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Synthesis and Gas Separation Performance of Triblock Copolymer Ion Gels with a Polymerized Ionic Liquid Mid-Block

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Supporting Information

Carbon dioxide removal from light gases (e.g., N_2, CH_4, and H_2) is an important technology widely used in applications such as natural gas sweetening, CO_2 recovery from coal-fire power plant exhausts, and hydrogen production.[1,2] Currently, four methods are used in CO_2 separation from gas mixtures: amine-based absorption, pressure-swing adsorption, cryogenic condensation, and membrane separation.[3] Of these, membrane separation technology can be economically advantageous over the other more energy-intensive methods, especially in small- and medium-scale separations, such as natural gas wells in remote areas.[2,4]

For efficient gas separation membranes, it is highly desirable to achieve both high permeability and high selectivity. Gas permeation through a polymeric membrane generally follows a solution-diffusion mechanism, and the permeability of the membrane (P) is determined by the product of the solubility (S) and diffusivity (D) of the gas in the membrane.[5,6] Membrane selectivity α is the permeability ratio of two different gases in the same membrane, which, in turn, is determined by both the solubility ratio and diffusivity ratio:[4]

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{S_i}{S_j}\frac{D_i}{D_j} \qquad (1)$$

The particular ratio that contributes more to the selectivity of a membrane is determined by the gas pairs involved. It is important to distinguish between ideal selectivity and real selectivity, where the former is the permeability ratio of the two pure gases and the latter is the permeability ratio of two different components in gas mixtures. For polymeric CO_2 gas separation membranes, the real selectivity is often much lower than the ideal selectivity;[2] this loss of selectivity is generally attributed either to increased polymer chain segmental mobility due to the dissolved CO_2 (i.e., plasticization) or to the competitive sorption between two mixed gases.[7−10] For example, the ideal selectivity for CO_2/CH_4 in cellulose acetate, the most widely used CO_2 separation membrane material, can be as high as 80, but its real selectivity drops below four under mixed gas conditions due to membrane plasticization.[7]

Room temperature ionic liquids (RTIL) have attracted great interest because of their unique properties such as nonvolatility, high thermal stability, high ionic conductivity, and tunable solvation properties.[11−13] Recently, there are promising reports of ionic liquids as new CO_2-separation media,[14−17] for four primary reasons: (i) ionic liquids generally show a significant preferential solubility for CO_2 over other gases such as N_2 and CH_4, which enhances the S_i/S_j term in eq 1; (ii) gas solubility and selectivity can be easily tuned by changing the anion or cation in the ionic liquid or by incorporating certain functional groups; (iii) compared with conventional liquid membranes, the nonvolatile nature of ionic liquids prevents solvent loss due to evaporation; (iv) as liquids, the transport rates are high. Previous studies on supported ionic liquid membranes (SILM), which were prepared by filling porous membranes with RTIL, have demonstrated the viability of using ionic liquids in gas separation.[18] These SILMs generally show promising gas separation properties because of the high solubility difference for CO_2/CH_4 and CO_2/N_2 gas pairs.[15,19,20] However, these liquid membranes cannot withstand practical pressure drops in gas separation, as only weak capillary forces hold the ionic liquid in the pores.[14] To address this issue, efforts have been made on blending ionic liquids with compatible polymers, such as chemically cross-linked polymerized ionic liquids[21−23] and poly(vinylidene fluoride-*co*-hexafluoropropylene).[24,25] These composite materials have shown enhanced mechanical strength and favorable gas transport properties.

Recently, we reported gelation of ABA-type triblock copolymers in ionic liquids, where the A blocks are insoluble and the B block is soluble in the chosen ionic liquid.[26,27] Such a physically cross-linked ion gel only requires a few weight percent of polymer to achieve gelation, and the mechanical properties can be tuned by changing polymer weight fraction and molecular weight. Inspired by the enhanced transport properties of poly(RTIL)−RTIL composite materials developed by Noble and coworkers,[21−23] we have synthesized poly(styrene-*b*-1-[(2-acryloyloxy)ethyl]-3-butylimidazolium bis(trifluoromethylsulfonyl)amide-*b*-styrene) (denoted as PS−PIL−PS), a new triblock copolymer with an acrylate-based polymerized ionic liquid (PIL) mid-block. In this Communication, we reported the gas separation properties of the corresponding ion gel formed by the self-assembly of PS−PIL−PS in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][TFSA]). As the main components are ionic liquid and PIL, polymerized ionic liquid gel maintains most of the transport property of ionic liquid and shows an improved selectivity.

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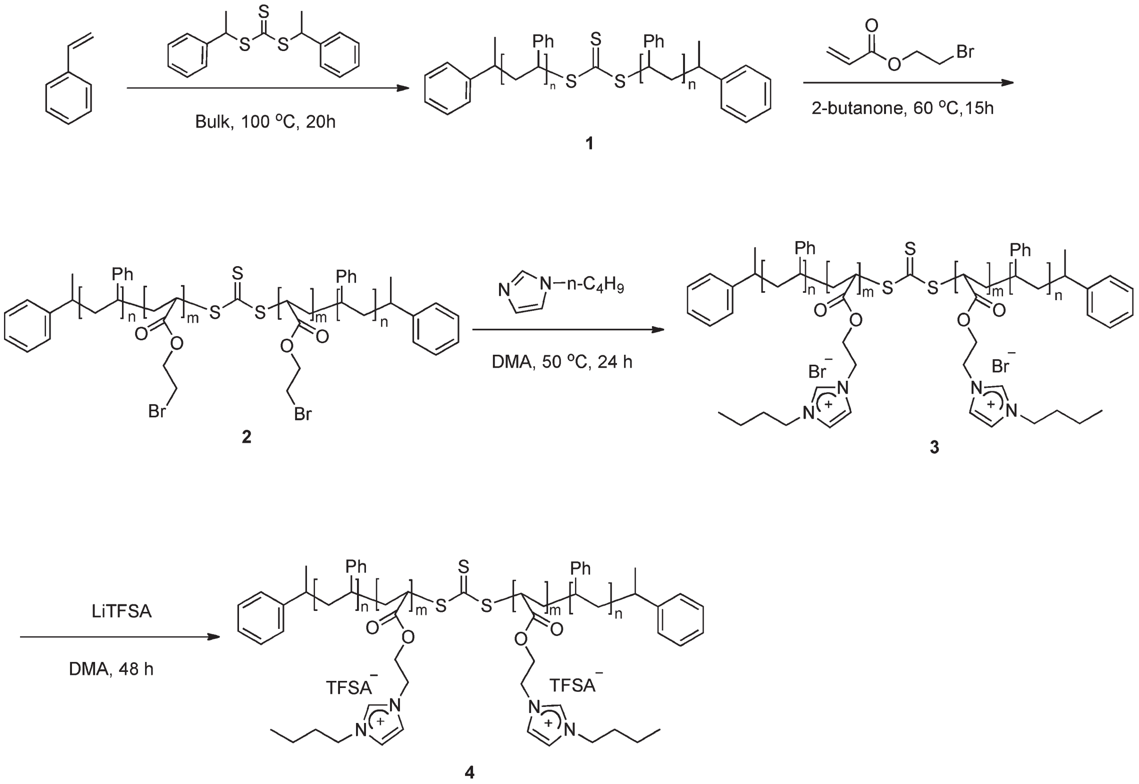
Scheme 1. Synthetic Route to the PS−PIL−PS Triblock Copolymer Using RAFT Polymerization



Scheme 1 shows the synthetic route to the PS−PIL−PS triblock copolymer. The polymer was synthesized through a two-step reversible addition−fragmentation chain transfer (RAFT) polymerization, followed by two functionalization steps to introduce ionic liquid functional groups. First, styrene was polymerized with *S*,*S*′-di(1-phenylethyl) trithiocarbonate,[28] a symmetric difunctional chain transfer agent (CTA), to yield a narrowly distributed polystyrene (PS). This CTA was specifically chosen because it has been reported to be suitable for polymerization of both styrene and acrylate monomers.[29] The resulting PS macro-CTA (**1**) was subsequently used to polymerize 2-bromoethyl acrylate (BrEA) into the mid-block. Then, a quarternization reaction between PS−PBrEA−PS (**2**) and 1-butylimidazole in dimethylacetamide (DMA) was employed to introduce ionic liquid functional groups into the side chains of the mid-block. Finally, through an anion exchange reaction with excess lithium bis(trifluoromethylsulfonyl)amide (LiTFSA), the target polymer (**4**) was obtained. Size exclusion chromatography and ^{1}H NMR spectroscopy were used to characterize each step of the reaction. The final triblock copolymer has an overall molecular weight of 260 kg/mol and a polydispersity index of 1.21. The two PS end-blocks each have a molecular weight of 4 kg/mol, and the PIL mid-block has a molecular weight of 252 kg/mol. The quarternization efficiency was at least 93%, determined by both ^{1}H NMR spectroscopy and elemental analysis (see Supporting Information). Both a silver nitrate test and elemental analysis showed that the anion exchange step from Br$^-$ to TFSA$^-$ is complete. The ionic liquid [EMIM][TFSA] was synthesized following a previously reported procedure.[30] Both polymers and ionic liquid were dried under vacuum at 70 °C for 48 h and stored in a desiccator before use.

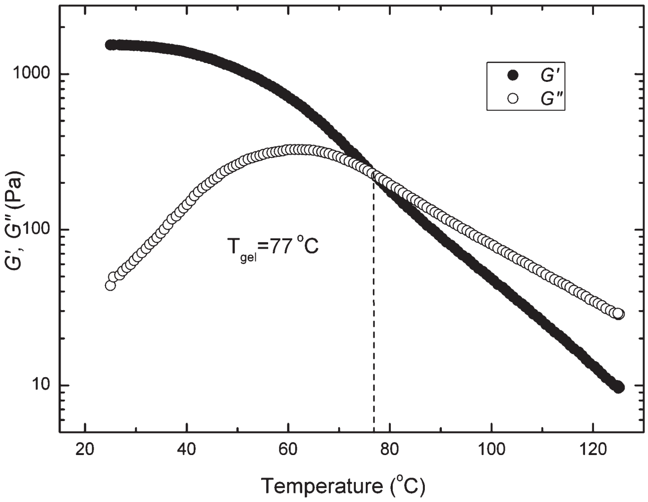


Figure 1. Temperature dependence of G' and G''.

The polymerized ionic liquid gel was prepared by dissolving a mixture of PS−PIL−PS and [EMIM][TFSA] (15/85 w/w) in tetrahydrofuran, followed by complete cosolvent evaporation. Rheological measurements were used to study the thermoreversible nature of the resulting ion gel. The dynamic moduli G' and G'' were measured at a frequency of 0.3 rad/s during a temperature ramp from 25 to 125 °C at a heating rate of 1 °C/min. As shown in Figure 1, the intersection of the G' and G'' curves indicates the critical gelation temperature at 77 °C, above which the gel will melt. This sol−gel transition is not unexpected according to the transient network theory.[31] Because the PS end-blocks are very short (less than 40 repeating units) and the glass transition temperature (T_g) of a 4 kg/mol PS is only 80 °C, their higher segmental mobility above T_g makes PS easier to dissociate and diffuse into the surrounding ionic liquid, leading to the gel melting. This thermoreversibility provides the possibility to process the ion gel at a higher temperature and use it at room temperature.

The gas separation performance of the ion gel was tested on a microporous PVDF membrane (0.45 μm pore size, 75% porosity) support. The pores of the PVDF membranes were filled with ion gel containing 15 wt % PS−PIL−PS to form a dense, dry membrane. Both pure gas and mixed gas permeation properties of the supported ion gel membrane were studied using a gas diffusion cell at room temperature with a pressure difference of ~30 psi.[32] Table 1 shows the permeation results for two different gas pairs: CO_2/N_2 and CO_2/CH_4. The gas permeability of CO_2, calculated by dividing the membrane permeability by the porosity of the support (0.75), was determined to be 985 barrers for the PIL gel containing 15 wt % of triblock copolymer, which is very close to the literature reported CO_2 permeability value of neat [EMIM][TFSA].[15,23] The permeability of N_2 and CH_4 was found to be 25 and 52 barrers, respectively. Interestingly, these observed values are significantly lower than those reported for neat [EMIM][TFSA]. In consequence, the block copolymer ion gel exhibits an ideal permselectivity of 19 for CO_2/CH_4 and 39 for CO_2/N_2, both of which are higher than the reported values for neat [EMIM][TFSA]. In a previous report, a cross-linked homopolymer of PIL of the same structure as the mid-block in this study was found to possess a higher selectivity than [EMIM][TFSA] for both CO_2/N_2 and CO_2/CH_4,[33] consistent with the results here.

As noted earlier, the real selectivity of polymeric gas separation membranes is often lower than the ideal selectivity due to the plasticization effect or competitive absorption. However, at the current experimental pressure, by using this ion gel, we observe that the real selectivity is almost the same as the ideal selectivity. In Table 2, the permeability of each gas is essentially the same with and without the presence of another gas. This result is understandable because the selectivity in the ion gel is determined by differential solubility in the ionic liquid, which is not significantly affected when exposed to a gas mixture. This result is also consistent with previous reports studying mixed gas selectivity on a SILM.[34,35] In polymer membranes there can be a major selectivity decrease at high pressure drops due to membrane plasticization. In our future work, we will explore

Table 1. Pure Gas Permeability and Ideal Selectivity of the Ion Gel

	permeability (barrer)[a]			ideal selectivity	
	CO_2	N_2	CH_4	CO_2/N_2	CO_2/CH_4
15% ion gel	985 ± 29	25 ± 2	52 ± 3	39	19
[EMIM][TFSA][b]	1000	44	90	21	11

[a] Permeability in barrers, units of 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg).
[b] Permeability data of pure ionic liquid from refs 14 and 23.

Table 2. Real Selectivity and Comparison between Pure and Mixed Gas Permeability

	permeability (barrer)[a]					
	CO_2		N_2	CH_4	real selectivity	
	CO_2 (N_2)	CO_2 (CH_4)	N_2 (CO_2)	CH_4 (CO_2)	CO_2/N_2	CO_2/CH_4
15% ion gel	985 ± 29		25 ± 2	52 ± 3	40	20
	1030 ± 24	1040 ± 23	26 ± 2	51 ± 2		

[a] Data in the first row are pure gas results and the second row are mixed gas results. The mixed gas permeability was tested on a 50/50 mixture with a background gas (listed in parentheses); see Supporting Information for further experimental details.

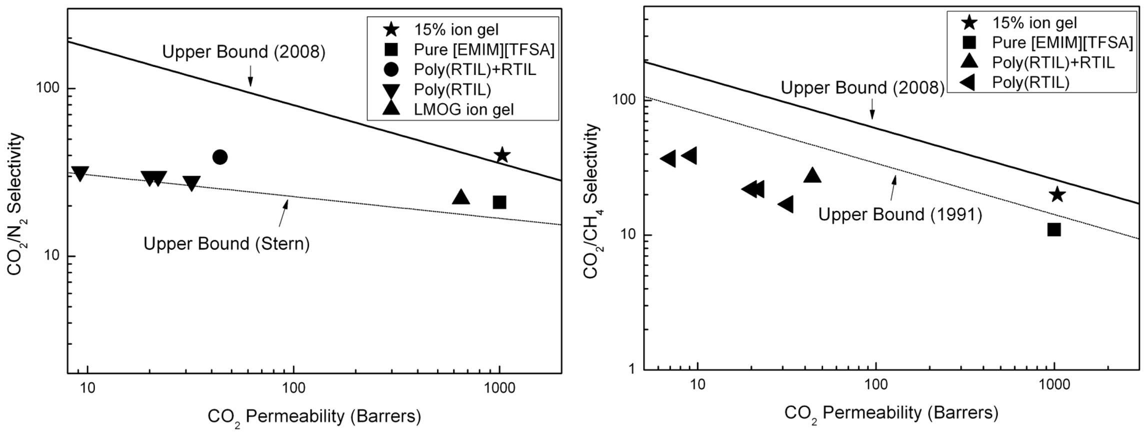


Figure 2. Robeson plot comparison with upper bound for various ionic liquid-related membrane materials: left, CO_2/N_2; right, CO_2/CH_4. Permeability data for the materials except the ion gel are from refs 22, 33, and 40. Upper bound (Stern) for CO_2/N_2 was generated from the data in ref 38, according to the method from ref 36. The other three upper bounds are adapted from refs 36 and 37.

whether a higher pressure drop influences the ion gel membrane performance.

The gas separation properties of this new type of ion gel can be compared with existing gas separation membranes on a Robeson plot, i.e., a log−log plot of selectivity vs permeability.[36−38] The empirical upper bound on the plot approximates the best permeability/selectivity combination for existing polymer membranes. As shown in Figure 2, the performance of the PIL gel lies above the upper bound for CO_2/N_2 and very close to the upper bound for CO_2/CH_4. This promising performance can be typically compared with recent reports of chemically cross-linked poly(RTIL) and poly(RTIL)−RTIL composite membranes.[23,33,39] The poly(RTIL) membrane shows high selectivity for CO_2 but has a very low permeability. By incorporating a certain amount of liquid (20% free IL), a poly(RTIL)−RTIL composite material exhibits increased CO_2 permeability (ca. 50 barrers) with little sacrifice on selectivity. However, as shown in Figure 2, the block copolymer ion gel shows a much higher permeability than these materials (ca. 100 times higher than cross-linked poly(RTIL) and ca. 20 times higher than poly(RTIL)−RTIL composites).

The favorable transport properties of ion gels stem from the fact that the major component is free ionic liquid (85%), and if we consider the swollen PIL in ionic liquid, the combined weight fraction of IL and swollen PIL is greater than 99%. Therefore, the ion gel achieves a liquid-like permeability in a solid-state material. Moreover, by incorporating a PIL as the mid-block, the selectivity has also been increased by almost a factor of 2 over the corresponding pure ionic liquid. One similar system is a physically cross-linked ion gel solidified by 12-hydroxystearic acid, a low-molecular-weight gelator (LMOG).[40] Because only 1.5% of gelators have been added, the local environment for gas permeation in the gel is not significantly affected. Therefore, this LMOG ion gel also exhibits excellent transport properties, close to the pure ionic liquid. However, we anticipate that the mechanical properties of these ion gel membranes can be tuned over a significant range by varying polymer concentration and molecular weight. Here, we also need to mention that this work is a proof-of-concept study to show the viability of using a triblock copolymer ion gel as a gas separation material. The current supported ion gel membrane is too thick for practical use. Therefore, the permeance of the ion gel membrane is limited by its thickness, and the permeation efficiency is also reduced by using a support. In future work, we will investigate the possibility to make ion gel into a thin film that has a more practical thickness ($\leq 1\ \mu m$) for gas separation. Also, a gas separation membrane needs to be stable under a higher pressure drop (>50 bar), which cannot be achieved with the current membrane. We will explore ways to enhance the mechanical strength, while retaining the attractive diffusivity and solubility characteristics, of these ion gels.

In summary, we have designed a new gas separation material with enhanced gas transport properties through gelation of PS−PIL−PS in an ionic liquid, [EMIM][TFSA]. The triblock copolymer is readily synthesized using RAFT polymerization and postpolymerization functionalization reactions. The thermoreversible nature of the ion gel offers the advantage of solvent-free processing in practical applications. More importantly, this new class of material exhibits both high permeability and high real selectivity for CO_2/N_2 and CO_2/CH_4 gas pairs, thus exhibiting great promise for future gas separation membranes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details for polymer synthesis, membrane preparation, gas separation experiments, and related calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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