Combined main-chain/side-chain ionic liquid crystalline polymer based on ‘jacketing’ effect: Design, synthesis, supra-molecular self-assembly and photophysical properties

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Abstract. Reasonably fabricating ordered structures of ionic polymers is very important for the development of novel functional materials. By combining the ions and liquid crystalline polymer, we successfully designed and synthesized a series of novel combined main-chain/side-chain ionic liquid crystalline polymer (MCSC-ILCPs) containing imidazolium groups and different counter-anions, poly (2,5-bis{[6-(4-butoxy-4'-imidazolium biphenyl)hexyl]oxycarbonyl}styrene salts) poly(BImBHCS-X) with the following types of counter-anions (Br^- , BF_4^- , PF_6^- and TFSI^-). Combined technologies confirmed the chemical structures of the monomers and polymers with imidazolium cation and different counter-anions. Differential scanning calorimetry (DSC), polarized light microscopy (PLM) and one- and two-dimensional wide-angle X-ray diffraction (1D and 2D WAXD) results illustrated that the LC structures and the transitions of ordered structures depended on the nature of the counter-anion employed. The polymers with Br^- and BF_4^- counter-anions exhibited smectic A (SmA) LC behavior below the isotropic temperature. The another one, poly(BImBHCS-TFSI) with the large volume of the TFSI^- anion destroyed the packing of the LC ordered structure resulting in an amorphous structure. The photophysical properties of the polymers prepared can be adjusted by tuning the ionic interaction of the polymers by switching the counter-anion.

Keywords: polymer synthesis, molecular engineering, ionic liquid crystalline polymer, phase behavior, supermolecular structure

1. Introduction

Ionic liquid crystalline polymers (ILCPs) are a class of macromolecular architectures with mesogenic groups and ionic species and they have attracted great interest in the fields of polymer chemistry and materials science lately [1–3]. The combination of electrostatic interaction with liquid crystalline (LC) ordering yields ILCPs with excellent mechanical properties, rheological processability, piezoelectric

performance, and optical variable performance [1–7]. Generally, ionic interaction promotes the ILCPs to form ionic clusters resulting in a reversible physical gelation [1, 8, 9]. Moreover, incorporation of the ions and selection of the type of ion chemistry can effectively improve the miscibility with other polymers. Therefore, ILCPs are versatile candidates to construct new high-performance functional mate-

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rials and micrometer/nanometer composite materials [10–20].

In terms of the chemical structure, ILCPs can be classified as a main-chain ionic liquid crystalline polymer (MC-ILCP) or a side-chain ionic liquid crystalline polymer (SC-ILCP) [1, 3, 6]. For the MC-ILCPs, the ionic liquid crystals (ILCs) are located in the main chain of polymer. Usually, this type polymer can be synthesized by a polycondensation reaction or non-covalent bond (such as hydrogen bonding, ionic bonds etc.). Incorporation of ion groups yields significant improvement in the polymer's transverse strength, compressive strength, and miscibility of polymers or other species in MC-ILCPs when compared to traditional main-chain liquid crystalline polymers (MCLCPs) [21, 22]. At the same time, the implementation of the ionic groups leads to better and more diverse thermal behavior, liquid crystal behavior, and photoelectric properties [23–26]. For example, the content of sulfonic acid in ILCPs not only dictates their glass transition temperature (T_g) and melting point (T_m), but also has been demonstrated to play an important role in their supramolecular structures [27, 28]. For MC-ILCPs with viologen, the LC properties can be controlled via tuning the main chain linkage position resulting in both thermotropic and lyotropic smectic phases [29]. For SC-ILCPs, their ILC mesogens are pendants located in the side chain or the ions are placed in the main chain and LC mesogens are situated in the side chain. Both of these ILCPs can be synthesized or assembled through free radical polymerization, silicon hydrogen addition, or non-covalent bond assembly [30–32]. Similarly to MC-ILCPs, the T_g , isotropic temperature (T_i), and LC behavior of the SC-ILCPs becomes varied due to the incorporation of the different cations and anions. For instance, SC-ILCPs with sulfonic groups and carboxylic groups can self-assemble to sandwich thermotropic smectic phase structure, but a similar structure with bromide anions displays nematic phase only [33, 34].

Side chain liquid crystalline polymers (SCLCPs) without ions can be divided into two classes according to the linkage type of mesogenic groups to the polymer backbone. These two classes are: i) terminally (end-on) SCLCPs [35, 36] or ii) laterally (side-on) SCLCPs [37, 38]. Normally, it is necessary to employ flexible spacers to decouple the interaction between the side chain and the backbone

of SCLCPs [39, 40]. However, when the flexible spacers were very short or a single carbon-carbon bond in the side-on in SCLCPs was utilized, these polymers still exhibited LC behaviors [41]. The typical example of such systems are the mesogen-jacketed LC polymers (MJLCPs), [42–46] whose bulky mesogenic units are laterally attached to the polymer backbone via non- or only short spacers. The significantly high steric hindrance forces the polymer chain to become stiff. In fact, the mesogens may not be necessary as long as the bulky side groups around the backbone are large enough. For example, poly[dialkyl vinylterephthalate] (PDAVT) with an appropriate alkyl length could form a 2D hexagonal columnar LC phase (Φ_H) [47]. Based on the PDAVT, a combined main-chain/side-chain LC polymer (MCSCSCLCP) poly(2,5-bis{[6-(4-butoxy-4'-oxy biphenyl) hexyl] oxy carbonyl} styrene) (PBBHCS) have been designed and synthesized. It is found that the MCSCSCLCP can exhibit hierarchical supra-molecular structures with orderings on both the nanometer and subnanometer length scales [48]. Herein, we intend to incorporate ions into this kind of MCSCSCLCP to construct a novel combined main-chain/side-chain ionic liquid crystalline polymer (MCSC-ILCPs). The introduction of ions adds additional interactions to the existing interaction of chain biphenyl mesogens and the polymer backbone leading to more complex behavior of the system. Thus, it is hypothesized that the resulting materials could display a larger array of structural configurations when processing as a function of temperature. Ultimately, our intention is to investigate these new materials to help us to understand the supra-molecule hierarchical assembly process and structure in ILCPs. The chemical structures of the system and the corresponding model are as shown in Figure 1. It is worth mentioning that previous work has revealed that the side chains with ions and the main chain of ILCPs cannot be totally phase separated. The two entities act as a whole to form a column type structure – specifically, the hexagonal columnar LC ordered structure form [49]. In this work, the PILC prepared derives from the MCSCSCLCP. This system differs from previous works because not only does the spacer induce side chain and main chain phase separation, but its unique characteristics can create different LC phases due to the ionic mesogens in side chain.

Figure 1. Chemical structures of MCSC-ILCPs poly(BImBHCS-X) ($X^- = \text{Br}^-, \text{BF}_4^-, \text{PF}_6^-$ and TFSI^-)

Herein, we report the design and synthesis of the novel MCSC-ILCPs poly(2,5-bis{[6-(4-butoxy-4'-imidazolium biphenyl) hexyl] oxy carbonyl} styrene salts) [denoted as poly (BImBHCS-X), $X^- = \text{Br}^-, \text{BF}_4^-, \text{PF}_6^-$ and TFSI^-] via radical polymerization. Detailed characterization of the thermal stability, phase transitions and LC ordered structures of ILCPs with different counter-anions were performed. The results showed that all the samples with varying counter-anions exhibited lamellar LC phase (SmA phase) except for the sample with TFSI^- . Additionally, these MCSC-ILCPs exhibited unique and enhanced fluorescence properties, which is able to promise a material for nanoscale technologies.

2. Experimental section

2.1. Instruments and measurements

Elemental analysis was carried out with an Elementar Vario EL instrument. ^1H NMR spectrum was taken at ambient temperature on a Bruker ARX400 spectrometer with chloroform-*d* (CDCl_3) as the solvent and tetramethylsilane (TMS) as the internal reference. Infrared spectroscopy was recorded on a PE Spectrum One FTIR spectrophotometer in KBr pellets over a range of 500–4000 cm^{-1} .

The apparent number-average M_w (M_n) and M_w distribution (M_w/M_n) were measured by a gel permeation chromatography (PL-GPC120). The μ -styragel columns used DMF as an eluent (1.0 mL/min) at 35°C. The calibration curve was obtained with linear polystyrene as standards.

Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument from room temperature to 600°C under nitrogen at a heating rate of

20°C/min. Differential scanning calorimetry (DSC) was performed on a TA DSC Q100 calorimeter under a continuous nitrogen purge and was recorded with a typical sample mass of 3–10 mg on the standard materials (indium and zinc) at different cooling and heating rates. LC texture was examined under polarized light microscopy (PLM) (Leica DM-LM-P) coupled with a Mettler-Toledo hot stage (FP82HT). The film was casted from chloroform solution and the thickness was approximately $\sim 10 \mu\text{m}$.

1D wide-angle X-ray diffraction (1D WAXD) experiments were performed on a Philips X' Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu K α) and an X' celerator detector. The reflection peak positions were calibrated with silicon powder ($2\theta > 15^\circ$) and silver behenate ($2\theta < 10^\circ$). The sample stage was set horizontally and a temperature control unit (Paar Physica TCU 100) in conjunction with the diffractometer was employed to study the structure evolutions as a function of temperature. The heating and cooling rates in the WAXD experiments were 10°C/min. The 2D WAXD experiments were performed with a Bruker D8Discover in a transmission mode using a GADDS detector. The point-focused X-ray beam was aligned perpendicular to both the shear direction and the shear gradient. For both diffractometers, the X-ray sources (Cu KR) were provided by 3 kW ceramic tubes, and the diffraction peak positions were calibrated with silicon powder ($2\theta > 15^\circ$) and silver behenate ($2\theta < 10^\circ$).

UV-Vis absorption spectra were recorded with a Shimadzu MultiSpec-1501 spectrophotometer. All fluorescence measurements were carried out on a Perkin-Elmer LS55 luminescence spectrometer with excitation slit set at 5.0 nm and emission slit set at 3.0 nm.

2.2. Materials

Tetrahydrofuran (THF), acetonitrile and N-methyl-2-pyrrolidone (NMP) were desiccated by anhydrous magnesium sulfate, then filtered and purified with vacuum distillation before use. N, N-dimethylformamide (DMF) was heated circumfluence with calcium hydride for 48 hours, then filtered and obtained with vacuum distillation. Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol before use. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) obtained from Aladdin was

dried under vacuum overnight. Other solvents and reagents were used as received from commercial sources.

2.3. Synthesis

The synthetic route of the monomers and polymers MCSC-ILCPs is given in Figure 2. The detailed synthesis and characterization of intermediates, monomers, and polymers are provided as following.

2.4. Synthesis of MCSC-PILCs

2.4.1. Synthesis of 4-bromo-4'-butoxy biphenyl

4-bromo-4'-hydroxy biphenyl 2.49 g (10 mmol), 1-butyl bromide 2.05 g (15 mmol), K_2CO_3 2.76 g (20 mmol), and with KI 0.33 g (2 mmol) were refluxed in DMF until TLC indicated full conversion. Reaction mixture was cooled and filtered, the filter residue was washed with acetone. Filtrate was collected and removed with rotating vaporizer apparatus. The amount of DMF was reduced to 25% by vacuum distillation and the concentrated solution was precipitated in a mass of distilled water and the precipitate was filtered and collected. The product was dried in a vacuum oven over night and purified by recrystallization from ethanol, yield 82% of a white solid. 1H NMR ($CDCl_3$) δ (ppm): 7.56–7.54 (d, 2H, Ar-H), 7.50–7.48 (d, 2H, Ar-H),

7.44–7.42 (d, 2H, Ar-H), 6.99–6.97 (d, 2H, Ar-H), 4.02 (t, 2H, $-OCH_2-$), 1.81 (m, 2H, $-CH_2-$), 1.54 (m, 2H, $-CH_2-$), 1.02–0.99 (t, 3H, $-CH_3$).

2.4.2. Synthesis of 4-butoxy-4'-imidazolyl biphenyl

4-bromo-4'-butoxy biphenyl 3.05 g (10 mmol), imidazole 1.02 g (15 mmol), K_2CO_3 2.76 g (20 mmol), and together with CuI 0.382 g (2 mmol) were put into a three-necked round bottom flask and stirred in dry N-methyl-2-pyrrolidone under nitrogen atmosphere at $190^\circ C$ for 24 h. The mixture was cooled down, filtered and washed with dichloromethane, and then the solvent was removed with rotate vaporizing apparatus. The remainder flowed through a short column filled with neutral aluminum oxide powder, and the residual liquid was precipitated in water and filter residue was collected. The solid product was dried in a vacuum oven over night, and then purified by recrystallization from hexane, yield 40.5% of a white or silver grey solid. 1H NMR ($CDCl_3$) δ (ppm): 8.03 (s, 1H, Im-H2), 7.70–7.68 (d, 2H, Ar-H), 7.56–7.54 (d, 2H, Ar-H), 7.48–7.46 (d, 2H, Ar-H), 7.37 (br s, 1H, Im-H4), 7.28 (br s, 1H, Im-H5), 7.03–7.01 (d, 2H, Ar-H), 4.04 (t, 2H, $-OCH_2-$), 1.82–1.81 (m, 2H, $-CH_2-$), 1.55 (m, 2H, $-CH_2-$), 1.03–1.02 (t, 3H, $-CH_3$).

Figure 2. Synthetic route of the ILCs and the corresponding MCSC-ILCPs

2.4.3. Synthesis of ω -(4-butoxy biphenyl-4'-imidazolium)-1-bromo hexane bromide

4-butoxy-4'-imidazolyl biphenyl 2.92 g (10 mmol), 1,6-dibromohexane 7.32 g (30 mmol), and together with dry acetonitrile were added into a round bottom flask and refluxed until TLC indicated full conversion. The mixture was cooled down and the solvent was removed by rotating vaporizer apparatus. The residual liquid was precipitated in ethyl acetate, and the solid was washed with THF at least three times and then dried in a vacuum oven over night. The collected product was dissolved in a little dichloromethane and purified by the silicon column using mixed solvent (dichloromethane:methanol = 10:1) as the eluent. The first ingredient was collected and the eluent was removed with rotate vaporizing apparatus, then the product dried in a vacuum oven gave a pale-grey viscous solid. Yield: 80.2%. ^1H NMR (CDCl_3) δ (ppm): 11.15 (s, 1H, Im-H2), 7.78–7.76 (d, 2H, Ar-H), 7.68–7.66 (d, 2H, Ar-H), 7.62 (br s, 1H, Im-H4), 7.50 (br s, 1H, Im-H5), 7.46–7.43 (d, 2H, Ar-H), 6.94–6.92 (d, 2H, Ar-H), 4.58–4.55 (t, 2H, $-\text{N}^+\text{CH}_2-$), 3.97–3.94 (t, 2H, $-\text{OCH}_2-$), 3.37–3.34 (t, 2H, $-\text{CH}_2\text{Br}$), 2.00–1.97 (m, 2H, $-\text{CH}_2-$), 1.83–1.71 (m, 4H, $-\text{CH}_2-$), 1.49–1.41 (m, 6H, $-\text{CH}_2-$), 0.96–0.92 (t, 3H, $-\text{CH}_3$).

2.4.4. Synthesis of 2-vinyl p-biphtalic acid

2-vinyl p-biphtalic acid was obtained by using the previous method from Zhang *et al.* [70]. ^1H NMR ($\text{DMSO}-d_6$) δ (ppm): 8.24 (s, 1H, Ar-H), 7.92 (d, 2H, Ar-H), 6.67 (d, 1H, $=\text{CH}-$), 5.75 (d, 1H, $=\text{CH}_2$), 5.42 (d, 1H, $=\text{CH}_2$).

2.4.5. Synthesis of monomers

2, 5-bis{[6-(4-butoxy-4'-imidazolium-biphenyl) hexyl] oxy carbonyl} styrene bis(bromide) (BImBHCS-Br)

2-vinyl p-biphtalic acid 0.96 g (5 mmol) and potassium hydrogen carbonate 1.0 g (10 mmol) were added into a 250 mL round bottom flask and stirred in DMF about 30 min until the vinyl p-biphtalic acid was dissolved completely. Then the ω -(4-butoxy biphenyl-4'-imidazolium)-1-bromo hexane bromide 6.70 g (12.5 mmol) and nitrobenzene 0.02 g (0.18 mmol) were input the flask and the mixture was stirred at 100°C until TLC indicated full conversion. After the reaction was over, the mixture was cooled down, filtered and the filtrate was added to ethyl acetate for precipitating. The resulting pre-

cipitate was collected and washed with THF five times. The crude product was separated through a silicon column by using the ethanol solution as the eluent until the first deserted ingredient outflow completely, and then exchanging mixed solvent (dichloromethane:methanol = 5:1) as the eluent. The previous outflowing ingredient was collected. By removing the solvent with rotate vaporizing apparatus, the product dried in a freeze drying gave a pale-yellow solid. Yield: 63.8%. ^1H NMR (CDCl_3) δ (ppm): 11.07 (s, 2H, Im-H2), 8.18 (s, 1H, Ar-H), 7.96–7.89 (d, 2H, Ar-H), 7.81–7.79 (d, 4H, Ar-H), 7.73 (s, 2H, Im-H4), 7.69–7.66 (d, 4H, Ar-H), 7.64 (s, 2H, Im-H5), 7.49–7.43 (d, 4H, Ar-H), 6.95 (d, 1H, $=\text{CH}-$), 6.93 (d, 4H, Ar-H), 5.74–5.70 (d, 1H, $=\text{CHH}$), 5.41–5.38 (d, 1H, $=\text{CHH}$), 4.61–4.57 (t, 4H, $-\text{N}^+\text{CH}_2-$), 4.30–4.28 (t, 4H, $-\text{COOCH}_2-$), 4.00–3.96 (t, 4H, $-\text{OCH}_2-$), 2.04 (m, 4H, $-\text{CH}_2-$), 1.79–1.76 (m, 8H, $-\text{CH}_2-$), 1.50 (m, 12H, $-\text{CH}_2-$), 0.99–0.96 (t, 6H, $-\text{CH}_3$).

FTIR (KBr): ν O-H/Br $\cdots$ H 3441 (s), Ar C-H 3054 (w), Im C-H 2957 (s), Ar C-H 2929 (s), $-\text{CH}_2-$ 2868 (s), $-\text{COO}$ 1718 (s), Ar C-H 1651 (m), C=C 1608 (m), Ar skeletal vibration 1560 (m), Im C=N 1499 (m), $-\text{CH}_2-$ 1465 (m), $-\text{CH}_3$ 1384 (m), Im C-N 1288 (m), C-O-C 1248 (s), Im skeletal vibration 1180 (w), Im C-N 1115 (m), Im C-N 1072 (m), C-O-C 1036 (w), Ar-CH=CH₂ 972 (w), Ar-CH=CH₂ 916 (w), Ar C-H 824 (m), Im C-H 760 (m), Ar C-H 618 (m) cm^{-1} .

Anal. Calcd for $\text{C}_{60}\text{H}_{70}\text{N}_4\text{O}_6\text{Br}_2$: C, 65.43; H, 6.41; N, 5.09; Found: C, 64.79; H, 6.54; N, 5.08.

Anion exchange reaction for other three monomers

Because the used anion-exchange reactions of the ILC monomers are similar, herein, we took the monomer BImBHCS- BF_4 as an example to illustrate the process. The monomer BImBHCS-Br 3.30 g (3 mmol) was dissolved in dichloromethane and sodium fluoroborate (NaBF_4) 1.65 g (15 mmol) dissolved in deionized water were mixed at a 250 mL round bottom flask under vigorous stirring for nearly 10 hours. After the reaction complete, the mixed solution was extracted with dichloromethane 50 mL by twice, and washed with deionized water 50 mL by five times until the eluent remained clear with the addition of an aqueous solution of AgNO_3 . The organic phase was collected and dried with MgSO_4 and filtered. The solvent was removed with rotate

vaporizing apparatus. The product was dried in a freeze dryer.

2,5-bis{[6-(4-butoxy-4'-imidazolium-biphenyl) hexyl] oxy carbonyl} styrene bis(fluoroborate) (BImB-HCS-BF₄) Yield: 89.5% of an off-white solid.

¹H NMR (CDCl₃) δ (ppm): 9.25 (s, 2H, Im-H2), 8.18 (s, 1H, Ar-H), 7.99–7.93 (d, 2H, Ar-H), 7.68 (d, 4H, Ar-H), 7.63 (s, 2H, Im-H4), 7.58–7.56 (d, 4H, Ar-H), 7.47 (s, 2H, Im-H5), 7.45–7.43 (d, 4H, Ar-H), 6.95 (d, 1H, =CH-), 6.93 (d, 4H, Ar-H), 5.75–5.71 (d, 1H, =CHH), 5.41–5.38 (d, 1H, =CHH), 4.35–4.32 (t, 4H, -N⁺CH₂-), 4.30–4.28 (t, 4H, -COOCH₂-), 4.00–3.97 (t, 4H, -OCH₂-), 1.98 (m, 4H, -CH₂-), 1.80–1.74 (m, 8H, -CH₂-), 1.52–1.49 (m, 12H, -CH₂-), 1.01–0.98 (t, 6H, -CH₃).

FTIR (KBr): ν O-H 3437 (s), Im C-H 3152 (w), Ar C-H 3042 (w), Im C-H 2956 (s), Ar C-H 2927 (s), -CH₂- 2869 (s), -COO 1718 (s), Ar C-H 1640 (w), C=C 1607 (m), Ar skeletal vibration 1563 (m), Im C=N 1499 (w), -CH₂- 1465 (s), -CH₃ 1382 (m), Im C-N 1289 (m), C-O-C 1248 (s), Im skeletal vibration 1180 (m), Im C-N 1114 (m), BF₄⁻ 1068 (s), Ar-CH=CH₂ 972 (w), Ar-CH=CH₂ 917 (w), Ar C-H 823 (s), Im C-H 761 (m), Ar C-H 621 (m) cm⁻¹.

Anal. Calcd for C₆₀H₇₀N₄O₆B₂F₈: C, 64.49; H, 6.32; N, 5.02; Found: C, 64.79; H, 6.53; N, 4.82.

2,5-bis{[6-(4-butoxy-4'-imidazolium-biphenyl) hexyl] oxy carbonyl} styrene bis(hexafluorophosphate) (BImBHCS-PF₆) Yield: 88.2% of a light red solid.

¹H NMR (CDCl₃) δ (ppm): 8.86 (s, 2H, Im-H2), 8.18 (s, 1H, Ar-H), 7.99–7.92 (d, 2H, Ar-H), 7.61–7.59 (d, 4H, Ar-H), 7.51 (s, 2H, Im-H4), 7.48 (d, 4H, Ar-H), 7.44 (s, 2H, Im-H5), 7.42 (d, 4H, Ar-H), 6.95 (d, 1H, =CH-), 6.93 (d, 4H, Ar-H), 5.74–5.70 (d, 1H, =CHH), 5.40–5.37 (d, 1H, =CHH), 4.28 (t, 4H, -N⁺CH₂-), 4.28 (t, 4H, -COOCH₂-), 4.00–3.97 (t, 4H, -OCH₂-), 1.97 (m, 4H, -CH₂-), 1.81–1.74 (m, 8H, -CH₂-), 1.55–1.47 (m, 12H, -CH₂-), 1.01–0.98 (t, 6H, -CH₃).

FTIR (KBr): ν O-H 3445 (s), Im C-H 3160 (w), Im C-H 2957 (m), Ar C-H 2931 (m), -CH₂- 2870 (m), -COO 1717 (s), Ar C-H 1670 (s), C=C 1607 (m), Ar skeletal vibration 1564 (w), Im C=N 1499 (s), -CH₂- 1467 (w), -CH₃ 1383 (w), Im C-N 1291 (w), C-O-C 1248 (s), Im skeletal vibration 1181 (w), Im C-N 1119 (m), Im C-N 1076 (m), Ar-CH=CH₂ 972 (w), Ar-CH=CH₂ 919 (w), PF₆⁻ 842 (vs), Im C-H 762 (w), Ar C-H 622 (m) cm⁻¹.

Anal. Calcd for C₆₀H₇₀N₄O₆F₁₂P₂: C, 58.42; H, 5.72; N, 4.54; Found: C, 58.78; H, 5.62; N, 4.48.

2,5-bis{[6-(4-butoxy-4'-imidazolium-biphenyl) hexyl] oxy carbonyl} styrene bis [bis (trifluoromethanesulfonyl) imide] (BImBHCS-TFSI) Yield: 88.0% of a yellowish solid.

¹H NMR (CDCl₃) δ (ppm): 9.12 (s, 2H, Im-H2), 8.21 (s, 1H, Ar-H), 7.94–7.89 (d, 2H, Ar-H), 7.69–7.67 (d, 4H, Ar-H), 7.58 (s, 2H, Im-H4), 7.56–7.54 (d, 4H, Ar-H), 7.50 (s, 2H, Im-H5), 7.48 (d, 4H, Ar-H), 6.98 (d, 1H, =CH-), 6.96 (d, 4H, Ar-H), 5.75–5.71 (d, 1H, =CHH), 5.40–5.38 (d, 1H, =CHH), 4.33 (t, 4H, -N⁺CH₂-), 4.32 (t, 4H, -COOCH₂-), 4.01–3.98 (t, 4H, -OCH₂-), 1.99 (m, 4H, -CH₂-), 1.78–1.77 (m, 8H, -CH₂-), 1.56–1.48 (m, 12H, -CH₂-), 1.01–0.97 (t, 6H, -CH₃).

FTIR (KBr): ν O-H 3450 (s), Im C-H 3139 (w), Im C-H 2954 (m), Ar C-H 2926 (s), -CH₂- 2867 (m), -COO 1700 (s), Ar C-H 1673 (w), C=C 1605 (m), Ar skeletal vibration 1566 (w), Im C=N 1499 (m), -CH₂- 1465 (m), -CH₃ 1384 (w), TFSI⁻ 1354 (s), Im C-N 1280 (m), C-O-C 1242 (m), TFSI⁻ 1178 (s), Im C-N 1135 (m), TFSI⁻ 1056 (s), Ar-CH=CH₂ 973 (w), Ar-CH=CH₂ 916 (w), Ar C-H 824 (s), Im C-H 760 (w), TFSI⁻ 738 (w), Ar C-H 614 (s) cm⁻¹.

Anal. Calcd for C₆₄H₇₀N₆O₁₄F₁₂S₄: C, 51.12; H, 4.70; N, 5.59; Found: C, 51.44; H, 4.77; N, 5.56.

2.4.6. Synthesis of MCSC-PILCs

Poly (2, 5-bis {[6-(4-butoxy-4'-imidazolium-biphenyl) hexyl] oxy carbonyl} styrene salts) [poly(BImBHCS-X)] (X⁻ = Br⁻, BF₄⁻, PF₆⁻ and TFSI⁻). Via conventional radical polymerization, all of the MCSC-PILCs were obtained. And due to all the polymer reaction process was similar. So, a typical polymerization procedure for poly(BImB-HCS-Br) was carried out as an example. The monomer BImBHCS-Br 1.10 g (1 mmol), 1 mg/mL DMF solution of AIBN 1.65 mL and together with the purified DMF 1.05 mL were input a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed off under vacuum. Polymerization was carried out at 70°C for 40 h. Then the tube was opened, and the reaction mixture was diluted with a few dichloromethane, and then it was precipitated in methanol. The polymer was purified by washed with methanol three times and frozen for drying to a constant weight. The other counter-anions polymers were obtained by the same way

except the precipitator and purification reagent of poly(BImBHCS–TFSI) was diethyl ether.

3. Results and discussion

3.1. Synthesis of monomers

In this work, we have successfully designed and synthesized the targeted MCSC-ILCPs via a multistep reactions route. The monomers with different counter-anions were synthesized as shown in the Figure 2. First, we synthesized the monomer with Br^- counter-anion, and then the other monomers with different counter-anions were obtained by an anion-exchange process. [50]. Figure 3 shows the ^1H NMR spectra of the monomers with different counter-anions. It was evident that the chemical shifts present at 6.95, 5.74–5.70, and 5.41–5.38 ppm (denoted j, l and m, respectively) represented the characteristic resonance peaks of the vinyl substituent of monomers. Completion of the anion-

exchange step was determined by the changes in the assigned peaks. For example, the 2-substituent proton hydrogen in imidazolium (denoted a) of the monomers with different counter-anions exhibited different chemical shifts depending on the type of counter-anion used. The chemical shift of the 2-substituent proton hydrogen in imidazolium were presented at 11.07, 9.25, 8.86, and 9.12 ppm for the monomers contained Br^- , BF_4^- , PF_6^- and TFSI^- , respectively. The order of the chemical shifts of the 2-substituent proton hydrogen in imidazolium monomers was monomer with $\text{Br}^- >$ monomer with $\text{BF}_4^- >$ monomer with $\text{PF}_6^- >$ monomer with TFSI^- . Because large counter-anions provided better shielding, it resulted in the chemical shift being moved towards the high-field after the anion exchange step [51, 52].

At the same time, FTIR was utilized to confirm the NMR results and the chemical structure of the mate-

Figure 3. ^1H NMR spectra of ILC monomers BImBHCS–X ($\text{X}^- = \text{Br}^-$, BF_4^- , PF_6^- and TFSI^-)

rials prepared. The characteristic stretching vibration peaks observed for the different counter-anions were as follows: 1068 cm^{-1} for BF_4^- , 842 cm^{-1} for PF_6^- , and 1354 , and 1178 , 1056 , 738 cm^{-1} for TFSI^- . Because residual water was present in the sample, the stretching for Br^- could not be discerned from the FTIR spectrum. Both the NMR and FTIR results were in good agreement with data found in the literatures [53, 54]. To recap, the combination of ^1H NMR and FTIR experiments demonstrated that the ionic liquid crystals side chain monomers with different anions were successfully prepared and the anion-exchange step was successfully achieved.

3.2. Synthesis of MCSC-ILCPs poly(BImBHCS-X) with different counter-anions

In this study, all monomers with vinyl substituent were polymerized via a simple radical polymerization method. Herein, the polymer poly(BImBHCS- BF_4) was used as an example to describe the process. ^1H NMR spectra of ILC monomer BImBHCS- BF_4 and the corresponding MCSC-PILC poly(BImB-

HCS- BF_4) are depicted in Figure 4. It was observed that the characteristic chemical shifts of the vinyl substituent of BImBHCS- BF_4 were present at 6.95, 5.75–5.71 and 5.41–5.38 ppm (denoted as j, l and m respectively). After polymerization these characteristic resonance peaks disappeared completely. Moreover, compared to the ILC monomer BImBHCS- BF_4 , the chemical shift peaks of poly(BImBHCS- BF_4) became quite broad, which was consistent with the anticipated polymer structure.

To further confirm the chemical structures of the MCSC-ILCPs, we carried out the experiment of FTIR spectroscopic to analyze the materials. As mentioned above, we used the same monomer BImBHCS- BF_4 and the corresponding polymer poly(BImBHCS- BF_4) as the example to illustrate the process. The characteristic peaks of the monomer BImBHCS- BF_4 , such as 1607 cm^{-1} , was assigned to C=C stretching-vibration, the peaks of 972 and 916 cm^{-1} was assigned to C-H out-of-plane bending vibration of the vinyl which completely disappeared after polymerization. In addition, restraint of the intra-molecular motion within the polymer material

Figure 4. ^1H NMR spectra of BImBHCS- BF_4 and the corresponding poly(BImBHCS- BF_4)

Table 1. Molecular characteristics and the phase transition temperatures of poly(BImBHCS-X)

Sample	M_n ($\cdot 10^4$) ^a	M_w/M_n ^a	T_g^b [°C]	T_i^b [°C]
poly(BImBHCS-Br)	6.7	2.15	93	—
poly(BImBHCS-BF ₄)	5.0	1.59	72	—
poly(BImBHCS-PF ₆)	4.2	1.32	85	182
poly(BImBHCS-PTFSI)	4.0	1.21	36	—

^aDetermined from GPC results, linear PS as standards.^bEvaluated by DSC at a rate of 10°C/min under cooling.

resulted in a reduction of the intensity of the infrared peaks when compared to the corresponding monomer after polymerization. The FTIR spectra were in good agreement with the results from ¹H NMR spectroscopy. Moreover, the molecular weight and number distribution and polydispersity of MCSC-ILCPs poly(BImBHCS-X) with different counter-anions were determined using gel permeation chromatography (GPC). The results from gel permeation chromatography are shown in Table 1.

3.3. Thermal properties and liquid crystal ordered structures

Before studying phase behavior and phase structure, we first investigated the thermal stability of MCSC-ILCP. Figure 5 depicts the thermal stability of the materials with different counter-anions under a nitrogen atmosphere. The results indicated that all the samples had excellent thermal stability because the samples' decomposition temperatures were above 320°C except that of poly(BImBHCS-Br) at about 275°C. The thermal stability order for the series of polymers with different counter-anions was: poly(BImBHCS-TFSI), poly(BImBHCS-PF₆), poly(BImBHCS-BF₄) and poly(BImBHCS-Br), and this ordering was consistent with the nature of the type of counter-anions in poly(BImBHCS-X) [55]. DSC was used to investigate the phase transitions of the MCSC-ILCPs. Figure 6a gives a set of DSC traces for MCSC-ILCPs that correspond to the first cooling and second heating (which were recorded at the rate of 10°C/min). These curves were collected after erasing the initial thermal history of the sample. Only one T_g for these MCSC-ILCPs could be observed during the whole cooling and heating process except for the sample poly(BImBHCS-PF₆), which exhibited an additional phase transition temperature. Moreover, we used the sample poly(BImBHCS-BF₄) as an example to further investigate the phase transition behavior with different heat-

Figure 5. TGA thermograms of poly(BImBHCS-X) ($X^- = \text{Br}^-, \text{BF}_4^-, \text{PF}_6^-$ and TFSI^-) at a rate of 10°C/min in nitrogen flow

ing and cooling rates of 2.5, 5, 10, and 20°C/min. However, the data in Figure 6b only showed a single glass transitions T_g . Based on the DSC results, the order of the T_g is poly(BImBHCS-Br) > poly(BImBHCS-PF₆) > poly(BImBHCS-BF₄) > poly(BImBHCS-TFSI). The observed T_g trend resulted from the different nucleophilicity and steric effect of counter-anions [56]. For example, the TFSI⁻ anion, which has relatively large steric hindrance and weak nucleophilicity, aided in the segment-movement strengthening of the material [57, 58], and thus this material (poly(BImBHCS-TFSI)) gave the lowest T_g temperature among the four samples.

To study the LC properties of the class of MCSC-ILCPs prepared herein, we performed PLM to investigate their birefringence phenomena. First, the thin film of poly(BImBHCS-X) ($X^- = \text{Br}^-, \text{BF}_4^-, \text{PF}_6^-$ and TFSI^-) were drop casted from chloroform solution. As shown in Figure 7, each of the polymers exhibited strong birefringences upon heating except for poly(BImBHCS-TFSI), which indicated the existence of LC phases. Moreover, the samples MCSC-ILCPs poly(BImBHCS-Br) and poly(BImBHCS-BF₄) always maintained their birefringences during heating and cooling process until decomposition. For the sample poly(BImBHCS-PF₆), the birefringences disappeared after the temperature exceeded 182°C during the heating process. Subsequently, the texture would reappear again during the cooling process. For sample poly(BImBHCS-TFSI), no birefringences were found during the whole consecutive heating and cooling process. The appropriate volume size of the counter-anions Br^- ,

Figure 6. DSC thermograms of poly(BImBHCS-X) ($X^- = \text{Br}^-$, BF_4^- , PF_6^- and TFSI^-) at a rate of 10 °C/min (a) and poly(BImBHCS- BF_4) at different rates (b)

BF_4^- and PF_6^- facilitated LC formation, but the TFSI^- counter-anion hindered the polymer to form the ordered structure because of its large volume. [59]. Note that the polymer PBBHCS with similar chemical structure of MCSC-ILCPs poly(BImBHCS-X) could exhibit typical different color fan texture, indicating highly ordered structure, but none of the poly(BImBHCS-X) samples exhibited any typical texture. It was obvious that the incorporation of counter-anions significantly restrained the formation of textures.

1D WAXD experiment was performed to identify the LC ordered structures of MCSC-ILCPs. Figure 8 presents the X-ray patterns of these polymers with different counter-anions. It was clearly found that all of the samples rendered an amorphous halo near 22° in high-angle region. This observation was attributed to the lack of long-range order at the sub-nanometer length scale. On the other hand, there were other three sharp diffractions at 2θ of 1.77, 3.56 and 5.34° for poly(BImBHCS-Br) and at 2θ of 1.85, 3.72 and 5.58° for poly(BImBHCS- BF_4) in the low-angle region. The q ratio ($q = 4\pi \cdot \sin(\theta/\lambda)$) of the diffractions were 1:2:3, so these peaks were assigned to the (001), (002) and (003) plane of smectic phase (lamellar structure). Furthermore, there

were two diffractions peaks at 2θ of 1.94 and 3.89° for the sample poly(BImBHCS- PF_6) and its q ratio remained 1:2 ratio, which was attributed to (001) and (002) plane. Meanwhile, we roughly estimated the spacing of the layer was 6.00 nm for these MCSC-ILCPs according to the all-trans conformation, but according to 1D WAXD data it revealed that the d-spacings were 4.98, 4.77 and 4.55 nm for poly(BImBHCS-Br), poly(BImBHCS- BF_4) and poly(BImBHCS- PF_6), respectively. Therefore, we speculated that the SmA or SmC phases had formed. However, no sharp diffraction peak was detected in the low-angle and high-angle region for poly(BImBHCS-TFSI), only two scattering halos in the 2θ region between 2 and 35° were observed, which indicated the absence of the highly ordered structures.

Variable-temperature WAXD experiments were performed to elucidate LC ordered structures of MCSC-ILCPs under different temperatures. The previous discussed WAXD results established that poly(BImBHCS- BF_4) had similar LC properties and ordered structure to that of poly(BImBHCS-Br). Therefore, we used the polymer poly(BImBHCS- BF_4) as a model sample to describe the LC ordered structure transition upon temperature evolution. As

Figure 7. Representative textures of poly(BImBHCS–Br) (a), poly(BImBHCS–BF₄) (b), poly(BImBHCS–PF₆) (c) and poly(BImBHCS–TFSI) (d) during heating (200× magnification)

shown in Figure 9a, the sample of poly(BImBHCS–BF₄) rendered an amorphous halo in the high angle region and two sharp peaks at 2θ of 1.85 and 3.72° assigned to (001) and (002) in the low angle region at low temperature during the heating process. With

Figure 8. 1D WAXD powder patterns of poly(BImBHCS–X) (X[–] = Br[–], BF₄[–], PF₆[–] and TFSI[–])

the increasing of temperature, the peaks become sharper and their intensity gradually became stronger but there was relatively no shift in the peak position. At the same time, a new peak at 5.58° was observed and it was assigned to (003). Furthermore, none of the diffraction peaks disappeared until heating the sample to the decomposition temperature. This observed behavior mimicked the known transitional behavior of MJLCPs. However, in the case of the sample poly(BImBHCS–PF₆), there were some differences with the WAXD experiment results. As shown in Figure 9b, only two shape diffraction peaks of 1.94 and 3.89° in the low angle region assigned to (001) and (002) remained when changing the temperature and the third diffraction peak did not always appear when increasing the temperature. When the temperature exceeded 182°C, all of the diffraction peaks disappeared indicating the arrival of isotropic phase. During the cooling process, the

Figure 9. 1D WAXD powder patterns of poly(BImBHCS- BF_4) (a) and poly(BImBHCS- PF_6) (b) under heating

process was observed to be reversible because the sample poly(BImBHCS- PF_6) displayed lamellar diffraction peaks upon cooling. As for the sample poly(BImBHCS-TFSI), no diffraction peaks were observed during both the heating and cooling processes. The X-ray scattering results were consistent with the results of DSC and PLM.

To confirm the precise LC ordered structure of the MCSC-ILCPs poly(BImBHCS- X) ($\text{X}^- = \text{Br}^-$, BF_4^- and PF_6^-), 2D WAXD experiments were performed. Figure 10a schematically shows the sheared sample

with the shear direction and shear gradient. The pattern for this sample poly(BImBHCS- PF_6) is shown in Figure 10b. From the result, it was found that there are two pairs of sharp diffraction arcs at 2θ of 1.94° and 3.89° assigned to (001) and (002) in the equator and the q ratio remains 1:2, which corresponded to the d -spacing of 4.55 and 2.27 nm, respectively. Meanwhile, a pair of diffuse halos displayed in the meridian region, indicated that the side-chain was laterally aligned. We can speculate the layer normal of the LC phase was perpendicular to the shear

Figure 10. (a) Schematic drawing of the sheared sample with the shear direction and shear gradient, respectively; (b) 2D WAXD pattern of the oriented sample poly(BImBHCS- PF_6) obtained at room temperature; (c) schematic drawing of the proposed supra-molecular structures for MCSC-ILCPs poly(BImBHCS- X) with counter-anions Br^- , BF_4^- , PF_6^-

direction. This result strongly demonstrated that the polymer formed SmA phase ordered structure, and the side chain partially overlapped between each other. Unfortunately, the other samples poly(BImBHCS–Br) and poly(BImBHCS–BF₄) did not display any orientation during the heating process up to decomposition. The lack of observed orientation was ascribed to the softening of the material. Based on this result, we did not obtain the 2D WAXD patterns of these two samples.

The previous MCSC-LCP PBBHCS displayed a fascinating hierarchical ordered structure with both double orderings on the nanometer and subnanometer scales. The nanoscale length structure in PBBHCS was assigned to the main chain, and the subnanoscale length structure resulted from the biphenyl side group being orthogonal to the main chain [48]. However, it was not unexpected to find no high-ordered structures in the MCSC-ILCPs samples because the biphenyl mesogen were directly attached to imidazole moieties in the side groups. Usually, this attachment should be helpful for enhancing the order structure, but the results demonstrated the opposite result. This effect was ascribed to the incorporated ions, which have weakened the construction of the LC phase. When the counter-anions inserted themselves in the imidazole group, the intermolecular space increased resulting in a decreased of the molecular stacking interaction. Based on these results, we propose that high-ordered structures cannot manifest themselves in this system. Therefore, the volume of the counter-anions in these polymers demonstrated a strong influence on the stability of LC ordered structure. For example, the samples poly(BImBHCS–Br) and poly(BImBHCS–BF₄) with relative small volume have stable LC ordered structure when varying the temperature. The volume of PF₆[–] is bigger than that of Br[–] and BF₄[–] [57, 58] and the poly(BImBHCS–PF₆) exhibited an isotropic transition temperature during the heating process. The counter-anion TFSI[–] had the largest volume and not only can it weaken the intramolecular stacking of biphenyl but it was shown to destroy the scaffold of main chain LC properties. Thus, the LC ordered structures in the polymer with counter-anion TFSI[–] did not always appear during the heating and cooling process in DSC scans.

Combined with the aforementioned results, it was easy to identify the three distinct classes of phase behavior in poly(BImBHCS–X) (X[–] = Br[–], BF₄[–],

PF₆[–] and TFSI[–]) samples. The changes in phase behavior occurred by changing the counter-anion in poly(BImBHCS–X). As for MCSC-ILCPs poly(BImBHCS–X) with counter-anions Br[–] and BF₄[–], the smectic phase always remained during the heating and cooling process except when they thermally decomposed. This result was consistent with the traditional MJLCPs. When the counter-anion was PF₆[–], this kind of MCSC-ILCP still maintained its smectic phase, but revealed an isotropic phase at the higher temperature. For the poly(BImBHCS–X) sample with counter-anion TFSI[–], it was determined that this sample cannot exhibit a LC phase and it only presented the isotropic status during the heating and cooling process. It is worth noting that the main chain of these MCSC-ILCPs should be columnar in spite of the incorporation of counter-anions. A number of studies have proved that MJLCPs had a rod-like columnar main chain due to the steric hindrance originating from the bulky side groups [41]. Although there was no direct evidence to indicate a columnar main chain in our MCSC-ILCPs system, the polyethylene main chain directly linked to the terephthalate unit was expected to impose a strong steric hindrance on the sample leading to a rod-like columnar structure [48, 49]. Therefore, the main chain of these MCSC-ILCPs should be rod-like columnar because of the ‘Jacketing’ effect. The proposed smectic structures for this class of polymers prepared herein are depicted in Figure 10c.

3.4. The photophysical properties of MCSC-ILCPs poly(BImBHCS–X)

Ultraviolet-Visible (UV-Vis) and fluorescence experiments were carried out to investigate the photophysical properties of MCSC-ILCPs poly(BImBHCS–X). Figure 11 is the UV-Vis spectra of the MCSC-ILCPs poly(BImBHCS–X) (X[–] = Br[–], BF₄[–], PF₆[–] and TFSI[–]) and MCSC-LCP PBBHCS in thin films. It can be found that PBBHCS without ions incorporated into them displayed a sharp absorption maximum at 285 nm, which was indicative of π - π^* transitions of aromatic rings [26, 60]. However, the samples poly(BImBHCS–X) (X[–] = Br[–], BF₄[–], PF₆[–] and TFSI[–]) yielded a broad absorption maxima at 290 nm, which were essentially independent of the structures of counter-anions [61, 62]. It indicates that the absorption bands of the samples originate from the same electronic transitions [63]. Compared to PBBHCS, the slight bathochromic

shift of the characteristic absorption peak for the poly(BImBHCS–X) was found. The results come from the extended planarization of the imidazole heterocycle and biphenyl group [64, 65].

Figure 11. UV-Vis spectra of the MCSC-ILCPs poly(BImBHCS–X) in thin films. For comparison, the UV-Vis spectrum of PBBHCS is also included

The fluorescence emission spectra of the MCSC-ILCPs poly(BImBHCS–X) ($X^- = \text{Br}^-$, BF_4^- , PF_6^- and TFSI^-) and MCSCILCP PBBHCS in CH_2Cl_2 and in thin films at excitation wavelength of 290 nm are given in Figures 12a and 12b, respectively. In Figure 12a, we found that the sample MCSCILCP PBBHCS only gave two weak emission peaks located at 410 and 435 nm in CH_2Cl_2 . However, the emission spectra of MCSC-ILCPs poly(BImBHCS–X) ($X^- = \text{Br}^-$, BF_4^- , PF_6^- and TFSI^-) displayed some difference from that of PBBHCS. For instance, the emission peak positions for the poly(BImBHCS–X) ($X^- = \text{Br}^-$, BF_4^- , PF_6^- and TFSI^-) samples were located at 420 and 435 nm indicating an obvious bathochromic shift when compared to PBBHCS. This shift originated from the extended planar conjugated system of imidazole heterocycle and biphenyl group [64, 65]. In Figure 12b, the spectra of these samples in thin films showed some new transitions which corresponded to the obvious emission peaks at 360, 420 and 485 nm, respectively. However, for poly(BImBHCS–X), there were some interesting changes. Emission signals were observed at 393, 390, 393 and 393 nm for poly(BImBHCS–Br), poly(BImBHCS– BF_4), poly(BImBHCS– PF_6) and poly(BImBHCS–TFSI), respectively. Compared to the emission of PBBHCS, the emissions from poly(BImBHCS–X) were obviously red-shifted which

Figure 12. Emission spectra of MCSC-ILCPs poly(BImBHCS–X) ($X^- = \text{Br}^-$, BF_4^- , PF_6^- and TFSI^-) and PBBHCS at excitation wavelength of 290 nm: (a) in CH_2Cl_2 and (b) in thin films

derived from the electron richness of the imidazole heterocycle [64, 65]. In addition, the positions of the other two emission peaks present at 420 and 485 nm for poly(BImBHCS–Br), poly(BImBHCS–BF₄), poly(BImBHCS–PF₆) and poly(BImBHCS–TFSI) changed little compared to that of PBBHCS. Meanwhile, the emission peak intensity of poly(BImBHCS–X) ($X^- = Br^-, BF_4^-, PF_6^-$ and TFSI⁻) was much stronger than that of PBBHCS. This indicated that the counter-anions inserted into the polymer samples hindered the strong high-ordering packing of the side chain biphenyl mesogens, which resulted in the absence of fluorescence quenching [66–69]. The fluorescence emission spectra results were consistent with the previous results describing the structures of the MCSC-ILCPs poly(BImBHCS–X).

4. Conclusions

In this article, we successfully designed and synthesized a series of novel MCSC-ILCPs poly(BImBHCS–X) ($X^- = Br^-, BF_4^-, PF_6^-$ and TFSI⁻) via radical polymerization. Each synthesized MCSC-ILCPs displayed phase transitions and LC properties and these material characteristics were strongly influenced by the type of counter-anion used. Due to the strong intermolecular interplay, MCSC-ILCPs formed lamellar ordered structures except for the poly(BImBHCS–TFSI) sample. Additionally, the poly(BImBHCS–PF₆) sample had isotropic phase besides the LC phase. Moreover, we found that the photophysical properties of poly(BImBHCS–X) were well-consistent with their chemical structure but practically independent on the types of counter-anions they contained. The LC property of MJLCPs depended on their molecular weight [48]. Herein, all monomers of the MCSC-ILCPs poly(BImBHCS–X) ($X^- = Br^-, BF_4^-, PF_6^-$ and TFSI⁻) having vinyl substituent were polymerized to control the polymer molecule chain length utilizing the ‘controlled/living’ radical polymerization method. This approach offered a new method to investigate the influence of the side chain length of the MCSC-ILCPs on the supra-molecular construction, LC behavior and photophysical properties. Continued studies with these materials (e.g., examining ion and electrical conductivity properties, optical properties, etc.) are underway and the relative results will be reported in subsequent articles.

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