



# Triazole-based ionene exhibiting tunable structure and ionic conductivity obtained via cycloaddition reaction: A new polyelectrolyte for electrochromic devices



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## ABSTRACT

Main-chain poly(ionic liquid)s based on 1,2,3-triazole with pentaoxyethylene spacer was developed via copper-catalyzed alkyne-azide cycloaddition (CuAAC) of a novel azide/alkyne-terminal monomer and subsequently quaternized by alkyl halides followed by anion exchanges with several fluorinated salts. Introduction of the extended ethylene oxide fragments  $[-(\text{CH}_2\text{CH}_2\text{O})_5-]$  has made this new PIL with methyl substituent and bis (trifluoromethane)sulfonimide counteranion exhibit ionic conductivity of  $1.16 \times 10^{-4} \text{ S cm}^{-1}$  at  $30^\circ\text{C}$ . This new electrolyte efficiently switches an electrochromic device (ECD) with 18% optical contrast from its transparent state to a colored state in 4.75 s and while bleaching takes 11.8 s. The development of this polyelectrolyte with simple structure and excellent physical and thermal properties is promising for the design of new all-solid state energy efficient smart windows and devices and other electrochemical device applications.

## 1. Introduction

Ionic liquids (ILs), organic salts with low melting point ( $< 100^\circ\text{C}$ ), are widely explored due to their chemical stability, low flammability, negligible vapor pressure, high ionic conductivity, and wide electrochemical window [1]. In the last decade, ionic liquids (ILs), having remarkable properties, have been regarded as highly potent materials for energy storage and energy conversion applications specifically in the electrochemical field [2,3]. Currently, the use of ionic liquids as electrolytes is improving the performance, speed, cyclability and long term stability of various electrochemical devices [4]. However, ionic liquid-based electrolytes are intrinsically liquids and still present some drawbacks that are difficult to overcome, such as the need of thorough encapsulation due to leakage. In those cases, solid or quasi-solid electrolytes such as polymer electrolytes have important advantages including mechanical stability, safety and simple processing. Lately, the combination of polymers with ionic liquids has been regarded as a hot topic in the field of polymer science in general particularly in the field of polymer electrolytes [5–8]. Poly(ionic liquid)s or PILs have drawn attention from researchers in the fields of polymer chemistry and materials science, not only due to the combination of the IL's exceptional properties with the macromolecular architecture, but likewise the creation of new properties and functions. PILs are polyelectrolytes which possess charged species in each of the repeating units.

Accordingly, the cationic or anionic moieties are constrained to the repeating units in the polymer chain. It is worth mentioning that while ILs are commonly liquid near room temperature, PILs are in fact solid in general, except for some [9]. However, despite their remarkable versatility, PILs are still limited in terms of their application in electrochemical devices due to their ionic conductivity. Currently synthesized PILs possess a solid state conductivity in the order of  $10^{-5}$  to  $10^{-11} \text{ S/cm}$  [4]. To date, the maximum solid state conductivity measured in dry conditions for thoroughly purified PIL having high molecular mass is around  $7 \times 10^{-5} \text{ S cm}^{-1}$  at  $30^\circ\text{C}$  [10].

In the last decade, many significant efforts have been made in designing innovative polymer electrolytes based on PILs. Countless number of combinations of anions and cations, as well as variations in the nature and structure of the main polymer backbone and spacer, paved the way to the synthesis of a wide array of ionic monomers and optimization of the macromolecules architecture with the aim of producing a PIL with enhanced solid state conductivity. The type of cation, the nature of heterocycles as well as its substitutes contribute significantly to the conductivity of the PIL. The influence of the anion nature is also important. For polyanions that contain the same pyrrolidinium cation, the conductivity is dictated by two factors: the size and the delocalization of the attached anion. Playing a strong influence on the bulk polymer ionic conductivity is the position of the cation in the PILs structure. In general, when cation is located inside or near the

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main polymer chain, it leads to lower conductivity as compared with polymer analogues that have ions linked by flexible spacer. Second established rule is that, insertion of longer spacer length leads to higher ionic conductivity. Furthermore, the nature of the main polymer chain also influences PIL's bulk ionic conductivity. The chain's flexibility as well as its ability to interact with ions (in terms of ion dissociation) enhances the overall conductivity of the PIL.

Regardless of all these improvements and enormous experimental data, PILs still need to overcome some limitations in order to compete with the state-of-the-art electrolytes. As stated above, the maximum solid state conductivity for PIL is in the order of  $10^{-5} \text{ S cm}^{-1}$ . This value, apparently, is generally below the requirements of many electrochemical devices. Most of these devices require  $> 10^{-4} \text{ S cm}^{-1}$  ionic conductivity to allow efficient performance. Devices like batteries, supercapacitors, dye sensitized solar cells, fuel cells, electrochromic devices etc. need fast ion mobility within their systems to deliver state-of-the-art performances.

Hence, this work aims to develop PILs with enhanced properties from the polymerization via copper catalyzed azide-alkyne cycloaddition (CuAAC) of an azide/alkyne-terminal monomer with penta-oxethylene fragments. The parent poly(1,2,3-triazole) undergoes quaternization with pendant substituents (methyl and butyl) followed by anion exchange (iodide, bis(trifluoromethane)sulfonimide, hexafluorophosphate, or tetrafluoroborate). In order to understand the structure-property relationships among the newly designed PILs, their physical, thermal and electrochemical properties were determined by nuclear magnetic resonance spectroscopy (NMR), fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and electrochemical impedance spectroscopy (EIS). The PIL synthesized in this work was used to create an all-solid state ECD whose electrochemical performance was evaluated.

## 2. Experimental

### 2.1. Chemicals

Sodium hydride (NaH, 95%), triethylamine (TEA,  $\geq 99.5\%$ ), methanesulfonyl chloride (MsCl,  $\geq 99.7\%$ ), copper (I) iodide triethylphosphite ( $\text{CuIP}(\text{OEt})_3$ , 97%), bis(trifluoromethane)sulfonimide lithium salt ( $\text{LiNTf}_2$ , 97%), iodomethane ( $\text{CH}_3\text{I}$ , 99.5%), and acetonitrile ( $\text{CH}_3\text{CN}$ , 99.8%) were supplied by Sigma-Aldrich. Pentaethylene glycol (PEG, 98 + %), propargyl bromide ( $\text{C}_3\text{H}_3\text{Br}$ , 97%), sodium azide ( $\text{NaN}_3$ , 99%), 1-iodobutane ( $\text{C}_4\text{H}_9\text{I}$ , 99%), and Celite were purchased from Alfa Aesar. Lithium hexafluorophosphate ( $\text{LiPF}_6$ , 98%), silver tetrafluoroborate ( $\text{AgBF}_4$ , 99%), and tetrahydrofuran (THF) were from Acros Organics. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ , 99%), hydrochloric acid (HCl), N,N-dimethylformamide (DMF), and methanol (MeOH) were provided by Showa. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and diethyl ether ( $\text{Et}_2\text{O}$ ) were purchased from Samchun and chloroform ( $\text{CHCl}_3$ ) was from Burdick and Jackson. All reagents were used without any further purification.

### 2.2. Synthesis of terminal alkyne-azide monomer

#### 2.2.1. Azido-PEG-alkyne 2 synthesis

A mixture of NaH (0.016 mol) and THF (84 ml) was prepared in flask with stirring, and a solution of PEG (0.023 mol) in THF (112.0 ml) was added into the mixture in 30 min. For 1 h, the mixture was allowed to react at room temperature.  $\text{C}_3\text{H}_3\text{Br}$  (0.026 mol) in THF (84 ml) solution was added into the reaction in 1 h and the mixture was allowed to react for additional hour. It was allowed to react further for 15 h at  $60^\circ\text{C}$ . Subsequently, it was quenched with a solution of 3% HCl, and THF solvent was evaporated using rotary drier under vacuum. The resulting material was extracted with  $\text{CH}_2\text{Cl}_2$  (280 ml) from the aqueous layer and was washed with 10% brine. Organic layer was dried using  $\text{Na}_2\text{SO}_4$  and concentrated using rotary evaporator. By silica gel column chromatography,

pure product was obtained as a clear yellowish oil PEG-alkyne **1** (3.0 g, 48.0%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 4.17 (m, 2H,  $\text{OCH}_2\text{C}\equiv\text{CH}$ ), 3.66–3.56 (m, 18H,  $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 3.54–3.51 (m, 2H,  $\text{OCH}_2\text{CH}_2\text{OH}$ ), 2.90 (br. s, 1H,  $\text{CH}_2\text{CH}_2\text{OH}$ ), 2.46–2.35 (m, 1H,  $\text{OCH}_2\text{C}\equiv\text{CH}$ ).

A solution of **1** (0.011 mol) and TEA (0.017 mol) in  $\text{CH}_2\text{Cl}_2$  (54 ml) was prepared. MsCl (0.012 mol) in  $\text{CH}_2\text{Cl}_2$  (34 ml) was added at  $0^\circ\text{C}$  in 30 min. For 2 h of continuous stirring, mixture was allowed to react. It was subsequently concentrated and thoroughly dried in vacuum. In DMF (100 ml), the product was allowed to react with  $\text{NaN}_3$  (0.056 mol) for 2 h at room temperature. The entire mixture was filtered over celite to obtain a clear solution. It was concentrated and dried under vacuum. Then the resulting material was purified using silica gel chromatography to obtain monomer **2** (2.13 g, 65.0%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 4.21–4.14 (m, 2H,  $\text{OCH}_2\text{C}\equiv\text{CH}$ ), 3.68–3.50 (m, 16H,  $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$ ), 3.40–3.33 (m, 2H,  $\text{OCH}_2\text{CH}_2\text{N}_3$ ), 2.43–2.39 (m, 1H,  $\text{OCH}_2\text{C}\equiv\text{CH}$ ), 1.95–1.92 (m, 2H,  $\text{OCH}_2\text{CH}_2\text{N}_3$ ).

### 2.3. Synthesis of PIL

#### 2.3.1. Poly(4-PEG-1,2,3-triazole) 3 synthesis

A solution of **2** (0.007 mol),  $\text{CuIP}(\text{OEt})_3$  (0.00015 mol), and TEA (0.007 mol) in  $\text{CHCl}_3$  (2 ml) was allowed to react in the dark at  $60^\circ\text{C}$  for 67 h. Mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , and product was precipitated in  $\text{Et}_2\text{O}$  (3 times) before drying in vacuum to obtain **3** as viscous brown material (2.07 g, 94.1%,  $M_n = 8.2 \text{ kDa}$ ,  $\text{Đ} = 1.08$ , THF).  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 8.00 (s, 1H,  $\text{OCH}_2\text{C}\equiv\text{CH}$ ), 4.52–4.40 (m, 4H,  $\text{OCH}_2\text{C}\equiv\text{CH}$  and  $\text{OCH}_2\text{CH}_2\text{N}$ ), 3.79–3.70 (m, 2H,  $\text{OCH}_2\text{CH}_2\text{N}$ ), 3.51–3.39 (m, 16H,  $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$ ).

### 2.4. Quaternization of PIL

#### 2.4.1. Poly(3-methyl-4-PEG-1,2,3-triazolium iodide) 4 synthesis

A mixture of **3** (630 mg) and  $\text{CH}_3\text{I}$  (4200 mg) was allowed to react in  $\text{CH}_2\text{Cl}_2$  (24 ml) at  $60^\circ\text{C}$  for 48 h.  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{I}$  residuals were evaporated in vacuum. Resulting material was dissolved in  $\text{CH}_3\text{CN}$ , precipitated in  $\text{Et}_2\text{O}$  2 times and completely dried in vacuum to obtain PIL **4** as amber-colored viscous material (0.75 g, 81.0%).  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 8.85 (s, 1H,  $\text{OCH}_2\text{C}\equiv\text{CH}$ ), 4.83–4.74 (m, 4H,  $\text{OCH}_2\text{C}\equiv\text{CH}$  and  $\text{OCH}_2\text{CH}_2\text{N}$ ), 4.29–4.21 (m, 3H,  $\text{NCH}_3$ ), 3.91–3.87 (m, 2H,  $\text{OCH}_2\text{CH}_2\text{N}$ ), 3.67–3.42 (m, 16H,  $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$ ).

#### 2.4.2. Poly(3-butyl-4-PEG-1,2,3-triazolium iodide) 5 synthesis

A mixture of **3** (790 mg) and  $\text{C}_4\text{H}_9\text{I}$  (1700 mg) was stirred in DMF (32.67) at  $80^\circ\text{C}$  for 68 h. DMF and  $\text{C}_4\text{H}_9\text{I}$  residuals were evaporated under vacuum. Product was dissolved in MeOH, precipitated in  $\text{Et}_2\text{O}$  (2 times) and dried under vacuum to yield **5** as amber-colored viscous material (1.27 g, 99.8%).  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 8.89 (s, 1H,  $\text{OCH}_2\text{C}\equiv\text{CH}$ ), 4.85–4.75 (m, 4H,  $\text{OCH}_2\text{C}\equiv\text{CH}$  and  $\text{OCH}_2\text{CH}_2\text{N}$ ), 4.60–4.54 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.92–3.88 (m, 2H,  $\text{OCH}_2\text{CH}_2\text{N}$ ), 3.64–3.42 (m, 16H,  $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$ ), 1.91–1.82 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.35–1.23 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.91–0.84 (m, 3H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ).

### 2.5. Anion metathesis

#### 2.5.1. Poly(3-methyl-4-PEG-1,2,3-triazolium bis(trifluoromethane)sulfonimide) 6 synthesis

A mixture of PIL **4** (420 mg) and  $\text{LiNTf}_2$  (350 mg) was allowed to react in water ( $\text{H}_2\text{O}$ , 9.7 ml) at  $40^\circ\text{C}$  for 16 h. Water was decanted and the material deposited on the flask was washed abundantly with MeOH. It was dissolved in acetone and precipitated in MeOH (2 times). Product was dissolved in  $\text{CH}_3\text{CN}$  and the solution was filtered with 0.45  $\mu\text{m}$  Teflon filter. It was totally dried to get an amber-colored material

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