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Liquid Crystals Today

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713681230>

Materials Highlights

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To cite this Article Imrie, Corrie T.(1995) 'Materials Highlights', *Liquid Crystals Today*, 5: 2, 3 — 4

To link to this Article: DOI: 10.1080/13583149508047592

URL: <http://dx.doi.org/10.1080/13583149508047592>

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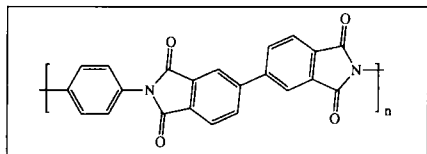
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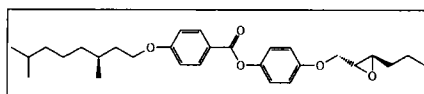
Materials Highlights

Corrie T. Imrie, University of Aberdeen

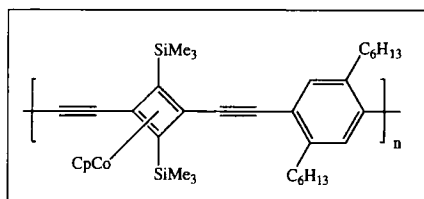
The alignment of liquid crystals in display devices is normally achieved using rubbed polyimide films. It has been known for many years that buffing the polymer with a cloth gives rise to alignment in the rubbing direction. The molecular origins of this important effect, however, have been the subject of considerable speculation. Toney and his colleagues (*Nature* 1995 **374** 709) have used grazing-incidence X-ray scattering (GIXS) to determine the effect of rubbing on the near-surface region of the polyimide films. The polyamic acid ester, **1**, of bisphenylene-dianhydride and *p*-phenylenediamine was used in this study. The results for two films of different thicknesses, 6 nm and 200 nm respectively, were discussed. These studies show that for the thicker film, the majority of the polymer chains within 5 nm of the surface are aligned in the rubbing direction while for the thinner film essentially all the macromolecular chains become aligned. This high degree of alignment is quite remarkable given the small loads applied during rubbing and the fact that the temperature at which the experiments were performed was several hundred degrees below the polymer's glass transition temperature. The authors proposed that the oriented macromolecular chains at the film surface serve as a molecular template in aligning the liquid crystal molecules.



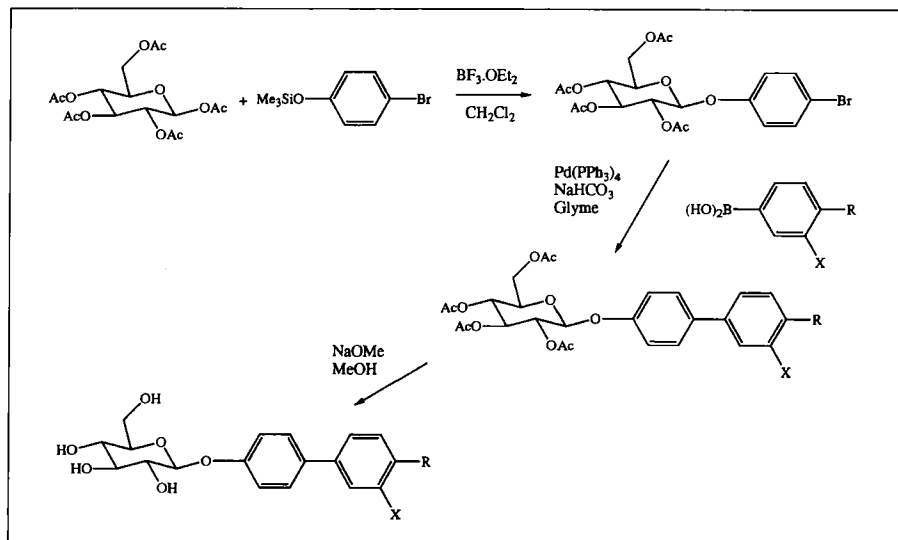
The question of the surface alignment of liquid crystals has been addressed also by Walba and his co-workers (*Science* 1995 **267** 1144) who used scanning tunnelling microscopy (STM) to obtain near-atomic resolution images of a chiral liquid crystal, **2**, adsorbed on graphite. This particular mesogenic compound was chosen, in part, because it contains functional groups not previously studied using STM. These studies revealed the formation of a two-dimensional heteroepitaxial crystal on the surface. Studies such as this should provide the basis for developing a greater understanding of the liquid crystal–solid interface.



Low molar mass metallomesogens have attracted considerable research interest in recent years. By contrast their polymeric counterparts have received much less attention. Altmann and Bunz (*Angew. Chem. Int. Ed. Engl.* 1995 **34** 569) have reported the first example of a thermotropic organometallic mesogenic polymer, **3**, which is constructed around 1,3-diethynylcyclobutadiene (cyclopentadienyl)cobalt. The polymer undergoes two transitions: at 115°C the side chains melt and at 160°C a nematic phase forms. Decomposition occurred before the clearing transition.



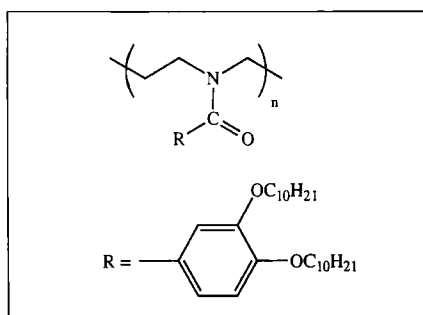
The clearing temperatures of amphiphilic carbohydrate-based liquid crystals are known to be enhanced by the introduction of rigid moieties, such as benzene or cyclohexane, into the hydrophobic chain. Synthetic difficulties have precluded extending the length of this rigid unit but Müller and Tschierske (*J. Chem. Soc., Chem. Commun.* 1995 645) have now described a synthetic route for the preparation of such materials, see Scheme 1. The key step in this scheme is the palladium-catalysed cross-coupling of



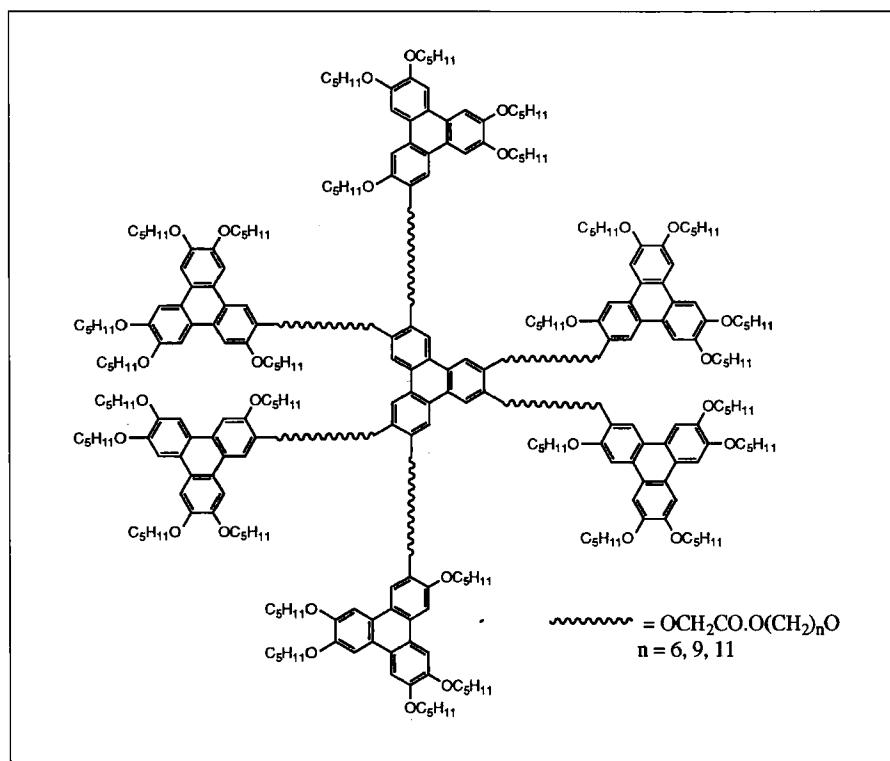
a 4-bromophenyl-β-O-D-tetraacetylglucoside with a boronic acid derivative. A wide range of materials have been prepared using this methodology and these reveal that the tetraacetate intermediates are not liquid crystalline whereas the glucosides are enantiotropic liquid crystals with high clearing temperatures. The authors consider hydrogen bonding between the hydroxy groups to be at the root of mesophase formation but liquid crystallinity is further enhanced by the anisotropic interactions between the biphenyl groups.

Hexagonal columnar mesophases are exhibited by a range of differing molecular structures including disk-shaped molecules, rigid macromolecules with flexible side-chains and macrocyclic oligoamines. Recently, open chain *N*-acylated oligoamines were reported also to exhibit hexagonal columnar behaviour (Stebani, U., *et al. Adv. Mater.* 1994 **6** 572). In these compounds hydrogen bonding between the terminal amide units result in a disk-like structure. Ringsdorf and his colleagues (*Angew. Chem. Int. Ed. Engl.* 1995 **34** 795) have now shown that a linear *N*-acylated poly(ethylenimine), **4**, also exhibits columnar hexagonal phases. The authors propose that the polymer may form a helical structure driven by the steric requirements of the bulky side-chains, and note that these polymers form the bridge between hexagonal columnar phases comprising of disk-like molecules and those formed by linear rigid polymers.

Continuing with the theme of columnar hexagonal mesophases,



Ringsdorf and his co-workers (*Liq. Crystals* 1995 **18** 185) have reported a novel class of discotic liquid crystals in which a central core is flanked by a further six discotic moieties and termed such molecules star-like. This molecular architecture was realized using triphenylene cores, **5**, and the authors noted that the arrangement of the discs within the molecule was analogous to that within a hexagonal columnar phase. These materials do indeed exhibit hexagonal columnar phases and their clearing temperatures are significantly higher than that of a model compound consisting of just a single triphenylene core. This enhanced mesophase stability was attributed to the pre-organization of the triphenylene units at the molecular level. The authors note that there exists



two possible packing arrangements for molecules of this type: the molecules either arrange into discrete columns or are mixed between columns. The authors

propose that the latter arrangement is favoured by these systems but suggest that chemical modification could result in the former arrangement being observed.

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