SUPRAMOLECULAR SIDE-CHAIN LIQUID CRYSTAL POLYMERS

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Supramolecular liquid crystals are mixtures in which specific non-covalent interactions between *differing* species give rise to either enhanced or induced liquid crystalline behaviour and such systems are attracting increasing interest as a means of developing novel mesogenic materials. The principal objective of the research programme was to determine the extent to which specific non-covalent interactions could be used to control the liquid crystalline behaviour of side-chain polymers. The research focused on two types of interaction: hydrogen bonding and charge transfer.

A detailed study was performed of the phase behaviour of binary mixtures of mesogenic acids and conventional polymers such as poly(4-vinyl pyridine), poly(2-vinyl pyridine) (P2VP) and polystyrene. These systems exhibited very limited miscibility and tended to phase separate. The liquid crystallinity observed for these mixtures was, therefore, attributed to phase separated acid regions. The interphase regions in these blends were stabilised via hydrogen bonding between the unlike components. This interpretation was in stark contrast to claims in the literature that these systems yielded supramolecular side-chain liquid crystal polymers. We attempted to enhance the miscibility of this type of system by using complementary units containing multiple binding sites but such systems were also essentially immiscible.

It became clear that the mesogenic groups were inherently insoluble in the polymer matrix and this was largely responsible for the observed phase separation in the acid-polymer mixtures. In order to overcome this difficulty, we developed a template approach in order to realise supramolecular side-chain liquid crystal polymers. The key structural factor is the introduction of mesogenic side-chains to the polymeric receptor which assist in miscibilising the low molar mass substrate; template polymers were prepared containing both 4-vinyl pyridine and 2-vinyl pyridine segments. The templates containing 4-vinyl pyridine were the most effective in enhancing liquid crystalline behaviour. Thus, it appears that the covalently bound mesogenic side-chains not only acts as solubilisers for the mesogenic acids but also impart a degree of selectivity into the complex formation. In addition, we have also studied blends in which the mesogenic groups in the substrate exhibit a specific electron-donor-acceptor interaction with those in the template polymer.

The study of the role of non-covalent interactions in determining liquid crystalline behaviour has been restricted to the effects on transition temperatures and, to a lesser extent, phase type. To the best of our knowledge, the control of the degree of molecular order within the mesophase, an important parameter in electro-optic technologies, had not been attempted using non-covalent interactions between unlike species. In low molar mass systems, it is well-known that dimeric liquid crystals comprising two mesogenic groups linked *via* a flexible spacer exhibit mesophases having unusually high degrees of order. Thus, we characterised the thermal behaviour of mixtures in which hydrogen bond formation gave rise to a supramolecular side-chain liquid crystal polymer containing two mesogenic groups per side-chain. These supramolecular complexes did indeed exhibit mesophases in which the translational and orientational ordering were unusually high.

Two classes of systems were investigated for which it was expected that charge-transfer interactions would give rise to supramolecular liquid crystal polymers. The first of these involved blending discotic side-chain liquid crystal polymers with various electron acceptors and enhanced liquid crystalline behaviour was observed. This study included the development of a new synthetic methodology for the preparation of discotic side chain polymers. The second general system involved blends of electron deficient polymers with triphenylene derivatives; surprisingly many of these mixtures gave amorphous materials which are to be evaluated in terms of their photoconductivity.

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