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Supramolecular main-chain liquid crystalline polymers and networks with competitive hydrogen bonding: networks and linear polymers created from *tris*- and *bis*-functionalised pyridyl networking agents

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A series of supramolecular polymers and networks with variable liquid crystalline characteristics have been created. These species are formed through the benzoic acid/pyridine hydrogen bonding of a flexible *bis*-acid and a mixture of a rigid *bis*-pyridyl and non-mesogenic *tris*- and *bis*-pyridyl molecules. The *tris* networked systems displayed liquid crystalline characteristics up to and including 31.0% netpoint inclusion. Above this concentration, only crystalline and melting behaviours were observed. The *bis*-containing polymer system displayed liquid crystalline characteristics up to and including 22.5% inclusion. The phenomenon observed in the *tris* system would seem to be linked to a statistical correlation of hydrogen bond acceptors and donors. The elimination of liquid crystallinity at lower concentrations of the *bis*-pyridyl dopant could be attributed to the lower melting nature of that species. Smectic phases were found in both series of complexes in loadings up to 10% of the non-liquid crystalline component. There was also no observed phase segregation of the species after multiple heat/cool cycles and extended periods of time in the isotropic state. This would indicate that the thermodynamically more stable mesogenic phase cannot out-compete the non-liquid crystalline network.

Keywords: hydrogen bond; liquid crystal; polymer; network

1. Introduction

The application of supramolecular interactions, such as hydrogen bonding, to form liquid crystals is an area of considerable scientific interest [1–8]. Hydrogen bonding has been used to form small molecule liquid crystals [1, 9], as well as main-chain [10–15] and side-chain [16–17] mesogenic polymers, and calamitic [1–18], discotic [19, 20] and banana-shaped [21] liquid crystals. The benzoic acid and pyridine assembly is one of the most commonly used associations – the resulting hydrogen bond is strong enough to maintain structure at the temperatures needed to form a thermotropic mesogen.

Mesogenic networks are a more recent innovation [22–30]. A large body of work has been produced in this field since its inception. There are a variety of these systems, differentiated mainly by the location of the liquid crystalline component in respect of the polymeric network. One such category is the main-chain liquid crystalline elastomer, a system that couples the ordering of the liquid crystalline phase with the binding force of the network.

Supramolecular chemistry, specifically hydrogen bonding, has also been applied to the field of polymer and network formation and modification. A body of work has been generated involving the formation of networks and polymers using multiple hydrogen bonds [31–33]. The structural integrity of the supramolecular systems often exceeds that of the analogous covalent species [31]. While this observation seemed counterintuitive (systems created through more stable associations would be stronger than those made through weaker associations), the rationale for this phenomenon was that the supramolecular species was capable of *macroscale reorganisation,* and capable of achieving a more thermodynamically favourable conformation by cleaving the hydrogen bonds and reforming in a more stable state. The covalent species has bonds that are relatively permanent and therefore ‘locked’ into a potentially less favoured structure.

The application of controlled crosslink density to supramolecular networks and the effects on liquid crystallinity has been previously explored [34, 35]. In these reports, two series of hydrogen bonded networks were made: one based on *bis*- and *tris*-functionalised benzoic acid species and *bis*-pyridyl acceptors, and a second formed through benzoic acid groups pendant to a covalently formed polymer chain and mono- or *bis*-pyridyl species. In both these reports, the authors described the formation of liquid crystalline phases at significant crosslink density.

Previous work [36, 37] in our laboratory involved a flexible *bis*-acid and a mixture of a rigid *bis*-pyridyl and a non-mesogenic tetra-pyridyl species. These produced supramolecular networks with variable liquid crystalline characteristics. Systems displayed

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liquid crystalline characteristics up to 22.5% netpoint inclusion. Above this concentration, only crystalline and melting behaviours were observed. This observed phenomenon would seem to be linked to the statistical correlation of hydrogen bond acceptors and donors. It was interesting to note that during all the thermal treatments of the complexes, no phase segregation was optically observed. The complex stayed intimately mixed through the entire analysis. This indicated that the materials were not separating into mesogenic and non-mesogenic regions with repeated scission of the hydrogen bond.

Here we report the formation of a series of supramolecular mesogenic networks and polymers from increasing netpoint inclusion of non-mesogenic flexible *bis*- and *tris*-functionalised pyridyl systems. The mesogenic portions of these systems arise from a hydrogen bonded interaction between a *bis*-benzoic acid and a rigid *bis*-pyridyl system.

2. Results and discussion

2.1 Materials used

Materials used in this study included:

- tetraethyleneglycoxy bis-(4-benzoic acid) (4EOBBA);
- 1,2-di(pyridylethylene) (2-RP);
- 1,1,1-tris(4-pyridloxymethylene)ethane (3-PD);
- 2,2-dimethyl-1,3-di-(4-pyridyloxy)propane (2-PD).

The synthesises of 3-PD and 2-PD are described later in this paper. All compounds used in this study can be found in Scheme 1.

All the compounds were characterised before and after complexation with spectral (^{1}H NMR, FT-IR) data. The hydrogen bond complexes were formed by thoroughly mixing equimolar quantities of the hydrogen bond donor and acceptor in the molten state for two minutes under an inert atmosphere (argon). These mixtures were allowed to cool slowly to room temperature to form the liquid crystalline materials. Hydrogen bond formation was confirmed through infrared spectroscopy by the presence of two characteristic stretching bands (centred around 2500 cm^{-1} and 1950 cm^{-1}).

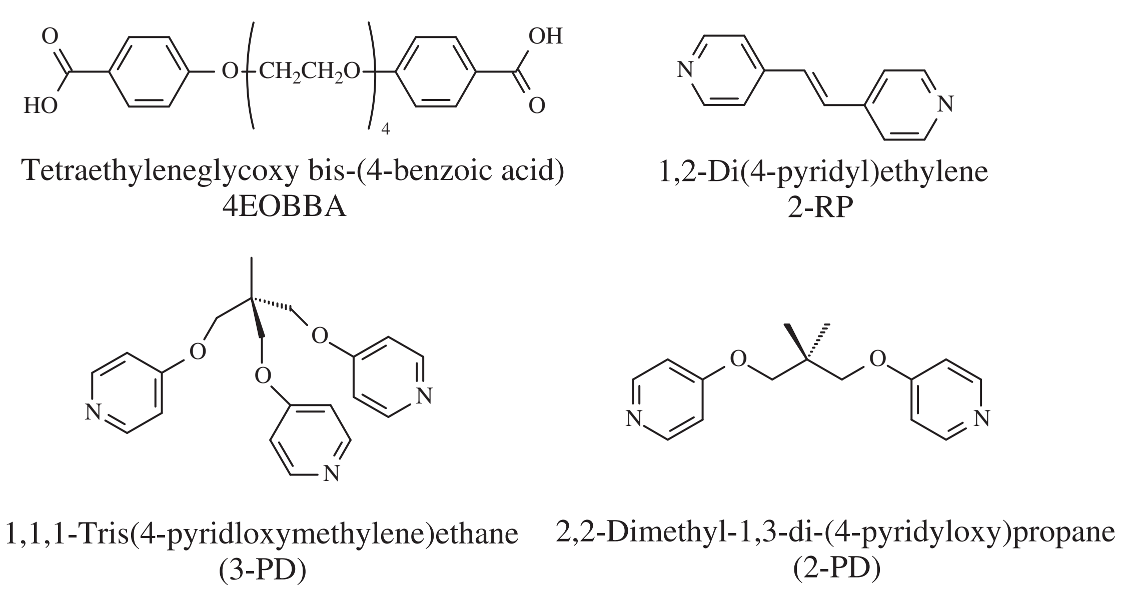
2.2 Thermal properties

A summary of all thermal transitions observed in the cooling cycles is presented in Tables 1 and 2. All heating and cooling rates were 10°C/min. Representative thermograms and thermal optical images for 3-PD and 2-PD systems are provided in Figures 1–4.

There was no observed phase discrimination in any of these materials after multiple heat/cool cycles or isothermal treatments for image acquisition. Repeated cleavage and reformation of the hydrogen bond did not form one phase preferentially. This would indicate that the lability of the hydrogen bond did not allow for the mesogenic portions to out-compete the non-mesogenic agent and therefore did not allow for the preferential formation of the thermodynamically more stable liquid crystalline system.

2.3 General results for all systems

All phase transitions are repeatable over several heat/cool cycles. The parent polymeric system



Tetraethyleneglycoxy bis-(4-benzoic acid)
4EOBBA

1,2-Di(4-pyridyl)ethylene
2-RP

1,1,1-Tris(4-pyridloxymethylene)ethane
(3-PD)

2,2-Dimethyl-1,3-di-(4-pyridyloxy)propane
(2-PD)

Scheme 1. Materials used.

Table 1. Collected thermal phase transitions for 4EOBBA/2-RP/3-PD networks (°C).

Trans	K I	I N	I K	N S	N K	S K
5%	160.3	155.2		145.1		134.8
10%	161.5	156.6		149.4		140.3
15%	158.8	142.5			136.5	
20%	159.3	145.5			140.9	
30%	157.2	141.9			136.8	
31%	159.4	146.5			140.9	
32%	155.6		134.5			
33%	156.2		136.4			
50%	154.9		135.5			
100%	142.5		76.5			

Notes: K = crystalline, N = nematic, S = smectic, I = isotropic.

Table 2. Collected thermal phase transitions for 4EOBBA/2-RP/2-PD polymers (°C).

Trans	K I	I N	I K	N S	N K	S K
2.5%	166.2	160.7		152.5		140.9
5.0%	166.4	159.8		151.8		142.7
10%	164.4	154.1		149.5		142.2
15%	166.2	149.0			141.4	
17.5%	160.6	148.4			138.7	
20%	161.3	142.9			141.0	
22.5%	162.0	143.8			138.1	
25%	166.6		146.1			
30%	154.5		133.2			
50%	150.4		127.9			
100%			76.0			

Notes: K = crystalline, N = nematic, S = smectic, I = isotropic.

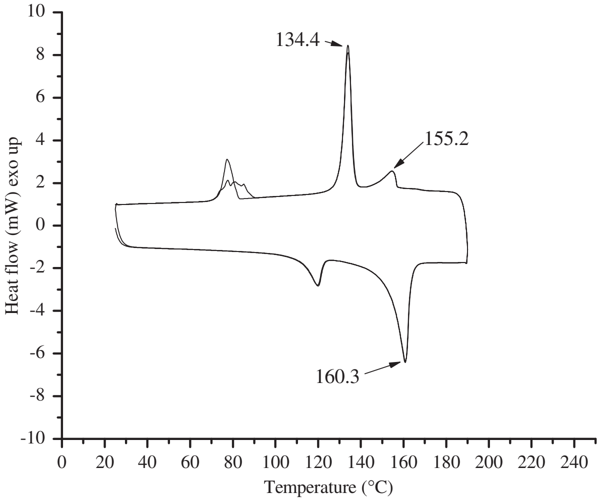


Figure 1. Differential scanning calorimetric thermogram for 5% 3-PD network.

(0% network) has been previously reported [15] and the observed phase transitions (K175.8I174.4N167.7S157.0K) were in general agreement with that report. The parent completely networked system has also

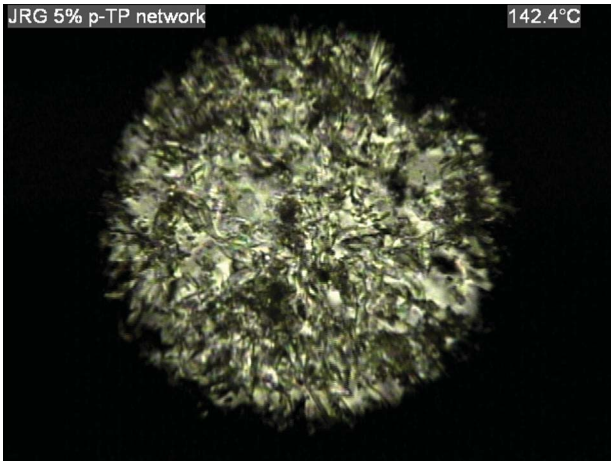


Figure 2. Thermal optical micrographs of 5% 3-PD polymer (colour version online).

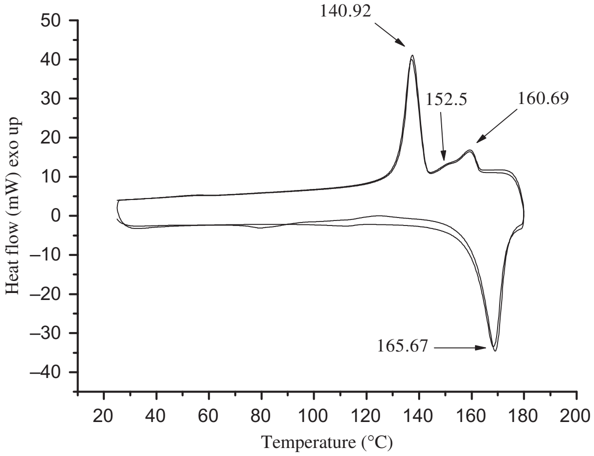


Figure 3. Differential scanning calorimetric thermogram for 2.5% 2-PD polymer.

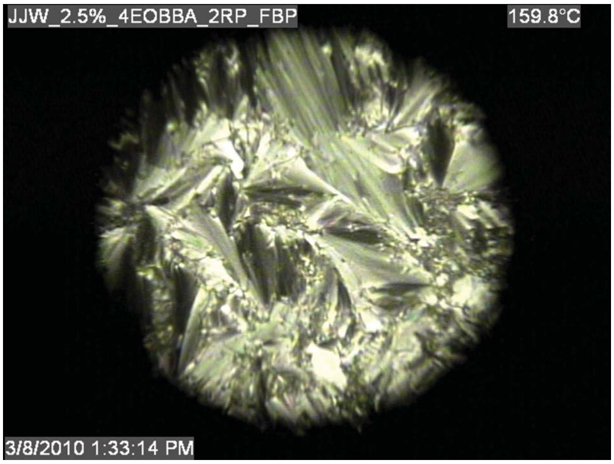


Figure 4. Thermal optical micrographs of 2.5% 2-PD polymer (colour version online).

been previously reported [33, 38–39] and has no mesogenic transitions – only melting and crystallisation behaviour (K145.7I92.9K).

It should be noted that, in all cases, the concentration of the pyridyl nitrogens was kept constant with respect to the acid protons. The total number of hydrogen bond acceptors, arising from either the mesogenic or the non-mesogenic pyridyl species, was in molar balance with the hydrogen bond donors. The lack of mesogenicity arising from the 2-PD and 3-PD species should not be attributed to its flexibility; 4-alkyl pyridines have shown the ability to form liquid crystalline complexes with benzoic acid hydrogen bond donors [38–39]. Rather, the geometry around the central atom of the 3-PD molecule is too constrained and the chain length to the pyridyl groups is too short to form a liquid crystalline phase.

The presence of a more ordered, layered smectic structure at 10% loadings of the non liquid crystalline 3-PD and 2-PD molecule was observed. Our previous work using a tetra-pyridyl of analogous shape showed the smectic phase disappearing between 8.5% and 10% inclusion. Nematic to smectic transition temperatures were similar between systems containing 2-PD and 3-PD. This seemed to indicate that the stability of the smectic phase is maintained at significant loadings of the pyridyl species. During all the thermal treatments of the systems, no phase separations were observed between the mesogenic and non-mesogenic portions. This is concurrent with behaviour observed in the previous 4-PD study [37] .

2.3.1 *Results of* tris-*functionalised (3-PD) mesogenic networks*

The hydrogen bond complexes display monotropic phases (nematic and smectic) by differential scanning calorimetry (DSC) and polarising light thermal optical microscopy (P-TOM). Phases are observed as the systems cool from the isotropic melt through the formation of nematic droplets, which resolve into materials with the Schlieren texture typical of the nematic phase. A smectic phase was observed in concentrations up to 10% of networking agent. The nematic phase was observed until concentrations up to 31%, with this limit displaying a frustrated nematic phase. At 32% and above, only melting and crystallisation behaviour was observed.

It was interesting to note that the liquid crystalline phase was present in such high concentrations of the non-mesogenic networking agent. It would seem that the lability of the hydrogen bond would allow for molecular reorganisation to allow the more stable mesogenic phase to form at higher concentrations than would normally be seen. The apparent cut-off for liquid crystallinity was 31%. This would correspond closely with the *tris*-functionalised nature of the crosslinking agent. This phenomenon would seem to arise from a similar statistical correlation as we have previously supposed [39]. At 33%, one of the benzoic acid components should be hydrogen bonded with one of the networking species, preventing the formation of a hydrogen bond with the rigid, mesogen-forming 2-RP species.

2.3.2 Bis-*functionalised mesogenic networks*

Polymers made from utilising 4EOBBA, 2-RP and 2-PD displayed trends and patterns similar to those observed in the 3-PD series of networks (monotropism, formation of nematic phases from the isotropic phase, etc.). Smectic phases were observed in the system until 10% inclusion of 2-PD (coincidentally identical to the concentration observed the 3-PD systems) and nematic phases were present at 22.5%. Concentrations of 2-PD inclusion at 25% and higher displayed no liquid crystallinity, simply melting and crystallisation behaviour. This is markedly lower than the expected 50% inclusion based on previous observations (3-PD at 31%, 4-PD at an identical 22.5%). One possibility for this depressed concentration is that the 2-PD system melts markedly lower (58.3°C) than either 4-PD (198.3°C) or 3-PD (125.5°C) molecules. Transition temperatures between the 3-PD and 4-PD containing complexes are very similar until higher concentrations of 2-PD are reached (30% above), indicating that only high concentrations of the 2-PD species were lowering the melting/recrystallisation temperatures of the complexes. One supposition for this was that, as the concentration of the lower melting 2-PD is increased in a sample, the complexes entered into the isotropic state sooner. In essence, this caused an eutectic mixture, which became an isotropic melt at lower temperatures than complexes with a lower loading of 2-PD and therefore inhibited the formation and duration of the liquid crystalline phase.

3. Experimental

3.1 Characterisation

Phase transitions were observed using an Olympus BHT polarising light microscope equipped with a Mettler-Toledo FP82-HT thermal optical hot stage connected to a Mettler Toledo FP90 control unit. DSC thermograms were obtained from a Mettler-Toledo STAR e1 DSC. A heating/cooling rate of 10°C/min was used in all analyses. Infrared spectroscopy was carried out using a Nicolet Avatar 360 FT-IR. ^{1}H spectra were recorded on a JEOL Eclipse 400 MHz FT-NMR spectrometer using TMS as an internal standard.

3.2 Materials

Reagent grade reactants and solvents were used as received from Aldrich Chemical Company (Milwaukee, WI). Spectrographic grade solvents were used for all measurements. Tetraethyleneglycoxy bis-4-benzoic acid (4EOBBA) was synthesised according to literature procedures [39]. 1,2-Di(4-pyridyl)ethylene (2-RP) was purchased from Aldrich Chemical Company and used as received.

3.3 Synthesis

3.3.1 Synthesis of 1,1,1-tris(methylene p*-toluenesulphonyl)ethane*

p-Toluenesulphonyl chloride (22.1 g, 0.12 mol) and 1,1,1-tris(hydroxymethyl) ethane (3.9798 g, 0.03 mol) were dissolved in 100 mL pyridine. The mixture was stirred for 20 h. The rose-coloured solution and white precipitate were poured into 3 L water and chilled for 24 h. The resulting precipitate was isolated via vacuum filtration and recrystallised from chloroform and methanol. Tm: 102.5°C. Yield: 12.5079 g (0.0215 mol), 65.0% yield. ^{1}H NMR data (CDCL$_3$): 7.69 (6H d, Ar–H, β to sulphur), 7.35 (6H d, Ar–H, γ to sulphur), 3.76 (6H s, C–CH_2–O–S), 2.47 (9H, s, Ar–CH_3), 0.89 (3H, s, H_3C–C– (CH$_2$–Tos)$_3$).

3.3.2 Synthesis of 1,1,1-tris(4-pyridloxymethylene) ethane

1,1,1-Tris(methylene *p*-toluenesulphonyl)ethane (9.8 g, 0.0169 mol), 4-hydroxy pyridine (5.3 g, 0.0558 mol) and caesium carbonate (18.2 g, 0.0558 mol) were combined in 15.0 mL dimethyl formamide (DMF). The mixture was refluxed with stirring for 24 h, then cooled and poured into 6 L of a water/ice mixture. This was refrigerated for 22 h; the resulting precipitate was filtered and the solid was recrystallised from methanol and water. Tm: 125.5°C. Yield: 1.2082 g (0.0034 mol), 20.0% yield. ^{1}H NMR (DMSO): 8.35 (6H, d, pyridine ring β to pyridyl nitrogen), 6.99 (6H d, Ar-H, γ to pyridyl nitrogen), 4.16 (6H s, C–CH_2–O–pyridine), methyl 1.24 (3H, s, H_3C–C– (CH$_2$–Tos)$_3$).

*3.3.3 Synthesis of 2,2-dimethyl-1,3-di-(*p*-toluenesulphonyl)propane*

2,2-Dimethyl-1,3-propanediol (7.1 g, 0.0684 mol) was combined with *p*-toluenesulphonyl chloride (26.5 g, 0.1389 mol) in 100 mL pyridine and stirred for 24 h. The pinkish-coloured solution and off-white precipitate were subsequently poured into 350 mL of water and cooled for 23 h. The resulting precipitate was vacuum-filtered and recrystallised from chloroform and methanol. Tm: 117.3°C. Yield: 12.7857 g (0.031 mol), 45.3% yield. ^{1}H NMR (CDCl$_3$): 7.75 (4H, d, Ar-H, β to sulphur), 7.35 (4H d, Ar–H, γ to sulphur), 3.72 (4H s, C–CH_2–O–S), 2.46 (6H, s, Ar–CH_3), 0.89 (6H, s, geminal dimethyl groups).

3.3.4 Synthesis of 2,2-dimethyl-1,3-di-(4-pyridyloxy) propane

2,2-Dimethyl-1,3-di-(*p*-toluenesulphonyl)propane (5.0 g, 0.0121 mol), 4-hydroxy pyridine (2.53 g, 0.0266 mol) and caesium carbonate (8.67 g, 0.0266 mol) were combined in 15.0 mL DMF. The mixture was refluxed with stirring for 24 h, then cooled and poured into 6 L of a water/ice mixture. This was refrigerated for 22 h and the resulting precipitate was filtered. The solid was recrystallised from methanol and water. Tm: 58.3°C. Yield: 0.69g (0.0027mol), 22.0% yield. ^{1}H NMR (DMSO): 8.35 (4H, d, pyridine ring β to pyridyl nitrogen), 6.96 (4H d, Ar–H, γ to pyridyl nitrogen), 3.93 (4H s, C–CH_2–O–pyridine), methyl 1.10 (6H, s, H_3C–C– (CH$_2$–Tos)$_3$).

4. Conclusions

Supramolecular networks and polymers have been formed utilising different types of pyridyl hydrogen bond acceptors – a *bis*-functionalised rigid species capable of forming a mesophase and flexible, non-mesogen-forming pyridyl species in *bis*- and *tris*- functionalities. Species containing the *tris* networks (3-PD) displayed liquid crystalline phases in loadings up to 31% inclusion. *Bis*-pyridyl species (2-PD) produced mesogenic phases up to 22.5% loading. The limits observed in the *tris* pyridyl containing systems seem to indicate a statistical correlation of available hydrogen bond acceptors in the networks; that is, the upper limit for loading of the networking agent is linked to the number of functional groups involved. *Bis*-pyridyl containing systems cleared liquid crystallinity at markedly lower concentrations than would be expected from any statistical correlation. One possible supposition for this phenomenon is the lower melting temperature for the 2-PD molecule. Smectic phases in both series were observed in up to 10% presence of the non-mesogenic pyridyl species, and had similar thermal transitions. It would seem that the more ordered, layered structure of the smectic phase is resilient to significant cross-linking or disruptive associations. As repeated heat/cool cycles did not force a phase segregation of the mesogenic and non-mesogenic systems, it would seem that the liquid crystalline components of the network cannot outcompete the networking agent for the hydrogen bond donors.

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