Highly Oriented Fibres of Discotic Liquid Crystals

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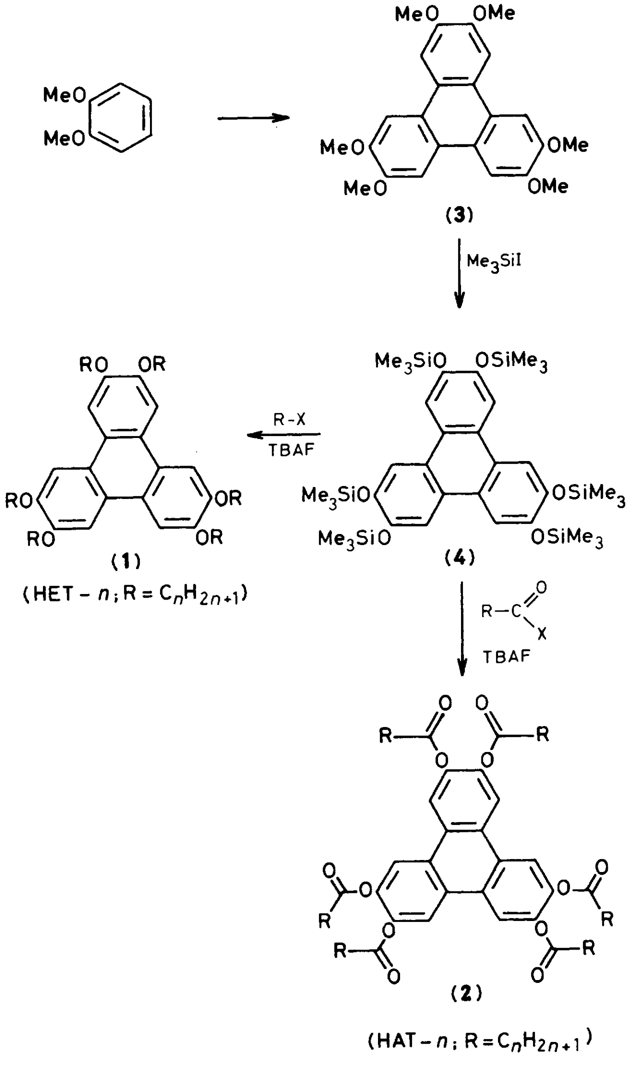
Highly aligned discotic liquid crystal fibres of hexa-alkoxytriphenylene (HET-*n*) and its ester derivative (HAT-*n*) can be drawn by a new strand technique; our synchrotron *X*-ray scattering study indicates the single crystal quality of these fibres.

The alignment of discotic liquid crystals (DLCs) is an active research area. Several alignment techniques including use of a rotating magnetic field[1] and various surface treatments[2] have resulted in limited degrees of alignment. We report here on highly oriented discotic liquid crystal fibres of hexa-alkoxytriphenylene [HET-*n*, (**1**)] and triphenylenehexa-n-alkanoate[3] [HAT-*n*, (**2**)] obtained by a new strand alignment technique. Our synchrotron *X*-ray scattering studies[4] demonstrate the single crystal quality of these fibres, while they are maintained at their fluid-like columnar phase temperatures. These results provide evidence of the most reliable technique to date for the alignment of DLCs.

The origin of our approach relies on the tendency of DLC ordering to occur at its mesophase temperature. Unlike the two-dimensional layered structure of smectic phases of rod-like liquid crystals, discotic liquid crystals exhibit a new kind of columnar liquid crystalline phase.[5] In the columnar phases, the disc-shaped molecules are irregularly stacked into infinite columns with long-range intercolumn positional order. We have, therefore, utilized the structural nature of these phases to orient the molecules.



Scheme 1

The two series of DLC used in this study were synthesized by a new route from a common intermediate of hexamethoxytriphenylene[6] (**3**), as shown in Scheme 1. The demethylation reaction of hexamethoxytriphenylene with trimethylsilyl iodide was carried out in a chloroform solution at its refluxing temperature. Without the isolation of intermediate (**4**), the reaction mixture was treated by very slow addition of tetrabutylammonium fluoride (TBAF) in tetrahydrofuran solution in the presence of an alkyl halide or alkanoyl chloride at 80 °C to afford triphenylenehexa-alkanoate (**2**) in a 72% yield or hexa-alkoxytriphenylene (**1**) in a 54% yield.

Freely suspended fibres[7] were drawn in a two-stage oven consisting of a mechanically operated pin and a reservoir cup. The temperature of both pin and cup was monitored to a stability of 0.01 °C. The metal pin was connected to a series of gears which provide a low, smooth pulling motion of the pin.

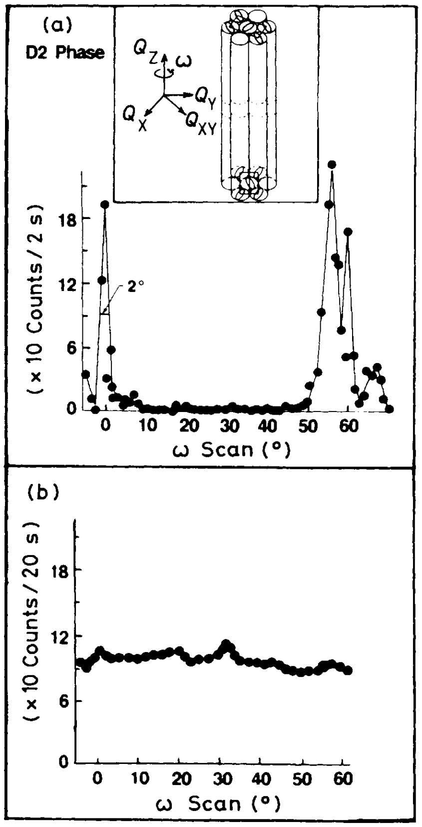


Figure 1. Synchrotron *X*-ray scattering data of an HAT-11 fibre.

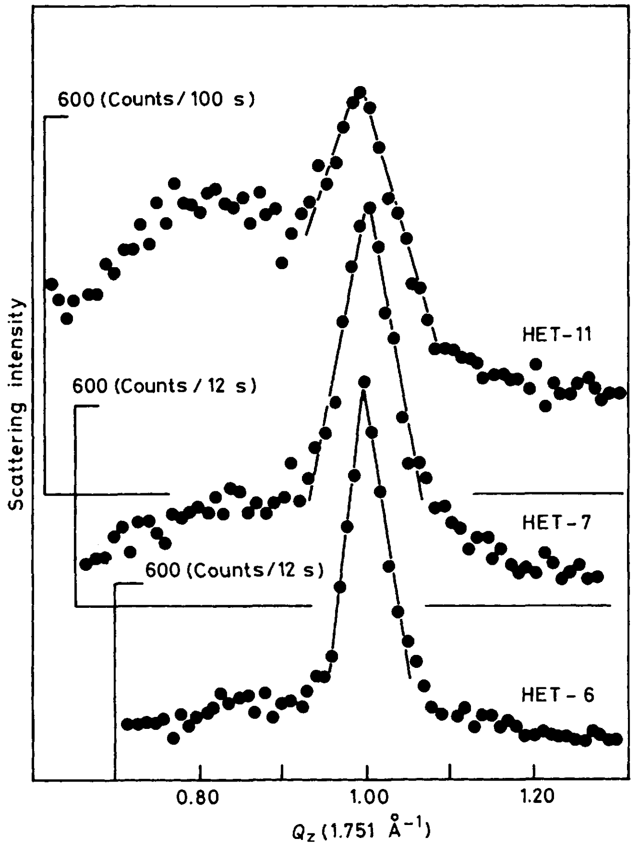


Figure 2. X-Ray scattering scan along the stacking direction of HET-n compounds. The strong structural evolution in the columns as a function of chain length is observed.

The process was operated at a narrow temperature range within the columnar phase of discotic liquid crystals (**1**) and (**2**). A typical fibre of 1—3 mm length with a diameter between 50 and 400 μm was obtained. The resulting colourless and semi-transparent fibres are apparently stable and isolatable. The ease of drawing depends on the length of alkyl substituent. Thus, a compound containing a higher alkyl tail is more easily drawn.

The single crystal quality of fibres of both (**1**) and (**2**) is substantiated by the synchrotron X-ray scattering studies. We show in Figure 1 the scattering data of an HAT-11 (**2**, n = 11) fibre at T = 112 °C in the D2 mesophase with the molecules packed into segregated columns with a hexagonal in-plane (the plane Q_{XY} perpendicular to the columnar axis Q_Z as shown in top panel to Figure 1a) structure. To determine the degree of the lattice mosacity, we carried out the usual crystallographic ω (rocking curve) scans through the in-plane hexagonal peaks by rotating the fibre about the Q_Z axis. Without the strand alignment, the ω scan shows a disoriented powder-like flat spectrum (Figure 1b). On the other hand, with the strand alignment of the sample, the ω scan (Figure 1a) shows two narrow bunches of peaks of width between 1 to 2° spaced by 60° (hexagonal periodicity). This indicates that the in-plane structure contains a few single column lattice domains separated by a few degrees. Annealing improves the mosaic width of the ω scan to between 0.15 and 0.3°.

The degree of liquid ordering of molecules inside columns of these DLC fibres has also been studied. Our X-ray scattering data reveal only a liquid-like short range ordering in HAT-n fibres. However, in the HET-n series of compounds, we find that the liquid peak (Figure 2) narrows as n (chain length) decreases indicating longer ranged intermolecular correlations. This correlation length increases significantly from 3—4 nearest neighbour to more than 12 nearest neighbour as n decreases from 11 to 6.

These results allow us to conclude that we are able to draw discotic liquid crystalline materials into highly aligned fibres possessing a nearly single crystal quality at their columnar mesophase temperature by a strand technique using a two-thermal-stage oven. Therefore, this strand technique is a reliable method to align discotic liquid crystals for studies of their physical properties.

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