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Communication

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A Simple and Universal Gel Permeation Chromatography Technique for Precise Molecular Weight Characterization of Well-Defined Poly(ionic liquid)s

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Supporting Information

ABSTRACT: Poly(ionic liquid)s (PILs) are an important class of technologically relevant materials. However, characterization of well-defined polyionic materials remains a challenge. Herein, we have developed a simple and versatile gel permeation chromatography (GPC) methodology for molecular weight (MW) characterization of PILs with a variety of anions. PILs with narrow MW distributions were synthesized via atom transfer radical polymerization, and the MWs obtained from GPC were further confirmed via nuclear magnetic resonance end group analysis.

Ionic liquids (ILs) are most commonly defined as salts with melting points below 100 °C, and are largely comprised of inorganic anions and asymmetric organic cations.[1] This ionic nature of ILs results in many unique properties, such as tunable solubility, negligible vapor pressure, wide electrochemical window, and high thermal stability. These attractive properties have prompted their use in battery electrolytes, fuel cells, capacitors, and gas and liquid separations.[2] The liquid nature of the ILs results in high diffusivity and conductivity with improved performance. However, the inherent lack of mechanical stability decreases the utility of such materials, and therefore polymeric/polymerized ionic liquids, or poly(ionic liquid)s (PILs),[3] have emerged as a possible alternative to ILs. PILs are generally solid materials with reduced mobility and significantly lower diffusion, which affects device performance. It has been proposed that diffusivity can be increased by reducing the dimensionality of ion diffusion.[4] Additionally, the reduction in dimensionality can lead to nanoconfinement, which has been shown to increase mobility and diffusion.[5] One potential way to realize these benefits is through phase separation of block copolymers. The first step to access such materials is the ability to synthesize and characterize PILs with precise molecular weights (MWs).

PILs have been prepared by controlled radical polymerization (CRP), including atom transfer radical polymerization (ATRP) and reversible addition−fragmentation chain-transfer (RAFT) polymerization[6] of styrenic, methacrylate, or *N*-vinylimidazolium-based IL monomers.[7] However, the presence of charged groups in PILs results in complicated and unreliable MW characterization via gel permeation chromatography (GPC). To overcome this difficulty, precursor polymers are typically synthesized first, and then modified to yield PILs. However, post-modification has its own drawbacks, as 100% modification is not guaranteed, and purification of the resulting mixtures is difficult or impossible.

Here we demonstrate that by simply adding salts containing the same anions as the PILs into the GPC eluents, the MW and molecular weight distribution (MWD) of PILs can be characterized. For example, as shown in Figure 1, the GPC peak of poly[1-(4-vinylbenzyl)-3-butylimidazolium bis(trifluoromethylsulfonyl)imide] (polyVBBI$^+$Tf$_2$N$^-$) was obtained with tetrahydrofuran (THF) containing 10 mM LiTf$_2$N as the eluent, while there was no polymer peak in many other tested GPC eluents, including pure THF; THF containing LiBr, triethylamine (TEA), tetrabutylammonium bromide (TBA-Br), or 1-butylimidazole; and *N*,*N*-dimethylformamide (DMF) containing LiBr. The disappearance of the GPC peak of PILs could be due to polymer aggregation on the column fillers caused by the ionic groups.[8] This is the first time, to the best of our knowledge, that a Tf$_2$N$^-$-containing PIL displayed normal peak in the GPC trace.

To facilitate GPC characterization of the PILs, we tried to obtain neutral polymers free of ionic groups from PILs by the derivatization technique.[9] GPC measurements of the samples obtained from attempted dequaternization of polyVBBI$^+$Tf$_2$N$^-$ via thermal degradation,[10] thiophenolate,[11] morpholine,[12] or NaOH[13] were unsuccessful, which might be attributed to the incomplete conversion and the presence of impurities. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) and electrospray ionization (ESI) mass spectrometry were also attempted, but the spectra of the polyVBBI$^+$Tf$_2$N$^-$ samples did not show well-defined peaks (Figures S9 and S10).

While these previous attempts did not succeed, it was found that simple addition of 10 mM LiTf$_2$N into the THF eluent resulted in "normal" GPC peaks of polyVBBI$^+$Tf$_2$N$^-$. The general chemical principle that *like dissolves like* explains this behavior in a figurative manner. In this case, the Tf$_2$N$^-$ anions in the GPC eluent appear to act as screening electrolyte that diminishes the polymer chain expansion (polyelectrolyte

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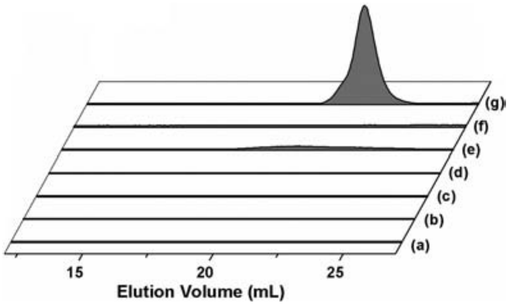


Figure 1. GPC traces of polyVBBI$^+$Tf$_2$N$^-$ measured with the eluent of (a) pure THF, (b) THF containing 10 mM LiBr, (c) THF containing 1 wt% triethylamine (TEA), (d) THF containing 1 wt% tetrabutylammonium bromide (TBA-Br), (e) THF containing 10 mM 1-butylimidazole, (f) DMF containing 50 mM LiBr, and (g) THF containing 10 mM LiTf$_2$N.

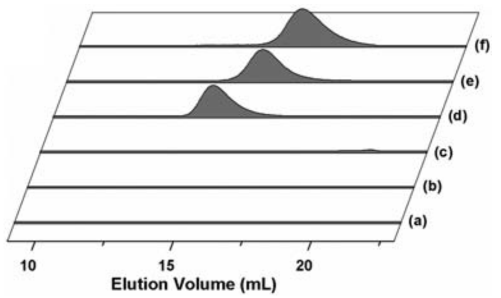
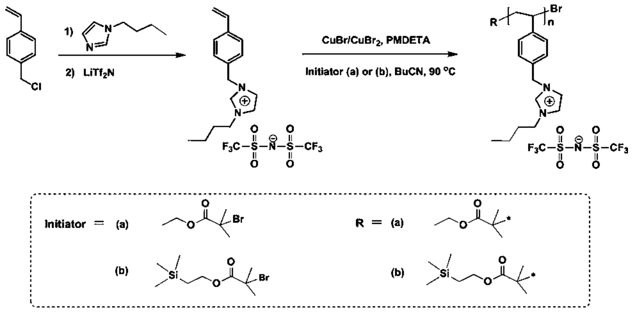


Figure 2. GPC traces of polyVBBI$^+$Tf$_2$N$^-$ measured with the eluent of (a) pure DMF and (d) DMF containing 10 mM LiTf$_2$N; polyVBBI$^+$PF$_6$$^-$ measured with the eluent of (b) pure DMF and (e) DMF containing 10 mM KPF$_6$; and polyVBBI$^+$BF$_4$$^-$ measured with the eluent of (c) pure DMF and (f) DMF containing 10 mM NaBF$_4$.

Scheme 1. Synthesis of Poly[1-(4-vinylbenzyl)-3-butylimidazolium bis(trifluoromethylsulfonyl)imide] (PolyVBBI$^+$Tf$_2$N$^-$) by ATRP



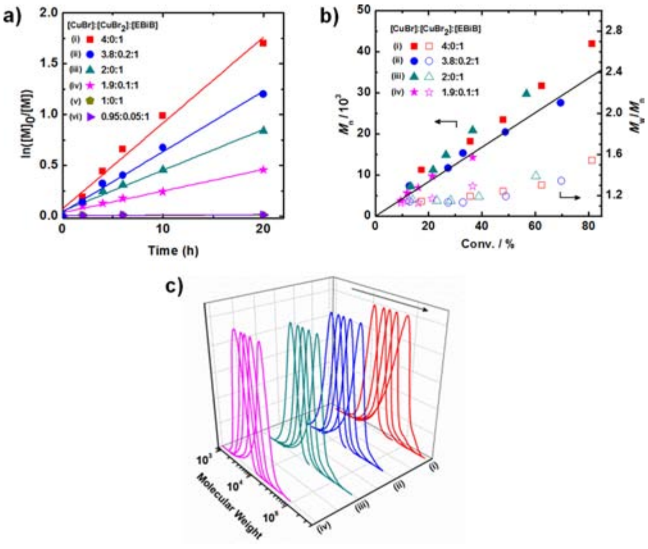


Figure 4. Kinetic plot of ln([M]$_0$/[M]) vs time (a), plot of M_n and M_w/M_n vs conversion (b), and GPC traces (calibrated with calibration curve in Figure 3c) (c) for ATRP of VBBI$^+$Tf$_2$N$^-$. Conditions: [VBBI$^+$Tf$_2$N$^-$]$_0$/[EBiB]$_0$/[CuBr]$_0$/[CuBr$_2$]$_0$/[PMDETA]$_0$ = 80/1/x/y/(x+y), VBBI$^+$Tf$_2$N$^-$/BuCN = 1/1 (w/w), 90 °C. (i) $x = 4$, $y = 0$; (ii) $x = 3.8$, $y = 0.2$; (iii) $x = 2$, $y = 0$; (iv) $x = 1.9$, $y = 0.1$; (v) $x = 1$, $y = 0$; (vi) $x = 0.95$, $y = 0.05$.

effect), as indicated by the measurement of the Mark–Houwink parameters (Figure S11). This effect decreases the association of ionic groups and reduces the polymer–column interactions, which are characteristic phenomena associated with polyelectrolytes.[14] Supporting this theory, GPC measurements of the PILs conducted with only nonionic species or salts with other types of anions, such as LiBr, TBA-Br, TEA, or 1-butylimidazole, did not produce peaks (Figure 1). Additionally, 1-butylimidazole can also be added into the LiTf$_2$N-containing THF eluent to obtain GPC peaks of polyVBBI$^+$Tf$_2$N$^-$, since the presence of imidazole could diminish the adsorption of the amino-containing polymers on the columns.[15] Moreover, the THF solution with a Tf$_2$N$^-$-containing IL, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, also worked well as a GPC eluent for PILs (Figure S8). The presence of the same type of anions and organic counterions in the GPC

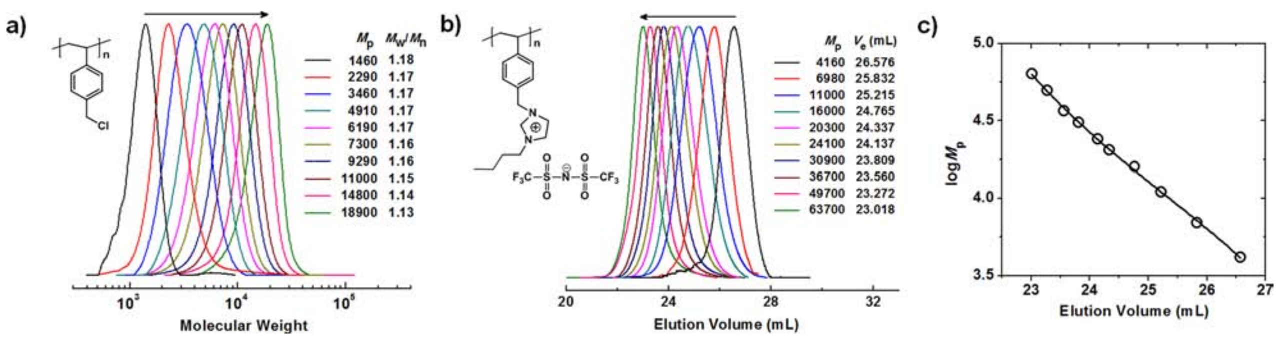


Figure 3. (a) GPC traces of polyVBC in THF calibrated using linear PS standards. (b) GPC traces of polyVBBI$^+$Tf$_2$N$^-_{\mathrm{RAFT}}$ standards in THF (containing 10 mM LiTf$_2$N and 10 mM 1-butylimidazole). (c) The GPC calibration curve using 10 polyVBBI$^+$Tf$_2$N$^-_{\mathrm{RAFT}}$ standards in THF (containing 10 mM LiTf$_2$N and 10 mM 1-butylimidazole) by a third-order polynomial fit of the data points.

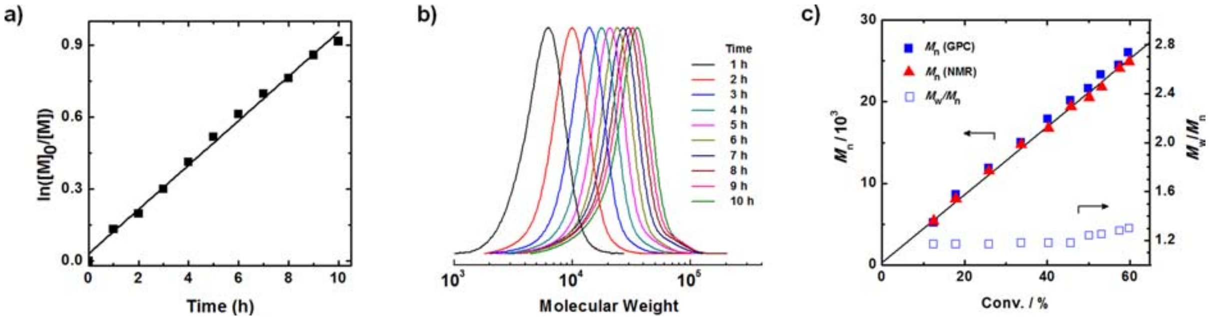


Figure 5. (a) Kinetic plot of ln([M]$_0$/[M]) vs time. (b) GPC traces of TMS-polyVBBI$^+$Tf$_2$N$^-$ in THF (containing 10 mM LiTf$_2$N and 10 mM 1-butylimidazole) calibrated using polyVBBI$^+$Tf$_2$N$^-_{\mathrm{RAFT}}$ standards. (c) Plot of M_n and M_w/M_n of TMS-polyVBBI$^+$Tf$_2$N$^-$ vs conversion using the M_n values obtained from GPC and ^{1}H NMR, respectively. Conditions: [VBBI$^+$Tf$_2$N$^-$]$_0$/[TMS-EBiB]$_0$/[CuBr]$_0$/[CuBr$_2$]$_0$/[PMDETA]$_0$ = 80/1/3.8/0.2/4, VBBI$^+$Tf$_2$N$^-$/BuCN = 1/1 (w/w), 90 °C.

eluent as those in the PILs could create a similar environment for the PILs, counterbalancing the effect of the ionic groups in the PILs on their flow behavior in the columns.[16] Furthermore, this appeared to be a universal method applicable to PILs with other types of complex anions (such as BF$_4^-$ and PF$_6^-$, but not simple Br$^-$) and other GPC eluents (such as DMF) (Figure 2).

A GPC calibration curve was generated by using polyVBBI$^+$Tf$_2$N$^-$ with known MW and narrow MWD as the standard. The PIL standards (denoted as polyVBBI$^+$Tf$_2$N$^-_{\mathrm{RAFT}}$) were prepared in a three-step process, by RAFT polymerization of 4-vinylbenzyl chloride (VBC) followed by quaternization with 1-butylimidazole and ion exchange with LiTf$_2$N, resulting in the same structure in the repeating unit as those directly synthesized by ATRP. The peak MW (M_p) and dispersity (M_w/M_n, where M_w and M_n stand for number- and weight-average MW, respectively) of the poly(4-vinylbenzyl chloride) (polyVBC) were obtained by GPC using pure THF as the eluent and calibrated with linear polystyrene (PS) standards. This allowed the M_p of the polyVBBI$^+$Tf$_2$N$^-_{\mathrm{RAFT}}$ to be calculated (Figure 3a,b) and a calibration curve established (Figure 3c). This calibration curve is essential for the accurate GPC characterization of PILs, since PILs have different hydrodynamic volumes compared to neutral polymer standards (e.g., PS, poly(methyl methacrylate) (PMMA), and poly(ethylene oxide) (PEO)) with the same MW, and thus the MWs of PILs obtained by GPC based on these normal calibration standards will be inaccurate.

To evaluate the reliability of such GPC methodology for MW characterization of PILs, a polymerization system was designed and studied using ATRP of Tf$_2$N$^-$-containing IL monomer. The IL monomer, 1-(4-vinylbenzyl)-3-butylimidazolium bis(trifluoromethylsulfonyl)imide (VBBI$^+$Tf$_2$N$^-$), was prepared by quaternization of VBC with 1-butylimidazole and then ion exchange with LiTf$_2$N. As shown in Scheme 1, the ATRP of VBBI$^+$Tf$_2$N$^-$ was conducted using ethyl 2-bromoisobutyrate (EBiB) as the initiator, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the ligand, butyronitrile (BuCN) as the solvent, and various activator/deactivator ratios. Linear semilogarithmic kinetic plots were observed when the ratio of ([CuBr]$_0$ + [CuBr$_2$]$_0$)/[EBiB]$_0$ was 4/1 and 2/1, with higher copper content leading to faster rate of polymerization (Figure 4a). However, when the ratio of ([CuBr]$_0$ + [CuBr$_2$]$_0$)/[EBiB]$_0$ was 1/1, there was no reaction. This was likely caused by the presence of trace amounts of residual chloride anions in the VBBI$^+$Tf$_2$N$^-$ that could suppress the activator (Cu$^+$/ligand).[17] When 5% CuBr$_2$ was initially added to the reaction medium, the polymerization rates became slower compared with those with pure CuBr.

The PILs synthesized by ATRP were characterized by GPC with the calibration curve in Figure 3c. The results showed that the M_n agreed well with theoretical M_n, and polymers with narrow MWD were produced (M_w/M_n ≈ 1.1−1.2) (Figure 4b,c). In contrast, when the VBBI$^+$Tf$_2$N$^-$ was polymerized by conventional radical polymerization, the resulting PILs showed the value of M_w/M_n as high as 2.42 (Figure S4).

In order to further check the reliability of this calibration method, the molar masses of the polyVBBI$^+$Tf$_2$N$^-$ were also measured by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. ATRP of VBBI$^+$Tf$_2$N$^-$ was conducted using a trimethylsilyl (TMS)-labeled ATRP initiator, TMS-EBiB (Scheme 1), which acts as the NMR marker for integration.[18] First-order kinetics was observed during the polymerization (Figure 5a), and the GPC traces displayed low M_w/M_n (1.1−1.3) (Figure 5b). The M_n values obtained by NMR end group analysis correlated very well with the theoretical M_n and those obtained by GPC (Figure 5c). Furthermore, the livingness of the system was demonstrated by chain extension of the polyVBBI$^+$Tf$_2$N$^-$-Br macroinitiator with styrene (Figure S7).

In summary, we established a universal GPC technique to evaluate MW of PILs using a GPC eluent containing bulky organic anions such as Tf$_2$N$^-$, BF$_4^-$, and PF$_6^-$. The accuracy of this approach was then verified using NMR end group analysis. Furthermore, ATRP of VBBI$^+$Tf$_2$N$^-$ was demonstrated to proceed in a well-controlled fashion, resulting in PILs with predetermined MW and narrow MWD (M_w/M_n ≈ 1.1−1.3). The novel approach developed in this work opens an avenue for the molecular characterization of PILs and the preparation of useful PILs materials for a wide range of applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, GPC measurement results, GPC calibration curves, GPC traces, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) This approach is similar to the vaccination process, in which the injection of vaccines stimulates the animal's immune system to develop adaptive immunity against a pathogen. Here, the conventional GPC eluent is "vaccinated" by injecting with salts (e.g., $LiTf_2N$) as the "vaccines" to make it endurable for the PILs containing the same type of anions.

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