

Supporting Information

High Temperature Imidazolium Ionic Polymer for Gas Chromatography

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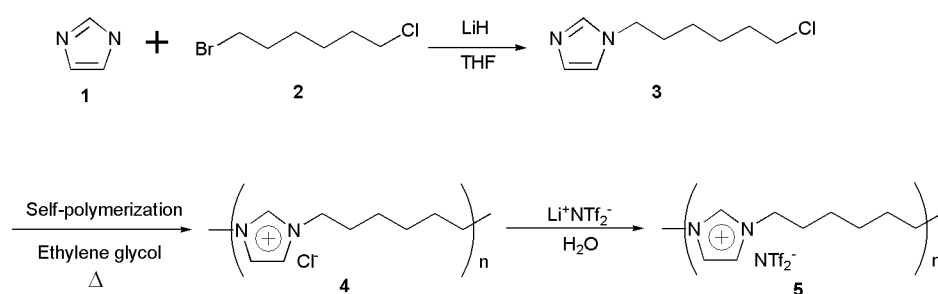
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Experimental:

Preparation of PImC₆NTf₂

The proposed PIL (PImC₆NTf₂) is prepared using a simple synthetic procedure¹. The procedure has three steps: 1) synthesis of monomer; 2) self-polymerization; 3) metathesis. Briefly, (1) 0.046 mol (3.17 g) of imidazole **1** was added into 10 mL of dry THF solution; 0.056 mol (0.45 g) of lithium hydride was dissolved in a 100 mL round-bottom flask containing 10 mL of dry THF solution and a stir-bar at 0 °C. The imidazole solution was slowly mixed with LiH solution at 0 °C under nitrogen atmosphere. 0.027 mol (5.39 g) of 1-bromo-6-chlorohexane **2** was slowly added into the mixture for reaction, which was carried out under nitrogen atmosphere for 24 h. Then, 10 mL of distilled water was added to terminate the reaction. The THF solvent was removed using an aspirator, and then the product was extracted several times using dichloromethane. After the removal of dichloromethane, the monomer 1-(6-chlorohexyl)imidazole (ImC₆Cl, **3**) was a transparent oily liquid. The yield of the monomer was around 95%. (2) Then, 0.02 mol of **3** was added into a 50 mL round-bottom flask containing 2 mL of ethylene glycol solution, which was then heated in an oil bath at 90 °C for 12 h. The solution was cooled to room temperature after the reaction completed. 10 mL of methanol was poured into the round-bottom flask to dissolve the product. The solution was transferred to 200 mL of acetone to cause precipitation. After the removal of acetone, the precipitate was washed using acetone three times, and then dried in a vacuum to obtain the polymer product as a white powder (polyhexylimidazolium chloride, PImC₆Cl, **4**). The yield of the polymers was around 90%. (3) 1 g of **4** was dissolved in 50 mL deionized water in a 250 mL round-bottom flask. Then, 100 mL of 0.35 M lithium bis-trifluoromethylsulfonylimide (LiNTf₂) was slowly added into agitatedly stirred **4** solution for metathesis. The reaction was carried out at room temperature for 12 h. The precipitate (PImC₆NTf₂, **5**) was first filtrated and washed using deionized water three times, and then dried at 80 °C in an oven for 12 h. The yield of the product was around 90%.



Scheme 1: Schematic illustrations of the synthesis procedures for $PImC_6NTf_2$.

*Characterizations for the monomer (ImC_6Cl , **3**) and polymer ($PImC_6Cl$, **4**):*

The monomer **3** was characterized using 1H NMR, ^{13}C NMR, and HRMS-FAB. The 1H NMR spectra (200 MHz) and ^{13}C NMR spectra (50 MHz) were recorded in deuterated chloroform; high resolution mass spectra (HRMS) were determined by using a JEOL JMS-700 mass spectrometer in fast atom bombardment (FAB) mode. The spectra of monomer **3** are listed below. The chloride containing polymers **4** was characterized using 1H NMR, the spectrum was recorded in deuterated water and is listed below:

*Spectral data of 1-(3-chlorohexyl)imidazole (ImC_6Cl , **3**):* 1H NMR spectra (200 MHz, $CDCl_3$): δ 7.42 (s, 1H), 7.02 (s, 1H), 6.87 (s, 1H), 3.90 (t, $J = 7.0$ Hz, 2H), 3.48 (t, $J = 6.6$ Hz, 2H), 1.84-1.56 (m, 4H), 1.52-1.20 (m, 4H); ^{13}C NMR spectra (50 MHz, $CDCl_3$): δ 137.2, 130.0, 119.0, 47.0, 45.0, 32.4, 31.1, 26.5, 26.0; HRMS-FAB: m/z $[M+H]^+$ calcd. for $C_9H_{16}N_2Cl$: 187.1002; found: 187.1000.

*Spectral data of $PImC_6Cl$, **4**:* 1H NMR spectra (200 MHz, D_2O): δ 8.80 (1H), 7.50 (2H), 4.20 (4H), 1.88 (4H), 1.36 (4H)

*Melting point test for the polymers ($PImC_6Cl$, **4** and $PImC_6NTf_2$, **5**):*

$PImC_6Cl$, **4: m.p.: 206 ± 2 °C.**

$PImC_6NTf_2$, **5: m.p.: 65 ± 1 °C.**

Preparation of $PImC_6NTf_2$ column

The $PImC_6NTf_2$ were dissolved in acetone at a concentration of 0.32 % (w/v) as the stationary phase solution. A 1 mL HPLC syringe (Hamilton Co., Reno NV. USA)

was used to inject the prepared stationary phase solution into untreated capillary fused silica tubing (10 m × 0.25 mm i.d.). One end of the tubing was then sealed with apiezon H grease. The other end was connected to the vacuum system. The tubing was immersed into a temperature controlled water bath (40 °C) and then a vacuum was started to let the acetone evaporate. The coating procedure took 18 h to complete. The PImC₆NTf₂ coated capillary column was installed into the GC injector and flushed with nitrogen (1 mL min⁻¹) for 3 h, then heated from 40 °C to 100 °C, held for 1 h, and then slowly heated again to 360 °C and held for 3 h. After conditioning, the column was ready for use. The column dimension is (10 m × 0.25 mm i.d. × 0.20 μm).

Aparatus

An Agilent gas chromatograph equipped with a flame ionization detector (6890N GC-FID, Agilent Technologies, USA) was used for the GC analyses. The system was controlled using Chem. Station. Nitrogen was used as the carrier gas. A mechanical pump was used for the vacuum system, and a water tank with a temperature controller was used during the static coating procedure. A thermal gravimetric analyzer TGA (TGA-50, Shimadzu, Japan) was used to analyze the decomposition temperature of ionic polymer.

Thermal gravimetric analysis

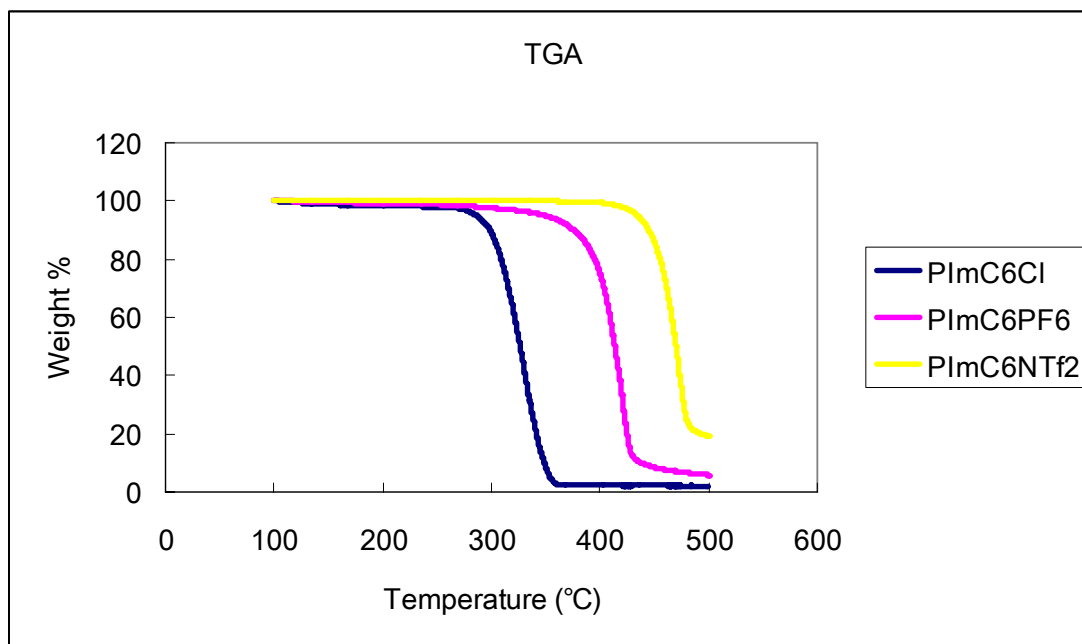


Fig. TGA results of three PILs: PImC₆Cl, PImC₆PF₆, and PImC₆NTf₂, Temperature program: 100 to 500 °C at a heating rate of 10 °Cmin⁻¹; N₂ flow rate: 20 mLmin⁻¹; platinum sample plate.

Column QC test

Column QC test

Column #	Retention factor	No. of tests	HETP (mm)
1	6.26±0.05	6	0.28
2	6.08±0.04	9	0.26
3	6.21±0.03	9	0.29

Standard: naphthalene; oven temperature: 100 °C; N₂ flow: 36 cm s⁻¹

Reference

1. Y. N. Hsieh, C. H. Kuei, Y. K. Chou, C. C. Liu, K. L. Leu, T. H. Yang, M. Y. Wang, and W. Y. Ho, *Tetrahedron Lett.* submitted.