Solid-State Covalent Cross-Linking of Polyimide Membranes for Carbon Dioxide Plasticization Reduction

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ABSTRACT: Solid-state covalent cross-linking of 6FDA-based polyimides with esterification reactions is shown to be effective in stabilizing membranes against CO_2 plasticization up to 40 atm feed pressure. The selection of cross-linking agent has a major impact on the cross-linking degree and the gas transport properties. A generalized cross-linking strategy is presented that enables analysis of the effects of the cross-linking agent structure and thermal treatment on pure gas permeation and sorption for CO_2 and CH_4 at 35 °C. The polyimide 6FDA-DAM:DABA 2:1 was cross-linked with ethylene glycol, 1,4-butylene glycol, 1,4-cyclohexanedimethanol, and 1,4-benzenedimethanol to illustrate these effects. The cross-linking degree is evaluated by a combination of solution ^1H NMR and solid-state IR spectroscopy. The annealing temperature is a significant factor in determining the membrane transport properties, since it affects the polymer chain rigidity and free volume distribution. It is believed that this cross-linking approach can be implemented in an industrial hollow fiber formation process since the reaction is shown to occur in the solid state, well below the glass transition temperature.

Introduction

Natural gas is the fastest growing primary energy source throughout the world, and its use is projected to increase 75% by 2020 from the 2002 level.[1] Natural gas is a very versatile feedstock, since it can be converted into a variety of products such as methanol, syngas (CO/H_2), and synthetic crude oil and diesel fuel via Fischer−Tropsch catalysis. It is also a cleaner burning fuel than coal or fuel oils for power plants and home heating, thus reducing sulfur oxide and particulate emissions.

As worldwide demand increases, new gas fields must be developed, many with high levels of CO_2. It is necessary to reduce CO_2 levels below 2 vol % in natural gas because it has no heating value and it causes corrosion in process equipment when in the presence of water (formation of carbonic acid). Amine absorption processes dominate the acid gas removal market, but membranes would be preferable in many cases if they are able to maintain good performance in the presence of aggressive feed streams. There is also significant economic advantage in building hybrid membrane/amine systems.[2]

Hydrocarbon loss is a major cost to gas treatment plants, and it tends to be higher for membranes than for absorption processes. Cellulose acetate membranes are the most commonly used materials for natural gas separations, but they only have CO_2/CH_4 separation factors of 12−15 in the field.[3] Polyimides tend to have high intrinsic separation factors for CO_2 over hydrocarbons (principally methane, ethane, and propane in natural gas), but they cannot maintain this selectivity in feeds with high partial pressures of CO_2 and condensable (C_3+) hydrocarbons. These rigid polymers primarily rely on differences in penetrant diffusion coefficients as their separation mechanism. The CO_2 and heavy hydrocarbons tend to plasticize the membranes, a process in which the polymer chain segmental mobility is increased by the sorption of the plasticizing penetrants and the diffusion selectivity is reduced.[4]

A recent field test showed that effective feed pretreatment is the most important factor for prolonging membrane life in natural gas sweetening applications.[5] However, pretreatment costs can be very significant, and periodically there are upset conditions where the pretreatment systems fail and the membrane is exposed to liquid hydrocarbons. Hydrocarbon aerosols can get past coalescing filters and mist eliminators, consequently damaging the membranes. The development of more solvent-resistant polymeric membrane materials such as those considered here would reduce the pretreatment costs, reduce hydrocarbon loss to the permeate, extend the life of the membrane modules, and ultimately expand the market for membrane systems.

Robust polymeric membranes could also be utilized in a variety of hydrocarbon separations. For example, 1,3-butadiene is currently separated from mixed butenes and butanes by extractive distillation. Polyimide membranes have excellent separation factors for butadiene over butane (and presumably a good selectivity for butadiene over 1-butene, 2-butene, and isobutene), but plasticization occurs at butadiene feed pressures above 0.5 atm at 50 °C.[6] The development of robust membrane materials may allow these polyimides to maintain attractive separation properties at feed pressures relevant for practical applications. Similar plasticization effects are seen for membrane separations of propylene/propane mixtures.[7]

Aromatic and aliphatic components in catalytically cracked naphtha streams are also typically separated by extractive distillation. Pervaporation membranes offer a potentially simple, low-cost alternative or comple-

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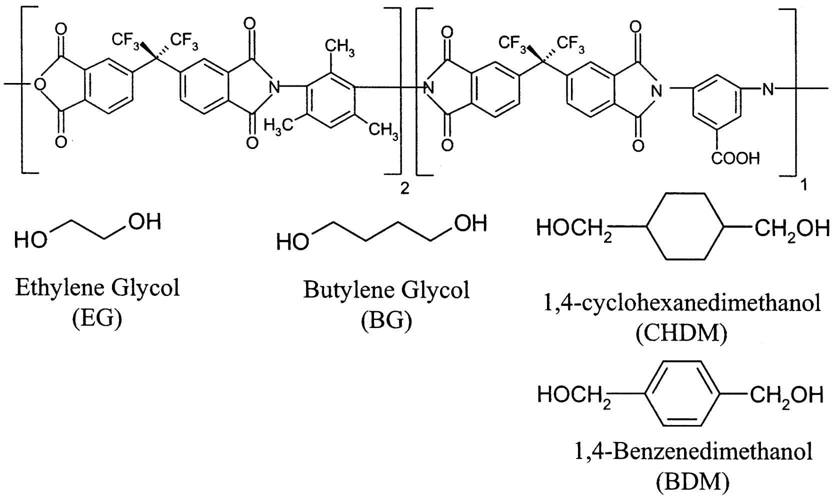

Figure 1. Polymer and cross-linking agent structures.

mentary separation technology to extractive distillation for these streams. Pervaporation would greatly benefit from the development of polymeric membranes that can withstand liquid organic feeds at temperatures of 120–250 °C.[8] Cross-linked polyimides have excellent thermal and chemical stability for these types of separations.[9]

The goal of our work is to minimize plasticization-induced permselectivity losses by cross-linking high-performance polyimides within a framework that could be implemented in the existing industrial process for hollow fiber membranes. Previously, we have reported on the development of a posttreatment procedure for the cross-linking of films containing carboxylic acids with ethylene glycol.[10,11] This approach led to good plasticization resistance, but the large uptake of ethylene glycol in the primary esterification reaction led to large swelling stresses and defects in the film during the removal of the glycol in the transesterification (cross-linking) reaction. When this procedure was applied to asymmetric hollow fibers, the fibers became brittle. The fibers have a delicate porous substructure, and the large uptake of a viscous, high-surface tension fluid is detrimental to this morphology. In this paper a new cross-linking approach is presented which is more general (less reliant on the physical properties of the cross-linking agent) and has better potential for leading to the development of cross-linked hollow fibers due to its more mild processing steps.

To make asymmetric hollow fibers from polyimides, these polymers need to be soluble in common solvents such as 1-methyl-2-pyrrolidinone (NMP) and tetrahydrofuran (THF). Much research has been reported on 6FDA-based polyimides because they have excellent gas separation properties[12] and they are soluble in common solvents. There also have been efforts in spinning 6FDA-based polyimides into hollow fibers.[13,14] The high solubility of these polymers is good from a processing standpoint, but it also means that they are particularly susceptible to plasticization, caused by strong swelling of the polymer matrix by condensable components.

The 6FDA-DAM:DABA 2:1 copolymer was chosen because it offers high permeability with a reasonable CO_2/CH_4 selectivity. Carbon dioxide has a high solubility in this polymer, so it is a rigorous test to see whether covalent cross-linking can inhibit plasticization in membranes where the CO_2 concentration is high.

This cross-linking approach is quite general since the cross-link density may be tuned by the amount of DABA incorporated into the polymer backbone and by selection of the diol cross-linking agent. The cross-linking is carried out in the solid state, thus minimizing the processing complications. This approach may also be attractive for applications where improved stability over wide temperature ranges can be obtained by cross-linking of polyimides, such as in prepregs and composite materials for aerospace systems.[15]

Background

Permeability is a measure of the membrane's intrinsic productivity, and selectivity is a measure of the separation efficiency. For dense films, the flux (n_A), normalized by the transmembrane partial pressure (Δp_A) and thickness (l), is defined as the permeability (P_A)

$$P_A = n_A \frac{l}{\Delta p_A} \tag{1}$$

Permeability values are reported in Barrers [1 barrer = 10^{-10} (cm^3 (STP) cm)/(cm^2 cmHg s)].

The *ideal* selectivity (i.e., pure gas feeds) between two gases A and B is defined as the ratio of their permeabilities

$$\alpha_{AB} = P_A/P_B \tag{2}$$

The permeability can be written as the product of the diffusion coefficient, D, and the solubility coefficient, $S_A = C_A/p_A$

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

From this relationship the *ideal* selectivity is

$$\alpha_{AB} = \frac{D_A S_A}{D_B S_B} = \alpha_D \alpha_S \tag{4}$$

Experimental Section

Polymer Synthesis and Characterization. Figure 1 shows the structures of the 6FDA-DAM:DABA 2:1 polyimide and the cross-linking agents. The polycondensation of (4,4′-hexafluoroisopropylidene)diphthalic anhydride (6FDA) with diaminomesitylene (DAM) and 3,5-diaminobenzoic acid (DABA) in NMP at room temperature was followed by a chemical imidization at 100 °C with an equimolar mixture of triethylamine and acetic anhydride, described in detail elsewhere.[16] The glass transition temperatures (T_g) were determined with

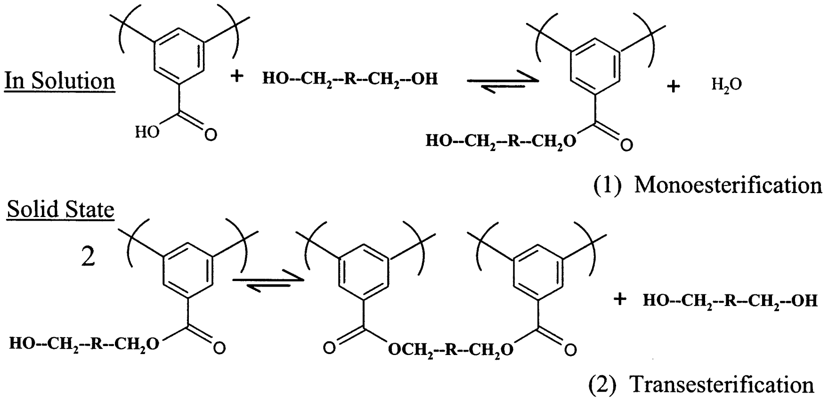

Figure 2. Covalent cross-linking scheme for DABA-containing poyimides.

a Perkin-Elmer DSC 7 with a heating rate of 20 °C/min under a N_2 purge, and the densities of the polymers were measured in a density gradient column filled with aqueous calcium nitrate solutions at 30 °C.

Films for permeation and sorption (40−70 μm thick) were prepared by casting filtered (0.2 μm pore size, Cole-Parmer) 2 wt % solutions of polymer in tetrahydrofuran (THF) onto a Teflon casting dish. After evaporation of the solvent, the film samples were dried at various temperatures under vacuum for 24 h.

The copolymer compositions and esterification conversions were measured with a Bruker AC250 ^{1}H NMR operating at 250 MHz with DMSO-d_6 as the solvent. The infrared (IR) spectra were obtained with a Nicolet Magnum 550 IR spectrometer with a N_2 purge. Samples for IR were prepared by making a 10−12 wt % polymer solution in 4-methyl-2-pentanone and adding drops of the solution onto a wafer spinning at 3000 rpm (Photo Resist spinner by Headway Research) until the film thickness was ~1 μm. These films were dried under the same conditions as those of the free-standing films.

Steady-state gas permeabilities were determined at 35 °C with a constant volume, variable pressure apparatus.[17] The membrane area was measured with Scion Image software, and the film thickness was measured with a micrometer (Ames). Permeation measurements for feed pressures above 15 atm were made once every 24 h for consistency in probing any slow relaxations involved in plasticization. Previously, it was shown that plasticization is a function of time and pressure, primarily with respect to changes in the diffusion coefficient.[11,18] Sorption measurements were made at 35 °C by the pressure decay method.[19]

Cross-Linking. The reaction scheme for covalent cross-linking of DABA-containing polyimides is shown in Figure 2. This mechanism is similar to that of solid-state polymerization of polyesters such as poly(ethylene terephthalate) and poly(butylene terephthalate).[20] The monoesterification reaction was carried out at 140 °C for 18 h in NMP with 5 mg of *p*-toluenesulfonic acid per gram of polymer for catalysis. The diol:DABA molar ratio was 40−70 in order to push the reaction equilibrium toward formation of the ester product. The reaction flask was fitted with a condenser and a continuous nitrogen purge. The esterification reaction is acid-catalyzed,[21] and it has been shown that *p*-toluenesulfonic acid increases the equilibrium conversion and speeds up the reaction kinetics for esterification reactions.[22]

After completion of the monoesterification reaction, the polymer solution was cooled to room temperature, and the polymer was precipitated in methanol, blended, washed, and dried at 70 °C for 24 h under vacuum. The temperature was kept low to prevent cross-linking of the polymer particles. The polymer was then cast into a film from THF, and the films were annealed at elevated temperatures under vacuum to activate the cross-linking reaction. In the transesterification step, the equilibrium was pushed to the formation of cross-links by pulling vacuum and removing the volatile diol from the film. All cross-linked films were annealed for 24 h under vacuum (at various temperatures).

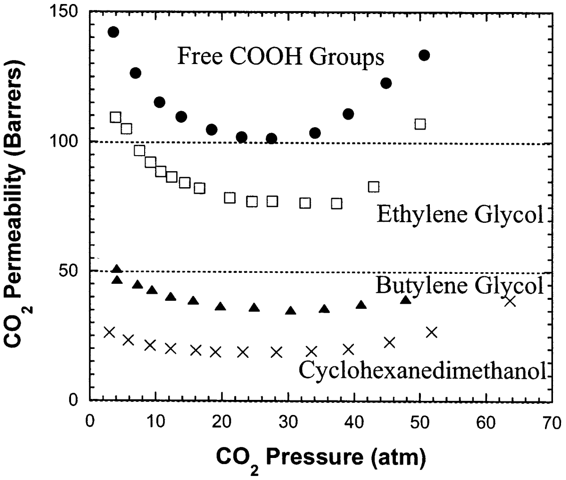

Figure 3. CO_2 permeation isotherms at 35 °C for various 6FDA-DAM:DABA 2:1 membranes untreated, cross-linked with ethylene glycol, butylene glycol, and 1,4-cyclohexanedimethanol.

Results and Discussion

Permeation. It is a common perception that cross-linking typically decreases the permeability of polymeric membranes.[23] In general, this expectation is fulfilled for rubbery polymers but not necessarily for glassy polymers. Indeed, it has been shown that cross-linking of DABA-containing copolyimides with ethylene glycol can lead to an *increase* in the permeability without sacrificing selectivity.[10,11] The effect of cross-linking on the membrane transport properties is highly dependent on the cross-link density, the polymer structure, and the properties of the cross-linking agent.

Pure gas CO_2 isotherms for the un-cross-linked and cross-linked 2:1 polymers are shown in Figure 3. It is clear that the physical properties of the cross-linking agent play a major role in determining the final cross-linking degree. The 6FDA-DAM:DABA 2:1 polymer has very high CO_2 sorption and diffusion coefficients. Previously, it was shown that cross-linking with ethylene glycol increased the CO_2 permeability of some polyimides with permeabilities that are 4 times[11] and 12 times[10] smaller than that of the un-cross-linked 2:1 polymer reported here. By starting with such an “open” polymer, it is not as easy to increase the permeability by inserting cross-linking agents between the polymer chains. In general, covalent cross-linking decreases the

Table 1. 6FDA-DAM:DABA Membrane Properties at 35 °C and 10 atm

polymer	cross-link agent	CO_2 permeability (Barrers)	CO_2/CH_4 ideal selectivity
6FDA-DAM	none	290	21
6FDA-DAM: DABA 2:1	none	127	29
2:1	ethylene glycol	90	30
2:1	butylene glycol	44	34
2:1	1,4-cyclohexane-dimethanol	21	30
1:2	none	29	45
6FDA-DABA[a] [40]	none	3.4	63

[a] Feed pressure of 2 atm.

sorption of CO_2 and CH_4, but changes in the permeability are mainly affected by changes in the diffusion coefficients.

Table 1 shows the effect of the copolymer composition on the CO_2 permeability and CO_2/CH_4 selectivity for a feed pressure of 10 atm. The untreated 6FDA-DAM:DABA membranes show the typical copolymer behavior. As more DABA is incorporated into the backbone, both permeabilities decrease, but the CO_2/CH_4 selectivity increases. The permeability/selectivity tradeoff for various esterification treatments of the 2:1 do not follow a simple relationship, as has been discussed.[24,25] The complex morphology of the cross-linked membranes is dependent on the cross-linking agent length and flexibility and the thermal treatment. These characteristics affect its reactivity in the solid state and the polymer packing characteristics (free volume distribution, etc.).

Sorption. The solubility coefficient for gas sorption in glassy polymers is often described by the dual mode model[26]

$$S_A = \frac{C_A}{p_A} = k_{DA} + \frac{C'_{HA} b_A}{1 + b_A p_A} \tag{5}$$

where C_A is the concentration, p_A is the partial pressure, k_{DA} is the Henry's law constant, C'_{HA} is the Langmuir capacity constant, and b_A is the Langmuir affinity constant.

The effect of cross-linking on the sorption of CH_4 and CO_2 is shown in Figure 4. These data indicate that cross-linking causes a significant decrease in the sorption of both gases and a reduction in the solubility selectivity. For a series of un-cross-linked glassy polymeric membranes, it has been reported that plasticization in permeation experiments occurs when the CO_2 concentration at the upstream face of the membrane is 37 ± 7 cm^3 (STP)/cm^3 polymer at 25 °C.[27] For the highly sorbing 6FDA-DAM:DABA 2:1 polymers, CO_2 concentrations in the cross-linked membranes may exceed 105 cm^3 (STP)/cm^3 without seeing plasticization in the permeation measurements. It seems likely, therefore, that control of the polymer chain segmental mobility, rather than an absolute sorption level, is the key to controlling plasticization, even in the presence of very high CO_2 concentrations.[11]

Interestingly, the sorption isotherms for the covalently cross-linked polymers tend to show an upturn at pressures above 25 atm, whereas the permeation isotherms remain flat. This is contrary to the conventional wisdom that the permeation isotherm will reach its minimum value at lower pressures than that of the sorption coefficient isotherm. Stern and Saxena modified the dual mode transport model with a diffusion coefficient that is an exponential function of concentration to describe this plasticization behavior.[28] Later, Mauze and Stern modified the model to replace the total concentration by the so-called "dissolved" concentration, neglecting the concentration associated with Langmuir sorption, while maintaining the exponential diffusion expression.[29] The response seen here in which the sorption isotherm shows an upturn while the permeability coefficient remains flat supports the expectation that the plasticization effects are primarily associated with the diffusion coefficient. It is significant that the thermal history of the polymer has a huge effect on this plasticization behavior, for both the un-cross-linked and monoester polymers.[30,31]

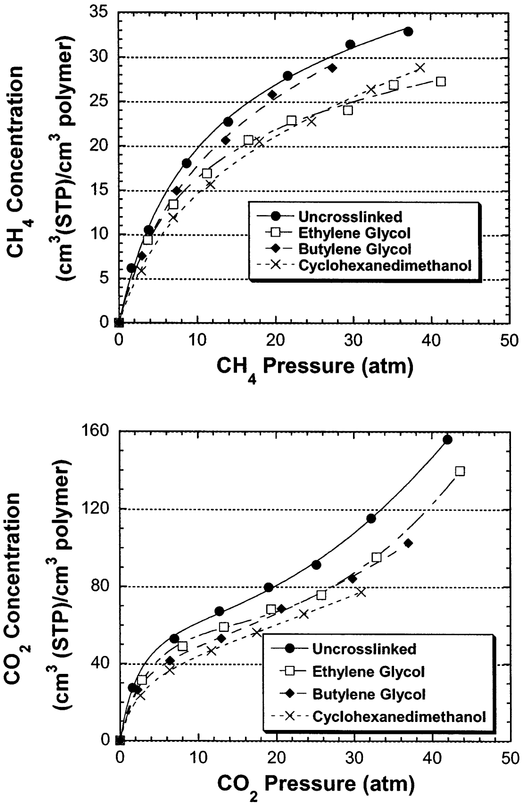

Figure 4. CH_4 and CO_2 sorption isotherms at 35 °C for various 6FDA-DAM:DABA 2:1 membranes untreated, cross-linked with ethylene glycol, butylene glycol, and 1,4-cyclohexanedimethanol.

Decoupling of Esterification and Cross-Linking Effects

Permeation. The data in Figure 5 show that the thermal treatment can significantly affect the permeability. The cross-link density for the films cross-linked with 1,4-cylohexanedimethanol (CHDM) and 1,4-butylene glycol (BG) increases at higher temperatures (as confirmed by IR spectroscopy) and so does the permeability, again contrary to the conventional view that cross-linking tends to decrease the permeability. These results were reproduced in pure gas permeation and confirmed with 50/50 CO_2/CH_4 mixed gas permeation (not described here). With annealing at 100 °C, the pendant ester groups occupy free volume and reduce the CO_2 permeability relative to that of the untreated polymer with free carboxylic acid groups. However, for annealing at 295 °C, it appears that the packing disruption introduced by insertion of the cross-linking

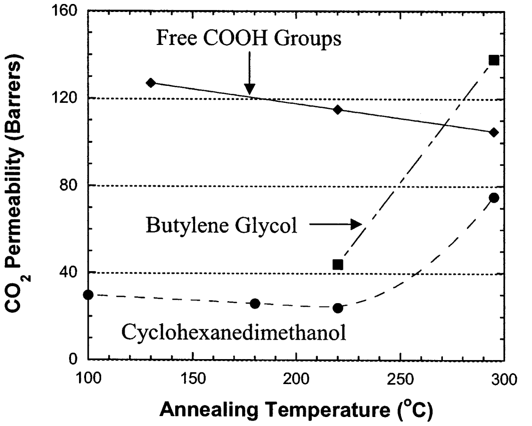

Figure 5. Effect of annealing temperature on CO_2 permeability isotherms for 6FDA-DAM:DABA 2:1 membranes, untreated and monoesterified. Permeabilities were measured at 10 atm and 35 °C.

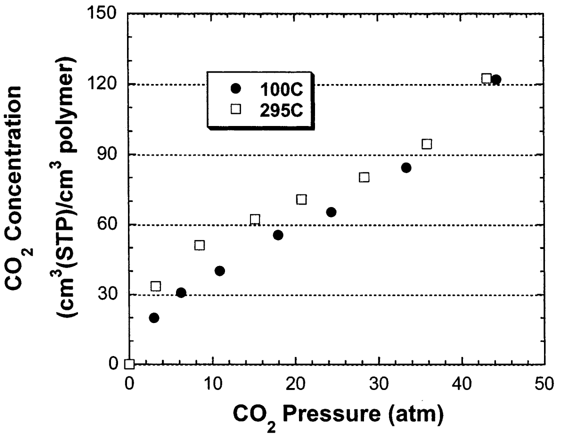

Figure 6. Effect of annealing temperature on CO_2 sorption at 35 °C in 6FDA-DAM:DABA 2:1 butylene glycol monoester.

molecules between the polymer chains tends to increase the permeability. The free volume may also increase due to the removal of pendant diol groups during the transesterification reaction. The increase in the permeability is consistent with the recently reported results for 6FDA-6FpDA:DABA-organosilicate membranes, which was performed independently from our research.[32] In their work, Hibsham et al. annealed the membranes at 400 °C, which was above the T_g, thus providing much more mobility for the cross-linking reactions to occur. These somewhat counterintuitive results provide a way to tune the free volume distribution and to stabilize membranes against plasticization.

Sorption. The data in Figure 4 suggest that cross-linking decreases the CO_2 sorption. However, the esterification treatments simultaneously change the polymer composition, confounding the true cause of the reduced sorption. By annealing monoester films at various temperatures, the effect of cross-link density on the sorption isotherms can be quantified. When the films are annealed at 100 °C, there is essentially no cross-linking. When the films are annealed at 295 °C, there is significant cross-linking.

Figure 6 shows the effect of the annealing temperature on the CO_2 sorption isotherms for the 6FDA-DAM:DABA 2:1 butylene glycol monoester. For a given starting monoester polymer, films that are annealed at higher temperatures and have more cross-linking have slightly *higher* sorption. To analyze the sorption within the dual mode framework, the model was fit for CO_2 pressures below 25 atm. Upon inspection of the dual mode parameters in Table 2, it is clear that greater cross-linking levels lead to an increase in the Langmuir capacity constant (C'_H) and a decrease in the Henry's law coefficient (k_D) values.

Table 2. CO_2 Dual Mode Sorption Parameters for 6FDA-DAM:DABA 2:1 Butylene Glycol Monoester at 35 °C[a]

annealing temp (°C)	k_D (cm^3 (STP)/cm^3 polymer atm)	C'_H (cm^3 (STP)/cm^3 polymer)	b (1/atm)
100	1.81	24.5	0.54
220	1.66	36.0	0.78
295	1.35	46.8	0.55

[a] The model was fit for pressures below 25 atm.

These sorption results are consistent with the permeation data (Figure 4), in that this cross-linking increases the concentration of trapped unrelaxed free volume, resulting in increased permeability and sorption via the hole-filling (Langmuir) mode. By keeping the chains rigid, the CO_2 sorption via the normally dissolved mode (Henry's law) associated with the more or less equilibrium packing of segments in the glassy matrix is depressed, and the CO_2 permeability is stabilized at feed pressures up to 50 atm. The key to controlling plasticization, therefore, is to control the polymer segmental mobility by controlling swelling, not sorption.[30]

Spectroscopic Investigation of Cross-Linking Degree

Cross-linking clearly has a significant impact on the transport properties of polyimide membranes. By dividing the esterification reactions into two steps (solution and solid state), the esterification yields in both reaction steps can be analyzed. In this way we can contrast the diol reactivity in the solution and solid phases to understand how to maximize the cross-linking conversion and to have a favorable tradeoff with the effect on transport properties.

NMR Spectroscopy. The degree of esterification may be quantified by ^1H NMR. The methylene proton nearest the ester bond appears at ~4.2−4.4 ppm in the spectra, and this does not overlap with any other peaks from the polymer or solvent. The conversion of carboxylic acids to esters may be calculated by taking the ratio of the area of this methylene peak with that of the aromatic protons compared with the theoretical ratios at complete conversion from the known copolymer composition. The aromatic proton from the DAM moiety is clearly resolved at 6.43 ppm, so the internal consistency of the conversion calculation can be checked by the inclusion and exclusion of this peak from the areas of the aromatic protons. A representative NMR spectrum of a monoester is shown in Figure 7, where the conversion is 100% for the 2:1 polymer esterified with butylene glycol. The conversion for this particular polymer may also be calculated from the peaks arising from the "a" and "b" protons in the butylene glycol moiety, as shown in Figure 7. Table 3 shows the monoester conversions for the various diols.

The monoesterification reaction in NMP gives the reactants good mobility to react, and the large excess of glycol (40−70 times the stoichiometric amount) should clearly favor the formation of the ester product. However, alcohols can form complexes with NMP, and

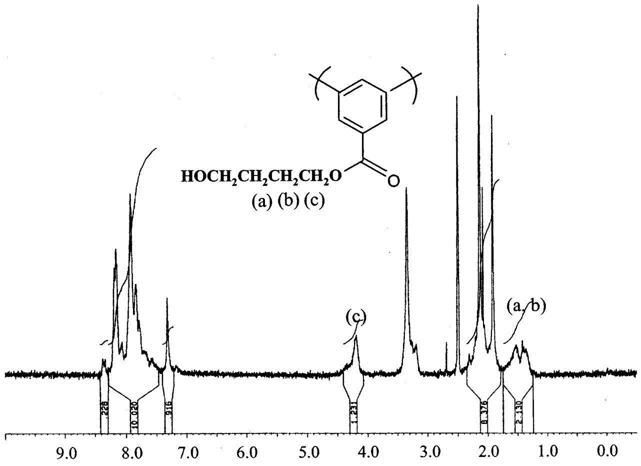

Figure 7. ^{1}H NMR spectrum for 6FDA-DAM:DABA 2:1 butylene glycol monoester.

Table 3. Monoester Conversions for DAM:DABA 2:1

cross-linking agent	conversion (%)
ethylene glycol	37
butylene glycol	100
1,4-cyclohexanedimethanol	50
1,4-benzenedimethanol	16

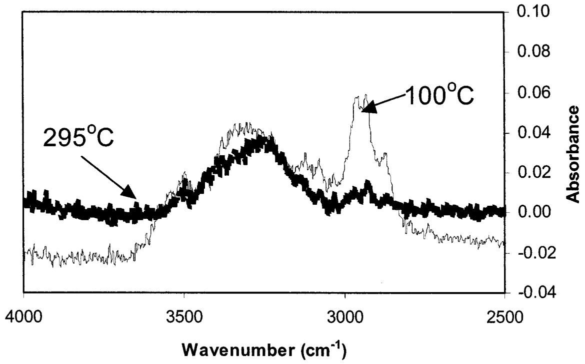

Figure 8. IR spectra for 6FDA-DAM:DABA 2:1 butylene glycol monoester annealed at 100 and 295 °C.

Table 4. Polymer Properties for 6FDA-DAM:DABA 2:1 with Various Chemical Treatments

cross-linking agent	thermal treatment (°C)	T_g (°C)	density (g/cm^3)	CO$_2$ permeability (Barrers)[a]	CO$_2$ diffusion coefficient (10^{-8} cm^2/s)[a]
none	220	364	1.388	115	14.3
butylene glycol	100	361	1.394	*b*	*b*
butylene glycol	220	363	*b*	44	6.89
butylene glycol	295	350	1.395	138	19.8

[a] Pure CO$_2$, feed pressure of 10 atm. [b] Not measured.

this may affect their reactivity in solution.[33] The aromatic ring in 1,4-benzenedimethanol is electron-withdrawing, and it shows the lowest conversion due to its poor nucleophilicity.

The monoesterification reaction is carried out at lower temperatures and with much lower acid concentrations than is typically used for esterification reactions with diols. An extensive review of esterification reactions by Fradet and Marechal showed that most lightly catalyzed esterifications of aromatic carboxylic acids have been carried out at temperatures above 180 °C.[34] To obtain higher conversions, the monoester reaction could be carried out at higher temperatures, and water could be distilled from the solution during the reaction.

IR Spectroscopy. When the monoester film is dried under vacuum at elevated temperatures, a transesterification (i.e., cross-linking) reaction is activated. In the glassy solid-state, the reactant mobility is much lower, and the equilibrium can only be pushed by removing the volatile glycol from the film. The cross-linking degree is, therefore, limited by the intrinsic reactivity of the alcohol group and its mobility in the solid state to attack the ester carbon atom. This is in contrast to the solid-state polymerizations of poly(ethylene terephthalate) and poly(butylene terephthalate) where the reaction temperature is well above the glass transition temperature, and there is much greater reactant mobility.[20] It is somewhat surprising that adequate segmental mobility exists well below the nominal glass transition temperature of the polymer (~365 °C) for the cross-linking process to occur, but the evidence is strong that this process occurs due to the free volume effects, plasticization resistance, and the IR results found here.

The O−H stretching absorption from the carboxylic acid in the DABA moiety and the pendant hydroxyl in the monoester is a broad peak in the region 3000−3600 cm^{-1}, agreeing well with the literature values.[35] The solid-state cross-linking reaction can be monitored by IR spectroscopy. Figure 8 shows the chemical modifications to the polymer by the monoesterification and transesterification reactions for the 2:1 polymer. The IR technique is only semiquantitative in determining the cross-linking degree, because the OH group can be involved in hydrogen bonding, thus complicating the quantitative analysis. The cross-linking conversion can be observed by the diminishing peaks at 3300 and 2950 cm^{-1} with the cross-linking reaction. These peaks correspond to the aliphatic C−H stretch and the O−H stretch from the BG moieties. The density of these groups is decreased as the transesterification cross-linking reaction proceeds.

T_g and Fractional Free Volume. For rubbery polymers, cross-linking typically increases the T_g of polymers.[36] However, covalent cross-linking of the copolyimides has a negligible impact on the glass transition temperature. It also appears that the T_g does not scale with the cross-link density because the BG monoester dried at 295 °C is much more highly cross-linked than the film annealed 100 °C, yet they have very similar T_g values. This is again contrary to conventional wisdom for more flexible polymer backbones.[36] The effect of cross-linking with butylene glycol on the copolyimide density, T_g, and CO$_2$ permeability and diffusivity is shown in Table 4.

It is rather surprising that the density does not change when the BG monoester is annealed at 295 °C, although the permeability and Langmuir capacity constant increase significantly, suggesting an increase in unrelaxed free volume. These results are consistent with the recently reported results on other polyimides cross-linked via a condensation reaction.[32] The occupied volume cannot be accurately calculated for the cross-linked samples because the yield of the cross-linking reaction has not been quantitatively determined. However, if the transesterification reaction went to completion, the polymer density should have decreased by 3%, which would be easily detected in the density measurement.

The permeability coefficients are likely to be related to the free volume distribution as well as the absolute amount of fractional free volume. Techniques such as positron annihilation lifetime spectroscopy (PALS) have shown good correlation with the CO_2 diffusion coefficient in polyimides[37] and may be promising for the cross-linked polyimides as well. It would be of great interest to see how cross-linking changes the free volume distribution via in-situ PALS in the presence of both plasticizing and noninteracting penetrants.[38,39]

Conclusions

A generalized solid-state covalent cross-linking procedure has been developed to analyze the effects of the length and flexibility of various diol cross-linking agents on polyimide membrane transport properties, especially under high-pressure feeds where plasticization needs to be suppressed. Cross-linking with butylene glycol and cyclohexanedimethanol is effective in controlling the CO_2 permeability up to 40 atm feed pressure by controlling the polymer chain mobility, not necessarily by suppressing sorption. The monoesterification and transesterification reactions were monitored with NMR and IR spectroscopy. Cross-linking tends to decrease sorption in the dissolution mode (Henry's law) and increase sorption in the hole-filling (Langmuir) mode. This increase in free volume is especially apparent when the membrane is cross-linked with butylene glycol at 295 °C, where the permeability increases by over a factor of 3 compared to that film annealed at 220 °C.

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