



# Manipulating ordered structure of ionic liquid crystalline polymers through tuning the alkyl spacer length



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## ABSTRACT

The fabrication of ordered structure is very important for the applications of ionic liquid crystalline polymers (ILCPs) or polymerized (ionic liquid crystal) (PILC). In this paper, we reported a facile approach to manipulate the ordered structure of ILCPs through adjusting the length of alkyl spacer. We designed and synthesized a series of ILCPs contained imidazolium, poly(2,5-bis{[*m*-(4-butoxy-4'-imidazolium phenyl) *m*-alkyl] oxy carbonyl} styrene bis (fluoroborate) salts) (denoted as P<sub>4-*m*</sub>-BF<sub>4</sub>, *m* represents the number of carbon in the alkyl spacers and *m* = 2, 4, 6, 10) via radical polymerization. Combined differential scanning calorimetry (DSC), polarized light microscopy (PLM), X-ray scattering, and two-dimensional wide-angle X-ray diffraction (2D WAXD), we found that the ordered structure of this ILCPs can transfer from smectic A phase (SmA) to hexagonal columnar ( $\Phi_H$ ) phase with the increase of spacer. Furthermore, these results were confirmed by reconstructed relative electron density map using fast fourier transform algorithm (FFT). The result revealed that the increase of alkyl spacer would affect the interaction between ions and side chain, and induce the packing of the side chains. It was evident that the alkyl spacer played an important role in the constructing of ordered structure and offered a new method to fabricate different ordered structure of ILCPs.

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## 1. Introduction

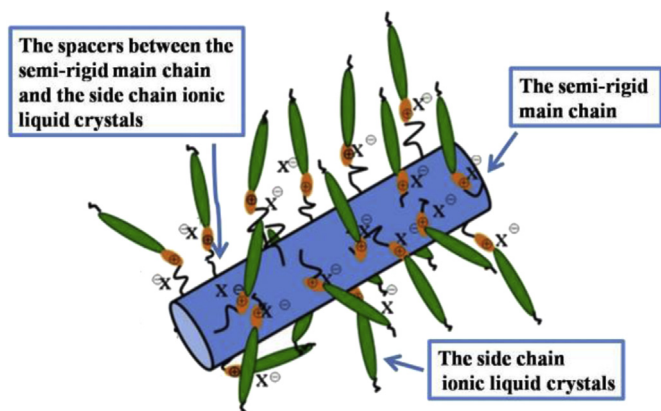
Ionic liquid crystalline polymers (ILCPs) or polymerized (ionic liquid crystal) (PILC) with the properties of combined ion-conductivity and the liquid crystal (LC) ordering have attracted tremendous attentions as promising applications in ionic conductive materials, piezoelectric materials, polymeric electrolytes, ionomeric membranes, photoelectric material and functional nanostructured materials and so on [1–21]. Ionic groups could promote inter- and intra-chain interactions and the interfacial adhesion, which improved the transverse, compressive strengths and miscibility significantly [22–29]. As a result, the physical properties such as the mechanical stability, thermal stability, processability, spatial controllability and electrochemical properties were improved [2,8,30–32]. On the other hand, the transformation of the ordering structures in ILCPs would result in different

properties, which directly impacted their promising application [1,4,9–12]. Thus, it became a very important topic to manipulate the ordered structure of ILCPs through controlling their chemical structures. Reasonable control of the interaction between the imidazolium ion and counter-anion in SCILCPs was an effective approach for tuning the ordered structures and LC behavior, and it resulted in one-dimensional (1D) lamellar, 2D hexagonal and three-dimensional (3D) cubic phase [30,33–37].

In previous research [38], ILCPs based on a “Jacketed” effect through Mesogen-jacketed LC polymer (MJLCP) yielded significantly high steric hindrance via the use of bulky side groups that forced the backbone to take a relatively extended and stiff chain conformation [39,40]. This approach allowed for the creation of a hexagonal columnar LC ordered structure due to the strong intramolecular interplay between the imidazolium cations and counter-anions. Although the kind of ILCPs can stabilize the LC phase contrasted to the corresponding LC polymer without ions, the phase structure cannot be adjusted through changing their structures. In order to reasonably control the ordered structure of ILCPs, we designed this kind of ILCPs containing ionic mesogens in their side group instead of alkyl chain with ions as shown in Scheme 1.

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**Scheme 1.** The molecular model of MCSCLCs based on "Jacketing" Effect.

Compared to previous ILCPs [38], the present ILCPs have similar chemical structure as the combined main-chain/side-chain LC polymer (MCSCLCP), whose main chain has the "Jacketed" effect and has strong interplay with the side chain. This combined effect promotes hierarchical supra-molecular structures with orderings on the nanometer and subnanometer length scales [41,42]. Thus, this special structure offers an approach to control the ordered properties for ILCPs. It is well known that the spacers between the main chain and side group could be readily controlled via a synthesis process through different halogenated hydrocarbon chain. According to the Finkelmann's principle [43] the inserted flexible spacer with a reasonable length could decouple the dynamics of the backbone and the side-chain mesogen, which lead to different LC phases, such as smectic A (SmA), and smectic C (SmC) [44–47]. Obviously, it offers more opportunities to design different materials through controlling the ordered structure of ILCPs.

In this article, we report the design and synthesis of poly(2,5-bis {[*m*-(4-butoxy-4'-imidazolium phenyl) *m*-alkyl] oxy carbonyl} styrene bis (fluoroborate) salts) with different spacers ( $P_{4-m}$ -BF<sub>4</sub>, *m* represents the number of carbon in the alkyl spacers and *m* = 2, 4, 6, 10). The synthesis of these materials is depicted in Scheme 2. It is worth mentioning that in this paper we only choose the anion BF<sub>4</sub><sup>-</sup> as the counter anion because ILCPs with BF<sub>4</sub><sup>-</sup> are proved to exhibit excellent ordered structures compared to other anions [38]. Additionally, we have investigated the phase transitions and LC ordered structures of  $P_{4-m}$ -BF<sub>4</sub> with the variation of the length of the alkyl spacer. It is very interesting that  $P_{4-2}$ -BF<sub>4</sub>,  $P_{4-4}$ -BF<sub>4</sub> and  $P_{4-6}$ -BF<sub>4</sub> formed smectic structures, but the  $P_{4-10}$ -BF<sub>4</sub> exhibited the  $\phi_H$  LC ordered structure. Thus, it is evident that the alkyl spacer played an important role in the constructing of LC ordered structure in this system.

## 2. Experimental section

### 2.1. Materials

N, N-dimethylformamide (DMF) was refluxed with calcium hydride for 48 h and evaporated with vacuum distillation. N-

methyl pyrrolidone (NMP), acetonitrile were dried, filtered and evaporated with vacuum distillation before use. 2, 2'-azo-bis-isobutyronitrile (AIBN) was purified by recrystallization from ethanol. Sodium tetrafluoroborate (NaBF<sub>4</sub>), 1, 2-dibromoethane, 1,4-dibromobutane, and 1,10-dibromodecane, were purchased from Aladdin. All other reagents were of commercial grade and were used as received.

### 2.2. Instruments and measurements

<sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded on a Bruker ARX400 spectrometer at room temperature, using deuterated chloroform (CDCl<sub>3</sub>) as the solvent and tetramethylsilane (TMS) as the internal standard.

Fourier transform infrared spectroscopy (FTIR) spectra in KBr pellets were recorded on a PE Spectrum One FTIR spectrometer.

The apparent number average MW (M<sub>n</sub>) and MW distribution (M<sub>w</sub>/M<sub>n</sub>) were measured by a gel permeation chromatography (PL-GPC120), using DMF as the eluant. The GPC calibration curve was obtained with linear polystyrene as standard.

The thermogravimetric analysis (TGA) was performed by means of a TA SDT 2960 instrument at a heating rate of 20 °C/min under nitrogen atmosphere.

Differential scanning calorimetry (DSC) examination was carried out on a TA DSC Q100 calorimeter with a programmed heating procedure in nitrogen. The temperature and heat flow were calibrated, using standard materials (indium and zinc) at different cooling and heating rates. The samples with a typical mass of 3–10 mg were encapsulated in sealed aluminum pans. Transition temperatures were taken from the second heating cycle.

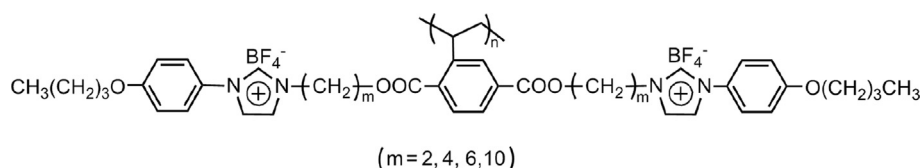
LC texture of the samples was examined under polarized light microscopy (PLM) (Leica DM-LM-P) equipped with a Mettler FP82HT hot stage and an FP80HT temperature controller.

X-ray scattering experiments were performed using a SAXSess instrument (Anton Paar) equipped with a Kratky block-collimation system. The X-ray was generated using a Philips PW3080 sealed-tube X-ray generator with the Cu target. Samples were placed in between aluminum foils which were folded and sandwiched in a steel sample holder. Scattering data were acquired for a 30 min exposure. The background scattering from aluminum foils was acquired and then subtracted from the sample profiles.

Two-dimensional wide-angle X-ray diffraction (2D WAXD) experiments were carried out on a Bruker D8 Discover diffractometer in a transmission mode using a GADDS detector. To perform the 2D WAXD experiments with the point-focused X-ray as the incident beam, we prepared the macroscopically oriented samples by mechanical shear at temperatures close to the samples' isotropic temperature.

### 2.3. Synthesis

The synthetic route of  $P_{4-m}$ -BF<sub>4</sub> is outlined in Scheme 3. And the detail information about the intermediate and monomers were shown in Supporting information.



**Scheme 2.** The chemical structures of ILCPs  $P_{4-m}$ -BF<sub>4</sub>.

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