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Calamitic and discotic mesophases formed by kinetically controlled rod–disc alternation of molecular shape in a triphenylene–azobenzene mesogenic system†

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A triphenylene mesogen with the peripheral azobenzene units was found to show kinetically controlled bimesomorphism, with a metastable smectic and a stable hexagonal columnar (Col$_h$) phases on cooling, which is caused by the rod–disc alternation of the molecular shape.

Calamitic (rod-shaped) and discotic (disc-shaped) molecules are well-known categories of typical liquid crystalline compounds. Therefore, the ratio of the longitudinal and lateral lengths of a calamitic molecule and the thickness and diameter of a discotic molecule are essentially important factors for the occurrence of liquid crystallinity.[1] Recent studies on supramolecular aggregates revealed a variety of compounds could form mesophases with some intermolecular specific interactions *via* making up a molecularly ordered cluster to give rod- and disc-shapes.[2]

On the other hand, a variant mesomorphism of one mesogenic molecule caused by a change in the molecular shape also can be seen for metallomesogens. Calamitic and discotic behaviour is observed based on the variable valency of metal ion.[3] Recent studies on mesomorphic dendrimers have revealed that the dendrimeric mesogens show a bimesomorphism of calamitic and discotic mesophases depending on the structures of the dendrimer core and the peripheral unit as well as the generation. Dendrimeric mesogens with peripheral rod-like mesogenic units have a strong tendency to form smectic layered phases.[4] However, one can see a generation dependence of the mesomorphism in two ways. In one way, the higher generations tend to show columnar mesophases[5] and in another case, the younger generations are likely to form columnar ones.[6]

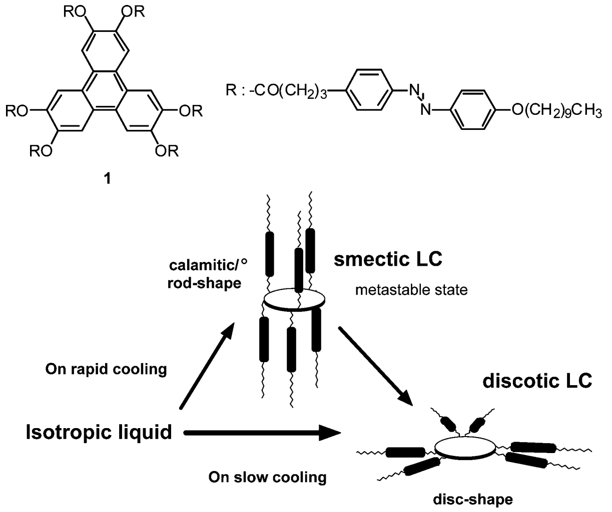
However, no mesogenic system has been reported that shows the change of mesomorphism between calamitic and discotic accompanied by a change in the molecular shape from rod-like to disc-like.

In this work, a novel mesogenic behaviour was found for a triphenylene mesogen with six long-chain azobenzene mesogenic moieties as the peripheral units. This compound shows a transient bimesomorphism (Sm–Col) due to the change in molecular shape between rod and disc which is dependent on the cooling rate from the isotropic (Iso) phase (Scheme 1).

The compound, 2,3,6,7,10,11-hexakis(4-*n*-decyloxyphenylazophenyl-4-propylenecarboxy)triphenylene (**1**) was synthesised by the esterification of the azobenzenecarboxylic acid and hexahydroxytriphenylene and purified by column chromatography followed by recrystallisation from ethanol.‡

It was found that **1** is a monotropic liquid crystal. However, the mesophase formed on cooling varies, depending strongly on the cooling rate from the Iso phase. When **1** is cooled down at 5 °C min^{-1}, the formation of "bâtonnets" was observed under crossed polarising condition of a microscope as shown in Fig. 1(a), which is a typical texture seen in the early stage of the growth of SmA/C phase from the isotropic melt.[7] However, the texture appearing on cooling at 1 °C min^{-1} showed a quite different type of texture from those of the Sm phases and it is similar to that of a Col mesophase formed by disc-shaped mesogens as seen in Fig. 1(b). A tiny difference in the isotropisation temperatures of these two mesophases was found (199.0 °C and 200.2 °C for the former and latter phases, respectively). The XRD measurement of the latter revealed that **1** shows a hexagonal columnar (Col$_h$) mesophase as shown in Fig. 2. The detected diffraction peaks showed the typical *d*-spacing ratio of Col$_h$ phase ($1 : 1/\surd 3 : 1/2 : 1/\surd 7$) for four reflections in the small angle region (49.0 Å, 28.0 Å, 24.5 Å and 18.0 Å). Furthermore, a broad halo was clearly observed at 4.5 Å, derived from the molten alkyl chains. The calculated lattice parameter, 56.6 Å is smaller than the expected diameter of the molecule (71 Å). A contact method with a known mesogen exhibiting SmA phase showed miscibility, indicating the former phase is a SmA phase.†

However, it was also observed that the "bâtonnets" phase is likely to gradually change to a Col phase when the sample was kept at the temperature at which the "bâtonnets" were formed (Fig. 1(c)). This indicates that this Sm phase is a thermodynamically metastable state and it is a transient layered structure. This phase was rather fluid like an ordinary smectic A phase. However, it was observed that cooling rates faster than 5 °C min^{-1} lead to formation of "bâtonnets" and a rate of 2–4 °C min^{-1} leads to the formation of both mesophases, while at 1 °C



Scheme 1

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† Electronic supplementary information (ESI) available: DSC traces and photos of mesophases. See http://www.rsc.org/suppdata/cc/b3/b301862h/

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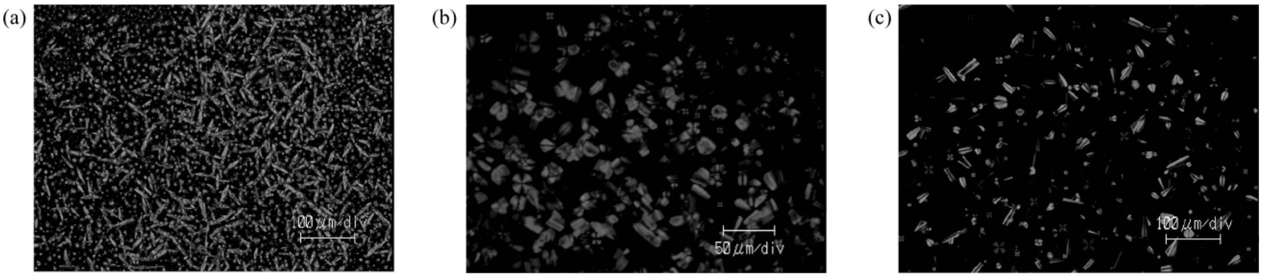


Fig. 1 Optical textures observed under crossed polarisers. On cooling at (a) 5 °C min^{-1} (199.1 °C), (b) 1 °C min^{-1} (199.5 °C), and (c) on standing of (a) at 199.1 °C for 100 min. An O-58 filter was used for texture observations.

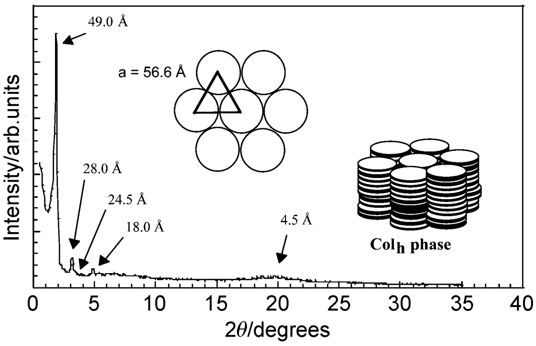
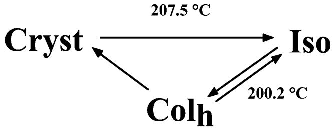


Fig. 2 X-Ray diffraction pattern at 195 °C for a mesophase obtained on cooling at 1 °C min^{-1}.



Scheme 2

min^{-1} only a Col$_h$ phase is formed. The "bâtonnets" phase could not be identified as a so-called discotic lamellar phase as its typical texture is still unknown and it is a highly viscous state.[8]

DSC measurements at 5 °C min^{-1} and 1 °C min^{-1} were also carried out. In the latter case, Col$_h$ phase formation was detected as an exothermic peak (ΔH = 15.5 kJ mol^{-1}) and in the former, an exothermic peak was observed with a shoulder in the lower temperature region.† This value is quite large in general as compared with typical Col$_h$–I transitions, probably due to the strong interaction among the azobenzene units. The thermodynamically most stable phase sequence is summarised in Scheme 2. Recently a similar type of mesogen with a different linkage group was reported to show mesomorphic behaviour. However, there is no mention of such unusual behaviour in the phase transition.[9]

This phenomenon could be interpreted by the consideration of a molecular shape change in the process of mesophase formation. The rod-shape is more favourable when the system is cooled at a relatively rapid rate, while the molecule is likely to be a disc-shape as a most stable conformation. The linkage between the triphenylene moiety and the peripheral azobenzenes is flexible and this allows such a conformational change in mesophase formation. Therefore, rod-shaped parts are more likely to recognise each other and form a smectic layered structure on rapid cooling, meaning that molecular recognition among the rod-shaped parts takes priority to that among the central core.

Finally, it was interestingly found in the texture observation that the *trans–cis* photoisomerisation of the azobenzene moieties in Col$_h$ mesophase induces an acceleration of the isothermal and spontaneous phase transition from Sm to Col and also Col to I phases. This may indicate that the photochemical change in the azo moieties no longer makes the molecules behave as rod-shaped because of the formation of the *cis*-isomer and the *cis*-contaminant molecules can act in the mesophase formation as disc-like, followed by isotropisation with further increase of *cis*-isomers.§

Notes and references

‡ ^{1}H-NMR (400 MHz, CDCl$_3$, δin ppm) :0.88 (t, 18H, J = 7.0 Hz, C=OCH$_2$CH$_2$(CH$_2$)$_7$$CH_3$),1.19–1.62 (m, 84H, OCH$_2CH_2$$(CH_2)_7$), 1.81 (quintet, 12H, J = 6.6 Hz, OCH$_2$$CH_2$), 2.13 (quintet, 12H, J = 7.5 Hz, C$_6$H$_4$CH$_2$CH$_2$$CH_2$), 2.62 (t, 12H, J = 7.5 Hz, C$_6$H$_4$CH$_2$$CH_2CH_2$), 2.78 (t, 12H, J = 7.5 Hz, C$_6$H$_4$$CH_2CH_2CH_2$), 4.01 (t, 2H, J = 6.6 Hz, OCH_2), 6.97 (d, 12H, J = 8.9 Hz, azobenzene-*H*), 7.30 (d, 12H, J = 8.3 Hz, azobenzene-*H*), 7.80 (d, 12H, J = 8.3 Hz, azobenzene-*H*), 7.87 (d, 12H, J = 8.9 Hz, azobenzene-*H*), 8.25 (s, 6H, triphenylene-*H*); IR (KBr, ν/cm^{-1}) 2923, 2854, 1764, 1602, 1252; MALDI TOF-MAS: 2765.57 for C$_{174}$H$_{216}$N$_{12}$O$_{18}$ = 2763.69; Elemental Analysis Calcd: C, 75.62; H, 7.88; N, 6.08. Found: C, 75.54; H, 7.85; N, 6.13%.

§ A 250 W Hg lamp was used for the light incidence with a bandpass filter (365 nm). The experiment was done at 197.1 °C.

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