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Supramolecular main-chain liquid crystalline polymers and networks with competitive hydrogen bonding

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Supramolecular main-chain liquid crystalline polymers and networks with competitive hydrogen bonding

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A series of supramolecular polymers and networks with variable liquid crystalline characteristics have been created. These species are formed though the benzoic acid/pyridine associations of a flexible bisacid and a mixture of a rigid bispyridyl and a non-mesogenic tetrapyridyl. The networked systems displayed liquid crystalline characteristics up to and including 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. 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. Computational analysis indicates no significant difference in hydrogen bond strength between the two different hydrogen bond acceptors.

Keywords: liquid crystals; networks; supramolecular; hydrogen bond

1. Introduction

The application of non-covalent or 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 [6, 10–14] and side-chain [15, 16] mesogenic polymers, and calamitic [1–17], discotic [18–20] and banana-shaped [21] liquid crystals. One of the most commonly used associations is the benzoic acid and pyridine assembly. The resulting hydrogen bond is linear and strong enough to maintain structure at the temperatures needed to form a thermotropic mesogen.

Mesogenic networks are a more recent innovation [22–29]. 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 with respect to 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.

It is important to note that supramolecular chemistry, specifically hydrogen bonding, has also been applied to the field of polymer formation and modification. A body of work has been generated involving the formation of networks and polymers using multiple hydrogen bonds [30–32, 35–36]. The structural integrity of the supramolecular systems often exceeds that of the analogous covalent species [30]. While this observation seemed strongly 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 [33, 34]. 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 of these reports, the authors described the formation of liquid crystalline phases at significant crosslink density.

Here we report the formation of a series of supramolecular mesogenic networks with increasing netpoint inclusion. The mesogenic portions of these systems arise from a hydrogen-bonded interaction between a bis-benzoic acid and a rigid bis-pyridyl system. A non-mesogenic pyridyl networking agent is used to introduce a network and potentially disrupt liquid crystallinity. These networks display mesogenic characteristics at a surprisingly high network concentration.

2. Results and discussion

2.1 Materials used

Materials used in this study including tetraethyleneglycoxy bis-(4-benzoic acid) (4EOBBA), tetrakis(4-

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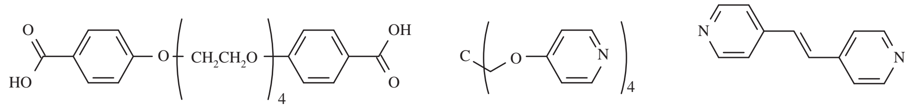

Tetraethyleneglycoxy bis-(4-benzoic acid)
4 EO BBA

Tetrakis(4-pyridyloxy
methylene)methane
p-TPPE

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

Scheme 1. Materials used.

pyridyoxymethane) (*p*-TPPE) and 1,2-di(pyridylethylene) (2RP), have been synthesised previously. All compounds used in this study can be found in Scheme 1.

All of 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 2 min under an inert atmosphere. 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 Table 1. All heating and cooling rates were 10°C min^{-1} unless otherwise noted. A representative thermogram and thermal optical image are provided in Figures 1 and 2.

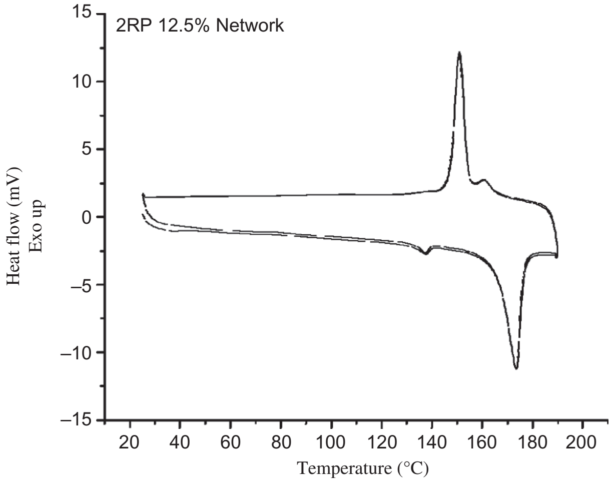

Figure 1. Differential scanning calorimetric thermogram for 12.5% network.

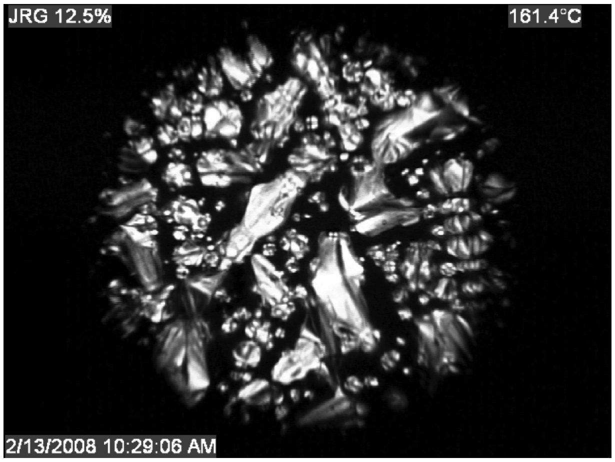

Figure 2. Thermal optical micrographs of 12.5% network.

Table 1. Collected thermal phase transitions (°C).

%	K I	I N	I K	N S	N K	S K
0	175.8	174.4		167.7		157
2.5	174.7	172.1		164.7		155.1
5	174.4	170.8		164.6		155.2
7.5	174.9	170.6		164.1		154.8
8.5	174.3	167.7		163.7		155.6
10	174.2	165.5			154.3	
12.5	172.6	160.7			151.9	
15	172.5	162.7			151.6	
20	172.2	160.6			152.4	
22.5	172.2	160.6*			152.4*	
25	172.1		152			
50	167.8		144			
75	163.3		138.7			
100	132.4		89.3			

Notes: K = crystalline, N = nematic, S = smectic, I = isotropic, *indicates a transient nematic phase.

2.2.1 *1,2-Di(4-pyridyl)ethylene (2RP) networks*

The hydrogen bond complexes display monotropic nematic phases and transitions 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. The phase transitions are repeatable over several heat/cool cycles. The parent polymeric system (0% network) has been previously reported [15] and the results presented here are in general agreement with that report. The phase transitions for the parent system are as follows: K175.8I174.4N167.7S157.0K. The parent completely networked system has also been previously reported [35, 36], and has no mesogenic transitions, only melting and crystallisation behaviour.

The networking agent (*p*-TPPE) was added in increasing concentrations to the system. It should be noted that in all cases, the concentration of the pyridyl nitrogens was kept constant with respect to the acid protons – that is, the total number of hydrogen bond acceptors, arising from either the mesogenic 2RP or the non-mesogenic p-TPPE, was in molar balance with the hydrogen bond donors. The lack of mesogenicity arising from the *p*-TPPE 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 [37, 38]. The geometry around the central atom of the *p*-TPPE molecule is too constrained and the chain length to the pyridyl groups is too short to form a liquid crystalline phase.

A smectic phase was observed in concentrations up to 8.5% of networking agent. The nematic phase was observed until concentrations up to 22.5%. The 22.5% data displayed a frustrated nematic phase, barely forming before crystallising. At 25% 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 form the more stable mesogenic phase at higher concentrations than would normally be seen.

At network concentrations amounts of 25% and above, no liquid crystalline characteristics were observed. It is curious to note that the apparent cut-off for liquid crystallinity was 22.5%, which would correspond closely with the tetrakis-functionalised nature of the crosslinking agent. This phenomenon may arise from a statistical correlation. At 25%, one of the benzoic acid components would always be hydrogen bonded with one of the networking species, preventing the formation of a hydrogen bond with the rigid 2RP species. This would therefore inhibit the formation of the mesogen.

There was no observed phase segregation in the materials after multiple heat/cool cycles or extended periods of time above the clearing temperature. Repeated scission and reformation of the hydrogen bond did not form one phase preferentially, excluding another. This would indicate that the lability of the system could not out-compete the formation of hydrogen bonds with the non-mesogenic networking agent and allow for the formation of the mesogenic phase in concentrations greater than 25%, and did not allow for the preferential formation of the thermodynamically more stable mesogenic system.

2.2.2 Computations

As the two hydrogen bond acceptors (2RP and *p*-TPPE) are fundamentally different in structure (a rigid, conjugated stilbazole and 4-alkoxy ether, respectively), density functional calculations were carried out to determine the relative strengths of bindings between each and the hydrogen bond donor (4EO BBA). Calculated hydrogen bond dissociation energies for complexes of donors 2RP and *p*-TPPE with acetic acid (a model for the hydrogen bond donor) differed less than 1 kcal mol^{-1} (17.5 kcal mol^{-1} versus 16.9 kcal mol^{-1}at the BP86/6–311+G** level of theory; and 17.4 kcal mol^{-1} versus 16.9 kcal mol^{-1} using B3LYP/6-311++G**). At this level of theory, total energy differences within 1 kcal mol^{-1} cannot be determined quantitatively, but are considered to be qualitatively similar. Therefore, calculated relative energies suggest that structural differences between 2RP and *p*-TPPE should not significantly change the affinity with which they can bind to a hydrogen bond donor.

3. Experimental details

3.1 Characterisation

Phase transitions were observed using an Olympus BHT polarising light microscope equipped with a Mettler-Toledo FP82-HT thermal optical hotstage connected to a Mettler Toledo FP90 control unit. Differential scanning calorimetry thermograms were obtained from a Mettler-Toledo STAR e1 DSC. A heating/cooling rate of 10°C min^{-1} was used in both analyses. Infrared spectroscopy was carried out using a Nicolet Avatar 360 FT-IR. 1H and 13C NMR 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, USA). Spectrographic grade solvents were used for all measurements. Tetraethyleneglycoxy bis-4-benzoic acid (4EO BBA) and tetrakis(4-pyridyloxy methylene)methane (*p*-TPPE) were synthesised according to literature procedures [36]. 1,2-Di(4-pyridyl)ethylene (2RP) was purchased from Aldrich Chemical Company and used as received.

3.3 *Computational methodologies*

To determine the relative affinity of two different hydrogen bond acceptors for a hydrogen bond donor, density functional calculations were performed using Gaussian 03 Rev E.01 [39]. Acetic acid was used as the model hydrogen bond donor in both cases, and the small complexes 2RP and *p*-TPPE were used as model hydrogen bond acceptors. Hydrogen bond dissociation energies were calculated from the total energies of the bound donor–acceptor complexes, relative to those of the isolated donor and acceptor molecules. Total energies were obtained at fully optimised geometries; zero point corrections were not applied. Two density functionals were used for comparison: the generalised gradient functional BP86 [40, 41], and the hybrid functional B3LYP [42]. It was found that the relative total energies were within +/– 0.1 kcal mol^{-1} when calculated using the double-zeta [43–52] 6-31+G* and triple-zeta [53, 54] 6–311++G** basis sets with diffuse [54–56] and polarisation [57] functions, indicating that the result was reasonably converged with respect to basis set size.

4. Conclusions

The supramolecular networks formed utilising two different types of pyridyl hydrogen bond acceptors (bis-functionalised, rigid, mesophase-forming and tetrakis-functionalised, non-mesogenic) displayed liquid crystalline characteristics in loading amounts up to 22.5%. At network concentration amounts of 25% and above, no liquid crystalline characteristics were observed. The limit of 25% may 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. 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 out-compete the networking agent for the hydrogen bond donors. Molecular modelling calculations indicate no significant difference between the systems in terms of hydrogen bond strength; that is, neither forms a stronger hydrogen bond to bias the competition.

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