



# Hydrogen-bonded liquid crystalline polymers containing poly(4-vinylpyridine) and dendron-like side chains: From lamellar to columnar phase



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## ABSTRACT

We investigated the phase behavior of a series of supramolecular polymer complexes  $P4VP(nCTB)_x$  in which poly(4-vinylpyridine) (P4VP) is hydrogen-bonded with dendron-like small molecules containing a phenolic end group ( $nCTB$ ,  $n = 6, 10, 12, 14$ ). Supramolecular lamellar and hexagonal columnar ( $\Phi_H$ ) structures were investigated via small angle X-ray scattering (SAXS), polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The stability of the lamellar and  $\Phi_H$  phases is dependent on the blending ratio of  $nCTB$  per vinylpyridine unit ( $x$ ), alkyl tail length ( $n$ ) and thermal treatment. The  $P4VP(6CTB)_x$  exhibit only a poorly ordered lamellar phase. Upon increasing  $x$ , the phase structure of the polymer complexes ( $n = 10, 12, 14$ ) can transform from the lamellar to the  $\Phi_H$  phase. As a result of the thermal dynamic nature of hydrogen bond and the conformation changing of P4VP during the thermal annealing, a non-reversible order-to-order transition from lamellar to  $\Phi_H$  phase appears when the volume fraction of the alkyl tails is 0.56–0.58.

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## 1. Introduction

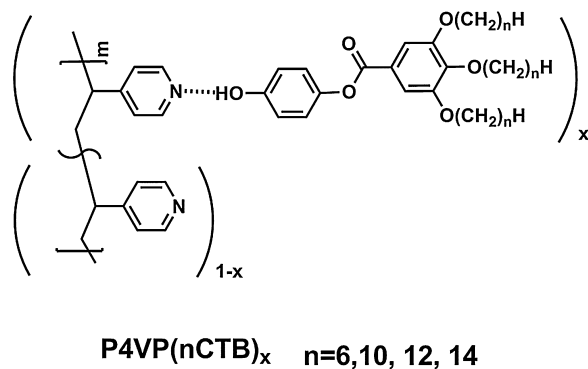
Supramolecular chemistry has attracted tremendous attention in materials science during the past decades because it can be used to build functional materials based on non-covalent interactions including hydrogen bonds, ionic interactions,  $\pi$ - $\pi$  stacking, or metal coordination [1–6]. Small molecules and polymer assemblies based on non-covalent interactions are an efficient way to construct various supramolecular side-chain polymers with mesomorphic properties and corresponding block copolymers with hierarchical self-assembled structures [7–10]. In this case, small molecules are frequently attached to the polymer backbone through non-covalent interactions and play the role of comb-like side chains in the resulting supramolecular polymers. Such supramolecular polymers and block copolymer systems offer promising advances in the construction of sophisticated architectures in incorporating desired functionality such as proton conductivity, electronically conducting nano wires, functional membranes, etc. [11–15]. Versus conventional side-chain liquid

crystalline polymers (SCLCPs) constructed with covalent bonds, it is more convenient to modulate the grafting density of the side chains by simply controlling the composition of small molecules in supramolecular LCs. On the other hand, choosing different substituent groups for the small molecules and polymers could modulate the strength of non-covalent interactions – this will further affect the phase behaviors of supramolecular complexes [16–17].

In addition to the degree of complexation and strength of non-covalent interactions, the shape and chemical structure of small molecules also controls the mesophase structures. In representative P4VP-based, supramolecular polymer systems, the P4VP-pentadecylphenol (PDP) [18] and P4VP-nonadecylphenol (NDP) [19] complexes can form mesomorphic lamellar structure despite of the amorphous nature of small molecular surfactants and P4VP. The self-assembly mechanism is similar to microphase separation of block copolymer systems. In addition to flexible linear surfactants, rod-like small molecules functionalized with hydroxyl or carboxylic end groups such as biphenyl derivatives [20–22], azophenols or azobenzene derivatives [23–25], and cholesteric derivatives [26–28] can also complex with P4VP homopolymers or P4VP-based block copolymers to produce lamellar (smectic) or nematic mesomorphic structures. Crystalline lamellar structure-

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**Scheme 1.** Supramolecular P4VP(*n*CTB)<sub>x</sub> complexes via hydrogen bonding.

sare formed when small molecules contain conjugated parts with strong intermolecular interactions such as oligothiophene [29–30] or perylenebisimide [31].

Besides those linear flexible surfactants and rod-like small molecules, dendron-like molecules have drawn much attention in the construction of supramolecular dendronized polymers [32–33]. Molecules that can complex with P4VP or P4VP-*b*-PS to achieve lamellar and columnar phases include: wedge-shaped molecules with sulfonic acid end groups [34], benzoic acid-type small molecules such as dendron-like 3,4,5-tri-benzyloxybenzoic acid and V-shaped acid with chiral tails [35], 4'-(3,4,5-trioctyloxybenzoyloxy) benzoic acid (TOB) [36–37], 3,4,5-tris(dodecyloxy) benzoic acid (TDBA) [38], 3,4,5-tris(hexadecyloxy) benzoic acid (THBA) [39] and toluene-based hemi-phasmid acid [40]. The structure depends on the degree of complexation of small molecules to polymers. Generally, when the degree of complexation is low, a lamellar structure is formed. By increasing the degree of complexation, the complex could form a columnar phase with hexagonal lattice symmetry in which each column is formed by a polymer chain surrounded with dendron-like molecular side chains. Similar composition-dependent structural changes have also been found in ionic interactions based on supramolecular complexes systems [41–42]. These studies indicate that various self-assembled ordered nano structures in supramolecular polymer systems can be achieved simply by means of molecular design of small molecules, which is then controlled by the blending ratio of the small molecular additives to the polymers. This is a promising strategy to construct and manipulate hierarchical architectures based on supramolecular approaches.

We recently reported a series of small molecules – *n*CBPs (*n* = 10, 12, 14) – that contain a phenolic head group, a bent-core rigid core, and three flexible alkyl tails [43–44]. When *n*CBP is complexed with P4VP, composition-dependent lamellar to columnar structural changes were observed. In addition, a non-reversible phase transition from lamellar to columnar structure was seen in some supramolecular complexes during thermal annealing. This indicates that hydrogen bonds are involved in the thermal dynamic behavior that occurs in this system. Inspired by the self-assembly behavior of P4VP(*n*CBP)<sub>x</sub>, we further reduced the size of the small molecules from bent-shaped *n*CBPs to a series of dendron-like molecules. These were named *n*CTBs (Scheme 1). They contain a short, rod-like rigid core attached by three alkyl tails. The P4VP(*n*CTB)<sub>x</sub> are formed through hydrogen bonds between the pyridine group of P4VP and the phenolic group of *n*CTBs. Here, *x* denotes the number of *n*CTB per vinylpyridine repeat unit, and *n* denotes the number of methylene groups per alkyl tail; *n* varies from 6 to 10, 12, and 14 carbons (Scheme 1). Self-assembly of supramolecular structures and thermal dynamic behaviors of P4VP(*n*CTB)<sub>x</sub> – especially for their structural change from lamellar to columnar phase – is a function of their degree of complexation, alkyl tail

length, and temperature. We investigated all of these parameters here.

## 2. Experimental

### 2.1. Materials

The 3,4,5-trihydroxybenzoic acid methyl ester (98%), 1-bromodecane (98%), K<sub>2</sub>CO<sub>3</sub>, KOH, ethanol (99.5%), ethylacetate (99.8%), acetone (99.9%), dichloromethane (99.5%), 4-(dimethylamino) pyridine (DMAP, 99%), *N,N*-dicyclohexylcarbodiimide (DCC, 95%), and 4-benzyloxyphenyl (99%) were used as received from Sinopharm Chemical Reagent Co., Ltd. Polymers of poly(4-vinylpyridine) (P4VP, weight-average molecular weight, *M*<sub>w</sub> = 5600) were purchased from Polymer Source Inc. and used after purification. The *n*CTB (*n* = 6, 10, 12, 14) was synthesized and purified in our lab. Their synthetic routes and characterization information are listed in the Supporting information.

### 2.2. Sample preparation.

The complexes of P4VP(*n*CTB)<sub>x</sub> were prepared in chloroform. The P4VP and *n*CTB were first dissolved separately in chloroform to form 5 wt% solutions, and then mixed together to form a homogeneous solution. After mechanical stirring for about 12 h at room temperature, the solvent was allowed to slowly evaporate for 24 h. The resulting samples were placed in a vacuum oven at 30 °C for 24 h to remove residual solvent.

### 2.3. Infrared spectroscopy

Attenuated total reflection (ATR) infrared measurements were performed using a Specac Golden Gate accessory with heated diamond-top-plate on a Bruker VECTOR22 FT-IR spectrometer equipped with a MCT-Adetector with 4 cm<sup>-1</sup> of resolution. The sample was prepared by solvent casting from chloroform onto a potassium bromide crystal. The solvent was removed and the sample was carefully dried. All FT-IR measurements were taken at room temperature. A variable temperature cell equipped with a temperature control unit (WK-1) was used for the temperature-dependent IR transmission measurements on a Nicolet6700FT-IR spectrometer equipped with a MCT-Adetector with 4 cm<sup>-1</sup> resolution. The heating runs were done step wise (heating rate 10 °C/min) from 25 to 190 °C. The spectra were measured under steady state at the given temperature.

### 2.4. Differential scanning calorimetry

The thermal behavior and phase transition temperatures of all the polymers were observed and obtained using a TA-Q200 DSC instrument. The temperature and heat flow were calibrated using standard materials (indium and zinc). Samples with a typical mass of ~5 mg were encapsulated in sealed aluminum pans and melted at 180 °C for 5 min to eliminate their thermal history. The DSC heating traces were recorded at 20 °C/min.

### 2.5. Polarized optical microscopy

The LC textures and birefringence values of the samples were examined under an Olympus polarized optical microscope (POM) BX51 equipped with a Linkam hot stage. The samples were made by sandwiching the dried polymer powder between a glass slide and a cover glass. Generally, several heating and cooling cycles with controlled rates were used to measure the phase transition by detecting the birefringence and morphology change of the sample

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