Cross-Linkable Polyimide Membrane for Natural Gas Purification and Carbon Dioxide Plasticization Reduction

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ABSTRACT: The ability of propanediol monoester cross-linkable (PDMC) polymer to effectively separate CO_2 from CH_4, and the polymer's stability against plasticization under high CO_2 pressures, was investigated. The cross-linked PDMC membranes were found to have significantly higher CO_2 permeability and slightly higher selectivity for the CO_2/CH_4 separation than the un-cross-linked PDMC membranes. Cross-linking temperature was found to have a significant impact on the permeation properties of the membranes. The PDMC membrane permeation results are compared with previous research that uses other cross-linking agents for CO_2 plasticization resistance and found to offer an excellent balance between extent of cross-linking and tradeoff between mechanical and transport properties. The cross-linked membranes not only outperform the un-cross-linked membranes with their enhanced transport properties but also provide vastly superior plasticization resistance against aggressive CO_2 steams. Un-cross-linked and cross-linked PDMC membranes were characterized via permeation (pure and mixed gas), density, T_g, and sorption measurements.

Introduction

Cross-linking has been shown to be an effective approach to stabilize properties of polymeric membranes used in carbon dioxide removal from natural gas mixtures.[1−4] The largest amount of polymer cross-linking research has been performed on polyimide membranes, which are attractive due to their intrinsically high CO_2/CH_4 selectivities and ease of chemical modification.[1−9] When considering polymer selection for cross-linkable membranes, a robust, processable, glassy polymer with a high glass transition temperature, T_g, is typically attractive. Research has also shown cross-linking to be a powerful approach to improve the performance of rubbery polymers;[10,11] however, this research focuses on the potential of glassy, polyimide membranes to purify natural gas mixtures and limit plasticization caused by aggressive carbon dioxide streams.

Polyimides modified with several different cross-linking agents were examined by Wind et al.[1] to assess the dependence of permeation properties on the size of cross-linking modifiers. Research reported here significantly extends work using this same polyimide backbone but explores an alternate cross-linking agent that enables optimized balancing of selectivity, permeability, and mechanical properties of the resultant material.

Experimental Methods

Polymer Synthesis. Polyimides based on selected dianhydrides and diamines have been found to be model cross-linkable polymers, particularly by Wind et al.[1−4] In this research, the anhydride used is (4,4′-hexafluoroisopropylidene) diphthalic anhydride (6FDA), and the two diamines used are 2,4,6-trimethyl-1,3-phenylenediamine (DAM) and 3,5-diaminobenzoic acid (DABA), which contains a carboxylic acid pendent group. The preferred cross-linking mechanism is implemented by reacting a diol with the carboxylic acid group within the polyimide and creating a monoester linkage on each DABA monomer. For this current research, 3:2 6FDA-DAM:DABA polyimide was synthesized using procedures reported earlier;[1−3] however, an alternate cross-linking agent, 1,3-propanediol, was explored. Because the reaction is water-sensitive, pure, dry reactants and glassware were assembled and maintained under an inert nitrogen atmosphere. All glassware was flamed prior to use, and all solvents were dried with molecular sieves.

Thermal imidization was used to force the ring closure via high temperatures (without the addition of catalyst).[3] The solvents used in the thermal imidization process are 1-methyl-2-pyrrolidinone (NMP) (anhydrous 99.5%, Aldrich) and *o*-dichlorobenzene (ODCB) (anhydrous 99%, Aldrich). The monomer mixture is reacted for 12 h at 180 °C and is covered in aluminum foil to exclude light, since the DAM monomer is especially sensitive to traces of oxygen in the presence of light. The thermal imidization process drives off water and forces the initial polymerization reaction and final ring closure to the imide. Following imidization, the polymer is precipitated, blended in methanol twice, and dried under vacuum at 100 °C.

Chemical modification of the polyimide, to introduce subsequent cross-linking, occurs prior to membrane formation via reaction of 1,3-propanediol with the carboxylic acid functionality on the DABA monomer in 6FDA-DAM:DABA (3:2). Following monoesterfication, the polyimide is referred to as PDMC (propanediol monoester cross-linkable) polymer.[12] The term "PDMC" will be used throughout this paper to describe cross-linkable or cross-linked 6FDA-DAM:DABA (3:2), which has been reacted with 1,3-propanediol.

The PDMC polymer was dried under vacuum at 100 °C and then dissolved in NMP in a reaction flask with an inert nitrogen atmosphere. *p*-Toluenesulfonic acid (98.5+% ACS Reagent, Aldrich) was used to catalyze the reaction (0.45 mol of PTSA/L of NMP). After adding the above-mentioned components, the mixture was heated to 100 °C, and 1,3-propanediol was added slowly in 70-fold excess of the stoichiometric amount required. The mixture was then heated to 140 °C and allowed to react for 18 h. Finally, the PDMC polymer was precipitated, blended in methanol, and carefully dried over several days under vacuum at 100 °C (see Figure 1).

Film Preparation and Cross-Linking. PDMC polymer was cast into a membrane prior to cross-linking by dissolving in tetrahydrofuran (THF) (anhydrous 99.9%, Aldrich) to create 35 wt % PDMC polymer solution. The solution was cast onto a substrate (Teflon) in an inert nitrogen environment, and the bulk of the solvent was evaporated. The membrane was then removed from the substrate and subsequently dried in a vacuum oven at 100 °C for 2 days to remove any remaining THF.

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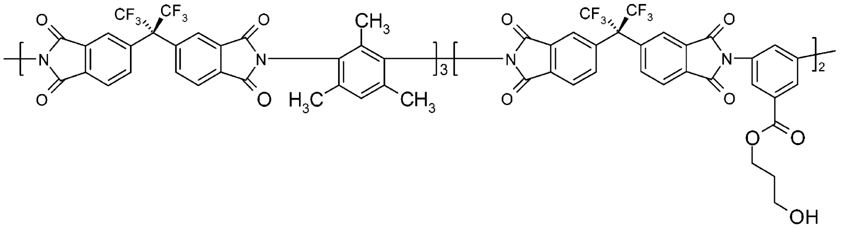

Figure 1. Structure of PDMC polymer (chemically modified 3:2 6FDA-DAM:DABA).

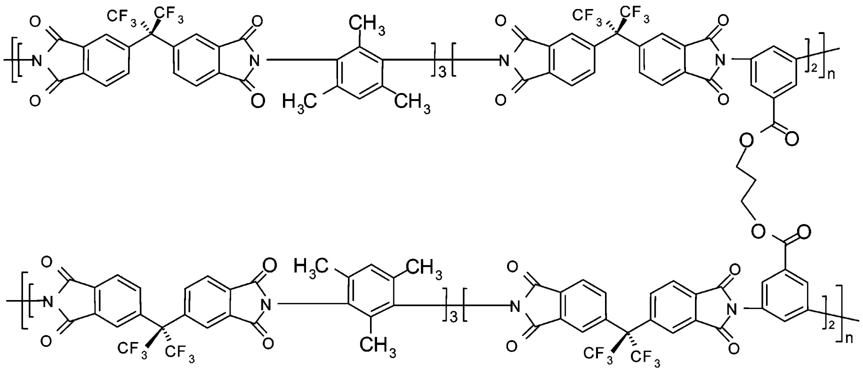

Figure 2. Cross-linked PDMC polymer chain.

Membrane cross-linking was achieved by heating to a temperature between 150 and 300 °C and annealing for 24 h under vacuum. Heating PDMC polymer induces transesterification of the monoester pendent groups attached to the DABA monomer, and these pendent groups react with each other to form cross-links within the polymer matrix[1−3] (see Figure 2). The cross-linking temperature has a direct effect on the membrane properties, and this will be addressed in the Results section. The membrane is then removed from the vacuum oven, and it is ready to be tested.

All permeation measurements were conducted in a variable-pressure, constant-volume apparatus, where the membrane can be housed between an upstream, capable of high-pressure gas introduction, and a downstream, which is kept under vacuum until experiments are initiated. The complete details of the permeation apparatus and its operation have been reported elsewhere.[13,14] Sorption experiments, using the pressure decay method, were also conducted for CO_2 and CH_4 using both un-cross-linked and cross-linked PDMC membranes.[15]

Results

Separation Properties of Cross-Linkable Membranes. Permeability and selectivity are the two key parameters commonly used to characterize polymeric membrane materials.[16−20] Permeability, P_A, reflects the intrinsic productivity of a membrane material and equals the penetrant diffusive flux through the membrane normalized by the difference in partial pressure across the membrane, Δp_A, multiplied by the thickness of the membrane, l:[16−20]

$$P_A = \frac{\text{flux}_A l}{\Delta p_A} \tag{1}$$

Permeability is given in units of barrer, defined as

$$\text{barrer} = 1 \times 10^{-10} \frac{\text{cm}^3\,(\text{STP})\,\text{cm}}{\text{cm}^2\ \text{s cmHg}} \tag{2}$$

Permeation occurs through polymer membranes via a coupled diffusion and sorption mechanism, so the permeability equals the product of the effective diffusion coefficient and sorption coefficient of component A in a given membrane:[16−19]

$$P_A = D_A S_A \tag{3}$$

Sorption in a membrane can be expressed as follows:

$$S_A = \frac{C_A}{p_A} \tag{4}$$

S_A is the sorption coefficient of component “A” in the membrane, C_A is the upstream concentration of component “A” sorbed into the membrane, and p_A is the corresponding partial pressure.[16−19] This equation assumes the downstream pressure is negligible in comparison to the upstream pressure, and these conditions were well-satisfied in the present study.

These equations reflect measures of the condensability, thermodynamic affinity, and kinetic mobility of penetrant “A” in the matrix between the upstream and downstream membrane face;[16,19] however, both coefficients may be a function of feed conditions. Complex effects due to competition between the feed components in mixtures containing carbon dioxide and methane are known, but the effects can be analyzed in terms of the so-called “dual mode sorption and transport models”.[21] Because of the higher affinity of CO_2 for unrelaxed volume in the glassy polymer, such competitive effects are typically apparent as a higher mixed gas selectivity vs pure gas apparent selectivity.

In certain cases, a bulk flow term may be required in the permeability calculation.[22] The separation processes and materials/gases addressed in this work do not involve such convective transport.[23] Such effects would reduce the observed mixed gas selectivity vs the pure gas permeability ratios. Such bulk flow terms are not expected to contribute significantly to the performance observed in the present study, and the mixed gas permeability ratios were actually above those of the pure gases, suggesting that only the competition effect mentioned above may be at play.

Table 1. Separation Properties of Un-Cross-Linked PDMC Membranes and PDMC Membranes Cross-Linked at 220 °C (Permeabilities in barrer; All Tests at ~65 psia and 35 °C)

membrane form	P_{CO_2}	α_{CO_2/CH_4}
un-cross-linked PDMC	17.1 ± 0.9	34.0 ± 0.5
cross-linked PDMC	57.5 ± 2.9	37.1 ± 0.7

Selectivity reflects the intrinsic capability of a polymer membrane to separate one gas from another, and for conditions of negligible downstream pressure, the ideal selectivity, $\alpha_{A/B}$, is given as[16−19]

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{5}$$

The preceding equation is used when the permeabilities of the two pure species are known, which are typically estimated from pure gas experiments. For permeation of actual mixed gases, "A" and "B", the mixed gas selectivity is given by the ratio of the mole fractions of the components in the permeate stream, y, and feed stream, x:[16−19]

$$\alpha_{A/B} = \frac{y_A/y_B}{x_A/x_B} \tag{6}$$

For conditions of negligible downstream pressure, eqs 5 and 6 are equivalent. In the case of polymer membranes, gas molecules diffuse via segmental motions in the polymer matrix. Clearly, molecules of smaller size and molecules with a high affinity for the polymer matrix are favored in transport via this diffusion−sorption mechanism.

Permeation measurements were typically conducted at ~65 psia and 35 °C, with the exception of selected high-pressure experiments to probe plasticization resistance (to be discussed later in the text). Membranes were tested with pure CO_2 and pure CH_4. Mixed gas permeations, which mimic contaminated natural gas feeds, were also run with a 90/10 CH_4/CO_2 gas mixture. Several samples of both un-cross-linked PDMC membranes and PDMC membranes cross-linked at 220 °C for 24 h were analyzed. The results are shown in Table 1. All permeability measurements have an error of ±5%.

There was no exceptional change in PDMC membrane selectivity upon cross-linking, though a measurably significant increase is apparent. The most profound effect of cross-linking on this polyimide is the significant, and highly attractive, increase in membrane permeability. CO_2 permeability increases over 3-fold from the un-cross-linked state to the samples cross-linked at 220 °C. These cross-linking separation property trends have been observed by other researchers.[1−3,22]

The increase in permeability is counterintuitive because cross-linking in rubbery matrices is typically associated with consolidation of the polymer matrix. While consolidation can also be measured in glassy matrices via density measurements, we and earlier researchers hypothesize that the monoester linkages in PDMC polymer redistribute segmental packing of polymer chains in the cross-linked form.[1] Charge-transfer complexes, which can occur when PDMC polymer is heated, may further align polymer chains in local domains through their own attractive forces.[1] Local segmental level "densification" and "de-densification" within the matrix may contribute to restructuring of the free volume distribution and matrix rigidity of the polymer, thereby enabling faster permeation of the smaller and more condensable CO_2. The effect is known to be dependent upon conditions and cross-linking agent, but the details responsible remain somewhat unclear at present. This fact notwithstanding, the effects are clearly significant, reproducible, and helpful for increasing membrane performance.

Table 2. Mixed Gas Data vs Pure Gas Data for PDMC Polymer Cross-Linked at 220 °C (Permeabilities in barrer; All Tests at ~65 psia and 35 °C)

permeation test	P_{CO_2}	α_{CO_2/CH_4}
mixed gas: 10/90 CO_2/CH_4	57.5 ± 2.9	44.8 ± 0.7
pure gas: CO_2 and CH_4 separately	57.5 ± 2.9	37.1 ± 0.7

Table 3. Separation Properties of Cross-Linked PDMC Membranes at Different Temperatures (Permeabilites in barrer; All Tests at 65 psia and 35 °C)

membrane form	cross-linking temp (°C)	P_{CO_2}	α_{CO_2/CH_4}
cross-linked PDMC	220	57.5 ± 2.9	37.1 ± 0.7
cross-linked PDMC	295	77.3 ± 3.9	39.9 ± 0.7

Permeation measurements with a mixture of 10.1% CO_2 and 89.9% CH_4 were performed to test for any competitive effects when both gases simultaneously permeate the PDMC polymer matrix. As CO_2 is both the more condensable and the smaller penetrant, it was presumed the mixed gas CO_2/CH_4 selectivity would be higher than the pure gas value in the absence of plasticization, since CO_2 may "out compete" CH_4, effectively slowing the transport of the bulkier molecule as it permeates through the matrix. Since these competition effects cannot be detected in pure gas measurements, the resulting CO_2/CH_4 selectivity should be higher for mixed gas measurements.[18] The results of the mixed gas permeation support this expectation, as shown in Table 2. Only PDMC polymer cross-linked at 220 °C was tested with mixed gas.

Previous research has shown that separation properties can vary with cross-linking temperature for cross-linkable polyimides.[1,3,25] For PDMC polymer, the minimum cross-linking temperature is 150 °C, though temperatures up to 300 °C have been explored.[25] Above the polymer glass transition (T_g is ~370 °C), the substructure of hollow fiber membrane modules will tend to collapse, so cross-linking temperatures for our dense films were studied at sub-T_g conditions of 220 and 295 °C. This approach allows consideration of conditions of practical importance for eventual applications as an asymmetric membrane. As expected, the selectivity increased slightly and permeability increased by 20 barrer (Table 3) at the higher cross-linking temperature where more complete rearrangements are facilitated.

A study of polyimide powder quantifying the percent of PDMC polymer cross-links at various cross-linking temperatures was completed by Wallace.[23] The current research represents the first dense film study of this material. One can visualize the matrix as progressing to a much more rigid selective environment with concomitant restriction of intersegmental packing and hindrance of chain motion. This favorable combination produces a nonconventional transport environment that favorably deviates from the typical behavior of solution-processable polymers that show reduced permeabilities with higher selectivities.

A permeation isotherm showing the plasticization resistance of the PDMC polymer was completed by testing CO_2 permeability up to 450 psia for both un-cross-linked and cross-linked membranes (Figure 3). An increase in CO_2 permeability with increasing CO_2 pressure is indicative of plasticization and typically signals a loss in size and shape discrimination in the polymer matrix. The isotherm suggests plasticization of the un-cross-linked PDMC membrane occurs at ~150 psia, while the PDMC membrane cross-linked at 220 °C does not show significant signs of plasticization up to ~450 psia. Resistance to 450 psia of pure CO_2 corresponds to several thousand pounds

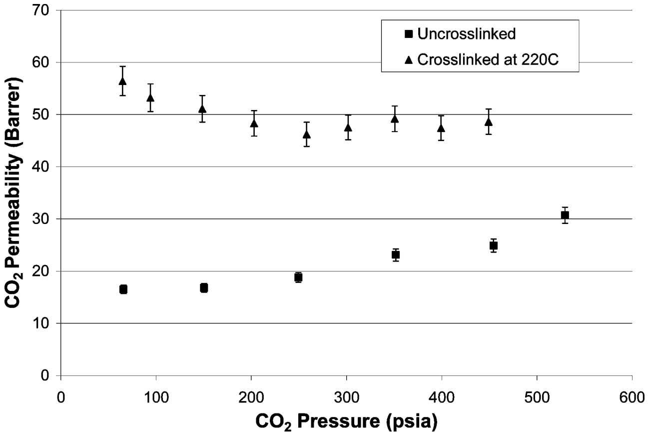

Figure 3. Permeation isotherm for PDMC membranes cross-linked at 220 °C and un-cross-linked PDMC membranes.

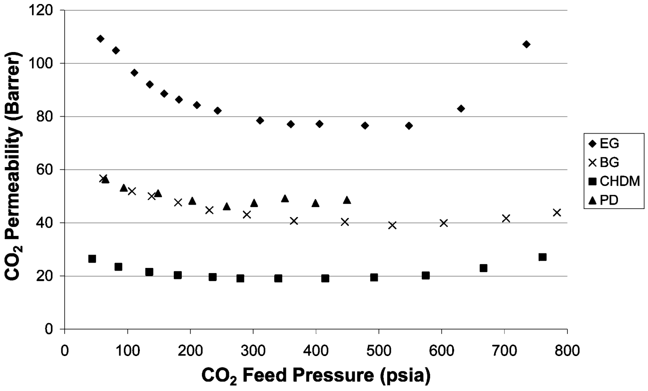

Figure 4. Transport properties of polyimides with various cross-linking agents, all cross-linked at 220 °C. EG = ethylene glycol, BG = butylene glycol, CHDM = 1,4-cyclohexanedimethanol, and PD = 1,3-propanediol (adapted from ref 3).

Table 4. Glass Transition Temperatures of Polyimides Used in This Work

polyimide	T_g (°C)
PDMC, cross-linked at 220 °C	365
3:2 6FDA-DAM:DABA	370

of natural gas for typical cases with 10−20% CO_2 feed content, even at extreme pressures, thereby making these materials of considerable practical importance.

Previous research was explored by Wind on cross-linkable polyimides similar to PDMC polymer.[1−4] Wind's research utilized monoester groups such as ethylene glycol, butylene glycol, and 1,4-cyclohexanedimethanol as cross-linking agents, as opposed to the 1,3-propanediol used in this work. Membranes monoesterified with ethylene glycol were the most permeable but had the lowest percentage of DABA groups successfully converted to monoesterified groups during polymer synthesis, 37% (evaluated via ^{1}H NMR). Butylene glycol had a monoester conversion of effectively 100%, but much lower membrane permeability. 1,4-Cyclohexanedimethanol was inferior with respect to monoester conversion, membrane permeability, and mechanical flexibility. The 1,3-propanediol cross-linker was used in this research after examining Wind's findings, presuming it would exhibit the positive physical and chemical properties of both the ethylene glycol and butylene glycol cross-linking agents and provide a desirable compromise in properties. Figure 4 displays the permeation isotherms of Wind's cross-linking agents vs 1,3-propanediol. It should be noted that Wind's work was conducted on a slightly different polyimide, 2:1 6FDA-DAM:DABA. The two polymers have very similar separation properties; however, since the DAM:DABA ratio is different for the two polymers considered, only general trends are considered in this comparison.

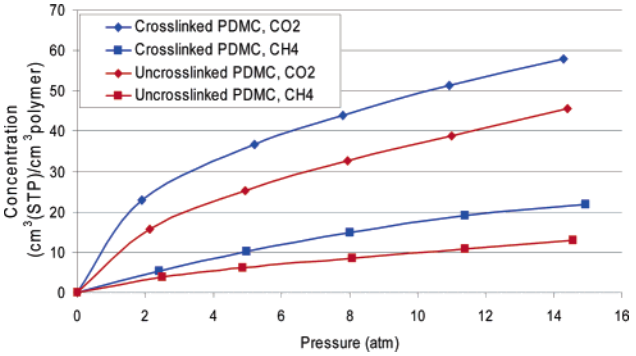

Figure 5. Equilibrium sorption of CO_2 and CH_4 in cross-linked PDMC polymer.

Figure 4 shows the 1,3-propanediol permeability isotherm does lie between the ethylene glycol and butylene glycol data, though it is much closer in value to the butylene glycol data. A high monoester conversion of 96% has been measured for the PDMC polymer using 1,3-propanediol as the cross-linking agent, which is also similar to the conversion associated with butylene glycol. A higher monoester reactivity, which promotes cross-linking, is preferred over enhanced permeation properties for this separation, to maximize plasticization resistance. We feel that both 1,3-propanediol and butylene glycol are attractive cross-linking agents for this system. Overall, the qualitatively greater flexibility noticed with the 1,3-propanediol vs the butylene glycol cross-linked samples recommends it as the preferred cross-linker. More detailed mechanical property and aging studies comparing these two diols would be interesting but are beyond the scope of this study.

Density Measurements. The densities of both the cross-linked and un-cross-linked versions of PDMC polymer were measured using a density gradient column with a density range of 1.320−1.410 g/cm^3. The average density of the cross-linked (220 °C) samples was 1.402 g/cm^3, which is slightly higher than the average of the un-cross-linked samples, which was 1.395 g/cm^3. This can be attributed to densification of the polymer matrix as cross-linking occurs and 1,3-propanediol groups are lost and is further physically evident by the fact that polymer films noticeably shrink during cross-linking. This coincides well with Wind's previous density measurements[1,2] and suggests that the increase in permeability without reduction in selectivity reflects a change in distribution of free volume, rather than a significant increase in the amount of free volume.

Glass Transition Temperatures of Polymers. Differential scanning calorimetry (DSC) was used to identify the glass transition temperatures of both PDMC polymer cross-linked at 220 °C and a nonmodified version of the PDMC polymer, 3:2 6FDA-DAM:DABA. Un-cross-linked PDMC polymer was not tested because it would begin to cross-link during the DSC heating cycle, resulting in an erroneous measurement. The 3:2 6FDA-DAM:DABA material is similar to the un-cross-linked polymer; only the chemical modification required for cross-linking has not been completed. The DSC apparatus used has an error of ±2 °C. The DSC results are shown in Table 4 and are in good agreement with T_g values for similar polymers.[3]

Sorption in PDMC Polymer. Sorption of CO_2 and CH_4 in cross-linked PDMC polymer (220 °C) was measured at up to 15 atm to verify the sorption selectivity of CO_2 vs CH_4 (Figure 5). Evidence for so-called "dual mode" sorption, Langmuir (hole-filling), and Henry's law (dissolution) behavior is apparent in the concave sorption isotherms.[26,27] Moreover, the tendency for CO_2 to sorb much more readily than CH_4 is intensified at elevated pressures in the cross-linked vs the un-cross-linked polymer as Langmuir sites are filled. These results agree well with previous research on similar polymers by Wind,[3] which shows lower sorption in the un-cross-linked polymer than in the cross-linked polymer for both gases (Figure 5).

Conclusions

Cross-linked PDMC polymer was found to be a particularly effective material for separating CO_2 from CH_4 in natural gas applications. The cross-linked polymer displayed permeabilities in excess of 75 barrer (for membranes cross-linked at 295 °C) and CO_2/CH_4 selectivities of almost 45 for mixed gas trials. The polymer's resistance to plasticization under high CO_2 pressures was investigated, and membranes cross-linked at 220 °C were stable up to at least 450 psia. In general, the cross-linked PDMC membranes were found to have significantly higher CO_2 permeability and slightly higher selectivity for the CO_2/CH_4 separation than the un-cross-linked PDMC membranes. Increasing the cross-linking temperature significantly enhanced the permeability of the membranes. When the PDMC membrane permeation results were compared with research that uses other cross-linking groups for CO_2 plasticization resistance, it was discovered that use of either 1,3-propanediol or butylene glycol yields an optimal cross-linked membrane. This is due to their high amount of initial reactivity with the polymer backbone, which leads to a higher amount of cross-linking in the membranes. The 1,3-propanediol studied here appears to be the preferred cross-linker, since it produces materials with qualitatively higher flexibility, which could be important in practical membrane applications. These nontraditional, cross-linked polymer membranes offer high productivity, good selectivity, and plasticization resistance against aggressive CO_2 streams and can perform in the versatile ranges that many industrial applications require.

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References and Notes

(1) Wind, J. D.; Sirand, S. M.; Paul, D. R.; Green, P. F.; Johnson, K. P.; Koros, W. J. *Macromolecules* **2003**, *36*, 1882−1888.
(2) Wind, J. D.; Staudt-Bickel, C.; Paul, D. R.; Koros, W. J. *Ind. Eng. Chem. Res.* **2002**, *41*, 6139−6148.
(3) Wind, J. D. University of Texas at Austin, Austin, TX, 2002; p 214.
(4) Wind, J. D.; Paul, D. R.; Koros, W. J. *J. Membr. Sci.* **2004**, *228*, 227−236.
(5) Cao, C.; Chung, T. S.; Liu, Y.; Wang, R.; Pramoda, K. P. *J. Membr. Sci.* **2003**, *216*, 257−268.
(6) Liu, Y.; Chung, T. S.; Wang, R.; Li, D. F.; Chng, M. L. *Ind. Eng. Chem. Res.* **2003**, *42*, 1190−1195.
(7) Tin, P. S.; Chung, T. S.; Liu, Y.; Wang, R.; Liu, S. L.; Pramoda, K. P. *J. Membr. Sci.* **2003**, *225*, 77−90.
(8) Liu, Y.; Wang, R.; Chung, T. S. *J. Membr. Sci.* **2001**, *189*, 231−239.
(9) Ren, J.; Wang, R.; Chung, T. S.; Li, D. F.; Liu, Y. *J. Membr. Sci.* **2003**, *222*, 133−147.
(10) Hagg, M. B. *J. Membr. Sci.* **2000**, *170*, 173−190.
(11) Eikeland, M. S.; Hagg, M. B.; Brook, M. A.; Ottoy, M.; Lindbrathen, A. *J. Appl. Polym. Sci.* **2002**, *85*, 2458−2470.
(12) Hillock, A. M. W. Georgia Institute of Technology, Atlanta, GA, 2005; p 199.
(13) Moore, T. T.; Damle, S.; Williams, P. J.; Koros, W. J. *J. Membr. Sci.* **2004**, *245*, 227−231.
(14) Damle, S.; Koros, W. J. *Ind. Eng. Chem. Res.* **2003**, *42*, 6389−6395.
(15) Costello, L. M.; Koros, W. J. *Ind. Eng. Chem. Res.* **1992**, *31*, 2708−2714.
(16) Koros, W. J.; Coleman, M. R.; Walker, D. R. B. *Annu. Rev. Mater. Sci.* **1992**, *22*, 47−89.
(17) Robeson, L. M. *Solid State Mater. Sci.* **1999**, *4*, 549−552.
(18) Koros, W. J.; Fleming, G. K.; Jordan, S. M.; Kim, T. H.; Hoehn, H. H. *Prog. Polym. Sci.* **1988**, *13*, 339−401.
(19) Koros, W. J., Chern, R. T., Rousseau, R., Eds.; *Handbook of Separation Process Technology*; John Wiley & Sons: New York, 1987; pp 862−953.
(20) Paul, D. R.; Morel, G. *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: New York, 1981; p 92.
(21) Koros, W. J.; Chern, R. T.; Stannett, V. T.; Hopfenberg, H. B. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1513−1530.
(22) Damle, S.; Koros, W. J. *AIChE J.* **2005**, *51*, 1396−1405.
(23) Kamaruddin, H. D.; Koros, W. J. *J. Membr. Sci.* **1997**, *135*, 147−159.
(24) Rezac, M. E.; Sorensen, E. T.; Beckham, H. W. *J. Membr. Sci.* **1997**, *136*, 249−259.
(25) Wallace, D. W. University of Texas at Austin, Austin, TX, 2004, p 202.
(26) Barrer, R. M. *J. Membr. Sci.* **1984**, *18*, 25−35.
(27) Costello, L. M.; Koros, W. J. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 136−146.

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