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## Poly(4-vinylpyridine)-based hydrogen bonded side-chain liquid crystal polymers

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## ABSTRACT

Novel liquid crystalline (LC) poly(4-vinylpyridine) (PVP)-based side-chain polymers were prepared from PVP and cyanobiphenyl (HOCnB) derivatives through intermolecular hydrogen-bonding between hydroxyl groups of the cyanobiphenyl derivatives and the nitrogen of PVP. PVP was used as a hydrogen bond acceptor polymer. A series of HOCnB having a linear alkoxy chain  $\text{HOCnH}_{2n+1}\text{O}$  ( $n = 2-6$ ) have been used as H-bond donor. The existence of H-bonding was confirmed using FTIR spectroscopy. The polymeric complexes behave as LC polymers and exhibit stable mesophases. DSC and optical microscopy were used to investigate LC behaviour. All PVP-LC-complexes exhibited stable and homogeneous nematic phases. On increasing spacer length or concentration of the hydrogen bonded mesogenic unit in the complex, the clearing temperature and the temperature range of the nematic phase increased. The binary phase diagram of the polymeric complexes PVP-HOCnB showed complete miscibility over the entire range of composition. Molecular interactions of self-assembled SCLCP presented the idea that various LC-complexes could be prepared through mixing a functionalised polymer with various low molar mass mesogens.

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## 1. Introduction

Side-chain liquid crystalline polymers (SCLCP) are usually prepared by covalently linking rigid mesogens to a polymer backbone through flexible spacers. In recent years, it has been recognized that molecular recognition processes between different molecular species through non-covalent interactions are advantageous for the design of functional molecular aggregates such as liquid crystals [1–6] as well as crystalline materials. Self-assembly through specific interactions, such as hydrogen-bonding [1,4,7] ionic, ionic-dipolar and charge transfer interactions [1], has been recognized as a new strategy for constructing side-chain liquid crystal polymers. The hydrogen-bonding

interaction is one of the most important and widely used non-covalent interactions in the design and construction of functional materials because biopolymers such as nucleic acids, polypeptide, and cellulose have hydrogen-bonding groups. The formation and dissociation of hydrogen bonds for these polymers play key roles in biological processes. Until now, there were three different SCLCP built via different molecular interactions. While conventional liquid crystalline polymers consist of only covalent bonds [1,2], the supramolecular polymeric liquid crystalline complexes contain a hydrogen-bonding mesogenic core [3,8,9] or a hydrogen-bonding linking moiety connecting the mesogenic molecule to the polymer [2].

A supramolecular host-guest polymer that is a new variation of structure has been successfully used to design SCLCP. Well-defined molecular structures with liquid crystalline properties were obtained via a simple self-assembly process between hydrogen-bonding donor and acceptor moieties. In previous studies, carboxylic and benzoic acid

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groups were widely used as hydrogen-bond donors while pyridine moieties were commonly used as hydrogen-bond acceptors. Complexes obtained through intermolecular hydrogen-bonding, include systems consisting of derivatives of carboxylic (such as benzoic) acid or pyridine [2,4,6], carboxylic acid–2,6-diaminopyridine, uracil–2,6-diaminopyridine, and carboxylic acid–pyridine-*N*-oxide [3]. Many processes in nature involve the participation of imidazole groups. Imidazole derivatives are useful as hydrogen-bonding components in connecting different molecular parts through the formation of stable hydrogen bonds. There are limited publications about supramolecular complexes formed through hydrogen-bonding between poly(4-vinylpyridine) as hydrogen bond acceptor and hydroxyalkoxycyanobiphenyl moieties as hydrogen bond donors.

The aim of present study is to attach several mesogenic cyanobiphenyl derivatives to a poly(4-vinylpyridine) backbone through H-bond interactions, between the hydroxyl group of cyanobiphenyl derivatives (HOCnB) and the pyridinium ion of poly(4-vinylpyridine). Fig. 1 shows the structures used to construct a variety of new SCLCP through self-assembly involving intermolecular hydrogen bonds. The SCLCP was characterised using differential scanning calorimetry (DSC), polarising optical microscopy (POM) to determine whether the liquid crystalline and thermal properties of the supramolecular complexes are dependent on the spacer length, and the composition of the complexes.

Building ordered structures with tailor-made optical, electrical, magnetic and mechanical properties is important for material science [10–12]. The physically side-chain liquid crystalline systems with region of order and disorder are fundamental of this research. The novel method of ordering is based on supramolecular assemblies through molecular recognition. These new structure–property–morphology models will be of benefit to the many potential applications of these materials.

## 2. Experimental

### 2.1. Materials

Poly(4-vinylpyridine) ( $M_n = 6\,000\text{ g mol}^{-1}$ ), 4'-hydroxy-4-cyanobiphenyl, tetrabutylammonium hydrogen (TBAH) sulfate, *n*-bromo(chloro)-1-alkanol (98%), other reagents

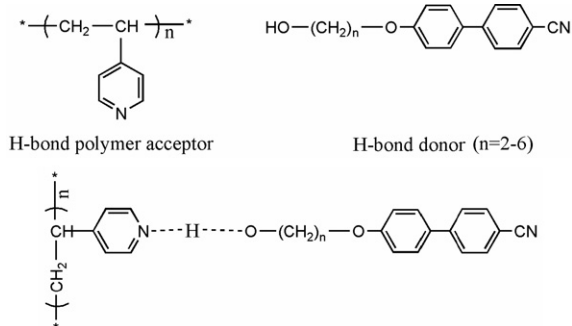


Fig. 1. Chemical structures of poly(4-vinylpyridine) and 4'-alkoxy-4-cyanobiphenyl, and the hydrogen bonded liquid crystal complex.

were used without further purification, *N,N*-dimethylformamide (DMF) (all from Sigma-Aldrich, Australia) was treated with potassium hydroxide, then dried by azeotropic distillation with benzene and distilled under reduced pressure.

The synthesis of 4'-(*n*-oxy-4-cyanobiphenyl)alkanoates is outlined. The first step consisted of nucleophilic displacement of the halide of *n*-haloalkan-1-ol with 4'-hydroxy-4-cyanobiphenyl according to a procedure described in the literature [13,14].

### 2.2. Preparation of hydrogen-bonded complexes

All complexes examined in the present study were prepared by an evaporation technique. The evaporation technique, in which the H-bond donor, a linear chain  $HOCnH_{2n+1}O$  ( $n = 2-6$ ), and PVP as a hydrogen bond acceptor polymer, are dissolved in the solvent DMF. Controlled evaporation of the solvent causes phase separation of the LC hydrogen-bonded liquid crystalline polymer complexes. From pyridine solution containing equimolar amounts of hydrogen-bond donor and acceptor moieties followed by drying in vacuo at 60 °C. Polymeric binary complexes containing two different 4'-(*n*-hydroxyalkoxy)-4-cyanobiphenyl derivatives were made from pyridine solution containing equimolar amounts of the pyridine unit of PVP and the hydroxy group of mixtures of HOC3B and HOC6B. Binary mixtures of monomeric and polymeric complexes were prepared from a pyridine solution of equimolar mixtures of a hydrogen-bond acceptor of PVP and hydrogen bond donor of HOCnB.

### 2.3. Characterization

Differential scanning calorimetry of films was obtained using a Perkin-Elmer Pyris 1 DSC with Intercooler 2P, under an inert nitrogen atmosphere (nitrogen flow  $20\text{ mL min}^{-1}$ ) throughout the analysis. About 5–10 mg (Perkin-Elmer AD-2Z Auto balance) of material was placed in a 30  $\mu\text{L}$  aluminum pan and hermetically sealed. Indium and zinc were used for temperature calibration, indium for heat flow calibration and the furnace was calibrated according to the manufacturer's instructions. DSC scans were obtained with reference to an empty aluminum pan and Pyris Software 3.81 was used.

The samples were heated and subsequently cooled in the range between 25 °C and 150 °C heating and cooling rates were  $10\text{ }^\circ\text{C min}^{-1}$ . After the first heating cycle, the samples were held at 150 °C for 10 min to obtain identical thermal histories for all polymers before the second cooling/heating cycle. Melting temperature ( $T_m$ ) was measured at the peak of the change in the heat capacity. The morphologies (the resolution: 10.2 million pixels) of PVP–HOCnB films were observed using a Nikon Labophot 2 optical microscope with polarising filters and a Mettler FP90 hot stage and images were captured using a Nikon D40 digital camera. The solvent cast PVP–HOCnB films were mounted on glass slides and covered by cover slips. The specimens were first heated on a hot-stage from room temperature to 150 °C at a rate of  $10\text{ }^\circ\text{C min}^{-1}$  and maintained at this temperature for 10 min before cooling.

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