



# Effects of main chain and acceptor content on phase behaviors of hydrogen-bonded main-chain/side-chain combined liquid crystalline polymers



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## ABSTRACT

Main-chain/side-chain combined liquid crystalline polymers (MCSCCLCPs) are usually difficult to synthesize and their degrees of polymerization are relatively low, which bring difficulties in studying their structure–property relationships. In order to solve this problem, we prepared a new series of MCSCCLCPs containing mesogen-jacketed liquid crystalline polymer (MJLCP) main chains via hydrogen-bonding (H–B). A pyridine derivative with a triphenylene (Tp) unit is the H–B acceptor. In addition to the temperature dependence, the phase behavior of the resulting complex is strongly influenced by the content of the H–B acceptor and the rigidity of the side-chain core of the MJLCP. The resulting complexes exhibit different phase structures: (1) a columnar nematic phase or a smectic A (SmA) phase formed by the supramolecular MJLCP chain as a whole; (2) hierarchical nanostructures including a hexagonal columnar phase or a SmA phase of the whole polymer chain plus a discotic nematic phase associated with the Tp moieties.

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## 1. Introduction

Liquid crystal (LC), a typical soft matter with mesophase structures between the three-dimensionally ordered crystal and isotropic liquid state, can exhibit phase structures with one-dimensional (1D) or two-dimensional (2D) order on the length scale of about 1–10 nm. Liquid crystalline polymers (LCPs) have received much attention because of their potential applications in fields such as electro-optic materials, catalysis, nano-templates, etc. [1–6]. In the past decades, scientists have paid attention to the strategies in the design and synthesis of LCPs by selecting different mesogenic groups, varying the location of the mesogen, changing the length of the flexible spacer, and so on, in order to obtain more

controllable and complex structures [7–10]. Main-chain/side-chain combined LCP (MCSCCLCP), a hybrid structure which combines the chemical features of both main-chain liquid crystalline polymer (MCLCP) and side-chain liquid crystalline polymer (SCLCP), may have more complex phase behaviors compared to conventional MCLCPs and SCLCPs [11]. Since the first example reported by Ringsdorf et al. [12], many MCSCCLCPs have been synthesized and investigated [13–16]. Generally, in MCSCCLCPs, the main chain is a rigid rod or rod-like chain composed of mesogenic groups and flexible spacers, while the side chain usually contains a mesogenic group linked to the main-chain repeating unit through a flexible spacer. The typical method to obtain this kind of MCSCCLCP is condensation polymerization, and thus the molecular weight (MW) and the polydispersity index (PDI) of the polymer are not easily controllable.

Mesogen-jacketed liquid crystalline polymers (MJLCPs) are, chemically speaking, SCLCPs with a very short spacer or a single carbon–carbon bond between the backbone and the laterally attached bulky side group [17,18]. The “jacketing” effect or the steric effect makes the backbone of the MJLCP more or less extended, and

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the polymer chain as a whole acts like a supramolecular rod. Therefore, MJLCPs are more like MCLCPs rather than SCLCPs from a physical point of view. Xie et al. investigated an MCSCLCP based on an MJLCP main chain, poly(2,5-bis{[6-(4-butoxy-40-oxy-biphenyl)hexyl]oxy-carbonyl}styrene) (PBBHCS), which was synthesized using free radical polymerization [19]. Biphenyl groups are incorporated into the side chain. At low temperatures PBBHCS exhibits a hierarchical supramolecular structure with double orderings on different length scales. The main chain constructs a rectangular scaffold on the nanometer length scale, and the biphenyl-containing side chains form a smectic E (SmE)-like structure on the subnanometer length scale [20]. Zhu et al. studied another MJLCP-based MCSCLCP PPNV, which incorporates triphenylene (Tp) units into the side chain [21,22]. PPNV also exhibits hierarchical supramolecular structures in which the main chain forms the columnar structure and the Tp units in the side chain form a discotic nematic ( $N_D$ ) phase. However, the MW of the monomer of PPNV is high, and the fraction of the polymerizable styrene unit is relatively low in the monomer, both of which will lead to a smaller degree of polymerization (DP) in preparation by atom transfer radical polymerization (ATRP). It brings difficulties in studying the structure–property relationship of this and other similar MCSCLCPs.

Another useful and simple method to building LCPs is via hydrogen bonding. During the past few decades, main-chain, side-chain, and network LCPs have been designed and prepared by using hydrogen bonding [23–28]. Xu et al. synthesized a new series of MJLCPs, utilizing hydrogen bonding, and the resulting complexes form a smectic A (SmA) or columnar nematic ( $Col_n$ ) phase [29]. Huang et al. prepared hydrogen-bonded MCSCLCPs with a pyridine group-containing MCLCP and two ligands having the carboxylic acid group (–COOH), and they investigated the influence of the side-chain mesogen on the phase behavior of the MCSCLCPs [15]. However, to the best of our knowledge, the influence of main-chain mesogen on the phase behavior of MCSCLCPs prepared via hydrogen bonding has never been investigated. Therefore, the design and preparation of new MCSCLCPs based on different MJLCP main chains using hydrogen bonding are appealing and promising.

In this work, we designed and prepared new hydrogen-bonded MCSCLCPs (see Chart 1) based on MJLCP main chains. The main chains, which are used as the hydrogen-bonding donors, are two mesogen-jacketed polyelectrolytes (MJPEs) containing two –COOH groups in the side chain, poly(vinyl terephthalic acid) (PVTA) and poly[2,5-bis(4-carboxylic phenyl)styrene] (PBCPS). And a pyridine derivative containing a Tp unit, 4-(6-(3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yloxy)hexyloxy)pyridine (PHTC<sub>6</sub>, where 6 is the number of the methylene units between pyridine and Tp) is the hydrogen-bonding acceptor. One of our objectives is to explore the possibility of preparing MCSCLCPs based on MJLCP main chains via hydrogen bonding. The other objective is to study the influences of the main chain and the content of the pyridine derivative on the phase behaviors of these MCSCLCPs.

Self-assembled phase structures of the MJPE-ligand complexes in bulk were investigated using various techniques. The complexes

with different compositions are denoted as PVTA(PHTC<sub>6</sub>)<sub>x</sub> and PBCPS(PHTC<sub>6</sub>)<sub>x</sub> (where the value of x indicates the molar ratio of PHTC<sub>6</sub> to the –COOH group in the MJPE repeating unit). We mainly focused on complexes with x ranging from 0.5 to 1, where macro-phase separation did not occur.

## 2. Materials and methods

### 2.1. Materials

Dimethyl formamide (DMF) was refluxed over potassium hydroxide and distilled out before use. Tetrahydrofuran (THF) was refluxed over sodium under argon and distilled before use. Chlorobenzene was washed by H<sub>2</sub>SO<sub>4</sub> and then distilled under a reduced pressure. All other reagents were used as received from commercial sources.

### 2.2. Measurements

All the measurements, such as <sup>1</sup>H NMR spectrometry, mass spectrometry (MS), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), FTIR spectroscopy, polarized light microscopy (PLM), small-angle X-ray scattering (SAXS), and 2D wide-angle X-ray diffraction (WAXD) experiments, were performed according to the procedures previously described [30,31].

### 2.3. Synthesis of the MJPEs

The chemical structures and synthetic procedures of the monomers and polymers are illustrated in Scheme 1. The experimental details are described as follows.

#### 2.3.1. Synthesis of di-tert-butyl 2-vinylterephthalate (TBVT)

2-Vinylbenzene-1,4-dioic acid was synthesized according to the procedure reported previously [32]. 2-Vinylbenzene-1,4-dioic acid (1.92 g, 10.0 mmol), 2-methylpropan-2-ol (2.22 g, 30.0 mmol), *N,N*-dicyclohexylcarbodiimide (DCC, 10.6 g, 50.0 mmol), *N,N*-dimethylpyridin-4-amine (DMAP, 0.120 g, 1.00 mmol), and 50 mL of dry dichloromethane were added into a 100 mL round-bottomed flask, and then the mixture was stirred at ambient temperature for 24 h. The insoluble material was removed by filtration, and the solvent was evaporated under a reduced pressure. The product was purified by passing through a silica gel column with dichloromethane and petroleum ether (v:v, 1:3) as the eluent. The obtained monomer was a light yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 1.67 (s, 18H), 5.37–5.41 (d, 1H), 5.70–5.76 (d, 1H), 7.33–7.43 (p, 1H), 7.80–7.82 (d, 1H), 7.87–7.90 (d, 1H), 8.16 (s, 1H). MS (EI, m/z): 304.2 (M<sup>+</sup>).

#### 2.3.2. Synthesis of methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate

2,5-Dibromostyrene was synthesized according to the previously reported method [33]. 4-(Methoxycarbonyl)phenylboronic

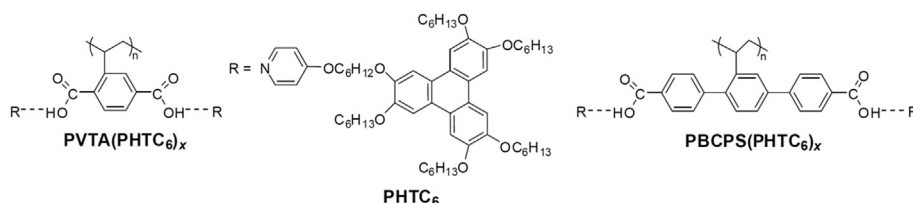


Chart 1. Chemical structures of the supramolecular MCSCLCPs.

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