Templated synthesis of cyclic poly(ionic liquid)s

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Abstract

Charged cyclic polymers, e.g. cyclic DNAs and polypeptides, play enabling roles in organisms, but their synthesis was challenging due to the well-known “polyelectrolyte effect”. To tackle the challenge, we developed a templated method to synthesize a library of imidazolium and pyridinium based cyclic poly(ionic liquid)s. Cyclic templates, cyclic polyimidazole and poly(2-pyridine), were synthesized first through ring-closure method by light-induced Diels–Alder click reaction. Through quaternization of cyclic templates followed by anion metathesis, the cyclic poly(ionic liquid)s were synthesized, which paired with varied counter anions.

Keywords: Cyclic polymers, Cyclic poly(ionic liquid)s, Ring-closure, Counter-anion exchange.
1. Introduction

Cyclic polymers (CPs) feature unique properties compared to their linear counterparts [1-4], such as lower melt viscosity, smaller hydrodynamic volume and modulated crystallization kinetics, leading to functional materials ranging from gels [5], micelles [6], to nanotubes [7], etc. CPs are normally synthesized through ring-expansion and/or ring-closure methods [8-10]. In contrast to the vast majority of synthetic CPs that are neutral, biology is replete with natural cyclic polymers bearing charge, such as cyclic deoxyribonucleic acid [11-13] and circular polypeptides [14-16], which were discovered in virus and bacterial [17,18], etc. The combination of charge and cyclic topology is crucial for properties such as self-replication [13], biological recognition [11] and activities [14]. As such, charged cyclic polymers, i.e., cyclic polyelectrolytes, are emerging topics attracting growing interest from both the chemistry and materials perspectives. For example, cyclic cationic poly((2-dimethylamino)ethylmethacrylate) exhibited reduced cytotoxicity than its linear counterparts in gene transfer processes [19]. In this context, we are particularly interested in cyclic poly(ionic liquid)s (CPILs), given that PILs is a subclass of ionic polymers highlighting beneficial properties [20-24] including surface activity, adaptive solubility, ionic conductivity, wide electrochemical windows, etc. As an emerging family of functional polymers, PILs have been exploited as membranes [25-28], self-assembly [29-31], ion conductors [32,33], structured carbon [34,35], advanced catalysis [36-38], etc. In this regard, CPILs can exhibit some novel properties than the linear counterparts, such as smaller hydrodynamic volume, unique diffusion dynamic [39], and higher biological activity [19]. As such, CPILs are potentially applicable for self-assembled entities with unique rheological properties, improved bioactivities, and advanced conducting abilities.

Different from neutral CPs synthesized by ring-closure cyclization at extremely diluted polymer solutions [40], synthesis of CPILs suffers from the so-called “polyelectrolyte effect” [41,42]. Under this circumstance, the electrostatic repulsion of charged chains renders collision of chain ends in dilute solution particularly difficult [43,44], thus impeding effective ring-closure. The ring-closure cyclization efficiency could be improved by increasing the polymer solution concentration, at the price of the enhanced intermolecular reaction and polycondensation byproducts. As an alternative approach, the ring-expansion method is more suited for monomers of specific chemical
structures, such as strain olefin [45,46] and lactones [47,48], precluding the majority of ionic liquid monomers such as the most extensively studied the imidazolium ones. Putting together, the synthesis of CPILs is an attractive topic but never reported so far.

Herein, we developed a templated method to synthesize CPILs (Scheme 1). Neutral cyclic polymer templates were synthesized first, which were subsequently quaternized and ion exchanged to yield target CPILs. This “template first” strategy skipped the adverse “polyelectrolyte effect” involved in the ring-closure method. In detail, linear poly(2-vinylpyridine) (LP2VP) and poly(1-(4-vinylbenzyl)imidazole) (LPVBIm) were synthesized by Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization, followed through cyclization reaction by Diels-Alder click reaction of orthoquinodimethane and dithioester chain ends under UV light (365 nm) [49]. Thereafter, cyclic poly(1-cyanomethyl-2-vinylpyridine bromine) (CP2VP-Br) and cyclic poly(1-cyanomethyl-(4-vinylbenzyl)imidazole bromine) (CPVBIm-Br), were synthesized by quaternization of the cyclic polymer precursors with bromoacetonitrile (BrCH₂CN). Subsequently, a library of CPILs paired with different counter anions was obtained by counter-ion exchange. They are termed CP2VP-X and CPVBIm-X, where X is tetrafluoroborate (BF₄), hexafluorophosphate (PF₆), or bis(trifluoro-methanesulfonyl)imide (Tf₂N).

2. Experimental

2.1 Materials

Glyoxaline, 4-(chloromethyl)styrene, bromoacetonitrile, sodium tetrafluoroborate (NaBF₄), potassium hexafluorophosphate (KPF₆), lithium bis(trifluoro-methanesulfonyl)imide (LiTf₂N), sodium tetrphenylborate (NaB(Ph)₄) and methyl
orange (MO), sodium hydroxide, imidazole, 4-vinylbenzyl chloride, were purchased as reagent grade from Aldrich, Acros, Alfa Aesar, Aladdin, and used as received. Petroleum ether, methanol, diethyl ether, acetonitrile, dichloromethane (DCM), tetrahydrofuran (THF), hexane, chloroform (CHCl₃), N,N-Dimethylformamide (DMF) were purchased as regent grade from Beijing Chemical Reagent Co. and used as received unless otherwise noted. 2-vinyl pyridine (2VP) were dried over CaH₂ and distilled before use. 2,2’-Azoisobutyronitrile (AIBN) was recrystallized from ethanol and stored at 4 °C. RAFT agent (3-(2-formyl-3-methylphenoxy)propyl 4-cyano-4-((phenylcarbonothioyl)thio)pentanoate) [49], and N-(4-vinylbenzyl)-imidazole (VBIm) [50], were synthesized according to the previous literatures. A low-pressure mercury lamp (120 W) (CEL-LPH120-254, Beijing China Education Au-light co. Ltd) was used as the UV light source.

2.2 Characterization

¹H-NMR spectrum were recorded on a Bruker Avance 400 spectrometer at room temperature. Ultraviolet Spectrum were recorded using a TU-1901 Ultraviolet Spectrophotometer. FT-IR spectrum were recorded on a Thermo Nicolet iS5 Spectrometer at room temperature. Gel permeation chromatography (GPC) in DMF was conducted on a system comprised of a Waters 515 HPLC pump, and a Waters 2414 RI detector equipped with four Waters Styragel columns (HT 2, HT 3, HT 4, and HT 5). DMF with 0.01 M LiBr was used as the eluent at a flow rate of 1.0 ml/min. Polystyrene standards were used for the calibration. Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Biflex III spectrometer equipped with a 337 nm nitrogen laser. Inductively coupled plasma mass spectrometry (ICP-MS) were recorded on a PerkinElmer NexION 300X. Elemental analysis (C, H, N, S) was performed on a Flash EA1112 from Thermo Quest Italia S.P.A.

2.3 Synthesis of LP2VP

RAFT agent (45.5 mg, 0.1 mmol) and AIBN (3.6 g 0.22 mmol) were dissolved in 2VP (3.15 g, 30 mmol) on stirring under inert atmosphere. The clear solution was degassed via three freeze-thaw-pump cycles. After stirring at 60 °C for 7.5 h, the reaction was terminated by exposure to air. Polymer was precipitated from DCM
solvent into the excess of hexane three times. After drying overnight in a vacuum oven at room temperature, the light red powder was obtained with a monomer conversion of 15.2% from $^1$H-NMR with a yield of 83.2%.

2.4 Synthesis of LPVBlm

RAFT agent (45.5 mg, 0.1 mmol) and AIBN (3.28 g 0.2 mmol) were dissolved in VBIm (1.84 g, 10 mmol) on stirring under inert atmosphere. The clear solution was degassed via three freeze-thaw-pump cycles. After stirring at 60 °C for 17 h, the reaction was terminated by exposure to air. Polymer was precipitated from DCM solvent into the excess of diethyl ether three times. After drying overnight in a vacuum oven at room temperature, the light red powder was obtained with a monomer conversion of 32.2% from $^1$H-NMR with a yield of 90.2%.

2.5 Synthesis of cyclic poly(2-vinylpyridine) (CP2VP)

After dissolving linear precursors (50 mg) in acetonitrile (1000 ml), the solution was stirred under UV light irradiation for 9 h at room temperature. Pure cyclic polymers were conveniently collected by evaporation of solvent. Repeat the procedure 5 times until enough CP2VP were obtained for quaternization.

2.6 Synthesis of cyclic poly(1-(4-vinylbenzyl)imidazole) (CPVBlm)

Follow similar procedures in “synthesis of CP2VP”, but with less linear precursors (20 mg) in acetonitrile (1000 ml).

2.7 Synthesis of CP2VP-Br

A solution of CP2VP (200 mg) in bromoacetonitrile (5 ml) was stirred at 60 °C for 3 days. After the reaction, the solution was precipitated in diethyl ether (50 ml), and then the precipitations were collected. The precipitations were re-dissolved in water (1 ml), and precipitated in THF (20 ml) again. After 3 dissolving-precipitations circles, the CP2VP-Br was obtained upon vacuum oven at room temperature overnight.

2.8 Synthesis of CPVBlm-Br

A mixture solution of CPVBlm (200 mg) with bromoacetonitrile (3 ml) in NMP (2
ml) was stirred at 60 °C for 1 days. After the reaction, the solution was dropped into diethyl ether (50 ml), and then precipitations were collected. The precipitations were re-dissolved in water (1 ml), and precipitated in THF (20 ml) again. After 3 dissolving-precipitations circles, the CPVBIm-Br was obtained upon vacuum oven at room temperature overnight.

2.9 Synthesis of Various Cyclic PILs

Ten different cyclic PILs were prepared following identical counter-ion exchange procedures, with molar ratios of 2:1 (salts : PILs). The dissolved PILs solution (e.g. 50 mg CP2VP-Br/CPVBIm-Br in 2 ml water) were dropped into salt solution (e.g. 36 mg NaBF₄ in 2ml water), and after filtration, the precipitations were washed 3 times with water, and dried in vacuum oven at room temperature overnight for next steps.

2.10 Calculation of counter-ion exchange efficiency

The efficiency of counter-ion exchange (E%) is defined as the ratio between exchanged ionic groups and ionic pyridine or imidazole units (equation 1 below).

\[
E\% = \frac{\text{exchanged ionic groups}}{\text{ionic pyridine or imidazole units}} \times 100\%
\]  

(1)

3. Results and discussions

3.1 Synthesis and characterization of cyclic templates

GPC characterization of LP2VP (Fig. 1A black) reveal a well-defined, monomodal, and symmetric elution trace, indicative of the successful RAFT polymerization with fine control over molecular weight distribution. The whole GPC trace of CP2VP (Fig. 1A red) remains the same to LP2VP but shifts to a lower molecular weight regime. It indicates a smaller hydrodynamic radius of CP2VP and the corresponding apparent molecular weight (\(M_n=11490\), PDI=1.15) in comparison to LP2VP precursor (\(M_n=14020\), PDI=1.12). MALDI-TOF mass spectrum of LP2VP (Fig. 2A) and CP2VP (Fig. 2B) indicates that the absolute molecular weights are similar for both cases expanding from 4500 to 7500 and centering at 6000. Combining the much smaller apparent \(M_n\) of CP2VP than that of linear precursor from GPC, the successful cyclization is demonstrated [51-53]. Chemical structures of CP2VP were characterized by UV-Vis spectra (Fig. 3) and \(^1\)H NMR (Fig. 4), whereas the \(\pi-\pi^*\) adsorption peak of
the thiocarbonyl moiety at 305 nm disappears after ring closure reaction (Fig. 3A red arrow). Additionally, the NMR signal of orthoquinodimethane end group in LP2VP (at 10.66 ppm, H₆ in Fig. 4A) vanishes after Diels-Alder ring-closure reaction (Fig. 4B), in good agreement with the UV-Vis results.

![Fig. 1](image1.png)  
**Fig. 1** A) GPC traces of (A) LP2VP and CP2VP, and (B) LPVBlm and CPVBlm. Eluent: DMF; calibration standard: polystyrene.

![Fig. 2](image2.png)  
**Fig 2.** MALDI–TOF mass spectrum for LP2VP precursor and the corresponding CP2VP.

![Fig. 3](image3.png)  
**Fig 3.** UV-vis spectrum of (A) LP2VP (black) and the resultant CP2VP (red) in DCM, (B) LPVBlm (black) and the resultant CPVBlm (red) in DCM.
Fig 4. $^1$H NMR spectrum of LP2VP (A), CP2VP (B), LPVBIm (C) and CPVBIm (D) in CDCl$_3$.

Similar results were also found for the synthesis of cyclic PVBIm (CPVBIm) from its linear counterpart LPVBIm. The GPC traces (Fig. 1B) in a well-defined, monomodal, and symmetrical shape are observed for LPVBIm ($M_n=8870$, PDI=1.26) and CPVBIm ($M_n=7540$, PDI=1.30), respectively. Moreover, the disappearance of orthoquinodimethane and thiocarbonyl group as a result of Diels-Alder ring closure reaction was confirmed by $^1$H NMR (Fig. 4D) and UV-vis (Fig. 3B), respectively. These results all support the successful synthesis of CP2VP and CPVBIm.

3.2 Synthesis and characterization of cyclic PILs

The two targeted CPIls, i.e. CP2VP-Br and CPVBIm-Br, were synthesized by quaternization of CP2VP and CPVBIm with BrCH$_2$CN, which is an active quaternizing agent with beneficial hydrophilicity for improving anion metathesis efficiency. In their $^1$H NMR spectrum, new signals of Hb (5.90 ppm, Fig. 5B) and Hc (5.50 ppm, Fig. 5D) appear for CP2VP-Br and CPVBIm-Br. Both signals can be assigned to the newly formed -CH$_2$-CN groups, as a result of the quaternization of CP2VP and CPVBIm by BrCH$_2$CN. Through the area integration ratio between Hb (-CH$_2$-CN) and H$_a$ (pyridine...
units), the quaternization degree of CP2VP is calculated to be ca. 60%. In a similar way, the quaternization degree of CPVBIm-Br is ca. 95%, i.e. being more efficient than CP2VP. From FT-IR spectrum (Fig. 6), two new absorption bands (dashed rectangles) are seen at 1200 cm\(^{-1}\) and 2200 cm\(^{-1}\), which are assigned to the vibration mode of newly formed \(-CH_2-CN\), in good agreement with the NMR results (Fig. 5).

**Fig. 5** \(^1\)H NMR spectrum of A) CP2VP and C) CPVBIm in CDCl\(_3\); B) CP2VP-Br and D) CPVBIm-Br in DMSO-\(d_6\).

**Fig. 6** FT-IR spectrum of CP2VP (A, in black), CP2VP-Br (A, in red), CPVBIm (B, in black) and CPVBIm-Br (B, in red).
3.3 Synthesis and characterization of various cyclic PILs

Counter-anion exchange was conducted to expand the structural spectrum of the as-synthesized CPILs. The successful synthesis of CP2VP- B(Ph)₄/MO and CPVBIm-B(Ph)₄/MO (MO ~ methyl orange) were verified by ¹H NMR spectrum (Fig. 7), whereas the exchange efficiency was also calculated. For both CP2VP-X (Fig. 8A) and CPVBIm-X (Fig. 8B), characteristic bands of each counter anions (BF₄⁻, PF₆⁻, Tf₂N⁻, B(Ph)₄⁻, MO⁻) are clearly seen from FT-IR curves of the corresponding CPIL-X after counter-ion exchange (dashed rectangles, Fig. 8). The efficiency of counter-ion exchange, defined as the ratio of exchanged repeating ionic units to their overall repeating ionic unit, was further quantified (Fig. 9). The exchange efficiency from Br⁻ to Tf₂N⁻ is 71.3% and 76.2% for CP2VP-X and CPVBIm-X respectively, and the exchange efficiency of B(Ph)₄⁺ for both polymers is less than 85%. Notably, the anion exchange degree of CP2VP-Br or CPVBIm-Br with MO anion are 99.1% and 98.1%, respectively, and this quantitative exchange is in agreement with previous works [54,55]. Moreover, the ion exchange degree of CP2VP-Br and CPVBIm-Br with BF₄⁻ are 81.4% and 93.4%, respectively, as determined by ICP-MS.

Fig 7. ¹H NMR spectrum of CPILs: A) CP2VP-B(Ph)₄; B) CP2VP-MO; C) CPVBIm-B(Ph)₄; D) CPVBIm-MO; in DMSO-$_{d6}$. 
Fig. 8 FT-IR spectrum of CP2VP-Br (A, in purple), CP2VP-BF4 (A, in black), CP2VP-PF6 (A, in red), CP2VP-Tf2N (A, in blue), CP2VP-B(Ph)4 (A, in red purple), CP2VP-MO (A, in navy), CPVBIm-Br (B, in purple), CPVBIm-BF4 (B, in black), CPVBIm-PF6 (B, in red), CPVBIm-Tf2N (B, in blue), CPVBIm-B(Ph)4 (B, in red purple), CPVBIm-MO (B, in navy blue).
Fig. 9 Efficiency of counter-ion exchange of CP2VP-Br and CPVBIm-Br with varied anions (BF\textsuperscript{4}-, Tf\textsubscript{2}N\textsuperscript{-}, B(Ph)\textsubscript{4}-, MO\textsuperscript{-}). a) determined from ICP-MS. b) determined from NMR. c) determined from Element analysis.

4. Conclusions

A templated method was proposed to synthesize pyridinium and imidazolium based cyclic PILs paired with various counter anions. LP2VP and LPVBIm were synthesized by RAFT polymerization, and the ring-closure was accomplished with quantitation through the UV induced Diels-Alder reaction. Quaternization of CP2VP and CPVBIm yielded CPIls whose counter anions could be effectively exchanged with other organic anions such as BF\textsuperscript{4}-, PF\textsuperscript{6}-, Tf\textsubscript{2}N\textsuperscript{-}, B(Ph)\textsubscript{4}- and MO\textsuperscript{-}. Given that both the cations (pyridinium and imidazolium) and anions are most frequently used for ionic liquids and PILs, this work paves the synthetic path to a broad spectrum of CPIls with enriched topology, self-assembly and implication potentials, which have not been addressed due to the lack of suitable synthetic tools.

Conflicts of interest

There are no conflicts to declare.

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Supplementary Information

Experimental

Materials

Glyoxaline, 4-(chloromethyl)styrene, bromoacetonitrile, sodium tetrafluoroborate (NaBF₄), potassium hexafluorophosphate (KPF₆), lithium bis(trifluoromethanesulfonyl)imide (LiTf₂N), sodium tetrphenylborate (NaB(Ph)₄) and methyl orange (MO), sodium hydroxide, imidazole, 4-vinylbenzyl chloride, were purchased as reagent grade from Aldrich, Acros, Alfa Aesar, Aladdin, and used as received. Petroleum ether, methanol, diethyl ether, acetonitrile, dichloromethane (DCM), tetrahydrofuran (THF), hexane, chloroform (CHCl₃), N,N-Dimethylformamide (DMF) were purchased as regent grade from Beijing Chemical Reagent Co. and used as received unless otherwise noted. 2-vinyl pyridine (2VP) were dried over CaH₂ and distilled before use. 2,2’-Azoisobutyronitrile (AIBN) was recrystallized from ethanol and stored at 4 °C. N-(4-vinylbenzyl)-imidazole¹, RAFT agent² were synthesized according to the previous literatures. A low-pressure mercury lamp (120 W) (CEL-LPH120-254, Beijing China Education Au-light co. Ltd) was used as the UV light source.

Characterization

¹H-NMR spectra were recorded on a Bruker Avance 400 spectrometer at room temperature.

Ultraviolet Spectra were recorded using a TU-1901 Ultraviolet Spectrophotometer.

FT-IR spectra were recorded on a Thermo Nicolet Avatar-330 Spectrometer at room temperature.

Gel permeation chromatography (GPC) in DMF was conducted on a system comprised of a Waters 515 HPLC pump, and a Waters 2414 RI detector equipped with four Waters Styragel columns (HT 2, HT 3, HT 4, and HT 5). DMF with 0.01 M LiBr was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for the calibration.

1. Preparation of LP2VP

A mixed solution of 2VP (3.15 g, 30 mmol), RAFT agent 1 (45.5 mg, 0.1 mmol) and AIBN (3.6 g 0.22 mmol) was degassed via three freeze-thaw-pump cycles. After stirring at 60 °C for 7.5 h, the reaction was terminated by exposure to air. Polymer was precipitated from an excess of hexane three times. After drying overnight in a vacuum oven at room temperature, the light red product was obtained with a monomer conversion of 15.2% from ¹H-NMR.
2. Preparation of LPVBIm

A mixed solution of VBIm (1.84 g, 10 mmol), RAFT agent I (45.5 mg, 0.1 mmol) and AIBN (3.28 g 0.2 mmol) was degassed via three freeze-thaw-pump cycles. After stirring at 60 °C for 17 h, the reaction was terminated by exposure to air. Polymer was precipitated from an excess of diethyl ether three times. After drying overnight in a vacuum oven at room temperature, the light red product was obtained with a monomer conversion of 32.2% from 1H-NMR.

3. Preparation of CP2VP

After dissolving linear precursors (50 mg) in acetonitrile (1000 mL), the solution was stirred under UV light irradiation for 9 h at room temperature. Pure cyclic polymers were conveniently collected by evaporation of solvent. Repeat the procedure until enough cyclic P2VP were obtained for quaternization.

4. Preparation of CPVBIm

Follow similar procedures in “preparation of cyclic P2VP”, but with less linear precursors (20 mg) in acetonitrile (1000 mL).

5. Preparation of CP2VP-Br

A solution of cyclic P2VP (200 mg) in bromoacetonitrile (5 ml) was stirred at 60 °C for 3 days. After the reaction, the solution was precipitated in diethyl ether (50 ml), and then concentrated and the precipitations were collected. The precipitations were re-dissolved in water (1 ml), and precipitate in THF (20 ml) again. After 3 dissolving-precipitation circle, the CP2VP-Br was obtained upon vacuum dry.

6. Preparation of CPVBIm-Br

A mixture solution of cyclic P2VP (200 mg) with bromoacetonitrile (3 ml) in NMP (2 ml) was stirred at 60 °C for 1 days. After the reaction, the solution was dropped into diethyl ether (50 ml), and then concentrated and the precipitations were collected. The precipitations were re-dissolved in water (1 ml), and precipitate in THF (20 ml) again. After 3 dissolving-precipitation circle, the CPVBIm-Br was obtained upon vacuum dry.

7. Preparation of Various Cyclic PILs

Ten different cyclic PILs were prepared following identical counter-ion exchange procedures, with molar ratios of 2:1 (salts : PILs). The dissolved PILs solutions (e.g. 50 mg CP2VP-Br/CPVBIm-Br in 2 mL water) were dropped into salt solutions (e.g. 36 mg NaBF₄ in 2mL water), and after filtration, the precipitations were washed 3 times with water, and dried in vacuum for next steps.
8. Calculation of counter-ion exchange efficiency

According to the definition of the efficiency of counter-ion exchange, the formula can be shown as (1):

\[
E\% = \frac{\text{exchanged ionic groups}}{\text{ionic pyridine or imidazole units}} \times 100\%
\]  

(1)

8.1. The efficiency of counter-ion exchange for CP2VP-Tf2N and CPVBIIm-Tf2N by elemental analysis.

Because the efficiency of quaternization of CP2VP-Br was 60%, name is, only 60% pyridine ring unit on the polymer have been ionized. The CP2VP-Tf2N structure was shown in Figure S1. The formula to calculate the content of sulfur was shown in (2), where 64 is the mass of sulfur, 105 is the mass of pyridine ring, 225 is the mass of unexchanged ionic group, 425 is the mass of exchanged ionic group, and \(x\) was 0.4, and \(y + z\) was 0.6, \(E\%\) was \(z/0.6\). The results of elemental analysis was 10.43%, So the efficiency of counter-ion exchange for CP2VP-Tf2N is 71.3%.

\[
\text{Content of Sulfur} = \frac{z \times 64}{x \times 105 + y \times 225 + z \times 425} \times 100\%
\]  

(2)

\[
= \frac{E \times 0.6 \times 64}{0.4 \times 105 + (0.6 - 0.6 \times E) \times 225 + E \times 0.6 \times 425} \times 100\%
\]

Similarly, because the efficiency of quaternization of CPVBIIm-Br was 94%, \(i.e.,\) only 94% imidazole unit along the polymer backbone have been ionized. The CPVBIIm-Tf2N structure was shown in Figure S2. The formula to calculate the content of Sulfur was shown in (3), where 64 is the mass of sulfur, 184 is mass of the neutral group, 304 is the mass of unexchanged ionic group, 504 is the mass of the exchanged ionic group, and \(x\) was 0.06, and \(y + z\) was 0.94, \(E\%\) was \(z/0.94\). The result of elemental analysis was 10.51%, so the efficiency of counter-ion exchange for CPVBIIm-Tf2N is 76.2%.
Figure S2 The structure of CPVBIm-Tf₂N.

Content of Sulfur

\[
\begin{align*}
&= \frac{z \times 64}{x \times 184 + y \times 304 + z \times 504} \times 100\% \\
&= \frac{E \times 0.94 \times 64}{0.06 \times 184 + (0.94 - 0.94 \times E) \times 304 + E \times 0.94 \times 504} \times 100\%
\end{align*}
\]  

8.2. The efficiency of counter-ion exchange for CP2VP-BF₄ and CPVBIm-BF₄ by the ICP-MS.

Similarly, the efficiency of counter-ion exchange for CP2VP-BF₄ and CPVBIm-BF₄ could be calculated by the content of boron, which was determined by ICP-MS. The calculation process was the same like E% calculated by content of sulfur for CP2VP-Tf₂N and CPVBIm-Tf₂N.

For CP2VP-BF₄, formula is (4), and the results of ICP-MS was 2.978%, so the efficiency of counter-ion exchange for CP2VP-BF₄ is 81.4%.

Content of Boron

\[
\begin{align*}
&= \frac{z \times 11}{x \times 105 + y \times 225 + z \times 232} \times 100\% \\
&= \frac{E \times 0.6 \times 11}{0.4 \times 105 + (0.6 - 0.6 \times E) \times 225 + E \times 0.6 \times 232} \times 100\%
\end{align*}
\]  

For CPVBIm-BF₄, formula is (5), and the results of ICP-MS was 3.187%, so the efficiency of counter-ion exchange for CPVBIm-BF₄ is 93.4%.

Content of Boron

\[
\begin{align*}
&= \frac{z \times 11}{x \times 184 + y \times 304 + z \times 311} \times 100\% \\
&= \frac{E \times 0.94 \times 11}{0.06 \times 184 + (0.94 - 0.94 \times E) \times 304 + E \times 0.94 \times 311} \times 100\%
\end{align*}
\]
Figure S3 ¹H NMR spectra of linear P2VP (A), cyclic P2VP (B), linear PVBlm (C) and cyclic PVBlm (D) in CDCl₃.

Figure S4 UV-vis spectra of (A) linear P2VP (black) and the resultant cyclic P2VP (red) in DCM, (B) linear PVBlm (black) and the resultant cyclic PVBlm (red) in DCM.
Figure S5 $^1$H NMR spectra of CPIILs: A) CP2VP-B(Ph)$_4$; B) CP2VP-MO; C) CP2VP-BF$_4$; D) CP2VP-PF$_6$; E) CP2VP-Tf$_2$N; F) CPVBlm-B(Ph)$_4$; G) CPVBlm-MO; H) CPVBlm-BF$_4$; I) CPVBlm-PF$_6$; J) CPVBlm-Tf$_2$N; in DMSO-$d_6$. 
Table S1 The content of Nitrogen, Carbon, Hydrogen, Sulfur of CP2VP-Tf$_2$N and CPVBIm-Tf$_2$N.

| SAMPLE       | DATA  |
|--------------|-------|
|              | N /%  | C /%  | H /%  | S /%  |
| CP2VP-Tf$_2$N| 7.80  | 43.56 | 3.67  | 10.99 |
|              | 7.81  | 43.66 | 3.57  | 10.60 |
|              | 7.80  | 43.55 | 3.48  | 10.26 |
| CPVBIm-Tf$_2$N| 10.58 | 37.73 | 2.35  | 11.02 |
|              | 10.57 | 37.36 | 2.27  | 10.42 |
|              | 10.67 | 37.35 | 2.22  | 10.60 |

Table S2 The content of Boron of CP2VP-BF$_4$ and CPVBIm-BF$_4$.

| Order number | CP2VP-BF$_4$ | CPVBIm-BF$_4$ |
|--------------|--------------|---------------|
| Sample(g)    | 0.0455       | 0.0099        |
| Volume of solution(mL) | 50           | 50            |
| Concentration of solution (mg/L) | 2.710        | 6.31          |
| Dilution rate | 10           | 1             |
| Concentration of Boron of sample (%) | **2.978**    | **3.187**     |

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