

Gas Separation Characteristics of New Membrane Materials Based on Poly(ethylene Glycol)-Crosslinked Polymers and Ionic Liquids

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Received October 6, 2011

Abstract—Gas transport characteristics (permeability and diffusion and solubility coefficients for CO₂, O₂, N₂, H₂) of new crosslinked membrane materials synthesized by copolymerization of poly(ethylene glycol) dimethacrylate and poly(ethylene glycol) methyl ether methacrylate in the presence of various ionic liquids have been studied. Comparison of the characteristics of specimens with and without ionic liquids has revealed that the presence of ionic liquids enhances the permeability of the membranes, especially to CO₂. It has been shown that the enhancement of the CO₂ permeability of films incorporating ionic liquid is due to an increase in CO₂ solubility and the increase in selectivity for pairs of gases containing CO₂ is determined by thermodynamic selectivity of separation.

Keywords: membranes, permeability, selectivity, crosslinked polymers, ionic liquids

DOI: 10.1134/S0965544112070031

INTRODUCTION

Searching for effective methods of selective recovery of carbon dioxide from CO₂-containing mixtures is one of the tasks on the front burner of modern membrane technologies. At present, gas separation membranes that contain ionic liquids (ILs) as a selective medium or an additive for the polymeric matrix are a subject of intensive development for CO₂ recovery from gas mixtures. Ionic liquids differ from usual organic solvents and water by low vapor pressure (i.e., nonvolatility), thermal and chemical stability, and an extensive range of the liquid state. In addition, their structure is easy to design for imparting certain properties. These characteristics were used for transition from traditional liquid membranes [1] to a new and more stable type of supported ionic liquid membranes (SILMs), which contain an ionic liquid (IL) as a low-volatility transport medium [2–5]. Such membranes, as a rule, are obtained by impregnation of porous (microfiltration, ultrafiltration, and reverse-osmosis) polymer membranes with ILs.

Most studies concerning the application of ILs to CO₂ absorption have been performed during the last five years, in which ILs with the quaternized or aprotic imidazolium cation have been basically used [2]. Some of them exhibit high permeability for CO₂ (about 1000 Barrer) and a selectivity for the CO₂/N₂ mixture greater than 50 [3]. At present, the main problem of SILMs is instability of transport characteristics

in time because of exudation of IL from the membrane. One of the possible ways to overcome the drawbacks of SILM is designing new membrane materials on the basis of crosslinked polymers (see the title of the article) and ionic liquids [6].

In this work we used a copolymer of polyethylene glycol mono- and dimethacrylates as the polymeric matrix. Preliminary studies showed [7] that exudation of ILs with time is not observed in such crosslinked polymer materials; moreover, the concentration of ILs can be varied within a wide range during the synthesis. This opens up a possibility for further search for membrane materials of this kind such sort aimed at improving their transport characteristics. In this context, the aim of the present study was to investigate the gas separation characteristics of some novel crosslinked polymer membrane materials containing various ILs.

EXPERIMENTAL

1-Methylimidazole (Acros Organics, 99%) was distilled over CaH₂ under argon before experiments. Poly(ethylene glycol) dimethacrylate (DMPEG, $M_n = 750$ g/mol, Aldrich, 98%), poly(ethylene glycol) methyl ether methacrylate (MPEG, $M_n = 475$ g/mol, Aldrich, 98%), and 1,1,2-trichloroethane (Acros Organics, 98%) were used without additional purification. 2,2'-Azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was purified by recrystallization from methanol.

Synthesis of Ionic Liquids

The ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (MeEtIm)⁺(CF₃SO₂)₂N⁻ – and 1-ethyl-3-methylimidazolium trifluoromethylsulfonate

(MeEtIm)⁺CF₃SO₃⁻, used as a filler for polymeric membranes were synthesized as described elsewhere [8, 9]. Their structure was confirmed by elemental analysis, ¹H NMR, and IR data.

The ionic liquid 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (MeEtIm)⁺(CF₃CF₂)₃PF₃⁻ (Merck KGaA PC-RL, >99%) was used without preliminary purification.

Synthesis of Membrane Materials

The membranes were obtained by polymerization of the monomers in 1,1,2-trichloroethane in the presence of IL according to the following procedure. A solution was prepared by dissolving 1.4 g of DMPEG, 0.7 g of MPEG, 1.05 g of the corresponding IL (50 wt %), and 0.063 g of AIBN (3 wt %) (initiator of radical polymerization) in 0.5 mL of 1,1,2-trichloroethane with stirring in an inert atmosphere. The solution was degassed using the freezing (liquid nitrogen)–pumping–thawing technique. Then it was loaded in a mold consisting of two glass plates clamped together with a U-shaped Teflon spacer of 80 × 80 × 0.5 mm (length × width × thickness). The mold was held for 15 h at 60°C. The obtained film was taken out and dried in vacuum at 80°C for 20 h.

Dynamic mechanical thermal analysis (DMTA) of the copolymer films (specimen dimensions length × width × thickness = 15 × 8 × 0.45 mm) was carried out on a TA Instruments Q800 analyzer in the tension mode (stretching from 0.05 to 0.07%; preliminary load was 10⁻² N) at a frequency of 1 Hz and a heating rate of 3.0°C/min in the range of -90 to +150°C. The mechanical loss tangent (tan δ) was determined as tan δ = E''/E' where E' is the storage modulus and E'' is the loss modulus.

The transport parameters of the membrane films for H₂, O₂, N₂, and CO₂ were evaluated by a mass-spectrometric procedure [10]. The permeability coefficient was calculated by the equation:

$$P = JI/(A\Delta p),$$

where *J* is the penetrant flux through a membrane, *l* is the membrane thickness, *A* is the membrane surface area through which mass transfer occurs, and Δ*p* is the pressure differential across the membrane. The experiments were carried out at room temperature, an upstream pressure in the range of 0.1–1 atm, and a downstream pressure 10⁻³ mmHg; thus, the back diffusion of the penetrant can be neglected. The measure of the permeability coefficient (*P*) was the change in time of ionic current for a certain ion (usually, the most abundant) in a mass spectrum of the given gas

after reaching a stationary state by the diffusion process. The diffusion coefficients (*D*) for O₂, N₂, and CO₂ were determined by the time lag θ method using the Daynes–Barrer equation:

$$D = l^2/6\theta.$$

The diffusion coefficients for H₂ were not determined because of a small time lag (1–3 s). The measurement errors for *P* and *D* were 5 and 10%, respectively.

From the values of *P* and *D* obtained for O₂, N₂, and CO₂, the solubility coefficient *S* was determined according to the formula

$$P = DS.$$

The ideal separation or selectivity factor α_{*ij*} = *P_i*/*P_j* for a pair of gases *i* and *j* and the diffusion selectivity (α_{*ij*}^{*D*}) and solubility (α_{*ij*}^{*S*}) factors were calculated from these *P*, *D*, and *S* values.

RESULTS AND DISCUSSION

It is known that polyethylene oxide dissolves well various ionic compounds including alkali metal salts [11]. However, it tends to crystallize and to lose its mechanical properties. In this work, we took a DMPEG-based polymer as an alternative to polyethylene oxide (Fig. 1). Its characteristic feature is the formation of a crosslinked non-crystallizable polymer with a low glass transition temperature (*T_g* or *T_α* is the temperature of a maximum in the loss tangent according to DMTA), which is -22.5°C. Therefore, the DMPEG polymer at room temperature exists in the rubbery state, which ensures that the ions of both salts dissolved in the polymer and ionic liquids retain their high mobility. This, in turn makes it possible to obtain an IL-filled crosslinked polymer matrix with properties close to those of the IL itself. By DMPEG polymerization in the presence of 50 wt % (MeEtIm)⁺(CF₃SO₂)₂N⁻, transparent colorless films were obtained. However, their mechanical strength was insufficient for use as gas separation membranes.

To increase the mechanical strength of the polymer membrane and to further lower its *T_g*, a DMPEG–MPEG copolymer in a 2 : 1 ratio (by mass) was obtained (Fig. 1). According to DMTA data, *T_g* of the copolymer film was -33.9°C. We also synthesized DMPEG–MPEG copolymer membranes containing 50 wt % different ILs. The ILs used for this purpose had perfluorinated anions, namely: 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide (MeEtIm)⁺(CF₃SO₂)₂N⁻, trifluoromethylsulfonate (MeEtIm)⁺CF₃SO₃⁻, and tris-(pentafluoroethyl)trifluorophosphate (MeEtIm)⁺(CF₃CF₂)₃PF₃⁻ (Fig. 1). This choice was determined by high solubility of CO₂ in these ILs [12].

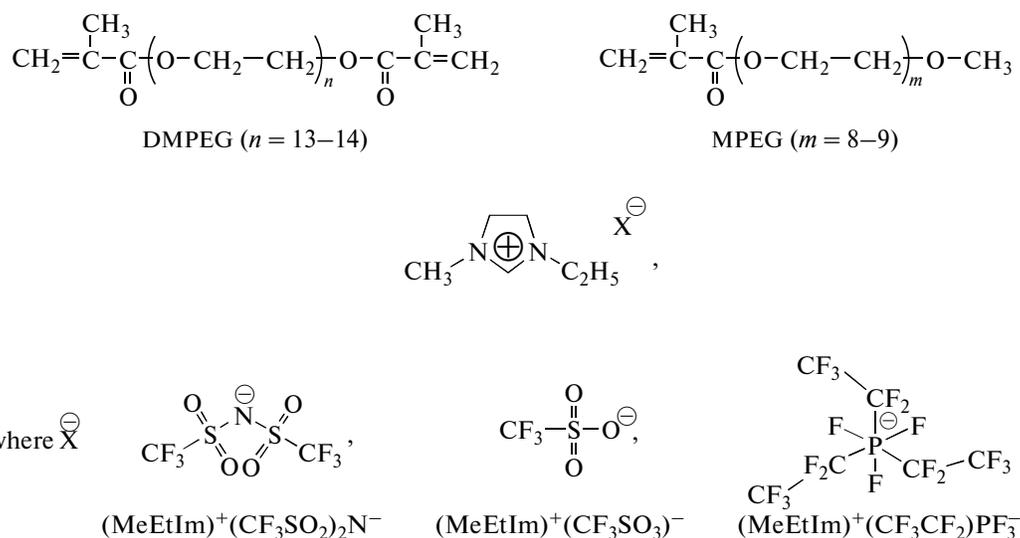


Fig. 1. Chemical structure of the monomers and ILs used in the work.

Note that T_g of copolymer films filled with 50 wt % IL almost coincides with T_g of the unfilled DMPEG–MPEG membrane and is -34.5 , -33.8 , or -29.2°C for the films containing (MeEtIm)⁺CF₃SO₃⁻, (MeEtIm)⁺(CF₃SO₂)₂N⁻,

or (MeEtIm)⁺(CF₃CF₂)₃PF₃⁻, respectively. This fact along with invariability of the storage modulus of the films (~ 2600 MPa for unfilled membrane and 2100–2540 MPa for filled membranes at -60°C) suggests strong interaction of the chosen ILs with the polymer,

which, in turn, results in good retention of IL inside the polymer membrane.

The permeability coefficients and values for the ideal selectivity of gas separation for the investigated materials are given in Table 1.

In comparison with I, specimens II–IV synthesized in the presence of IL exhibit a significant increase in the permeability coefficient for all gases and, especially, CO₂. Owing to the increase in $P(\text{CO}_2)$, the gas separation selectivity in pairs of gases containing CO₂ also increases. The gas separation selectivity for gases inert towards IL $\alpha(\text{O}_2/\text{N}_2)$ and $\alpha(\text{H}_2/\text{N}_2)$ correlates with data obtained for crosslinked rubbers [13]. Unlike the case of specimen I, the pair CO₂/N₂ data in the Robeson diagram (Fig. 2) for specimens II–IV containing IL lie close to the higher bound of distribution reported in 1991 [13] (curve *b*, Fig. 2). Nevertheless, the data for the IL-containing specimens are in the common “cloud of points” relative to the upper bound of distribution published in 2008 [14] (curve *a*, Fig. 2).

In the Robeson plot for CO₂/O₂ (Fig. 3), the data for specimens II–IV containing IL, in contrast to specimen I, lie near or above the higher bound constructed according to the data published in 1999 [15].

Most polymers generally exhibit a gas separation selectivity of $P(\text{H}_2) > P(\text{CO}_2)$; i.e., $\alpha(\text{H}_2/\text{CO}_2) > 1$. However, the reverse is observed for highly permeable polymers: $P(\text{H}_2) < P(\text{CO}_2)$; i.e. $\alpha(\text{CO}_2/\text{H}_2) > 1$. For example, $\alpha(\text{CO}_2/\text{H}_2) \sim 3$ for the superpermeable glassy polymer poly(trimethylsilyl)propyne (PTMSP) [16] and ranges from 5 to 8 for some rubbers, such as PEBAX[®], $\alpha(\text{CO}_2/\text{H}_2)$ [17]. Thus, the data obtained for IL-containing specimens II–IV (Table 2) are in the region of quite high $\alpha(\text{CO}_2/\text{H}_2)$ separation selectivity.

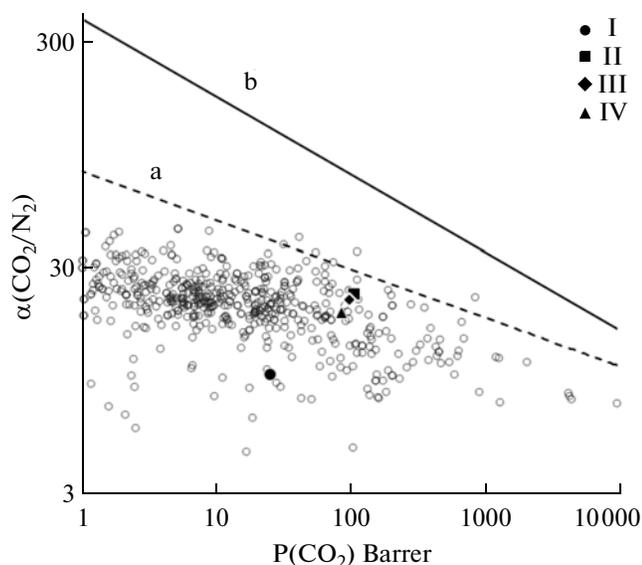


Fig. 2. Robeson plot for the CO₂/N₂ pair of gases. The upper bound of distribution according to (a) [13] and (b) [14].

Table 1. Permeability coefficients P [Barrer*] and values of ideal separation selectivity for test materials and gases

	Polymer membrane			
	I**	II*** [(MeEtIm) ⁺ (CF ₃ SO ₂) ₂ N ⁻]	III*** [(MeEtIm) ⁺ (CF ₃ CF ₂) ₃ PF ₃ ⁻]	IV*** [(MeEtIm) ⁺ CF ₃ SO ₃ ⁻]
$P(\text{H}_2)$	11.4	17.6	18.2	22.6
$P(\text{CO}_2)$	26.1	106	98.3	85.6
$P(\text{O}_2)$	5.4	8.8	8.7	8.5
$P(\text{N}_2)$	2.6	4.5	4.5	4.4
$\alpha(\text{CO}_2/\text{N}_2)$	10	23.6	21.8	19.5
$\alpha(\text{CO}_2/\text{O}_2)$	5	12	11.3	10.1
$\alpha(\text{CO}_2/\text{H}_2)$	2.3	6	5.4	3.8
$\alpha(\text{O}_2/\text{N}_2)$	2.1	1.9	1.9	1.9
$\alpha(\text{H}_2/\text{N}_2)$	4.4	3.9	4	5.1

* 1 Barrer = 10^{-10} cm³ (STP) cm/(cm² s cmHg).

** IL-free membrane.

*** IL-filled membrane, the IL content is 50 wt %.

The diffusion coefficients and diffusion selectivities of the test materials are given in Table 2.

In comparison with specimen *I* synthesized without ILs, there is no significant changes in the diffusion coefficient of CO₂ in specimens II–IV synthesized in the presence of ILs. Small changes in $D(\text{CO}_2)$ and diffusion selectivity for gases, including those inert towards ILs ($\alpha^D(\text{O}_2/\text{N}_2)$), suggest that the thermodynamic mechanism of enhancement of gas separation selectivity of polymer materials containing IL as compared with the IL-free materials. In other words, the observed growth in carbon dioxide permeability is mainly due to changes in solubility coefficients. The invariability of the diffusion selectivity values listed in Table 2 means that changes in diffusion coefficients for other gases are the same as for CO₂.

The solubility coefficients and solubility selectivities of the test materials are given in Table 3.

There are a significant increase in the CO₂ solubility coefficient and an increase in solubility selectivity for the CO₂-containing gas pair in specimens II–IV with encapsulated ILs, as compared with specimen *I*. Thus, it has been experimentally shown that the enhancement of permeability and selectivity for CO₂ in the IL-containing specimens is due to the increase in thermodynamic separation selectivity, a finding that can appear useful for the further development of polymer membrane materials as applied to separation of CO₂-containing pairs of gases. The maximal increase

in thermodynamic gas separation selectivity for the pairs of gases containing CO₂ was observed for the IL with the bis(trifluoromethylsulfonyl)imide anion in agreement with published data on CO₂ absorption in ILs [18]. Therefore, it is reasonable to continue the search for advanced membrane materials on the basis of ILs for separation of CO₂-containing pairs of gases by varying the nature of the crosslinked polymer

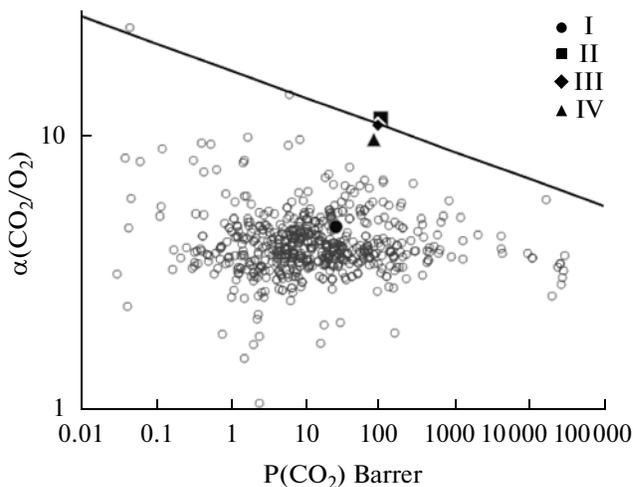


Fig. 3. Robeson plot for the CO₂/O₂ pair of gases. The upper bound according to [15].

Table 2. Diffusion coefficients $D \times 10^8$, cm²/s and values of diffusion selectivity for test materials and gases

	Polymer membrane			
	I*	II** [(MeEtIm) ⁺ (CF ₃ SO ₂) ₂ N ⁻]	III** [(MeEtIm) ⁺ (CF ₃ CF ₂) ₃ PF ₃ ⁻]	IV** [(MeEtIm) ⁺ CF ₃ SO ₃ ⁻]
$D(\text{CO}_2)$	43	66	54	46
$D(\text{N}_2)$	64	93	90	85
$D(\text{O}_2)$	96	156	93	115
$\alpha^D(\text{CO}_2/\text{N}_2)$	0.68	0.72	0.6	0.54
$\alpha^D(\text{CO}_2/\text{O}_2)$	0.45	0.43	0.58	0.4
$\alpha^D(\text{O}_2/\text{N}_2)$	1.5	1.7	1.0	1.4

* IL-free membrane.

** IL-filled membrane, the IL content is 50 wt %.

Table 3. Solubility coefficients $S \times 10^3$, cm³(STP)/cm³ cmHg and values of solubility selectivity for test materials and gases

	Polymer membrane			
	I*	II** [(MeEtIm) ⁺ (CF ₃ SO ₂) ₂ N ⁻]	III** [(MeEtIm) ⁺ (CF ₃ CF ₂) ₃ PF ₃ ⁻]	IV** [(MeEtIm) ⁺ CF ₃ SO ₃ ⁻]
$S(\text{CO}_2)$	6.0	16	18	19
$S(\text{N}_2)$	0.4	0.5	0.5	0.5
$S(\text{O}_2)$	0.6	0.6	0.9	0.7
$\alpha^S(\text{CO}_2/\text{N}_2)$	15	32	35	36
$\alpha^S(\text{CO}_2/\text{O}_2)$	11	28	20	25
$\alpha^S(\text{O}_2/\text{N}_2)$	1.4	1.1	1.8	1.4

* IL-free membrane.

** IL-filled membrane, the IL content is 50 wt %.

matrix itself and the nature and concentration of ionic liquid.

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