Zhang, W., Willa, C., Sun, J.-k., Guterman, R., Taubert, A., & Yuan, J. (2017). Polytriazolium poly(ionic liquid) bearing triiodide anions: Synthesis, basic properties and electrochemical behaviors. *Polymer*. doi:10.1016/j.polymer.2017.07.059.

Polytriazolium poly(ionic liquid) bearing triiodide anions: Synthesis, basic properties and electrochemical behaviors

Abstract

4-Methyl-1-vinyl-1,2,4-triazolium triiodide ionic liquid and its polymer poly(4-methyl-1-vinyl-1,2,4-triazolium) triiodide were prepared for the first time from their iodide precursors *via* the reaction of iodide (I^-) with elemental iodine (I_2). The change from iodide to triiodide (I_3^-) was found to introduce particular variations in the physical properties of these two compounds, including lower melting point/glass transition temperature and altered solubility. The compounds were characterized by single-crystal X-ray diffraction, elemental analysis, and their electrochemical properties examined in solution and in the solid-state. Compared with their iodide analogues, the triiodide salts exhibited lower electrical impedance and higher current in the cyclic voltammetry. We found that poly(4-methyl-1,2,4-triazolium triiodide) was proven to be a promising solid polymer electrolyte candidate.

Polytriazolium poly(ionic liquid) bearing triiodide anions: synthesis, basic properties and electrochemical behaviors

Weiyi Zhang,† Christoph Willa,‡ Jian-Ke Sun,† Ryan Guterman,† Andreas Taubert,§ Jiayin Yuan*†‖
†Max-Planck-Institute of Colloids and Interfaces, D-14476 Potsdam, Germany
‡Laboratory for Multifunctional Materials, Department of Materials, ETH Zurich
Vladimir-Prelog-Weg 5, 8093 Zurich, Switzerland
§Institute of Chemistry, University of Potsdam, D-14476 Potsdam, Germany
‖Department of Chemistry & Biomolecular Science & Center for Advanced Materials Processing (CAMP), Clarkson University, 8 Clarkson Avenue, Potsdam, New York 13699, United States
E-mail: Jiayin.Yuan@mpikg.mpg.de

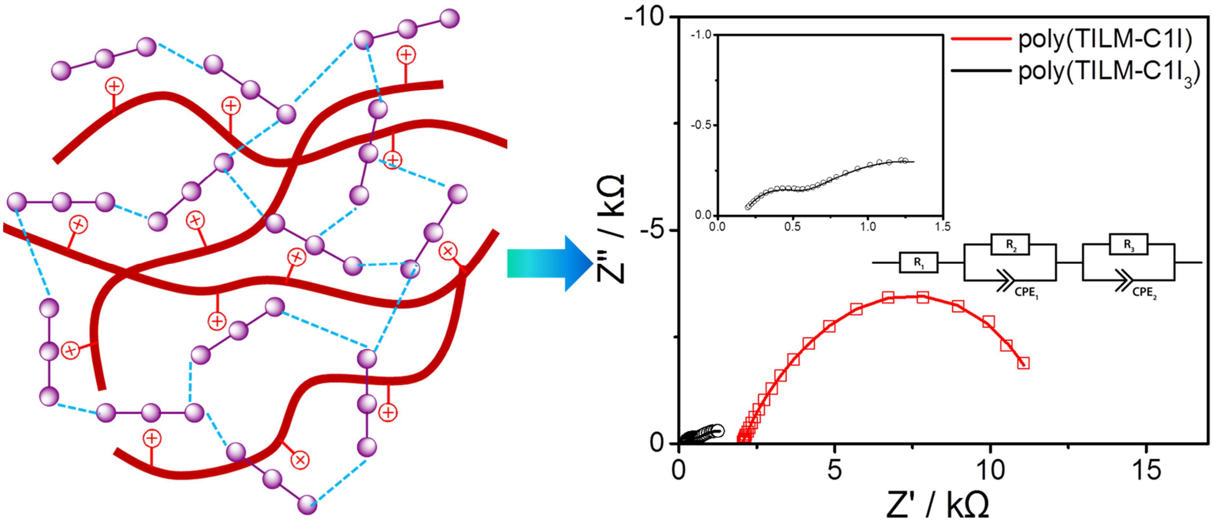
Highlights

1. PILs bearing a triiodide anion have been synthesized for the first time.

2. The replacement of I^- by I_3^- resulted in dramatic property change of PILs.

3. PILs bearing a triiodide anion show low resistance as solid electrolyte.

TOC



Abstract

4-Methyl-1-vinyl-1,2,4-triazolium triiodide ionic liquid and its polymer poly(4-methyl-1-vinyl-1,2,4-triazolium) triiodide were prepared for the first time from their iodide precursors *via* the reaction of iodide (I^-) with elemental iodine (I_2). The change from iodide to triiodide (I_3^-) was found to introduce particular variations in the physical properties of these two compounds, including lower melting point/glass transition temperature and altered solubility. The compounds were characterized by single-crystal X-ray diffraction, elemental analysis, and their electrochemical properties examined in solution and in the solid-state. Compared with their iodide analogues, the triiodide salts exhibited lower electrical impedance and higher current in the cyclic voltammetry. We found that poly(4-methyl-1,2,4-triazolium triiodide) was proven to be a promising solid polymer electrolyte candidate.

1. Introduction

Poly(ionic liquid)s (PILs) are an emerging class of functional polymers that are comprised of ionically charged repeating units typically used in ionic liquid chemistry.[1-3] These materials are normally obtained from the polymerization of ionic liquids (ILs), or post-modification of extant polymers *via* ion metathesis, *N*-alkylation, or grafting ILs onto neutral polymers.[4-6] The marriage of ILs and polymers enables PILs to possess numerous useful properties, such as adjustable solubility in many organic solvents, relatively high ionic conductivity, and low glass transition temperature in comparison to classical polyelectrolytes. Currently, PILs find a variety of uses in materials applications.[7-15] The intrinsic physical and chemical properties of PILs are affected by their chemical structures and molecular characteristics, including the nature of both cations and anions, the relative positioning of the cation and anion in the polymer chain, linker length between main chain and pendant ionic groups, molecular weight, molecular weight distribution, main chain shape, *etc*. Among these, the molecular structure of both the cations and anions along with how they are combined into the polymer chains are of paramount importance. To date, cations from tetraalkylammonium, tetraalkylphosphonium, *N,N'*-dialkylpyrrolidinium *N,N'*-dialkylimidazolium and *N*-alklypyridinium, with anions from halides (Cl^-, Br^-, I^-), hydrophobic inorganics (N_3^-, BF_4^-, PF_6^-), or hydrophobic and hydrophilic organics ($(CF_3SO_2)_2N^-$, $CF_3SO_3^-$, $CF_3CO_2^-$, $CH_3CO_2^-$) are the most common choices.[16] The persistent need for polymers of task-specific functions nevertheless results in an endless search for unknown and less studied structures and functions. Recently, 1,2,4-triazolium-based PILs have been examined because of their unique properties and fine inner nanostructure in their colloidal nanoparticles.[17-20] Compared to imidazolium or 1,2,3-triazolium type PILs that have been intensively studied by Drockenmuller *et al.*,[21] The 1,2,4-triazolium-based species have shown so far higher hydrophilicity, stronger acidity due to two active protons in the cation ring, and enhanced metal ion loading capacity, which expanded the property window and application scope of PIL materials. It is further expected that upon anion metathesis/modification, new functions in 1,2,4-triazolium PILs will be discovered.

PILs due to its high ion density have been previously used by Ohno *et al.[22]* as macromolecular electrolytes for applications in supercapacitors, fuel cells, batteries, dye-sensitized solar cells, *etc*.[23-26] Generally speaking, PILs are thermodynamically more stable than conventional liquid-state or quasi-solid state electrolytes, and can be stable upon exposure to air when carrying hydrophobic anions, thus possessing a long shelf life. Chemically, the polymerizable cations or anions are covalently attached to the polymer backbone, and thus have limited, sometimes negligible mobility. The counter-ions of related PILs however are fairly mobile and can transport ions in the whole system, which make PILs a single-ion conductor.[27] In this context, we introduce poly(1,2,4-trizaolium) as a new solid-state polymer electrolyte bearing enhanced ion mobility and acidic protons.[28] Triiodide is incorporated into the 1,2,4-triazolium PIL as the counter-anion, which minimizes interactions between the heterocyclic cation ring and the anion due to its large size thus enhanced steric hindrance. While triiodide has been explored previously as additives to polymers due to its charge carrying properties,[29, 30] they have not been examined in the context of PILs. After the introduction of I_3^-, the electrochemical and thermal behaviors of the PILs were altered, and a highly ion conductive polyiodide "network" can be expected according to Grotthuss mechanism.[31] This makes triiodide-based PILs promising materials for high-performance polymer electrolyte.

2. Experimental Section

Materials

1-Vinyl-1,2,4-triazole (**1**, 98%), iodomethane (CH_3I, 99%), butylated hydroxytoluene (BHT, 98%), N.N'-azobisisobutyronitrile (AIBN, 98%, recrystallized from methanol), and all organic solvents were purchased from Sigma-Aldrich. Iodine (I_2, 99.8%) was obtained from Acros Organics. All solvents used are anhydrous. Graphite sheets were bought from LairdTech. The preparation method of iodide type ionic liquid monomer (TILMC1-I) and polymer (PTILMC1-I) was described in our previous work.[17]

Characterization Methods

Thermogravimetric analysis (TGA) experiments were carried out by a Netzsch TG209-F1 apparatus under a heating rate of 10 K min^{-1} with constant N_2 flow. Differential scanning calorimetry (DSC) measurements were conducted on a Perkin-Elmer DSC-1 instrument at a heating rate of 10 K min^{-1} under N_2 flow. The melting points were obtained from the heating curves and they were measured in the second heating cycle. Fourier transform infrared spectroscopy (FT-IR) spectra were measured and recorded on a BioRad 6000 FT-IR spectrometer; samples were used in solid states and measuring *via* a Single Reflection Diamond ATR. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker DPX-400 spectrometer in deuterated solvents using residual solvent as reference. Elemental analyses of triiodide compounds were measured by company Mikroanalytisches Laboratorium Kolbe (www.mikro-lab.de). The cyclic voltammetry (50 mV s^{-1}) were performed with a Gamry reference 3000 potentiostat at a voltage window of 0.0-2.0 V for all samples. The impedance spectra were recorded using the same device by applying a sine wave with amplitude of 10 mV over the frequency range from 0.1 or 0.5 Hz to 20 kHz. The data was fitted using ZPlot software from Scribner Associates Inc. Single crystal X-ray diffraction was conducted by Gemini A Ultra X-ray Diffraction System (from Rigaku Oxford Diffraction), with detector Altas CCD.

Synthesis of 4-methyl-1-vinyl-1,2,4-triazolium triiodide (TILMC1-I_3)

A 50 mL round-bottom flask was filled with a mixture of 4-methyl-1-vinyl-1,2,4-triazolium iodide (2 g, 4.21 mmol) and iodine (1.07 g, 4.21 mmol) with 30 mL acetone. After stirring for 24 h, a small fraction of solid residue was filtered and the liquor was poured into cyclohexane resulting in the formation of a brown precipitate, which was washed with cyclohexane (3 x 20 mL) dried *in vacuo*, and identified as TILMC1-I_3 (4.10 g, 99.0%). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 10.21 (s, 1H), 9.19 (s, 1H), 7.49 (dd, 1H, J_1=16 Hz, J_2=8 Hz), 6.01 (d, 1H, J=16 Hz), 5.52 (d, 1H, J=8 Hz), 3.88(s, 3H); ^{13}C NMR (400 MHz, DMSO-d_6, δ, ppm): 146.02, 142.67, 129.63, 110.85, 35.34.

Synthesis of poly(4-methyl-1-vinyl-1,2,4-triazolium triiodide) (PTILMC1-I_3)

Following the same procedures described in the synthesis route of TILMC1-I_3, a dark brown solid (3.5 g, 98.5%) was obtained. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 10.03 (br, 1H), 9.12 (m, 1H), 4.45 (br, 1H), 3.91 (br, 3H), 2.34 (br, 2H). Elemental analysis, calculated: %C: 12.23; %H: 1.64; %N: 8.56; %I: 77.56, found: %C: 12.73; %H: 1.80; %N: 8.52; %I: 76.23.

Solubility tests

10 mg of the monomer/polymer was put into 1 mL of solvent (water, methanol, acetone, acetonitrile, THF, ethyl acetate, toluene, chloroform or DMF). After shaking for 10 min, the solubility of corresponding monomer/polymer at ambient temperature was checked.

Crystal growth

Single crystals of 4-methyl-1-vinyl-1,2,4-triazolium triiodide (TILMC1-I_3) were acquired by the vapor diffusion method: the monomer was dissolved in acetone and stored inside a 5 mL open vial, then the vial was fixed at the bottom of a 250 mL closed bottle with diethyl ether surrounded. After diethyl ether entered through the gas phase into acetone, crystals of the triiodide monomer slowly grew up. The single crystals were stored in the mother solution until testing.

All samples were treated at 80 °C under high vacuum prior to all electrochemical tests. All electrochemical tests were conducted at a relative humidity of 20% and a temperature of 25 °C.

3. Results and discussion

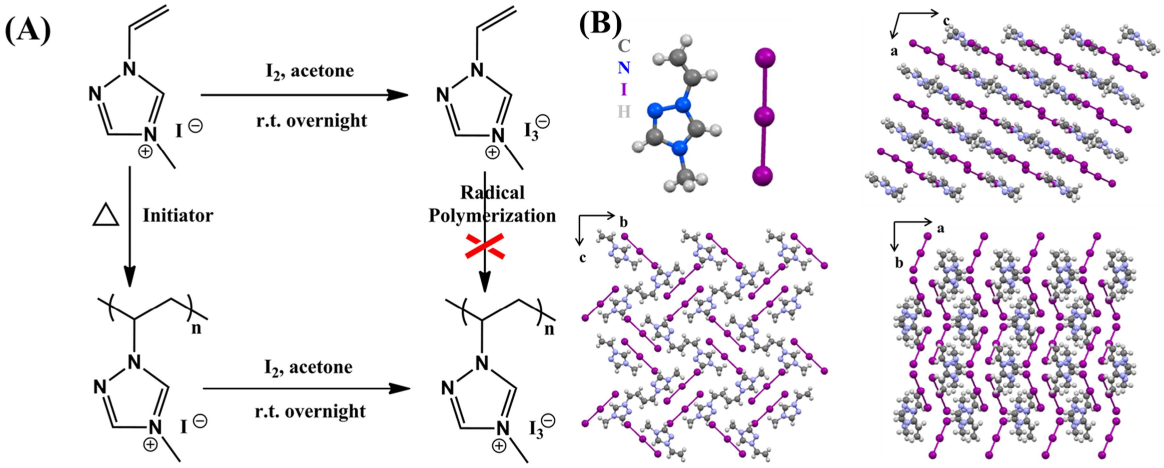


Figure 1. (A) Synthetic route towards 4-methyl-1-vinyl-1,2,4-triazolium triiodide monomer and poly(4-methyl-1-vinyl-1,2,4-triazolium triiodide). (B) Single crystal structure and crystallographic packing model of 4-methyl-1-vinyl-1,2,4-triazolium triiodide (CCDC 1436279 contains the supplementary crystallographic data for this article. These data can be found from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.)

The monomer 4-methyl-1-vinyl-1,2,4-triazolium triiodide (TILMC1-I_3) was synthesized directly from its iodide analogue. The synthesis route for 4-methyl-1-vinyl-1,2,4-triazolium iodide as well as poly(4-methyl-1-vinyl-1,2,4-triazolium iodide) was reported by us previously and used here directly as precursor.[17] Treatment of the IL monomer 4-methyl-1-vinyl-1,2,4-triazolium iodide with a 1:1 molar equivalent amount of I_2 produced I_3^- which can be viewed as the neutralization reaction of a Lewis base (I^-) and Lewis acid (I_2).[32] Triiodide-based IL was obtained as a solid powder *via* precipitation of the reaction mixture in cyclohexane to remove unreacted iodine. In order to elucidate the solid-state structure of TILMC1-I_3, single crystal X-ray diffraction of the single crystals grew from triiodide monomer-acetone solution was performed. As shown in **Table S1**, TILM-C1I_3 monomer crystallizes in the monoclinic space group $P2_1/c$, and cell parameters are a=7.2685(14) Å, *b*=11.616(4) Å, *c*=15.038(4) Å and *ß*=106.472(19)°. Single crystal data analysis reveals the successful formation of I_3^- anion in TILMC1-I_3. The distances for I-I bonds in I_3^- anion are 2.91 and 2.88 Å, and the I-I-I bending angle is 178.94(6)°, which are consistent with triiodide reported in the previous literatures.[33] **Figure 1B** shows the packing model of TILMC1-I_3 along *a*, *b* and *c* axes individually. It is clear that the I_3^- anions are sandwiched between the adjacent 1,2,4-triazolium planar rings, which further extend to supramolecular 3D "network" by the intermolecular electrostatic interaction. Owing to the Grotthuss mechanism, in which the charge transfer is achieved *via* construction and simultaneous destruction of covalent bonds among neighboring species, *i.e.* "hopping" of atoms instead of mass movement,[31, 34] enhanced transportation of I^- in such 3D supramolecular "network" is foreseeable for solid-state ILs. Additionally, the unique alignment of I_3^- anions finally result in a shorter distance of 4.4 Å between adjacent triiodide chains. Considering the radius of I^- (2.2 Å), bond length of I_2 (2.7 Å) and above mentioned "hopping" mechanism, the effective ion conduction can be inferentially expected in triiodide systems.

Since the radical quenching capability of triiodide is well-known[35] and prevented our repeated efforts for the direct radical polymerization of I_3^- containing monomers (Figure 1A), , post-modification of the iodide PIL was performed. Triiodide-based PILs were produced following the same procedure used for triiodide-based IL monomers, *i.e.* anion modification. While iodide-based polymer PTILMC1-I is insoluble in acetone, the addition of a stoichiometric equivalent of I_2 led to the formation of a transparent dark yellow solution in acetone plus a tiny fraction of residue solid (< 5 wt%) that was filtered off. After precipitation of the mixture solution in cyclohexane, further purification of the precipitate *via* dialysis in acetone (molecular weight cutoff / MWCO of 3500 Da) to remove impurities, dark brown powders were obtained when solvent was evaporated. The change in the solubility of the iodide PIL in acetone after the treatment of I_2 indicated that triiodide-based PILs were successfully synthesized, which was further identified by elemental analysis (**Table S2**).

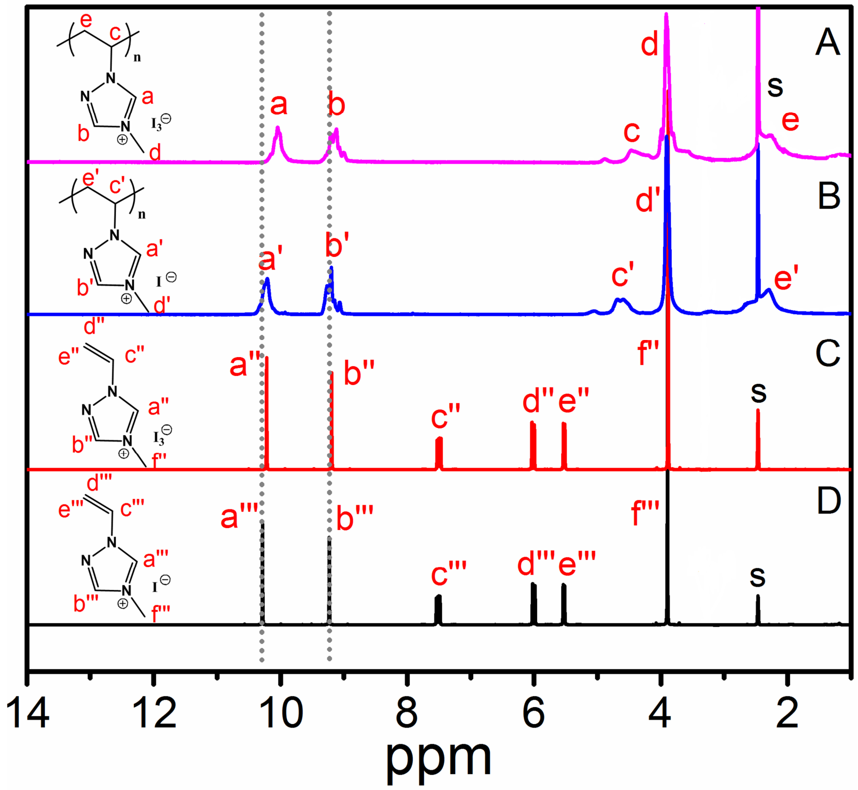


Figure 2. ^{1}H-NMR spectra of (A) poly(4-methyl-1-vinyl-1,2,4-triazolium triiodide); (B) poly(4-methyl-1-vinyl-1,2,4-triazolium iodide); (C) 4-methyl-1-vinyl-1,2,4-triazolium triiodide; and (D) 4-methyl-1-vinyl-1,2,4-triazolium iodide.

Slight differences were observed in the ^{1}H NMR spectra of the triiodide-based monomer and polymer relative to their iodide congeners. **Figure 2** shows that the resonances corresponding to two acidic protons in 1,2,4-triazolium rings are slightly more shielded when triiodide is present. This trend is consistent with other anion-exchanged PILs, where the replacement of anions may result in varied shielding of the protons.[36] In the enlarged view of the low field region the of PILs in **Figure S1**, peak *a* and *b* related to protons in 1,2,4-triazolium rings in PTILMC1-I$_3$ were more shielded in comparison to PTILMC1-I, from 10.23 (*a'*) to 10.03 ppm (*a*) and from 9.21 ppm (*b'*) to 9.11 ppm (*b*). Similar behaviors were observed as well for monomers TILM-C1I and TILM-C1I$_3$ from 10.28 (*a'''*) to 10.21 ppm (*a''*) and from 9.23 (*b'''*) to 9.19 ppm (*b''*). As reported, triiodide anions exist in an isolation state in solutions because they are electronically more stable instead of I$_2$-I$^-$ pair in solvents,[37, 38] we believe that the delocalized negative charge in triiodide *vs* iodide leads to weakened interaction of anions with hydrogens in the 1,2,4-triazolium heterocycle ring, which eventually results in shielding of those acidic protons.

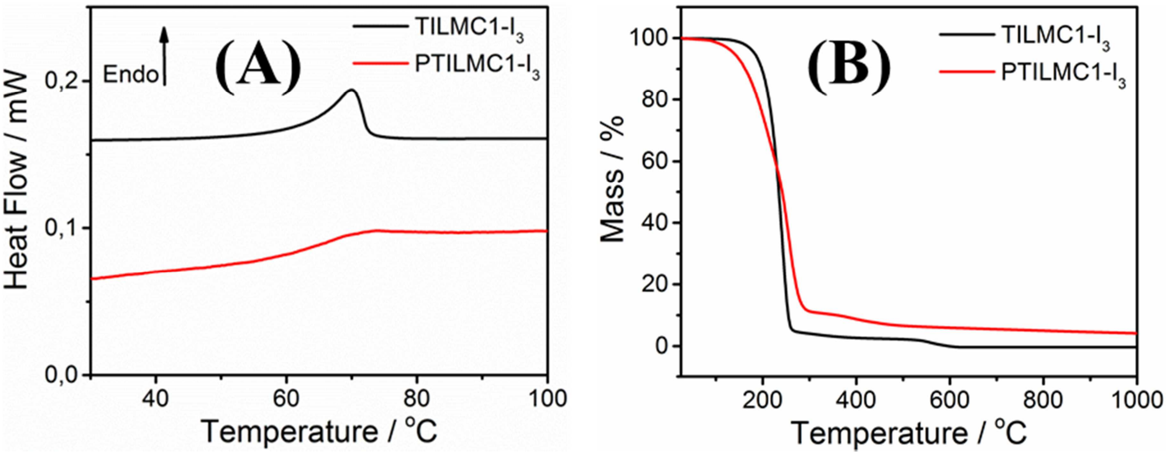


Figure 3. (A) DSC curves of PTILMC1-I_3 and TILMC1-I_3; (B) TGA curves of PTILMC1-I_3 and TILMC1-I_3.

The thermal behaviors of IL monomers and their polymers strongly depend on the types of cations, anions, and interactions between them. Differential scanning calorimetry (DSC, **Figure 3A**) and thermogravimetric analysis (TGA, under N_2, **Figure 3B**) were applied to measure the melting points, glass transition temperature (T_g), and thermal stabilities of the monomers/polymers. TILMC1-I_3 melts at ~70 °C, and is considered an IL by conventional definition of ILs. Owing to the inhibition effect of iodine and triiodide towards radical propagation, exothermal peak stands for thermal radical polymerization are not found until 100 °C. PTILMC1-I_3 possesses a T_g at ~68 °C, which is very close to the melting point of its monomer. Compared to PTILMC1-I which didn't show glass transition temperature before its thermal decomposition, PTILMC1-I_3 acquired T_g in consistent with the trend corroborated by the monomers. According to the thermal stability, triiodide PIL and IL here start to decompose (defined as 5 wt% mass loss) at 139 and 183 °C, respectively. Compared to their iodide analogues, the thermal stability of triiodide monomer is consistent with the iodide monomer (180 °C for TILMC1-I), while the major decomposition temperature of triiodide PIL is 175 °C, significantly lower than 237 °C for PTILMC1-I. This result may be explained by the dynamic equilibrium between triiodide and iodine + iodide in the solid PTILMC1-I_3. The boiling point of iodine is 184 °C, close to the observed decomposition temperature, at which iodine leaves the system and drives the equilibrium to the decomposition side.

Anion differences in PILs/ILs will not only induce variations in their thermal properties, but also in their hydrophilicity/hydrophobicity. **Table 1** exhibits the solubility of triiodide-based 1,2,4-triazolium type monomer and polymer performed at a concentration of 1.0 wt% at room temperature. In good accordance with their iodide analogues, both TILMC1-I_3 and PTILMC1-I_3 are insoluble in chloroform and toluene, and soluble in DMF/DMSO, which indicates the solubility in these hydrocarbon solvents is irrelevant or less relevant to anion types. Opposite to their iodide precursors, PTILMC1-I_3 and TILMC1-I_3 were both insoluble in water but soluble in tetrahydrofuran and acetone/acetonitrile. In addition, PTILMC1-I_3 and TILMC1-I_3 differentiate each other slightly in their solubility in methanol and ethyl acetate, in which only the triiodide monomer is soluble.

Table 1. Solubility of triiodide-type monomer and polymer in different solvents.

Compound	H_2O	MeOH	Acetone/ACN	THF	$CHCl_3$/toluene	EtOAc	DMF/DMSO
TILMC1-I	+	+	+	-	-	-	+
TILMC1-I_3	-	+	+	+	-	+	+
PTILMC1-I	+	-	-	-	-	-	+
PTILMC1-I_3	-	-	+	+	-	-	+

(+) – soluble at 1.0 wt%; (-) - insoluble at 1.0 wt%

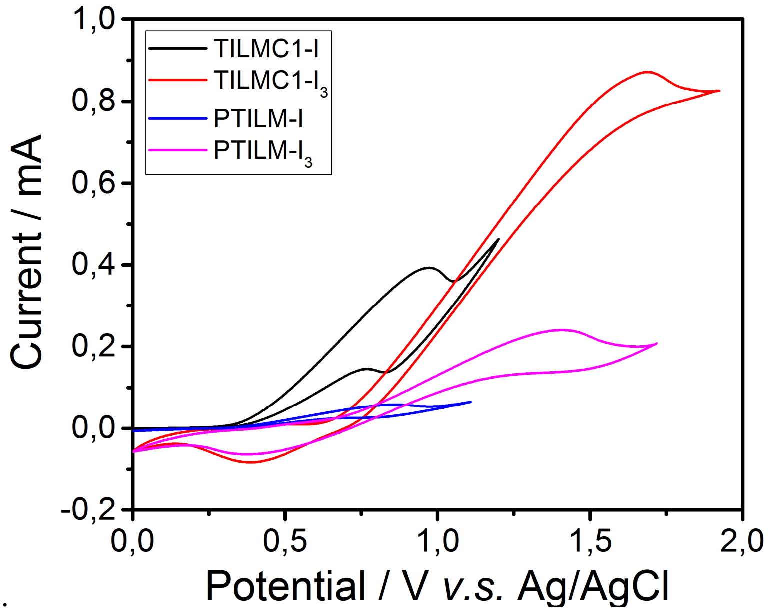


Figure 4. Cyclic voltammetry curves of TILMC1-I, TILMC1-I_3, PTILMC1-I and PTILMC1-I_3 (50 mmol in 10 mL DMF).

We studied the electrochemical nature of triiodide type IL and PIL by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses in DMF (with Ag/AgCl standard electrode and Pt/C electrode). The iodide-type TILMC1-I and PTILMC1-I samples were measured as references. Triiodide PIL/IL exhibit a higher current density than iodide counterparts (**Figure 4**), which is contributed possibly by the more ion-conductive triiodide species because of their better charge transportation ability *via* "hopping" of I^-. In this figure, all the CV profiles have a couple of redox peaks; for example, the plot of TILMC1-I_3 has an oxidation peak centered at 1.5 V, and the corresponding reduction peak around 0.4 V (vs.

Ag/AgCl). This indicates that these samples all have the redox activity during electrochemical cycling.

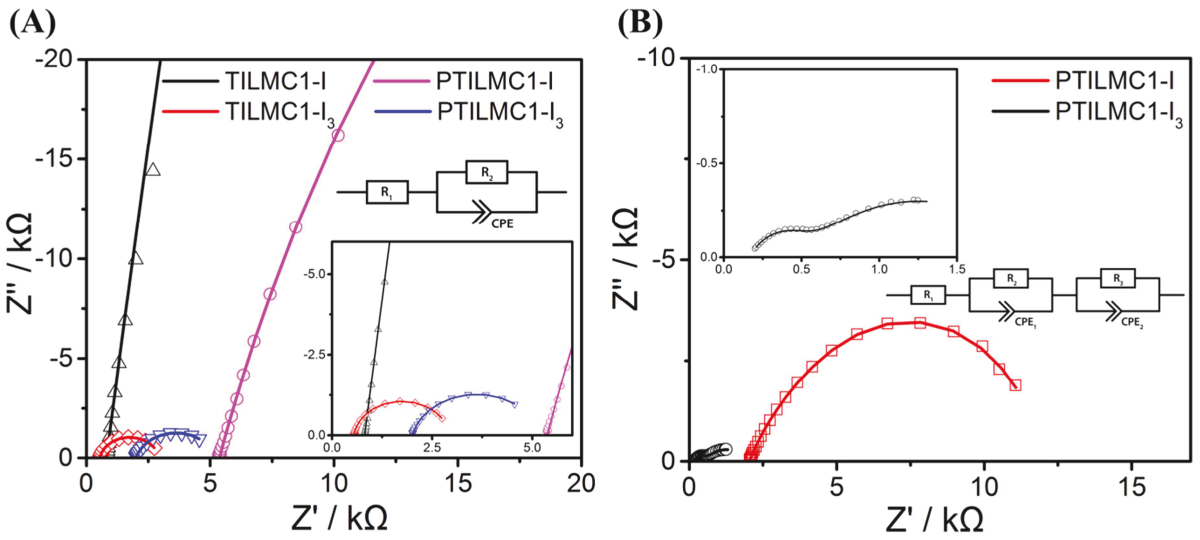


Figure 5. Nyquist plots from electrochemical impedance spectroscopy analysis of (A) 50mmol TILMC1-I, TILMC1-I_3, PTILMC1-I and PTILMC1-I_3 in 10 mL DMF and equivalent electrical circuit model used for fitting (inset); (B) 0.1 mol anhydrous PTILMC1-I and PTILMC1-I_3 sample with two blocking electrodes (graphite sheets, 6 cm x 1 cm; electrolyte area, 0.6-0.8 cm x 1 cm). Hollow symbols and solid lines represent experimental and fitting results, respectively.

Figure 5A shows the impedance data from iodide and triiodide-type IL and PIL in a Nyquist plot. We fit the experimental data using a Randles equivalent circuit (**Figure 5A**, inset) consisting of the electrolyte series resistance, R_1, in series with a $R_2||CPE_1$ circuit element representing the charge transfer resistance at the double layer from the electrode/electrolyte interface.[39, 40] The fitting results can be found in the supporting information (**Table 2**).

Table 2. Fitting results obtained from analysis of EIS data (**Figure 5A**).

Samples	R_1 (Ω)	R_2 (Ω)	CPE_1T (-)	CPE_2P (-)
TILM-C1I	814	$3.26 \cdot 10^6$	$1.72 \cdot 10^{-6}$	0.935
TILM-C1I_3	545	$2.40 \cdot 10^3$	$2.04 \cdot 10^{-6}$	0.918
poly(TILM-C1I)	$5.37 \cdot 10^3$	$225 \cdot 10^3$	$2.04 \cdot 10^{-6}$	0.866
poly(TILM-C1I_3)	$2.00 \cdot 10^3$	$3.22 \cdot 10^3$	$3.51 \cdot 10^{-6}$	0.851

It is apparent that the high frequency series resistance, R_1, is smaller for triiodide type samples when compared to iodide IL or PIL. This observation is in line with the idea that the presence of triiodide anion increases ion conductivity.[31] Polycations typically display lower mobility in solution than their respective monomers, *i.e.* the formed polymer chains are more restricted from free random motions according to chain tangling and shearing, thus R_1 for PILs is larger than for ILs. Regarding the double layer resistance, R_2, can be drastically reduced by using I_3^- and/or by polymerization. These results underline that triiodide type compounds outperform iodide type by displaying increased ion transportation ability. Since solid state electrolytes typically show better long-term stability properties than liquid electrolytes,[41] we further perform EIS measurements on bulk PTILMC1-I_3 and compared it with PTILMC1-I as a reference. Due to its low T_g (thus sticky) and relatively high electrochemical stability, it might be used as solid electrolyte and binder at the same time. **Figure 5B** shows the measured and fitted EIS data of solid PTILMC1-I and PTILMC1-I_3. As shown in the inset, the equivalent circuit consists of an ohmic resistor in series with two R||CPE circuits to mimic the influence of the electrode/electrolyte double-layer (R_2||CPE_1) as well as the charge transport resistance of the solid electrolyte (R_3||CPE_2) on the overall impedance.[42] The results from fitting can be found in supporting information (**Table 3**).

Table 3. Fitting results obtained from analysis of EIS data (**Figure 5B**).

Samples	R_1 (Ω)	R_2 (Ω)	CPE_1T (-)	CPE_1P (-)	R_3 (Ω)	CPE_2T (-)	CPE_2P (-)
poly(TILM-C1I)	$2.04 \cdot 10^3$	$2.64 \cdot 10^3$	$2.28 \cdot 10^{-5}$	0.656	$7.40 \cdot 10^3$	$1.33 \cdot 10^{-5}$	0.849
poly(TILM-C1I_3)	167	346	$6.98 \cdot 10^{-6}$	0.688	$1.49 \cdot 10^3$	$2.90 \cdot 10^{-4}$	0.482

We observe that the use of the triiodide anion results in significantly reduced R_1, R_2, and R_3 emphasizing the importance of I_3^- in the bulk as well as at the electrode/electrolyte interface. It was found that the value for CPE_2P is decreased from 0.85 to 0.48 when using I_3^- instead of I^-. It means that a transition from a capacitive-like circuit element to a diffusion-like element is observed.[43] We believe that our primary result is indicative of diffusion of ionic species through the Grotthuss mechanism when I_3^- is present. Based on above results, it is fair to say that poly(1-vinyl-1,2,4-triazolium triiodide) is a very promising material in the field of energy generation and conversion where it can be utilized as solid polymer electrolyte.[44]

4. Conclusions

In conclusion, a 1,2,4-triazolium triiodide-type PIL was synthesized from the iodide precursor for the first time. Compared to its iodide analogues, both triiodide type IL and PIL exhibit visibly different behaviors in solubility, thermal properties, and especially in electrochemical properties. According to the single crystal structure of TILMC1-I_3, we believe that the triiodide "network" can largely enhance conductivity and electrochemical efficiency of triiodide type PIL, and it has been confirmed by cyclic voltammetry test as well as EIS measurements both in solution and in bulk as solid electrolyte. Consequently, PTILMC1-I_3 as a new PIL is a promising candidate as solid polymer electrolyte for future energy devices to be investigated.

Supporting Information

Supporting Information is available from the authors.

Acknowledgements

The authors acknowledge financial support from the Max Planck Society and the grant of China Scholarship Council, the ERC starting grant NAPOLI-639720 and a Startup Grant from Clarkson University, USA. We thank Prof. Feihe Huang for the single crystal structure measurements, and Dr. Xuewan Wang for electrochemical measurements. Prof. Dr. Andreas Taubert thanks the grant of DFG TA571/13-1 within the framework of the DFG SPP 1708.

Keywords: poly(ionic liquid); solid polymer electrolyte; Grotthuss mechanism; triiodide "network".

References

[1] D. Mecerreyes, Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes, Progress in Polymer Science 36(12) (2011) 1629-1648.
[2] J. Yuan, D. Mecerreyes, M. Antonietti, Poly(ionic liquid)s: An update, Progress in Polymer Science 38(7) (2013) 1009-1036.
[3] J. Lu, F. Yan, J. Texter, Advanced applications of ionic liquids in polymer science, Progress in Polymer Science 34(5) (2009) 431-448.
[4] J. Yuan, M. Antonietti, Poly(ionic liquid)s: Polymers expanding classical property profiles, Polymer 52(7) (2011) 1469-1482.

[5] M. Weiss-Maurin, D. Cordella, C. Jerome, D. Taton, C. Detrembleur, Direct one-pot synthesis of poly(ionic liquid) nanogels by cobalt-mediated radical cross-linking copolymerization in organic or aqueous media, Polymer Chemistry 7(14) (2016) 2521-2530.

[6] H. He, D. Luebke, H. Nulwala, K. Matyjaszewski, Synthesis of Poly(ionic liquid)s by Atom Transfer Radical Polymerization with ppm of Cu Catalyst, Macromolecules 47(19) (2014) 6601-6609.

[7] X. Wang, Y. Zhou, Z. Guo, G. Chen, J. Li, Y. Shi, Y. Liu, J. Wang, Heterogeneous conversion of CO2 into cyclic carbonates at ambient pressure catalyzed by ionothermal-derived meso-macroporous hierarchical poly(ionic liquid)s, Chemical Science 6(12) (2015) 6916-6924.

[8] J. Pinaud, J. Vignolle, Y. Gnanou, D. Taton, Poly(N-heterocyclic-carbene)s and their CO2Adducts as Recyclable Polymer-Supported Organocatalysts for Benzoin Condensation and Transesterification Reactions, Macromolecules 44(7) (2011) 1900-1908.

[9] D. Cordella, A. Kermagoret, A. Debuigne, R. Riva, I. German, M. Isik, C. Jérôme, D. Mecerreyes, D. Taton, C. Detrembleur, Direct Route to Well-Defined Poly(ionic liquid)s by Controlled Radical Polymerization in Water, ACS Macro Letters 3(12) (2014) 1276-1280.

[10] F. Yan, J. Texter, Solvent-Reversible Poration in Ionic Liquid Copolymers, Angewandte Chemie 119(14) (2007) 2492-2495.

[11] J.R. Nykaza, A.M. Savage, Q. Pan, S. Wang, F.L. Beyer, M.H. Tang, C.Y. Li, Y.A. Elabd, Polymerized ionic liquid diblock copolymer as solid-state electrolyte and separator in lithium-ion battery, Polymer 101 (2016) 311-318.

[12] X. Sui, M.A. Hempenius, G.J. Vancso, Redox-Active Cross-Linkable Poly(ionic liquid)s, Journal of the American Chemical Society 134(9) (2012) 4023-4025.

[13] M.L. Hoarfrost, R.A. Segalman, Ionic Conductivity of Nanostructured Block Copolymer/Ionic Liquid Membranes, Macromolecules 44(13) (2011) 5281-5288.

[14] J.E. Bara, D.E. Camper, D.L. Gin, R.D. Noble, Room-Temperature Ionic Liquids and Composite Materials: Platform Technologies for CO2 Capture, Accounts of Chemical Research 43(1) (2010) 152-159.

[15] J.-K. Sun, M. Antonietti, J. Yuan, Nanoporous ionic organic networks: from synthesis to materials applications, Chemical Society Reviews 45(23) (2016) 6627-6656.

[16] R. Marcilla, J.A. Blazquez, R. Fernandez, H. Grande, J.A. Pomposo, D. Mecerreyes, Synthesis of Novel Polycations Using the Chemistry of Ionic Liquids, Macromolecular Chemistry and Physics 206(2) (2005) 299-304.

[17] W. Zhang, J. Yuan, Poly(1-Vinyl-1,2,4-triazolium) Poly(Ionic Liquid)s: Synthesis and the Unique Behavior in Loading Metal Ions, Macromolecular Rapid Communications 37(14) (2016) 1124-1129.

[18] W. Zhang, Z. Kochovski, Y. Lu, B.V.K.J. Schmidt, M. Antonietti, J. Yuan, Internal Morphology-Controllable Self-Assembly in Poly(Ionic Liquid) Nanoparticles, ACS Nano 10(8) (2016) 7731-7737.

[19] K. Nakabayashi, A. Umeda, Y. Sato, H. Mori, Synthesis of 1,2,4-triazolium salt-based polymers and block copolymers by RAFT polymerization: Ion conductivity and assembled structures, Polymer 96 (2016) 81-93.

[20] A.T. De La Hoz, K.M. Miller, Covalently crosslinked 1,2,4-triazolium-containing polyester networks prepared by Michael addition polymerization, Polymer 72 (2015) 1-9.

[21] M.M. Obadia, E. Drockenmuller, Poly(1,2,3-triazolium)s: a new class of functional polymer electrolytes, Chemical Communications 52(12) (2016) 2433-2450.

[22] O. Hiroyuki, I. Kaori, Room-Temperature Molten Salt Polymers as a Matrix for Fast Ion Conduction, Chemistry Letters 27(8) (1998) 751-752.

[23] B. Qiu, B. Lin, F. Yan, Ionic liquid/poly(ionic liquid)-based electrolytes for energy devices, Polymer International 62(3) (2013) 335-337.

[24] M. Döbbelin, I. Azcune, M. Bedu, A. Ruiz de Luzuriaga, A. Genua, V. Jovanovski, G. Cabañero, I. Odriozola, Synthesis of Pyrrolidinium-Based Poly(ionic liquid) Electrolytes with Poly(ethylene glycol) Side Chains, Chemistry of Materials 24(9) (2012) 1583-1590.

[25] X. Chen, J. Zhao, J. Zhang, L. Qiu, D. Xu, H. Zhang, X. Han, B. Sun, G. Fu, Y. Zhang, F. Yan, Bis-imidazolium based poly(ionic liquid) electrolytes for quasi-solid-state dye-sensitized solar cells, Journal of Materials Chemistry 22(34) (2012) 18018-18024.

[26] M. Díaz, A. Ortiz, I. Ortiz, Progress in the use of ionic liquids as electrolyte membranes in fuel cells, Journal of Membrane Science 469 (2014) 379-396.

[27] J. Wu, Z. Lan, J. Lin, M. Huang, Y. Huang, L. Fan, G. Luo, Electrolytes in Dye-Sensitized Solar Cells, Chemical Reviews 115(5) (2015) 2136-2173.

[28] R.S. Massey, C.J. Collett, A.G. Lindsay, A.D. Smith, A.C. O'Donoghue, Proton Transfer Reactions of Triazol-3-ylidenes: Kinetic Acidities and Carbon Acid pKa Values for Twenty Triazolium Salts in Aqueous Solution, Journal of the American Chemical Society 134(50) (2012) 20421-20432.

[29] H.C. Zur Loye, B.J. Heyen, H.O. Marcy, D.C. DeGroot, C.R. Kannewurf, D.F. Shriver, Dielectric response and conductivity of poly(propylene oxide) sodium polyiodide complexes. Discussion of charge transport by an ion relay mechanism, Chemistry of Materials 2(5) (1990) 603-609.

[30] L.C. Hardy, D.F. Shriver, Poly(ethylene oxide)-sodium polyiodide conductors: characterization, electrical conductivity, and photoresponse, Journal of the American Chemical Society 108(11) (1986) 2887-2893.

[31] J. Wu, S. Hao, Z. Lan, J. Lin, M. Huang, Y. Huang, P. Li, S. Yin, T. Sato, An All-Solid-State Dye-Sensitized Solar Cell-Based Poly(N-alkyl-4-vinyl-pyridine iodide) Electrolyte with Efficiency of 5.64%, Journal of the American Chemical Society 130(35) (2008) 11568-11569.

[32] A.F. Wells, Structural inorganic chemistry, Clarendon Press ; Oxford University Press, Oxford [Oxfordshire]; New York, 1984.

[33] P.H. Svensson, L. Kloo, Synthesis, Structure, and Bonding in Polyiodide and Metal Iodide−Iodine Systems, Chemical Reviews 103(5) (2003) 1649-1684.

[34] P. Deplano, J.R. Ferraro, M.L. Mercuri, E.F. Trogu, Structural and Raman spectroscopic studies as complementary tools in elucidating the nature of the bonding in polyiodides and in donor-I2 adducts, Coordination Chemistry Reviews 188(1) (1999) 71-95.

[35] C.C. Clark, A. Marton, R. Srinivasan, A.A. Narducci Sarjeant, G.J. Meyer, Triiodide Quenching of Ruthenium MLCT Excited State in Solution and on TiO2 Surfaces: An Alternate Pathway for Charge Recombination, Inorganic Chemistry 45(12) (2006) 4728-4734.

[36] R. Marcilla, J. Alberto Blazquez, J. Rodriguez, J.A. Pomposo, D. Mecerreyes, Tuning the solubility of polymerized ionic liquids by simple anion-exchange reactions, Journal of Polymer Science Part A: Polymer Chemistry 42(1) (2004) 208-212.

[37] T. Sugano, K. Yamada, G. Saito, M. Kinoshita, Polarized reflectance spectra of the organic conductors: α- and β-modifications of DI{bis(ethylenedithiolo)tetrathiafulvalene} triiodide, (BEDT-TTF)2I3, Solid State Communications 55(2) (1985) 137-141.

[38] R.J. Webb, T.Y. Dong, C.G. Pierpont, S.R. Boone, R.K. Chadha, D.N. Hendrickson, Extreme environmental sensitivity of the rate of intramolecular electron transfer in mixed-valence 1',1'''-dibenzylbiferrocenium triiodide, Journal of the American Chemical Society 113(13) (1991) 4806-4812.

[39] M.E. Orazem, I. Frateur, B. Tribollet, V. Vivier, S. Marcelin, N. Pébère, A.L. Bunge, E.A. White, D.P. Riemer, M. Musiani, Dielectric Properties of Materials Showing Constant-Phase-Element (CPE) Impedance Response, Journal of The Electrochemical Society 160(6) (2013) C215-C225.

[40] V.F. Lvovich, Examples of Ideal Equivalent Circuit Models, Impedance Spectroscopy, John Wiley & Sons, Inc.2012, pp. 49-57.

[41] J. Yuan, M. Antonietti, Poly(Ionic Liquid)s as Ionic Liquid-Based Innovative Polyelectrolytes, in: D. Mecerreyes (Ed.), Applications of Ionic Liquids in Polymer Science and Technology, Springer Berlin Heidelberg, Berlin, Heidelberg, 2015, pp. 47-67.

[42] I.D. Raistrick, D.R. Franceschetti, J.R. Macdonald, Theory, Impedance Spectroscopy, John Wiley & Sons, Inc.2005, pp. 27-128.

[43] N. Bonanos, B.C.H. Steele, E.P. Butler, Applications of Impedance Spectroscopy, Impedance Spectroscopy, John Wiley & Sons, Inc.2005, pp. 205-537.

[44] P. Wang, , S. M. Zakeeruddin, P. Exnar, I. Comte, M. Grätzel, Gelation of ionic liquid-based electrolytes with silica nanoparticles for quasi-solid-state dye-sensitized solar cells, Journal of the American Chemical Society, 125(5) (2003) 1166-1167.