed is a pseudo re-entrant phenomenon for the columnar phase. When the concentration of the hydrogen bonding unit, [HAT6-C10UC6], is increased in the binary mixture, the temperature range of the columnar phase decreases strongly until it disappears completely, only to re-appear with increasing [HAT6-C10UC6]. The structure of the two columnar phases are, however, not identical. We propose that the increasing presence of H-bonding urea containing alkyl tails initially disturbs the columns until they fully disappear while a further increase in concentration allows the formation of intra-columnar H-bonding which has a less destabilising effect on the mesophase formation. The WAXS results indeed indicate that the details of the structure of the two columnar phases is different and this will be examined in more detail to gain further understanding of the observed phenomena.

REFERENCES

[1] Chandrasekhar, S., Sadashiva, B. K., & Suresh, K. A. (1977). *Pramana*, *7*, 471.

[2] Kouwer, P. H., Jager, W. F., Mijs, W. J., & Picken, S. J. (2001). *Macromolecules*, *34*, 7582.

[3] Adam, D., Schuhmacher, P., Simmerer, J., Haussling, L., Siemensmeyer, K., Etzbachi, H., Ringsdorf, H., & Haarer, D. (2002). *Nature*, *371*, 141.

[4] Matsugana, Y., Miyajima, N., Nakayasu, Y., Sakai, S., & Yonenaga, M. (1988). *Bull. Chem. Soc. Jpn.*, *61*, 207.

[5] Setoguchi, Y., Monobe, H., Wan, W., Terasawa, N., Kiyohara, K., Nakamura, N., & Shimizu, Y. (2003). *Thin Solid Films*, *438–439*, 407.

[6] Gearba, R. I., Lehmann, M., Levin, J., Ivanov, D. A., Koch, M. H. J., Barbera, J., Debije, M. G., Piris, J., & Geerts, Y. H. (2003). *Adv. Mater.*, *15*, 1614.

[7] Destrade, C., Mondon, M. C., & Malthete, J. (1979). *J. de Physique*, *3*, 17.

[8] Beginn, U. (2003). *Prog. Polym. Sci.*, *28*, 1049.

[9] Radzihovsky, L. (1996). *Europhysics Letters*, *36*, 595.

[10] Destrade, C., Foucher, P., & Tinh, N. H. (1982). *Physics Letters*, *88A*, 187.

[11] Pietrasik, U., Szydlowska, J., Krowczynski, A., Pociecha, D., Gorecka, E., & Guillon, D. (2002). *J. Am. Chem. Soc.*, *124*, 8884.

[12] Fimmen, W., Glusen, B., Kettner, A., Wittenberg, M., & Wendorff, J. H. (1997). *Liquid Crystals*, *23*, 569.

[13] Allen, T. M., Diele, S., Harris, K. D. M., Hegmann, T., Kariuki, B. M., Lose, D., Preece, J. A., & Tschierske, C. (2001). *J. Mater. Chem.*, *11*, 302.