

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### Supramolecular side chain liquid crystal polymers II. Interaction of mesogenic acids and amorphous polymers

David Stewart<sup>a</sup>; Corrie T. Imrie<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Aberdeen, Scotland, UK

**To cite this Article** Stewart, David and Imrie, Corrie T.(1996) 'Supramolecular side chain liquid crystal polymers II. Interaction of mesogenic acids and amorphous polymers', *Liquid Crystals*, 20: 5, 619 – 625

**To link to this Article:** DOI: 10.1080/02678299608031151

**URL:** <http://dx.doi.org/10.1080/02678299608031151>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Supramolecular side chain liquid crystal polymers

## II. Interaction of mesogenic acids and amorphous polymers†

by DAVID STEWART and CORRIE T. IMRIE\*

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen  
AB9 2UE, Scotland, UK

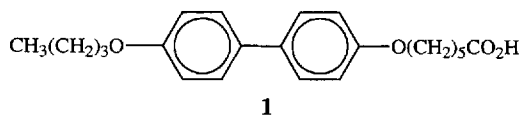
(Received 11 August 1995; in final form 24 September 1995; accepted 21 December 1995)

The thermal behaviour of blends of a low molar mass mesogenic acid, 6-(4-*n*-butyloxy-4'-oxybiphenyl)hexanoic acid (BOBPOHA) with polystyrene, poly(2-vinylpyridine) and poly(4-vinylpyridine) has been characterized. BOBPOHA exhibits a monotropic smectic A phase and is essentially immiscible with polystyrene. Thus, the transition temperatures of the acid are independent of blend composition. In contrast, the thermal properties of the acid are strongly modified on blending with poly(2-vinylpyridine) and poly(4-vinylpyridine). Molecular mixing occurs in these blends below approximately 0.2 mol fraction of acid. This miscibility is driven by the formation of hydrogen bonds between the pyridyl and acid moieties. At higher concentrations of acid, phase separation occurs. Liquid crystallinity is not observed in the miscible blends while in the immiscible blends mesomorphic behaviour is attributed to regions of phase separated acid.

### 1. Introduction

Side chain liquid crystal polymers are continuing to be the focus of considerable research activity. This arises not only from their considerable application potential in a wide range of electro-optic devices [1], but also because they provide a demanding challenge to our understanding of the molecular factors that promote self-organization in polymeric systems [2, 3]. A side chain liquid crystal polymer comprises three distinct structural units: a polymer backbone, a flexible spacer (usually an alkyl chain) and a mesogenic unit which is attached as a pendant to the polymer backbone via the spacer [2, 3]. In essence, the spacer partially decouples the tendency of the polymer backbones to adopt random coil conformations from that of the mesogenic groups to self-assemble into mesophases. The effects of varying the chemical nature of these structural units on the thermal properties of the polymer are well documented and form the basis of a set of empirical rules used in the rational design of new materials exhibiting targeted properties [2, 3]. Recently, a novel class of side chain liquid crystal polymers has been reported in which the novelty arises through the mode of linkage of the spacer to the polymer backbone [4]. In a conventional side chain liquid crystal polymer, the spacer is attached to the polymer backbone via a covalent linkage whereas in

this novel class of materials non-covalent interactions are employed to link the polymer and the side chain [4]. This is a quite different design strategy to that described by Fréchet, Kato and co-workers [5–7] in which hydrogen bonding is used to assemble the mesogenic unit. In order to achieve the former supramolecular assembly, the polymer and low molar mass side chain must possess complementary binding sites. Ujiie *et al.* [8–10] reported the first examples of this class of materials in which the side chain was attached to the macromolecule through an ionic interaction; for example, blends of a poly(vinyl sulphonate) anion and a cationic mesogenic side chain exhibit considerably enhanced clearing temperatures over those of the individual components [10]. Bazuin and Brandys [11, 12] have proposed that a much weaker interaction, the hydrogen bond, may also be used in the construction of these materials, citing the phase behaviour of mixtures of poly(4-vinylpyridine) (P4VP) and a mesogenic acid, 6-(4-*n*-butyloxy-4'-oxybiphenyl)hexanoic acid, 1:

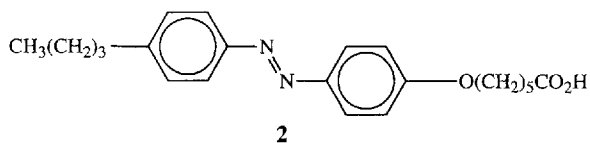


The authors initially interpreted the thermal behaviour of these mixtures in terms of the formation of a supramolecular side chain liquid crystal polymer [11], although later they modified this view [12]. To investigate the generality of this model, we investigated the

\* Author for correspondence.

†Part 1 in this series: D. Stewart and C. T. Imrie, 1995, *J. Mater. Chem.*, **5**, 223.

thermal behaviour of a structurally similar mesogenic acid, 6-(4-*n*-butylazobenzene-4'-oxy)hexanoic acid, **2** (BABOHA) not only with poly(4-vinylpyridine) (P4VP) but also with polystyrene (PS) and poly(2-vinylpyridine) (P2VP) [13].



The behaviour of these systems was not compatible with the formation of a supramolecular side chain liquid crystal polymer as proposed by Bazuin and Brandys [11]. Instead we suggested that only partial complexation of the polymer backbone by the acid occurs and this supramolecular copolymer is responsible for the observed modification of the thermal behaviour of the acid [13]. In order to investigate the apparent difference in behaviour between these two very similar systems, we have now undertaken a similar study using acid **1** in which the thermal behaviours of blends with polystyrene (PS), poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) have been characterized. The acronym used to refer to the mesogenic acid **1** is BOBPOHA.

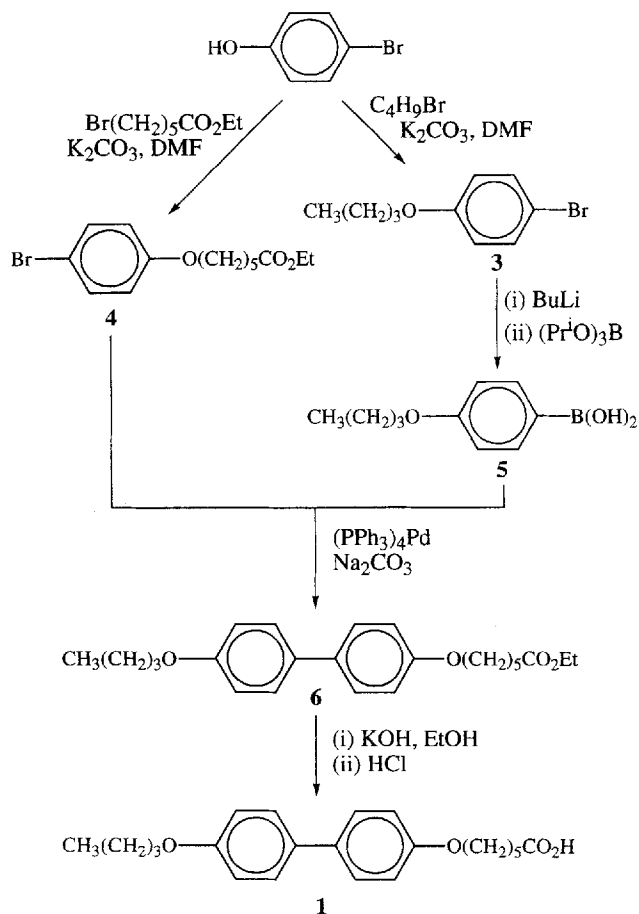
## 2. Experimental

BOBPOHA, **1**, was obtained via the synthetic route outlined in the Scheme. Attempts to synthesize BOBPOHA via the mono-substitution of 4,4'-dihydroxybiphenyl with 1-bromobutane and subsequent reaction of the product with ethyl 6-bromohexanoate, followed by alkaline hydrolysis, were unsuccessful.

### 2.1. 4-*n*-Butyloxybromobenzene, **3** [14]

A mixture of 4-bromophenol (20.1 g, 116 mmol), 1-bromobutane (16.6 g, 121 mmol), potassium carbonate (33.4 g, 242 mmol) and DMF (150 ml) was heated with stirring at 120°C overnight. The reaction mixture was allowed to cool, poured into water (1.5 L) and the resulting solution shaken twice with dichloromethane. The combined organic extracts were washed successively with water, 5 per cent aqueous NaOH solution and twice more with water. The organic layer was collected, dried over MgSO<sub>4</sub> and the solvent removed. The resulting liquid was distilled from calcium hydride under reduced pressure using a Kugelrohr apparatus. Yield: 19.9 g, 75 per cent.

<sup>1</sup>H NMR, δ(CDCl<sub>3</sub>) 6.9 and 7.1 (m, aromatic, 4H), 4.0 (t, ArOCH<sub>2</sub>-2H, *J*=6.7 Hz), 2.6 (m, ArOCH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 2H) 1.0-1.8 (m, ArOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 5H).



Scheme 1.

### 2.2. Ethyl 6-(4-bromophenoxy)hexanoate, **4**

A mixture of 4-bromophenol (10.0 g, 58 mmol), ethyl 6-bromohexanoate (13.3 g, 60 mmol), potassium carbonate (27.3 g, 198 mmol) and DMF (150 ml) was heated with stirring at 120°C overnight. The work-up of the reaction mixture was identical to that described for **3**. Yield: 10.9 g, 58 per cent.

IR (NaCl) 1743 cm<sup>-1</sup> (vs C=O). <sup>1</sup>H NMR, δ(CDCl<sub>3</sub>) 6.8 and 7.4 (m, aromatic, 4H), 4.1 (q, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 2H, *J*=7.1 Hz), 3.9 (t, ArOCH<sub>2</sub>, 2H, *J*=6.4 Hz), 2.3 (t, CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 2H, *J*=7.4 Hz), 1.3-1.9 (m, ArOCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>, 6H), 1.2 (t, CH<sub>3</sub>, 3H, *J*=7.1 Hz).

### 2.3. 4-*n*-Butyloxyphenylboronic acid, **5** [14]

**5** was prepared according to the method outlined by Gray *et al.* [15]. Thus, 4-*n*-butyloxybromobenzene, **3** (10.0 g, 44 mmol) was degassed on a vacuum line by the freeze-pump-thaw method. THF (50 ml) was distilled from Na/benzophenone onto **3** and the reaction vessel flushed with argon for 15 min. *n*-Butyl lithium (6.0 ml of 10.0 M solution in hexane) was injected at -80°C into the flask and the mixture left stirring under a positive

argon overpressure at  $-80^{\circ}\text{C}$  for 2 h. A solution of triisopropyl borate (28 ml, 121 mmol) in dry THF (30 ml) cooled to  $-80^{\circ}\text{C}$  was then injected into the reaction mixture. The stirred mixture was left under argon and allowed to warm to room temperature overnight. Hydrochloric acid (3 M, 60 ml) was added and the reaction mixture allowed to stir at room temperature for a further hour. The mixture was shaken twice with ether and the combined ethereal extracts were washed twice with water. The organic layer was dried over  $\text{MgSO}_4$  and the solvent removed. The crude product was recrystallized from ethanol and dried overnight under vacuum. Yield: 4.0 g, 47 per cent, mp  $130^{\circ}\text{C}$ .

$^1\text{H}$  NMR,  $\delta(\text{CDCl}_3)$  7.1 and 6.9 (m, aromatic, 4H), 4.0 (t,  $\text{ArOCH}_2$ , 2H,  $J=7.2$  Hz), 2.5 (m,  $\text{ArOCH}_2\text{-CH}_2\text{CH}_2\text{CH}_3$ , 2H), 0.9–1.8 (m,  $\text{ArO}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$ , 5H).

#### 2.4. Ethyl 6-(4-*n*-butyloxy-4'-oxybiphenyl)hexanoate, **6**

**6** was prepared according to the method described by Gray *et al.* [15]. Thus, a solution of **5** (3.2 g, 16.5 mmol) in ethanol (30 ml) was added to a stirred mixture of **4** (3.8 g, 13 mmol), tetrakis(triphenylphosphine)palladium(0) (0.49 g, 0.42 mmol), sodium carbonate (6.4 g, 60 mmol), benzene (30 ml) and water (30 ml). The resulting mixture was heated with stirring at  $95^{\circ}\text{C}$  for 24 h under a constant overpressure of argon. After cooling, the reaction mixture was shaken twice with ether and the combined ethereal extracts were washed with water, brine and finally twice more with water. The organic layer was dried over  $\text{MgSO}_4$  and the solvent removed. The resulting solid was recrystallized from ethanol and dried overnight under vacuum. Yield: 3.9 g, 80 per cent; mp  $100^{\circ}\text{C}$ .

IR (KBr)  $1736\text{ cm}^{-1}$  (vs C=O).  $^1\text{H}$  NMR,  $\delta(\text{CDCl}_3)$  7.5 and 6.9 (m, aromatic, 8H), 4.1 (q,  $\text{CO}_2\text{CH}_2\text{CH}_3$ , 2H,  $J=7.1$  Hz), 3.9 (t,  $\text{ArOCH}_2$ , 4H,  $J=6.5$  Hz), 2.3 (t,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ , 2H,  $J=7.4$  Hz), 1.9–1.2 (m,  $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OAr}$ ,  $\text{ArOCH}_2(\text{CH}_2)_3\text{CH}_2\text{CO}_2$ , 10H), 1.2 (t,  $\text{CO}_2\text{CH}_2\text{CH}_3$ , 3H,  $J=7.1$  Hz), 1.0 (t,  $\text{CH}_3(\text{CH}_2)_3\text{OAr}$ , 3H,  $J=7.3$  Hz).

#### 2.5. 6-(4-*n*-Butyloxy-4'-oxybiphenyl)hexanoic acid, **1**

A mixture of **6** (3.9 g, 10.0 mmol), potassium hydroxide (20 g, 357 mmol) ethanol (50 ml) and water (100 ml) was heated under reflux with stirring for 48 h. The reaction mixture was added to boiling water (1 l) and filtered hot. The hot filtrate was acidified with dilute hydrochloric acid and allowed to cool. The resulting precipitate was collected, recrystallized from ethanol and dried overnight under vacuum. Yield: 2.9 g, 80 per cent; mp  $161^{\circ}\text{C}$ , lit. value  $160^{\circ}\text{C}$  [12].

IR (KBr)  $1700$  (vs C=O).  $^1\text{H}$  NMR,  $\delta(\text{CDCl}_3)$  7.5 and 6.9 (m, aromatic, 8H), 4.0 (t,  $\text{ArOCH}_2$ , 4H,  $J=6.4$  Hz),

2.4 (t,  $\text{CH}_2\text{CO}_2\text{H}$ , 2H,  $J=7.3$  Hz), 1.4–2.0 (m,  $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OAr}$ ,  $\text{ArOCH}_2(\text{CH}_2)_3\text{CH}_2\text{CO}_2\text{H}$ , 10H), 1.0 (t,  $\text{CH}_3$ , 3H,  $J=7.3$  Hz).

#### 2.6. Polymers

Polystyrene (Aldrich molecular weight standard,  $M_v=45\,730$ ) and poly(2-vinylpyridine) (Polysciences, MW 200 000) were used without further purification. Poly(4-vinylpyridine) was prepared via a free radical mechanism as described previously [13].

#### 2.7. Blends

Blends of BOBPOHA with polystyrene and poly(2-vinylpyridine) were prepared by codissolving the components in THF and allowing the solvent to evaporate slowly. The blends with poly(4-vinylpyridine) were prepared in a similar manner using pyridine as the solvent. All the mixtures were dried under vacuum for at least 48 h prior to characterization.

#### 2.8. General

$^1\text{H}$  NMR spectra were recorded on samples dissolved in  $\text{CDCl}_3$ , using a Bruker AC-F 250 MHz NMR spectrometer. IR spectra were recorded using an ATI Mattson Genesis Series FTIR spectrometer. The IR spectra of the equimolar blends of BOBPOHA with each polymer were recorded as thin films on NaCl discs. Each film was heat treated under vacuum at  $150^{\circ}\text{C}$  for 20 min prior to characterization.

The thermal behaviour of the mixtures was characterized by differential scanning calorimetry using a Polymer Laboratories PL-DSC instrument equipped with an autocool accessory and calibrated using indium. The time-temperature profile was identical in each sample, namely heated from  $25^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ , held at  $200^{\circ}\text{C}$  for 3 min, cooled from 200 to  $-50^{\circ}\text{C}$ , held at  $-50^{\circ}\text{C}$  for 3 min and finally reheated from  $-50$  to  $200^{\circ}\text{C}$ . The heating and cooling rates in all cases were  $10^{\circ}\text{C min}^{-1}$ . Phase identification was performed by polarized light microscopy using an Olympus BH-2 optical microscope equipped with a Linkam THMS 600 heating stage and TMS 91 control unit.

### 3. Results and discussion

#### 3.1. BOBPOHA, **1**

BOBPOHA, **1**, melts directly into the isotropic phase at  $161^{\circ}\text{C}$ . On cooling, however, bâtonnets develop at  $155^{\circ}\text{C}$  which coalesce to give a well defined focal-conic fan texture. Thus the phase is assigned as a smectic A. This clearing temperature is almost  $20^{\circ}\text{C}$  higher than that first reported by Bazuin and Brandys [11], but in excellent agreement with their subsequent report [12]. It is interesting to note that if the carboxylic acid group in **1** is replaced by a methyl group then the resulting

compound would be expected to exhibit a clearing temperature of approximately 110°C [13]. The actual clearing temperature of **1** is considerably higher than this value, strongly suggesting that, as is well established in early literature, hydrogen bonded dimers enhance the thermal stability of mesophases; a similar argument was used to rationalize the high clearing temperature exhibited by **2** [13].

### 3.2. PS-BOBPOHA blends

The dependence of the transition temperatures, extracted from the DSC data, on the mol fraction of acid in the PS-BOBPOHA blend is shown in figure 1. The polystyrene used in these investigations exhibited a glass transition temperature ( $T_g$ ) at 102°C. The melting points and smectic A–isotropic transition temperatures are essentially constant over almost the entire composition range. For the 0.09 mol fraction of BOBPOHA mixture, small decreases in these temperatures are observed, while for the 0.06 mol fraction acid blend the melting point is further decreased and no liquid crystallinity is observed. Optical microscopy revealed that the isotropic phase exhibited by all these blends was phase separated, but for the crystal and smectic A phases, uniform textures were observed over the whole preparation. This suggests that one phase consists of droplets of BOBPOHA in a PS matrix, while in the second phase droplets of PS are dispersed in an acid matrix. The size of these droplets presumably lies below the resolving power of the microscope, resulting in the observation of uniform textures for the Cr and  $S_A$  phases. The  $T_g$  of PS is essentially constant after the addition of 0.06 mol fraction of acid. The absence of liquid crystallinity for the 0.06 mol fraction acid blend reflects a greater reduction in the clearing temperature of the acid than in its

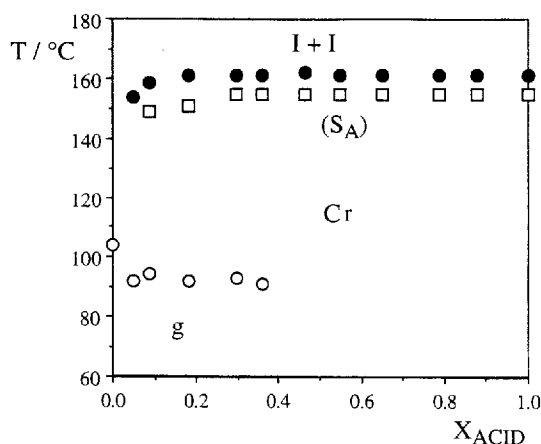


Figure 1. The dependence of the crystal–isotropic (●), smectic A–isotropic (□) and glass transition temperatures (○) on the mol fraction of BOBPOHA in the polystyrene-based blends. I isotropic;  $S_A$  smectic A; Cr crystal.

melting point. The smectic–isotropic transition is thermodynamically considerably weaker than the crystal–isotropic transition and, hence, more sensitive to the presence of small amounts of PS. The dependence of the enthalpy change, expressed per mol of acid, associated with the crystal–isotropic transition is shown in figure 2 and the melting enthalpy is, within experimental error, independent of blend composition. Similar behaviour is observed also for the smectic–isotropic enthalpy change, although the data are more scattered because these values are very small for the more dilute acid blends, making the associated error in their measurement relatively large.

The behaviour of this system is qualitatively identical to that we reported for blends of acid **2** with PS [13] and implies that the two components are essentially immiscible. Thus there exist no significant interactions between the two components and the system may, therefore, be used as a control against which blends containing interacting components may be compared.

### 3.3. P4VP-BOBPOHA blends

In contrast to the thermal behaviour of the PS-BOBPOHA system, see figure 1, the transition temperatures exhibited by the P4VP-BOBPOHA blends show a marked composition dependence, see figure 3. Indeed, blends containing less than 0.17 mol fraction of acid remained isotropic on cooling to room temperature, implying molecular mixing of the components. An even greater reduction is observed in the smectic–isotropic transition temperature, and liquid crystallinity is extinguished when the mol fraction of acid falls below 0.79. This does not simply reflect an increased tendency towards crystallization as the acid concentration is reduced, as the samples can be extensively supercooled. P4VP exhibited a  $T_g$  at 155°C and this falls rapidly as

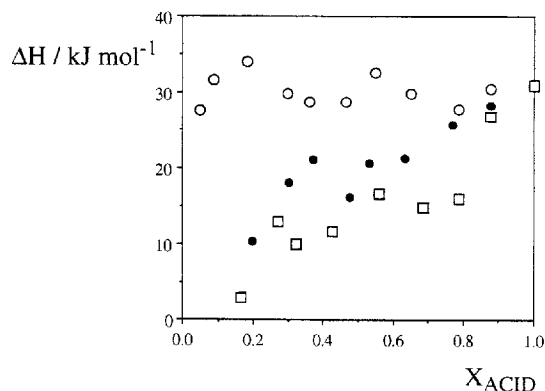


Figure 2. The dependence of the crystal–isotropic enthalpy, expressed per mol of acid, on the mol fraction of BOBPOHA in the blend. Polystyrene (○); poly(2-vinylpyridine) (●); poly(4-vinylpyridine) (□).

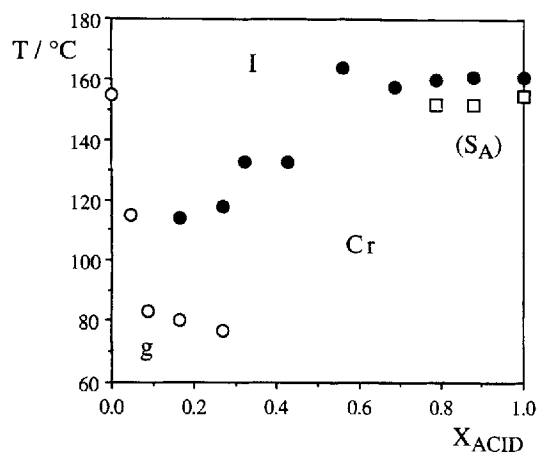


Figure 3. The dependence of the crystal–isotropic (●), smectic A–isotropic (□) and glass transition temperatures (○) on the mol fraction of BOBPOHA in the poly(4-vinylpyridine)-based blends. I isotropic; S<sub>A</sub> smectic A; Cr crystal.

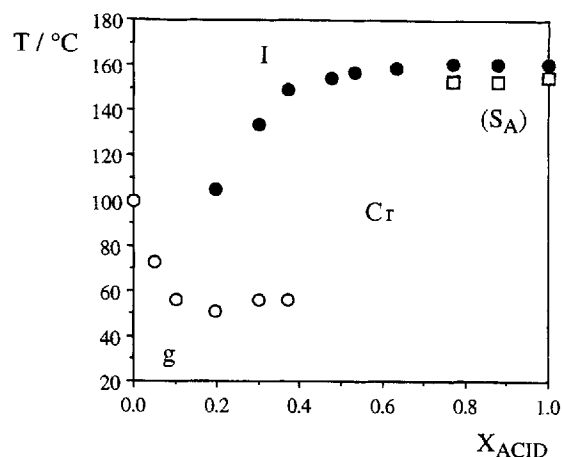


Figure 4. The dependence of the crystal–isotropic (●), smectic A–isotropic (□) and glass transition temperatures (○) on the mol fraction of BOBPOHA in the poly(2-vinylpyridine)-based blends. I isotropic; S<sub>A</sub> smectic A; Cr crystal.

the concentration of acid is increased before reaching a limiting value. It is important to note that no phase separation was observed in the isotropic phase for these blends. The enthalpy changes associated with the melting transition are shown in figure 2 and a strong dependence on composition is observed. The endotherm associated with the smectic–isotropic transition overlapped that corresponding to sample crystallization in all the blends exhibiting liquid crystallinity, and so it was not possible to measure the smectic–isotropic enthalpy. These thermal data are qualitatively identical to those obtained for the P4VP-2 blends [13] and indicate that the two components are, at least, partially miscible.

The P4VP-based blends generally exhibit two crystal–crystal modifications on reheating at *c.* 36°C and *c.* 135°C. The higher temperature transition appears to correspond approximately to a transition observed by Bazuin *et al.* [12] who assigned the phase between this and the melting point as a mesophase. We do not believe this assignment to be correct for two reasons: (i) the optical textures obtained are indicative of a crystal phase and (ii) the enthalpy associated with the melting transition is considerably larger than that associated with the transition at *c.* 135°C. The pure acid exhibits the lower temperature crystal–crystal transition but not the one at higher temperature.

### 3.4. P2VP-BOBPOHA blends

The dependence of the transition temperatures on blend composition for the P2VP-BOBPOHA system is shown in figure 4 and the behaviour is qualitatively similar to that exhibited by the P4VP-based blends, see figure 3. Specifically, the melting and smectic–isotropic transition temperatures decrease on increasing polymer

content. Liquid crystallinity was not observed for blends containing less than 0.77 mol fraction of acid, although all these blends could be extensively supercooled. Below 0.20 mol fraction of acid, no crystallization was observed, implying molecular mixing in these blends. The glass transition temperature of P2VP, 102°C, decreased rapidly as the acid content was increased before reaching a limiting value. The dependence of the enthalpy change associated with the melting transition on blend composition for the P2VP-BOBPOHA system, see figure 2, is also similar to that observed for the P4VP-based blends. For the 0.88 mol fraction of acid blend, it was possible to measure the smectic–isotropic enthalpy and this was considerably lower than that of the pure acid. Again these data are qualitatively identical to those observed for the P2VP-2 system [13] and imply some degree of miscibility between the two components. The P2VP-based blends do not exhibit the crystal–crystal modifications described for the P4VP-based mixtures and we will return to this observation later.

## 4. Comparison of systems

The thermal behaviour and its dependence on blend composition for the P2VP- and P4VP-based systems is strikingly similar but qualitatively different to that of the PS-BOBPOHA blends. This difference suggests some degree of miscibility in the former systems, while the latter is essentially immiscible. Infrared studies suggest that the driving force for miscibility is the formation of hydrogen bonds. This manifests itself in the spectra as a broadening of the carbonyl peak arising from a new band centred at *c.* 1725 cm<sup>-1</sup> which overlaps the band arising from the self-associated acid dimer at *c.* 1700 cm<sup>-1</sup>. In

addition a new band is observed in the spectrum at  $c. 1930 \text{ cm}^{-1}$ . Before we attempt to interpret these data, we must first consider the model proposed by Bazuin *et al.* [11, 12] to rationalize the thermal behaviour of this class of system. Figure 5 shows a schematic representation of the formation of the complex which is proposed to form between the acid and P4VP, and such a molecular arrangement may be expected to exhibit liquid crystalline behaviour. In such a model, however, steric factors involving the binding site on the backbone would be expected to exert considerable control over the formation of the supramolecular species. Our results have shown that the phase diagrams of the P2VP- and P4VP-based mixtures, see figures 3 and 4, are very similar and this observation is not in accord with the formation of complexes such as that shown in figure 5.

A more realistic model with which to interpret the data for this class of system allows for molecular mixing to occur below a given concentration of acid: for the P4VP blends below 0.17 and for the P2VP blends below 0.20 mol fraction of acid. This miscibility, driven by hydrogen bonding, results in an insufficient coverage of the backbone to promote liquid crystallinity. By analogy with conventional side-chain liquid crystal copolymers based on relatively rigid backbones containing mesogenic and non-mesogenic groups, approximately 0.5 mol fraction of mesogenic side chains must be present in order to observe mesomorphic behaviour [16]. As the concentration of acid in the blends is increased further, phase separation occurs. The interphase region is presumably diffuse and stabilized via hydrogen bonding; this is detected using IR spectroscopy. The thermal properties of the acid are modified by the presence of small amounts of dissolved polymer which effectively

acts as a crystal modifier [17, 18] and this accounts for the observation that the P2VP-based mixtures do not exhibit the crystal-crystal transitions observed for the analogous P4VP-based blends. It is well known that structural changes in polymeric crystal modifiers gives rise to changes in such transitions. Our interpretation of the data also successfully accounts for the dependence of the glass transition temperature on blend composition. The initial rapid decrease in  $T_g$  on the addition of the acid, see figures 3 and 4, is caused by the plasticizing effect of the solvated acid. The  $T_g$  values reach a limiting value, however, which appears to be coincident with the observation of the crystal phase and this strongly suggests a two phase morphology as we propose.

Recently, Malik *et al.* [19] have reported another structural variant of supramolecular side chain liquid crystal polymers in which the mesogenic group is attached to the spacer via a single hydrogen bond. The spacer presumably facilitates the formation of liquid crystallinity. In order to achieve supramolecular side chain liquid crystal polymers in which the side chain is non-covalently attached to the backbone, it appears necessary to design systems in which multiple hydrogen bonds form between the side chain and backbone. Such a strategy of multiple hydrogen bonding has been used to compatibilize immiscible components of a blend [20] and also to assemble mesogenic structures [21–23]. These systems are currently under investigation.

We are pleased to acknowledge support from the EPSRC (grant number GR/J32701), and from the University of Aberdeen Research Committee (the award of a grant to purchase the PL-DSC).

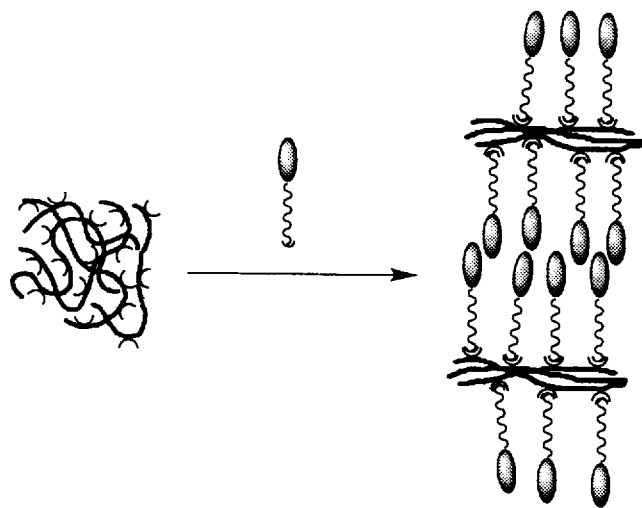


Figure 5. Schematic representation of a supramolecular side chain liquid crystal polymer.

## References

- [1] ATIARD, G. S., 1993, *Trends Polym. Sci.*, **1**, 79.
- [2] PERCEC, V., and PUGH, C., 1989, *Side Chain Liquid Crystal Polymers*, edited by C. B. McArdle (Glasgow: Blackie and Sons), Chap. 3.
- [3] PERCEC, V., and TOMAZOS, D., 1992, *Comprehensive Polymer Science*, First Supplement, edited by S. L. Aggarwal and S. Russo (Oxford: Pergamon Press), Chap. 14.
- [4] IMRIE, C. T., 1995, *Trends Polym. Sci.*, **3**, 22.
- [5] KATO, T., and FRÉCHET, J. M. J., 1989, *Macromolecules*, **22**, 3818.
- [6] KATO, T., and FRÉCHET, J. M. J., 1990, *Macromolecules*, **23**, 360.
- [7] KATO, T., KIHARA, H., URYU, T., FUJISHIMA, A., and FRÉCHET, J. M. J., 1992, *Macromolecules*, **25**, 6836.
- [8] UJIE, S., and IIMURA, K., 1991, *Chem. Lett.*, 411.
- [9] UJIE, S., TANAKA, Y., and IIMURA, K., 1991, *Chem. Lett.*, 1037.
- [10] UJIE, S., and IIMURA, K., 1992, *Macromolecules*, **25**, 3174.
- [11] BAZUIN, C. G., and BRANDYS, F. A., 1992, *Chem. Mater.*, **4**, 970.

- [12] BAZUIN, C. G., BRANDYS, F. A., EVE, T. M., and PLANTE, M., 1994, *Macromol. Symp.*, **84**, 183.
- [13] STEWART, D., and IMRIE, C. T., 1995, *J. Mater. Chem.*, **5**, 223.
- [14] HIRD, M., TOYNE, K. J., GRAY, G. W., DAY, S. E., and McDONNELL, D. G., 1993, *Liq. Cryst.*, **15**, 123.
- [15] GRAY, G. W., HIRD, M., LACEY, D., and TOYNE, K. J., 1989, *J. chem. Soc. Perkin Trans. II*, 2041.
- [16] CRAIG, A. A., and IMRIE, C. T., 1996, *J. Polym. Sci., Polym. Chem. Ed.* (in press).
- [17] DAVIDSON, I. G., and CAMERON, G. G., 1994, *Polym. Int.*, **34**, 443.
- [18] DAVIDSON, I. G., and CAMERON, G. G., 1994, *Polym. Int.*, **34**, 449.
- [19] MALIK, S., DHAL, P. K., and MASHELKAR, R. A., 1995, *Macromolecules*, **28**, 2159.
- [20] LANGE, R. F. M., and MELJER, E. W., 1995, *Macromolecules*, **28**, 782.
- [21] FOUQUEY, C., LEHN, J.-M., and LEVELUT, A.-M., 1990, *Adv. Mater.*, **2**, 254.
- [22] KOTERA, M., LEHN, J.-M., and VIGNERON, J.-P., 1994, *J. chem. Soc., chem. Commun.*, 197.
- [23] BRIENNE, M.-J., GABARD, J., LEHN, J.-M., and STIBOR, I., 1989, *J. chem. Soc., chem. Commun.*, 1868.