Highly Cross-linked Polyether-based 1,2,3-Triazolium Ion Conducting Membranes with Enhanced Gas Separation Properties

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Abstract

A series of cross-linked polyether-based 1,2,3-triazolium ion conducting membranes are prepared *via* the combination of thermally promoted Huisgen 1,3-dipolar cycloaddition of a dialkyne and a diazide poly(trimethylene ether glycol) monomers with *in-situ* *N*-alkylation of the resulting poly(1,2,3-triazole)s with varying contents of 1,10-diiododecane as cross-linking agent. The resulting free-standing membranes have T_g s below $-60\text{ }^{\circ}\text{C}$, T_d s up to $230\text{ }^{\circ}\text{C}$, and Young's modulus up to 4.2 MPa. The overall combined reaction kinetics were studied by DSC yielding an activation energy of 76 kJ/mol by the Kissinger method. These ion conducting membranes have conductivities up to 10^{-6} S/cm at $30\text{ }^{\circ}\text{C}$ under anhydrous conditions. They have potential to be used in CO_2 separation applications as they exhibit CO_2 permeability of 59-110 Barrer and CO_2/N_2 selectivity of 25-48.

KEYWORDS

poly(ionic liquid), 1,2,3-triazolium, cross-linked, ion conducting, polyether, CO_2 separation membrane.

HIGHLIGHTS

A monotopic approach yields cross-linked 1,2,3-triazolium-based membranes

Huisgen 1,3-dipolar azide-alkyne cycloaddition and *N*-alkylation are combined

Free-standing membranes with $T_g \sim -60\text{ }^{\circ}\text{C}$, $T_{d5} \sim 230\text{ }^{\circ}\text{C}$, $E' \sim 4\text{ MPa}$ are obtained

Anhydrous ionic conductivities $> 10^{-6}\text{ S/cm}$ at $30\text{ }^{\circ}\text{C}$ are reached

Membranes show CO_2 permeabilities of 59-110 Barrer and CO_2/N_2 selectivity of 25-48.

1. Introduction

Cross-linked elastomers are interesting three dimensional polymer networks that exhibit unique and tunable elasticity, water uptake, and small molecules transport properties. They have been studied for a wide range of applications from light emitting diode encapsulates, soft lens, separation membrane, and solid electrolyte applications.[1–8] Development of new facile synthetic approaches that can yield functional cross-linked materials is thus of wide considerable interest.

A large number of reactions has been used to access functional materials including ‘click’ reactions such as azide–alkyne dipolar cycloadditions, Diels–Alder cycloadditions, thiol–ene reactions etc. Within the cross-linked elastomers, those made of poly(ethylene glycol) (PEG) and poly(propylene oxide) (PPO) are notable due to their unique properties such as highly polarity and hydrophilicity yet they are compatible with many organic media. The ability to incorporate additional functionality in these systems is also highly desirable.

Copper-catalyzed azide-alkyne cycloaddition (CuAAC), the most widespread example of click reactions is an effective synthesis methodology for accessing highly functionalized polymer materials.[9–14] Moreover, the resulting 1,2,3-triazoles can be readily converted into 1,2,3-triazolium groups by simple *N*-alkylation with alkyl halides or other quaternizing agents.[15,16] The broad library of polymer materials containing 1,2,3-triazole groups thus provides a powerful toolbox of precursors able to tailor 1,2,3-triazolium-based poly(ionic liquid)s (TPILs) ionic conductors. Nulwala and coworkers prepared TPILs from the radical (co)polymerization of 4-vinyl-1,2,3-triazolium monomers, and investigated their properties with respect to their applications in gas separation technologies.[17–20] Drockenmuller and coworkers synthesized

TPILs by *N*-alkylation of poly(1,2,3-triazole)s obtained either by controlled radical polymerization,[21] or by copper-catalyzed azide-alkyne cycloaddition (CuAAC) of α -azide- ω -alkyne monomers.[14,22–24] They also reported a solvent- and catalyst-free one-step approach to prepare TPILs based on the thermal Huisgen 1,3-dipolar cycloaddition of an α -azide- ω -alkyne monomer in the presence of different quaternizing agents.[25,26] Although containing statistical mixtures of 1,3,4- and 1,3,5-trisubstituted 1,2,3-triazolium groups, the resulting TPILs exhibit thermal and ion conducting properties comparable to their regioisomeric analogs prepared from multistep synthetic methods. This versatile approach was recently applied to the synthesis of highly cross-linked ion conducting networks using a series of di-functionalized quaternizing agents, which served as cross-linkers.[27] This method provides a platform towards robust ionic soft materials with tunable functionalities and properties. Moreover, the resulting networks exhibit the valuable properties of vitrimers,[28] i.e. the ability to be reprocessed, reshaped and recycled. In this paper, we have applied this elegant one-step strategy to prepare a series of membranes with excellent ion conducting properties and gas separation performances by combining the AA + BB thermal polyaddition of diazide and dialkyne poly(trimethylene ether glycol) (PTMEG) monomers by Huisgen 1,3-dipolar cycloaddition with cross-linking of the resulting poly(1,2,3-triazole)s via *N*-alkylation using 1,8-diiododecane.

Membrane technology is a promising method for CO₂ separation because of the absence of a regeneration process, small footprint, and low capital cost.[29] However, challenges still remain in designing membranes with good mechanical properties, as well as excellent CO₂ permeability and selectivity. PEG-based polymeric membranes present potentials for CO₂ separation as they have high affinity towards CO₂ due to the ether segments.[30–40] However, they suffer from high crystallinity and weak mechanical strength.[41] PTMEG is a commercially available

starting material derived from renewable resources that is more hydrophobic than PEG.[42–45] PTMEG-based membranes are expected to be CO₂-philic enough because of their numerous ether groups. PIL membranes are a new class of materials that have been successfully applied to CO₂ separation.[46–50] The IL moieties in PIL membranes provide good CO₂ selectivity. However, low CO₂ permeability of these PIL membranes is the major challenge to be addressed to improve their gas separation performances. In this study, we used a one-step strategy to design cross-linked PIL membranes with robust mechanical properties which contain flexible PTMEG units for high CO₂ affinity and good CO₂ permeability.

2. Experimental Section

2.1 Materials

Poly(trimethylene ether glycol) (PTMEG, $M_w = 657$ g/mol, DuPont), methanesulfonyl chloride (MsCl, 99.5%, Acros Organics), triethylamine (Et₃N, 99%, Sigma-Aldrich), dichloromethane (DCM, >99.5%, Sigma-Aldrich), hydrochloric acid (HCl, tracemetal plus, Fisher Chemical), sodium chloride (NaCl, certified ACS, Fisher Chemical), magnesium sulfate (anhydrous, 99.5%, Fisher Chemical), sodium azide (NaN₃, laboratory grade, Fisher Chemical), dimethylformamide (DMF, Extra dry, 99.8%, Acros Organics), tetrahydrofuran (THF, HPLC grade, Fisher Chemical), sodium hydride (NaH, 95%, Sigma-Aldrich), propargyl bromide (80 wt% solution in toluene, Sigma-Aldrich), 1,10-diiododecane (>98.0%, TCI), and *bis*(trifluoromethane)sulfonamide lithium salt (LiNTf₂, 98+%, TCI) were used as received.

2.2 Characterization Methods

^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded at ambient temperature in CDCl_3 on a Bruker AVANCE III 300 spectrometer. Infrared spectroscopic data were collected on a Thermo Scientific Nicolet IR100 FT-IR spectrometer equipped with an ATR module with a resolution of 2 cm^{-1} , and a number of scans of 64. Thermogravimetric analysis (TGA) was employed to study the thermal stability of polymers using a TA instruments model Q500. Samples were heated from 25 to 600 °C at a heating rate of 10 °C/min under N_2 . A TA instruments Q2000 DSC equipped with liquid nitrogen cooling accessory was used to determine the glass transition temperatures (T_g s). T_g values were measured using the inflection point of the third heating cycle using a heating and cooling rate of 10 °C/min under N_2 . Dynamic mechanical analysis (DMA) were performed on a TA instruments model Q800 dynamic mechanical analyzer in tension mode at a frequency of 1 Hz, an oscillatory amplitude of 15 μm , and a temperature ramp of 3 °C/min over the range from -100 to 150 °C. Tensile test employed an Instron model 4400 Universal Testing System. The film samples were cut into rectangle shaped specimens ($50 \times 5 \times 0.4\text{ mm}^3$). Specimens were tested with a cross-head rate of 10 mm/min at ambient conditions using an initial gauge length of 15 mm. The repeated tensile test results were an average value of at least four specimens. A goniometer (260, Rame Hart) with Drop Image® software was used to determine the contact angle of de-ionized water on a dense polymer film. A 5 μL liquid droplet was dispensed onto the film to form a sessile drop, and after waiting 5 min for the drop to settle, the contact angle was recorded. The reported contact angle was the average of 5 trials.

2.3 Oligomer synthesis and membrane fabrication

Synthesis of α,ω -dimesyl PTMEG **1**.

A solution of MsCl (3.44 g, 30.0 mmol) in DCM (10 mL) was added dropwise to a mixture of PTMEG (6.51 g, 10.0 mmol) and Et₃N (4.20 mL, 30.0 mmol) in DCM (10 mL) with vigorous stirring at 0 °C. After the completion of addition, the mixture was stirred at 0 °C for 2 h and at room temperature for additional 2 h. The mixture was then concentrated to dryness and dissolved in DCM (100 mL). The organic phase was washed with 1M HCl solution (100 mL) and then NaCl saturated solution (100 mL). This procedure was repeated twice. The organic phase was dried overnight over anhydrous MgSO₄ and vacuum dried to afford an orange viscous liquid (7.48 g, 92.7%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 4.34 (t, *J* = 6.2 Hz, 4H, CH₃SO₃CH₂CH₂), 3.55-3.46 (m, 40H, CH₂OCH₂), 3.01 (s, 6H, CH₃SO₃), 2.00 (m, 4H, CH₃SO₃CH₂CH₂), 1.83 (m, 18H, OCH₂CH₂CH₂O). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 68.04-67.34 (20C), 66.04 (2C), 37.19 (2C), 30.10-29.25 (11C). FT-IR: ν (cm⁻¹) 2923, 2866, 2361, 1348, 1169, 1107, 932, 838, 781, 728, 527, 450.

Synthesis of α,ω-diazide PTMEG **2**.

A mixture of **1** (2.01 g, 2.49 mmol) and NaN₃ (0.806 g, 12.4 mmol) in DMF (10 mL) was heated at 65 °C for 15 h. The mixture was filtered and the solid was washed with THF. The filtrate was concentrated to dryness, washed with H₂O (50 mL) and extracted three times with DCM (3 × 50 mL). The organic phase was dried overnight over anhydrous MgSO₄ and dried under vacuum for 3 h to give a yellow liquid (1.40 g, 80.2%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 3.53-3.47 (m, 40 H, CH₂OCH₂), 3.39 (t, *J* = 6.8 Hz, 4H, CH₂N₃), 1.89-1.79 (m, 22H, OCH₂CH₂CH₂O). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 79.84 (2C), 74.09 (2C), 67.74-67.06 (22C), 57.99 (2C), 30.01-29.82 ppm (11C). FT-IR: ν (cm⁻¹) 2939, 2866, 2357, 2091, 1457, 1362, 1262, 1176, 1112, 945, 668, 528.

Synthesis of α,ω -dipropargyl PTMEG **3**.

DMF (10 mL) was added slowly to NaH (0.554 g, 23.1 mmol) in a flask under vigorous stirring. **1** (5.00 g, 7.69 mmol) was added to the mixture. After 1 h, propargyl bromide (2.29 g, 19.2 mmol) was added dropwise over 30 min. After additional 30 min, silica gel and DCM were added to the mixture and allowed stirring overnight. After filtration, the filtrate was washed with H₂O and extracted with DCM. The organic phase was dried overnight over anhydrous MgSO₄ and dried under vacuum for 5 h to give a brown liquid (3.22 g, 57.7%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 4.13 (d, J = 2.3 Hz, 4H, CH₂C $\equiv$ CH), 3.59 (t, J = 6.2 Hz, 4H, CH₂OCH₂C $\equiv$ CH), 3.51-3.45 (m, 40 H, CH₂OCH₂), 2.42 (t, J = 2.3 Hz, 2H, CH₂C $\equiv$ CH), 1.87-1.78 (m, 22H, OCH₂CH₂CH₂O). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 67.90-67.29 (20C), 48.44 (2C), 30.04-29.14 ppm (11C). FT-IR: ν (cm⁻¹) 3370, 2927, 2860, 1371, 1275, 1261, 1100, 1063, 918, 764, 750, 544.

General procedure for the preparation of cross-linked PTMEG membranes (**5**_{a-c})

A mixture of **2** (1.0 eq), **3** (1.0 eq), and **4** (0.5, 1.0, or 2.0 eq) was stirred at room temperature for 1 h. The mixture was casted on a glass plate and heated at 110 °C in an oven for 24 h to yield a yellow free-standing film. The film was washed with H₂O/MeOH (1:1) to remove any unreacted residues and dried at 110 °C under vacuum overnight.

General procedure for the preparation of membranes **6**_{a-c} by anion exchange

An iodide-containing membrane (**5_a**, **5_b**, or **5_c**, ca. 0.15 g) was added to a solution of LiNTf₂ (1.4 eq to the I⁻) and 5 mL of H₂O/MeOH (3:1). The mixture was stirred at 50 °C for 2 days. The resulting film was washed with H₂O/MeOH (1:1) and dried at 110 °C under vacuum overnight.

2.4 Thermal curing behavior

About 5 g of a mixture consisting of **2** (1.0 eq), **3** (1.0 eq), and **4** (1.0 eq) was stirred at room temperature for 1 h and served as a precursor for curing study. DSC capsules containing approximately 5 mg precursor were sealed under ambient conditions. These DSC capsules were heated at 110 °C in an oven for a 1 to 24 h and then quenched with liquid nitrogen to stop the curing process. DSC scans were then run at a ramp of 5 °C/min from -100 to 210 °C on all of the samples to see the changes in the heat of reaction (ΔH) and the glass transition temperature (T_g) of samples at different curing times.

2.5 Gas transport properties

The pure gas CO₂ and N₂ permeation tests were performed at room temperature using the isochoric (constant volume, variable-pressure) permeation system.[20] Upstream pressures were measured with a pressure transducer (Maximum pressure 150 psia, viatran Inc., Model-345) and accompanying readout (Dalec electronics digital panel). Downstream pressures were measured using a Baratron® 627D capacitance manometer with a maximum pressure output of 10 Torr (MKS, Wilmington, MA). The downstream volume was calibrated by using a standard simple mole balance method with known volume of stainless steel balls. The thicknesses of the membranes were measured using a micrometer (Marathon Electronic digital micrometer) several times and their average value was used for the calculation of permeabilities. The membrane was

loaded in the Millipore high pressure stainless 25 mm filter holder. The entire permeation system was de-gassed using a vacuum pump (Edwards nXDS 10i scroll pump) for 18 h and then the leak rate was measured by isolating the permeation system from the vacuum pump to obtain the accurate permeability measurements. The degassing step also result in ultra-dry conditions. The leak rate was much less than (at least 10 times) the steady state pressure rise of the gas permeation measurement. The feed gas is then introduced to the upstream side of the membrane, and the pressure rise in the downstream volume was recorded as a function of time. Two film samples were tested to get average permeation results in pure gas studies.

The permeation of a gas through the dense polymer can be described using the sorption-diffusion theory. The permeability of a gas, i , is given by: $P_i = D_i \times S_i$, where D_i and S_i represent the diffusion and solubility coefficients of component i , respectively. In terms of this model, the productivity of a membrane is defined by the permeability of the gas through the membrane and the ideal selectivity of the membrane is the ratio of the permeabilities of the individual gases. Permeability is calculated by taking a differentiation of pressure rise as a function of time and using the following equation:

$$P = \frac{V_d l}{p_2 A R T} \left(\frac{dp_1}{dt} \right)_{ss} - \frac{V_d l}{p_2 A R T} \left(\frac{dp_1}{dt} \right)_{leak} \quad (1)$$

Where, V_d = downstream volume (cm^3), l = film thickness (cm), p_2 = upstream absolute pressure (cmHg), A = film area (cm^2), T = temperature (K), R = gas constant ($\text{cm}^3 \text{ cmHg/mol K}$), $(dp_1/dt)_{ss}$ = rate of pressure rise under upstream pressure (cmHg/sec), $(dp_1/dt)_{leak}$ = rate of pressure rise under vacuum (cmHg/sec).

2.6 Ion conducting properties

Ionic conductivities were measured using a high resolution Alpha-Analyzer (Novocontrol GmbH) assisted by a Quatro temperature controller. Cross-linked membranes of known thickness were annealed at 110 °C under vacuum for ca. 24 h in order to eliminate solvent residuals and adsorbed water. The membranes were sandwiched between two platinum electrodes and were further annealed inside the spectrometer for 4 additional h at 110 °C under a pure nitrogen atmosphere in order to reach equilibration. The complex conductivity function $\sigma^*(\omega, T) = \sigma'(\omega, T) + i\sigma''(\omega, T)$ was continuously monitored during this second thermal annealing and measurements were started once a constant value of the complex conductivity function was attained. This affords well equilibrated samples and ensures the reliability and reproducibility of the measurements. $\sigma^*(\omega, T)$ was then measured in the 10^7 - 10^{-1} Hz range under nitrogen and isothermal conditions at temperatures ranging between 110 and –50 °C in steps of 10 °C. The thermal stability was set to be better than 0.1 K in absolute values with relative variations less than 0.2 K/min. The low applied voltage ($U = 0.1$ V) excludes the appearance of non-linear effects that can take place at the TPIL-electrode interfaces.

3. Results and Discussion

3.1. Oligomer synthesis and membrane fabrication

α,ω -Dihydroxy PTMEG having a number average degree of polymerization (DP_n) of 11 was chosen for the preparation of AA and BB monomers because the chain-ends can be easily converted into azide and alkyne functionalities via straightforward synthetic procedures, (Scheme 1).[9,18,51–53] To synthesize α,ω -diazide PTMEG **2**, the hydroxy groups from PTMEG were first converted to mesylate groups, which are effective leaving groups in nucleophilic substitution reactions, to afford oligomer **1** as an orange liquid. α,ω -Dimesyl

PTMEG **1** was then reacted with sodium azide to give α,ω -diazidePTMEG **2**, a yellow liquid in an overall yield of 74%. α,ω -Dipropargyl **3** was prepared by reacting PTMEG with propargyl bromide in the presence of NaH to afford a brown liquid in 58% yield. Chemical compositions of **1-3** were confirmed using ^1H , ^{13}C NMR (Figure S1-S2), and FT-IR (Figure S3).

Scheme 1. Preparation of ionic polymer membranes **5_{a-c}** and **6_{a-c}**.

Membrane fabrication is based on the thermally initiated AA+BB polyaddition α,ω -diazide and α,ω -dipropargyl PTMEGs **2** and **3** by Huisgen 1,3-dipolar cycloaddition in combination with *in-situ* *N*-alkylation of the resulting poly(1,2,3-triazole)s in the presence of varying amounts of 1,8-diiodooctane **4** difunctional cross-linker.[25] Compared to the commonly employed, multistep synthetic route (CuAAC followed by *N*-alkylation)[19,22] towards poly(1,2,3-triazolium)s, this versatile one-step method does not involve any catalyst, polymerization mediator or solvent. PTMEGs **2**, **3** and cross-linking agent **4** were mixed and then casted on a glass plate to obtain highly cross-linked membranes **5_{a-c}** which are yellow, rubbery and free-standing. Based on the curing behavior study by DSC (see section 3.2), the membranes were cured at 110 °C for 24 h to ensure the complete curing and sample equilibration. Three different membranes were prepared by maintaining the ratio between AA and BB monomers **2,3** at 1:1 (mol/mol) while increasing, from **5_a** to **5_c**, the content of cross-linker **4** from 0.5 to 2.0 equivalent with respect to monomers **2** or **3** (Table 1). By changing the cross-linker loading, and thus the number of 1,2,3-triazolium iodide moieties within the membranes, it is quite easy to manipulate the cross-linking densities of the resulting networks and consequently finely tune their thermal, mechanical, ion conducting, and gas separation properties (see discussions in sections 3.3-3.5). NTf₂-containing membranes **6_{a-c}** were then obtained by anion exchange using LiNTf₂ by immersing membranes **5_{a-c}** in a 3:1 mixture of water and methanol. Thermal properties (Table 2, and Figure S7) of these membranes confirmed that the anion exchange was successfully carried out.

3.2. Thermal curing behavior

The thermal curing for the preparation of membrane **5_b** ([**2**] = [**3**] = [**4**]) was studied using DSC, based on the Kissinger method reported previously.[54,55] It is important to state that there are

two reactions occurring at the same time i.e. the azide-alkyne Huisgen 1,3-dipolar cycloaddition of monomers **2,3** and the *N*-alkylation of the resulting poly(1,2,3-triazole)s by difunctional cross-linker **4**. DSC curve of the mixture of **2** and **3** in the absence of **4** (Figure S4, first heat) shows similar exothermic peak (120-200 °C) as the DSC curve of mixture of **2, 3**, and **4** (Figure 1a, 0 h). This indicates that the two reactions are likely occurring over the same temperature range. It is quite challenging to quantify each reaction separately therefore only the kinetics of the overall process are considered herein, mainly to assess the time required to achieve complete curing of the initial reactive mixtures. The first heat curves of samples (mixture of **2, 3**, and **4**) with different curing time are shown in Figure 1a. Glass transition temperatures (T_g s) increase from $T_{g0} = -83$ °C to $T_g = -62$ °C after 24 h of curing due to the increase in cross-link density of the network. DSC curves of the liquid mixture and after 1 h and 2 h of curing have cold crystallization peaks in the range of -60 to -40 °C followed by melting peaks at around 0 °C. These are likely associated with the crystallinity of PTMEG-based oligomers and as the cross-linking progresses the crystallization disappears. The splitting of cold crystallization peaks in 1 h and 2 h curves are possibly due to the delocalization of the crystals caused by the cross-links within the networks. The exothermic peaks indicate that for this ramp rate the curing reaction occurs at temperatures ranging from 120 to 200 °C. As the curing time increases, the intensity of the residual heat of reaction (ΔH) peak decreases and eventually disappears for 24 h of curing. From Figure 1b, we observe a dramatic decrease in ΔH in the first 6 h of curing. As the curing time further increases, ΔH decreases more slowly. Longer curing time leads to networks with higher cross-link density, higher viscosity, and thus slower reaction rates. At 24 h of curing time, the reaction is essentially completed with only a residual ΔH of 7 J/g. The 200 °C limit is close to the onset degradation temperature of these films and we do observed some sample

gassing/degradation above this temperature. This is consistent with the results from TGA measurements (see section 3.3). The activation energy (E_a) of the overall curing process is determined to be 76 kJ/mol using the Kissinger method (Figure S5 and S6 in the ESI). This value is consistent with the literature values (74 and 79 kJ/mol) for other polyadditions by thermal Huisgen 1,3-dipolar cycloaddition.[54]

Figure 1. a) DSC curves of first heat at increasing curing times, and b) T_g and residual heat of reaction vs. curing time. Dotted lines are guides to the eye.

3.3. Physical properties

Water contact angle measurements give an insight of the hydrophilic nature of the membranes surfaces (Table 1). **5_a** and **5_b** show similar water contact angle of *ca.* 53° while **5_c** has the smallest value (40°) among these polymers. **5_a** and **5_b** have similar amount of 1,2,3-triazolium groups mostly due to a comparable amount of cross-links. The most hydrophilic surface of **5_c** is probably because of the higher 1,2,3-triazolium content resulting both from elastically active cross-links and dangling chains. The more hydrophilic nature of sample **5_c** due to the higher

content of 1,2,3-triazolium iodide groups allows water to interact more easily with the ionic surface.

Thermal properties of polymer **5_{a-c}** and **6_{a-c}** were investigated using TGA and DSC. TGA curves (Figure 3a) show that polymers **5_{a-c}** start to degrade near 200 °C following a two-stage decomposition. First significant weight loss starts at ca. 230 °C while the second weight loss occurs near 350 °C. The first-stage weight loss is likely attributed to the decomposition of iodide moiety from the cross-linker **4** in these systems. The decomposition temperatures are similar to iodide-containing ionic liquids which tend to have lower thermal stability than hydrophobic and highly delocalized anions.[56] The weight loss attributed to the first stage decomposition increases as the cross-linker loading increases. This also suggests the strong correlation between first stage weight loss and 1,2,3-triazolium iodide content. The thermal stability could be significantly improved by simple ion exchange reaction between 1,2,3-triazolium iodide and LiNTf₂. Indeed, NTf₂-containing polymer **6_{a-c}** exhibited 50 to 100 °C increase in T_{d5} compared to their iodide-containing analogs **5_{a-c}** (Table 2 and Figure S7). According to DSC analysis, **5_{a-c}** and **6_{a-c}** showed single T_g s below -60 °C (Table 1, Figure 3b, and S7b) indicating highly flexible PTMEG-based polymer backbones. However, the range of cross-linker loading studied herein showed insignificant effect on T_g s observed from DSC.

DMA was utilized to explore thermomechanical behavior of polymers **5_{a-c}**. The T_g s were obtained from the major dissipation peaks of tan δ profiles. Compared to T_g s obtained from DSC, these values are approximately 10 °C higher (Table 1) and the effect of cross-linker loading is also insignificant. This difference in T_g values obtained from DSC and DMA is commonly observed because they use completely different methods to determine thermal transitions.[57] The temperature dependencies of the storage modulus (E') for polymers **5_{a-c}** are shown in Figure

3c. The lack of observable melting transition after the rubbery plateau at elevated temperature indicates the cross-linking characteristics of these membranes. Cross-link densities (ρ_x s) were estimated using the following equation:

$$\rho_x = E'/3RT \quad (2)$$

where E' is the storage modulus at temperature above T_g in Pa from DMA measurements (E' 's at 0 °C were used in this study), R is the gas constant (8.314 J mol⁻¹ K⁻¹), and T is the temperature (K).[58] The calculated ρ_x values are summarized in Table 1. **5_a** shows slightly higher cross-link density in comparison with **5_c**. And **5_b** has much higher value in comparison with **5_a** and **5_c**. This trend is expected based on the cross-linker loading. Figure 2 illustrates the cross-link density as an effect of cross-linker loading. For **5_a**, since the iodide functionalities from **4** are lower than the amount of formed 1,2,3-triazoles, cross-link density is limited by the amount of cross-linking units. For **5_b**, the theoretical ratio between iodide and 1,2,3-triazole groups is 1:1. Therefore, cross-link density of **5_b** is higher than **5_a**. In the case of **5_c**, iodide content is much higher than the 1,2,3-triazoles. As a result, most of the di-functionalized iodide compounds would only be able to react on one side and thus lead to a network having a high content of dangling chains and thus a lower cross-linking density. The effects of cross-linker loading on membrane properties are discussed in later sections.

Figure 2. Illustration of cross-link density as an effect of cross-linker loading.

The mechanical properties of membranes **5_{a-c}** were further investigated by tensile tests under ambient conditions (Table 1). The representative stress-strain curves are shown in Figure 3d. Membranes **5_{a-c}** have Young's modulus of 1.5-4.2 MPa and tensile strain at break of 53-76%. Among these membranes, **5_b** has the highest Young's modulus and lowest tensile strain at break, which is likely due to its highest cross-link density of the series. These results are consistent with the trend of cross-link densities found in thermomechanical study by DMA.

Figure 3. a) TGA curves, b) DSC curves of third heat, c) DMA storage modulus response, and d) stress-strain curves of polymer **5_{a-c}**.

Table 1. Thermal and physical properties of membranes **5_{a-c}**.

Polymer	Anion	2:3:4 Ratio ^{a)}	Cross-linker loading, wt%	Contact angle of water, °	$T_{g, b)}$ DSC, °C	$T_{g, c)}$ DMA, °C	$T_{d5, d)}$ °C	E' at 0 °C, ^{e)} MPa	ρ_x , ^{f)} mol/cm ³	Tensile Stress at Break, ^{g)} MPa	Tensile Strain at Break, ^{g)} %	Young's Modulus, ^{g)} MPa
5_a	I	1:1:0.5	12.1	50.9±8.2	−64	−55	233	1.88	276	1.0±0.3	76±28	2.6±0.5
5_b	I	1:1:1	21.6	54.9±1.3	−63	−51	222	2.85	418	1.3±0.2	53±17	4.2±0.2
5_c	I	1:1:2	35.6	39.6±3.0	−65	−56	207	0.88	129	0.5±0.2	67±23	1.5±0.2
6_a	NTf ₂	1:1:0.5	^{h)} −	−	−61	−	324	−	−	−	−	−
6_b	NTf ₂	1:1:1	−	−	−60	−	313	−	−	−	−	−
6_c	NTf ₂	1:1:2	−	−	−62	−	266	−	−	−	−	−

^{a)}Molar ratios between dialkyne, diazide, and diiodide; ^{b)}Determined by DSC; ^{c)}Determined by

DMA; ^{d)}Temperature at 5% weight loss from TGA. ^{e)}Storage modulus at 0 °C from DMA.

^{f)}Calculated from E' at °C using Equation 2. ^{g)}Determined by tensile test. ^{h)}Not measured.

3.4 Gas transport properties

The gas separation performances of polymers **5_{a-c}** and **6_b** were evaluated at room temperature using an isochoric gas permeation system. CO₂ permeability and CO₂/N₂ selectivity results are summarized in Table 2. Iodide-containing membranes **5_{a-c}** showed high CO₂ permeabilities in the range of 85-110 Barrer due to the flexible PTMEG-based polymer backbones. The high content of CO₂-philic ether groups afforded membranes with CO₂/N₂ selectivities ranging from 19 to 41. These data suggested the correlation between cross-link density and gas separation properties (both permeabilities and CO₂/N₂ selectivity). **5_b**, which contains the highest cross-link density, has the lowest CO₂ permeability and highest CO₂/N₂ selectivity. Compared to **5_a**, **5_c** has slightly lower CO₂ permeability but much enhanced CO₂/N₂ selectivity which might be due to the higher content of 1,2,3-triazolium moieties. The change from iodide to NTf₂ anion illustrated by the

preparation of membrane **6_b** further decreases permeabilities of CO₂ and N₂. The decrease in permeabilities is likely attributed to the blocking of gas transport by the larger NTf₂ anion.

Modifying and/or cross-linking the polyether-based membranes is thus an efficient approach to increase the CO₂ gas transport properties. Membranes **5_{a-c}** and **6_b** have good CO₂ permeability and high CO₂/N₂ selectivity due to the favorable interaction between the polar CO₂ with the polar ether and 1,2,3-triazolium moieties. Their gas transport properties are compared with the reported data from literature and showed in Figure 4 in comparison with Robeson upper bound.[59] The gas permeation properties of these membranes are promising because both the permeability and selectivity of the membranes are very close to the Robeson's upper bound curve. These membranes showed similar or higher gas transport properties compared to other reported polyether based membranes.[30,33–35,59–62] Optimization of the structure (e.g. chemical structure of the monomer, anion and difunctional cross-linker) and resulting properties of these membranes will likely further increase the permeability and selectivity. The preparation of thin membranes on porous supports with a sufficiently high flux to enable economical capture of CO₂ from flue gas is a challenge that remains to be met. These polyether ionic membranes have the potential to show higher gas fluxes since it is very easy to cast them into thin film while maintaining the good mechanical properties as shown by DMA analysis.

Table 2. Gas transport and ion conducting properties of polymer membranes **5_{a-c}** and **6_b**.

	CO ₂ Permeability, ^{a)} (Barrer)	N ₂ Permeability, ^{a)} (Barrer)	CO ₂ /N ₂ Selectivity ^{a)}	$\sigma_{DC}^{b)}$ at 30 °C (S/cm)	$\sigma_{\infty}^{c)}$ (S/cm)	$B^{c)}$ (K)	$T_0^{c)}$ (K)
5_a	113.2	6.0	18.9	3.6×10^{-7}	0.03	1556	164
5_b	86.0	2.1	40.9	3.0×10^{-7}	0.05	1668	164
5_c	96.5	2.7	36.4	1.1×10^{-6}	0.12	1648	160
6_b	59.2	1.2	47.6	3.9×10^{-6}	0.04	1289	164

^{a)}Determined by isochoric gas permeation system at room temperature. ^{b)} Obtained by BDS. ^{c)} Obtained by VFT fits of the experimental data using equation 3.

Figure 4. Comparison of the gas transport properties of the PTMEG-based ionic membranes **5_{a-c}** and **6_b** with the literature data of polyether based membranes.[30,33–35,59–62]

3.5. Ion conducting properties

The temperature dependence of ionic conductivity of cross-linked membranes **5_{a-c}** and **6_b** was then investigated under anhydrous conditions by broadband dielectric spectroscopy (BDS). For

each membrane of known thickness, the DC-conductivity (σ_{DC}) was derived from the plateau-value observed in the spectral dependence of the conductivity ($\sigma' = \omega \varepsilon'' \varepsilon_0$, where ω is the frequency, ε_0 the vacuum permittivity and ε'' the dielectric loss) measured at temperatures ranging from 110 to -50 °C and was reported as a function of reciprocal temperature (Figure 5). As generally observed for most polymer materials, σ_{DC} above T_g follows a Vogel-Fulcher-Tammann (VFT) dependence of the relaxation times, due to the correlation between the charge transport of the ionic species and the molecular mobility of the polymer matrix. Experimental σ_{DC} values reported in Figure 5 were thus fitted with the VFT equation (3),

$$\sigma_{DC} = \sigma_{\infty} \times \exp(-B/(T-T_0)) \quad (3)$$

where σ_{∞} is the conductivity in the limit of high temperatures, B is the fitting parameter related to the activation energy of ionic conduction and T_0 is the Vogel temperature which generally ranges between 30 to 70 K above T_g . σ_{DC} of the studied membranes at 30 °C under anhydrous conditions ranges from 3.0×10^{-7} to 3.9×10^{-6} S cm $^{-1}$ which is relatively high for non-doped ionic networks. σ_{DC} is almost constant for **5_a** and **5_b** (i.e. $[N_3]/[I] = 0.5$ and 1.0 , respectively) and a three-fold increase is observed for **5_c** (i.e. $[N_3]/[I] = 2.0$). Since T_g values are comparable for the three studied ratios, the superior σ_{DC} of **5_c** most probably stems from the higher content of ionic groups and the enhanced mobility provided by the increase in dangling chains of sample **5_c**. Besides, as commonly observed for PILs, a one order of magnitude increase is observed when iodide counter-anions are substituted by fluorinated NTf $_2$ anions. Membrane **6_b** has thus the highest anhydrous ionic conductivity of the studied series ($\sigma_{DC} = 3.9 \times 10^{-6}$ S cm $^{-1}$).

Figure 5. Direct current conductivity (σ_{DC}) versus reciprocal temperature for membranes **5_a** (open circles), **5_b** (solid squares), **5_c** (solid triangles) and **6_b** (open squares) measured by BDS under anhydrous conditions. The solid lines represent the best VFT fits of experimental data using equation 1 using σ_{∞} , B , T_0 values given in Table 2.

4. Conclusions

We have reported a facile one-step, solvent- and catalyst-free membrane fabrication method *via* thermal Huisgen 1,3-dipolar cycloaddition of a dialkyne and a diazide PTMEG-based monomers with *in-situ* *N*-alkylation of the resulting poly(1,2,3-triazole)s by 1,10-diiododecane. The kinetics of the overall process was explored using DSC and was found to have an activation energy of 76 kJ/mol. The resulting 1,2,3-triazolium-based cross-linked membranes have decomposition temperatures above 200 °C and their onset decomposition temperatures are increased (up to 91 °C) by the replacement of iodide anions by NTf₂ ones. These polymers show T_g s below –

60 °C, Young's modulus up to 4.2 MPa, and tensile strain at break up to 76%. The membranes are excellent candidates for CO₂ separation since they are highly CO₂ permeable (up to 110 Barrer) and show good CO₂ selectivities over N₂ (up to 41). σ_{DC} of membranes **5**_{a-c} and **6**_b at 30 °C under anhydrous conditions ranges from 3.0×10^{-7} to 3.9×10^{-6} S cm⁻¹. We also found that by varying the cross-linker loading, and thus the cross-link density and ionic group content as well as nature of the counter-anion affords a fine-tuning of thermal, mechanical properties, gas permeability, and ionic conductivity of these membranes. Further tuning of the membranes properties could be performed by the variation of the structural parameters of the constitutive building blocks (i.e. monomers, cross-linking agents and counter-anions).

Supporting Information: ¹H, ¹³C NMR, and FT-IR of **2**, **3**, and **4**; DSC curves of mixture of **2** and **3**; determination of activation energy; TGA and DSC curves of polymer **6**_{a-c}.

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GRAPHICAL ABSTRACT