Increased Molecular Weight of a Cross-Linkable Polyimide for Spinning Plasticization Resistant Hollow Fiber Membranes

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Received April 11, 2008; Revised Manuscript Received July 2, 2008

ABSTRACT: A propanediol monoester cross-linkable (PDMC) polyimide was synthesized for high-speed hollow fiber membrane spinning. The membranes were plasticization resistant and asymmetric, useful for natural gas purification. In fabricating the membrane material, it was found that significant chain scissioning could occur during the monoesterification reaction, which caused problems in subsequent membrane formation processes. Using NMR, GPC, and FTIR, it was observed that hydrolytic degradation occurs at the imide rings from the small amount of water produced during monoesterification. Workable synthesis conditions were found that enabled the cross-linkable polyimide to be synthesized with high conversions and without loss in the polymer molecular weight. The preservation of a high molecular weight (M_w >100 000) was shown to be favorable for hollow fiber membrane formation.

Introduction

For polymer membranes to be used in challenging gas separations, they must not only exhibit good separation properties but also be durable. Membranes are attractive for natural gas separations because of their ease of operation, compactness, and low maintenance costs. Aromatic polyimides are favorable because of their rigidity,[1] which makes them size and shape selective to penetrant molecules such as CO_2 over CH_4. However, to be used for natural gas purification, the membranes must be resistant to plasticization caused by exposure to high partial pressures of CO_2 and/or the presence of highly sorbing contaminants in the feed. Plasticization causes the polymer to swell and increases chain segmental motion, eventually causing the polymer to lose its size and shape discriminating ability.[2−4] This becomes apparent as a concomitant increase in permeability of both CO_2 and CH_4, simultaneously with a loss in CO_2/CH_4 selectivity. The loss in selectivity causes decreased product recovery, since more CH_4 product leaves with the CO_2 permeate.

Covalent cross-linking using a class of cross-linkable polyimides[2,3,5−17] has been shown to increase plasticization resistance mostly in dense films[2,3,5−13] by suppressing the degree of swelling and segmental chain mobility in the polymer, thereby preserving the selectivity of the membrane. This class of cross-linkable polyimides utilizes a diaminobenzoic acid (DABA) group in the polyimide backbone as a site for interchain cross-linking. The cross-linking agent is a diol such as ethylene glycol, 1,3-prodanediol, propylene glycol, 1,4-butanediol, or 1,4-cyclohexanedimethanol. The choice of the diol is dependent on its reactivity and affects the separation properties of the membrane made from it. The effects of the cross-linking agent has been studied by previous researchers,[5,7] and the choice for this study was 1,3-prodanediol based on work done by Hillock et al.[7] This material, termed "PDMC" (propanediol monoester cross-linkable), showed the best balance between its reactivity in cross-linking and resultant effects on transport properties in dense film membranes. This study focuses on extending the dense film success with this polymer to asymmetric hollow fibers, since this is an industrially preferred form of the membrane.[19,20] Asymmetric hollow fibers provide high fluxes required for productive separations due to the ability to reduce the separating layer to a thin integral "skin" on the outer surface of the membrane. Such small diameter, cylindrical morphologies also can provide high surface area to volume ratios and high packing densities, with the ability to withstand large transmembrane driving force pressure differences.

To achieve the economies of scale required to make the hollow fiber spinning process more cost-effective, spinning speeds greater than about 50 m/min are preferred.[20,21] In previous studies using these cross-linkable polymers, higher spinning speeds were not achieved due to low viscosity of the polymer solutions used in making the fibers.[14] There are ways that may alleviate this problem, such as with the use of viscosity-enhancing salts, e.g. lithium nitrate, or by increasing polymer concentration in the dopes. However, these methods have limitations and consequential negative effects on the transport properties of the final membrane if used extensively. Moreover, viscosity-enhancing salts alone do not create the level of polymer chain entanglement in solution required to get adequate viscoelasticity for high-tension spinning. A more direct approach by increasing the cross-linkable polymer molecular weight to enhance solution viscoelasticity and thus spinnability is addressed in this study.

To form membranes into high pressure, high surface area/volume hollow fibers, fiber dimensions of about 300 μm or less are preferred.[22,23] To achieve fibers with smaller radial dimensions, the fiber must withstand significant tension during drawing along the spin line. The tension applied during spinning is related to the nominal draw ratio, defined as the ratio of takeup rate to the rate of extrusion from the spinneret. In previous studies using these cross-linkable polymers, nominal draw ratios could only go as high as 9 before spin line breakage was observed due to the lack of dope strength.[14]

The reduced viscosities in previous studies reflected the relatively low polymer molecular weights, which were typically about 30 000 (M_w).[13,24] This work focuses on developing the PDMC polymer for spinning into highly productive asymmetric hollow fibers at industrially relevant spinning speeds and testing the resultant cross-linked fibers for plasticization resistance against high CO_2 pressures, typical of aggressive natural gas feeds. The viability of using the improved molecular weight in

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10.1021/ma800813w CCC: $40.75
Published on Web 08/16/2008

achieving the intrinsic polymer separation capabilities in defect-free hollow fiber membranes made from them is also demonstrated. Gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) spectroscopy, and Fourier transform infrared spectroscopy (FTIR) were used to monitor molecular weights, reaction yields, and functional groups, respectively, during the synthesis reactions to develop the high molecular weight cross-linkable polymer. Gas permeation was used to evaluate the cross-linked fiber performance for plasticization resistance and in determining the separation properties of the fibers made from the cross-linkable polymer.

The synthesis process occurs by condensation polymerization of monomer units in solution followed by imidization, which occurs thermally. The imidized polymer is subsequently subjected to another reaction, monoesterification, wherein the polyimide is made cross-linkable. During the monoesterification reaction, using the previous method, molecular weight was found to drop due to chain scission.[16,17] In this study, it was found that more rigorous elimination of the water produced in esterification plays a key role in preventing this loss in molecular weight. The effect of reducing the monoesterification catalyst concentration was also shown to be important in preventing the molecular weight loss. This article describes a practical optimization process in making such cross-linkable polyimides.

Background

Gas transport in polymer membranes is described as a solution-diffusion mechanism. Specifically, gas molecules dissolve into the polymer at the upstream, then diffuse under the influence of a chemical potential gradient, and finally desorb from the polymer at the downstream. Two key intrinsic properties, the so-called "permeability" and "selectivity", are commonly used to evaluate the performance of membranes. Permeability is a measure of the membrane material's intrinsic productivity and equals the fugacity and thickness normalized flux, described mathematically by the equation

$$P_i = \frac{n_i l}{\Delta f_i} \tag{1}$$

In eq 1, n_i represents the flux of component "*i*" gas molecules through the membrane, l represents the membrane thickness, and Δf_i is the transmembrane fugacity difference of component i that acts as the driving force across the membrane. In many cases, the fugacity is the same as the partial pressure. In asymmetric hollow fibers, the actual membrane thickness is not readily known, so productivity in these membranes is described by the permeance, which is simply the fugacity normalized flux as written in the equation

$$\left(\frac{P}{l}\right)_i = \frac{n_i}{(\Delta f_i)} \tag{2}$$

The permeability is commonly reported in the unit called barrer, which is defined as 10^{-10} [cm^3 (STP) cm]/[cm^2 s cmHg], and the permeance unit is commonly the GPU, which is defined as 10^{-6} [cm^3 (STP)]/[cm^2 s cmHg]. The permeability for such a sorption−diffusion process can also be described in terms of the governing kinetic and thermodynamic parameters, namely the diffusion coefficient, D_i, and the solubility coefficient, S_i, by the equation

$$P_i = D_i S_i \tag{3}$$

The selectivity or "permselectivity" is a measure of the membrane's separation capability or efficiency. The permselectivity of a membrane is described by the ratio of the component permeabilities or permeances:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{(P/l)_i}{(P/l)_j} = \frac{D_i S_i}{D_j S_j} \tag{4}$$

Experimental Section

Polymer Synthesis. The cross-linkable polyimide synthesis starts with synthesizing the polyimide backbone, namely 6FDA−DAM:DABA (3:2), via a polycondensation reaction by addition of the dianhydride, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), and diamines, 2,4,6-trimethyl-1,3-diaminobenzene (DAM) and 3,5-diaminobenzoic acid (DABA), in solution. The 6FDA and DAM monomers were purified by sublimation prior to use. The DABA monomer was used as received at 99.9% purity. The solvent typically used is *N*-methylpyrrolidone (NMP). In this study, the ratio of DAM to DABA is 3:2, which translates to a 40% DABA content of the diamines. The reaction stoichiometry can be adjusted to change the DABA content and thus the cross-link density since the DABA monomer is the site for cross-linking, but doing so has subsequent effects on processing. For instance, higher DABA contents make the polymer more hydrophilic, thereby increasing the time for a solution made from the polymer to phase separate in an aqueous medium such as the quench bath during fiber spinning. The polycondensation reaction is very sensitive to water, and care must be taken to ensure that there is minimal exposure to moisture. The reaction produces polyamic acid, the precursor to the polyimide. The polyamic acid is characterized by the presence of amide and carboxylic acid groups on the chain. To form the polyimide from the precursor, the reaction solution can be heated up to high temperatures (180−200 °C) in solution to form the imide rings on the polyimide, essentially dehydrating the polyamic acid. An azeotropic drying agent such as *o*-dichlorobenzene (*o*-DCB) is routinely used to aid in the removal of water formed from the reaction, thus driving the reaction forward. Here ∼2.5 mL of *o*-DCB per gram of polymer was used for imidization. Typically, the polyimide is precipitated and dried at 100 to 120 °C under vacuum prior to further processing. However, as will be discussed in the Results section, precipitation here is not necessary. The solids concentration of the polymer in solution is about 20 wt % during the polymerization reaction and about 13 wt % during imidization. The 6FDA, DAM, and DABA monomers and the reaction sequence are shown in Figure 1.

The cross-linking method pursued here occurs in two steps: (1) the creation of a monoester "cross-linkable" polyimide, which can be processed in solution into a membrane form, and (2) transesterification/cross-linking, which occurs in the solid state of the formed membrane. This eliminates the need to react the diol cross-linking agent with the polymer membrane in the solid state, which would require excessively swelling the membrane and may create defects in the membrane. This method also allows the process to be conveniently retrofitted into current membrane formation processes with a simple aqueous quench bath, with the cross-linking step taking place during final membrane drying.

Once the polyimide is made as described in the first paragraph of this section, a monoesterification reaction is performed in solution to form the cross-linkable polyimide. This is done by adding the cross-linking agent, 1,3-propanediol (40−70× stoichiometric amount), to the polyimide solution at about 140 °C for up to 18−24 h. The 1,3-propanediol molecules react with the pendant carboxylic acid group on the DABA moiety and give off water as the byproduct. The water produced is about 0.8% of the reaction solution, and the diol used is 40−70 times the molar amount of water produced. This is done in order to enable high conversions of the DABA groups to esters without the need to apply excessive amounts of heat, which might cross-link the polymer and render it insoluble and unable to process. High ester yields are necessary for achieving high cross-linking degrees. Esterification reactions are acid catalyzed,[25] and the amount of catalyst added is a crucial factor as discussed in the Results section. 5 mg of *p*-toluenesulfonic acid

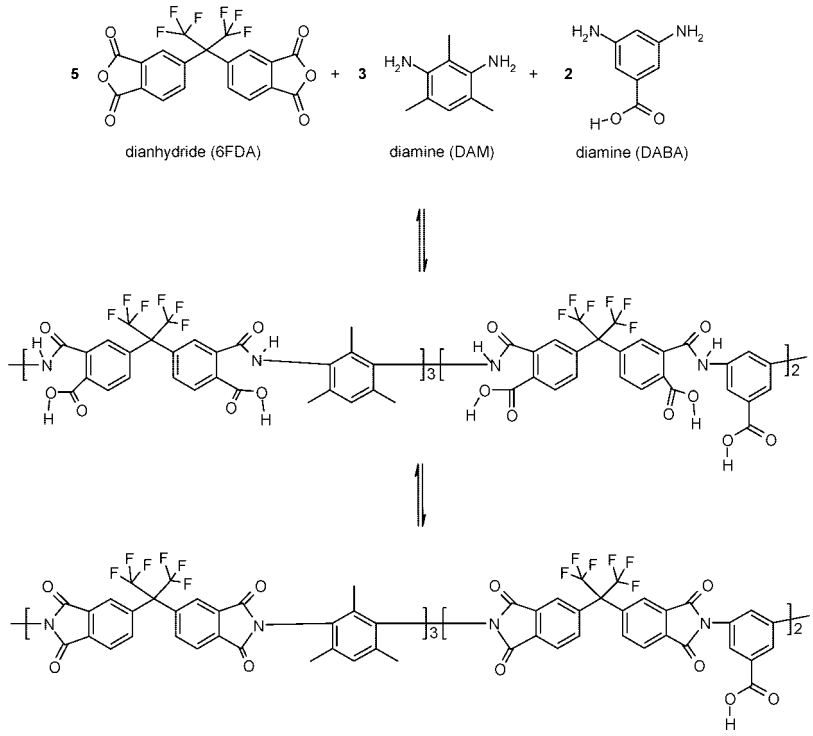

Figure 1. Synthesis steps for 6FDA−DAM:DABA (3:2) polyimide.

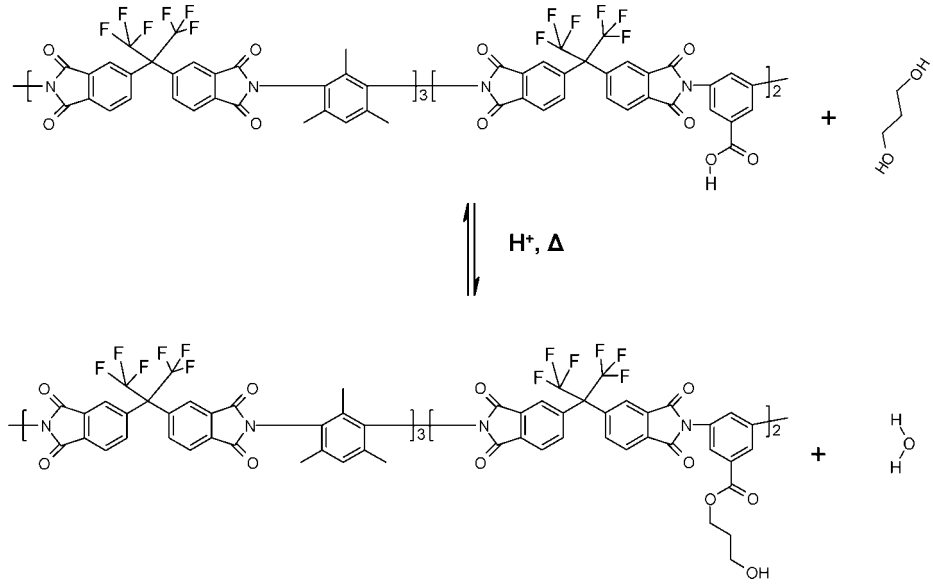

Figure 2. Monoesterification reaction for synthesizing 1,3-propanediol monoesterified cross-linkable (PDMC) polyimide (3:2).

(*p*-TSA) per gram of polymer has been used in earlier synthesis of these cross-linkable polyimides.[5,6,10,11,13] As noted earlier, the final cross-linkable polyimide obtained from the reaction of 1,3-prodanediol with the 6FDA−DAM:DABA (3:2) polyimide has been named "PDMC (3:2)", which stands for 1,3-propanediol monoesterified cross-linkable polyimide (3:2). The monoesterification reaction can be monitored via the ester yields, which can be done using solution ^{1}H NMR as described elsewhere.[5] The monoesterification reaction is shown in Figure 2.

The PDMC (3:2) polyimide can be subsequently made into the desired membrane form, i.e. a dense film or hollow fiber membrane, since the material is still soluble in common solvents. Once a membrane is made from the material, as described in the next section, cross-linking is carried out by simply heating the membrane in the solid state at temperatures above ∼150 °C under vacuum or an inert sweep gas to activate a transesterification reaction. Here, the pendant alcohol on one ester reacts with another ester to form a cross-link (see Figure 3 for a depiction of the transesterification/cross-linking between two polymer chain segments). Esterification reactions are reversible, and the reaction can be pushed to the formation of the cross-links by pulling vacuum or by using an inert sweep gas to take off the reaction byproduct, since there is not an excess of reactants in this case as there are during monoesterification. In theory, one 1,3-propanediol molecule is evolved to form one cross-link, assuming the monoesterification reaction goes to completion. In the case that the monoesterification reaction does not go to completion, the unconverted DABA groups are still capable of reacting with the alcohol on a pendant ester of a converted DABA group, thus giving off a water molecule instead of the diol. This enables a high degree of cross-linking as long as reasonably high (>60%) ester yields are obtained and adequate activation energy for cross-linking is reached. However, it is preferred that an ester yield of ∼90% or above is obtained. Analytical measurements of cross-linking conversion were not

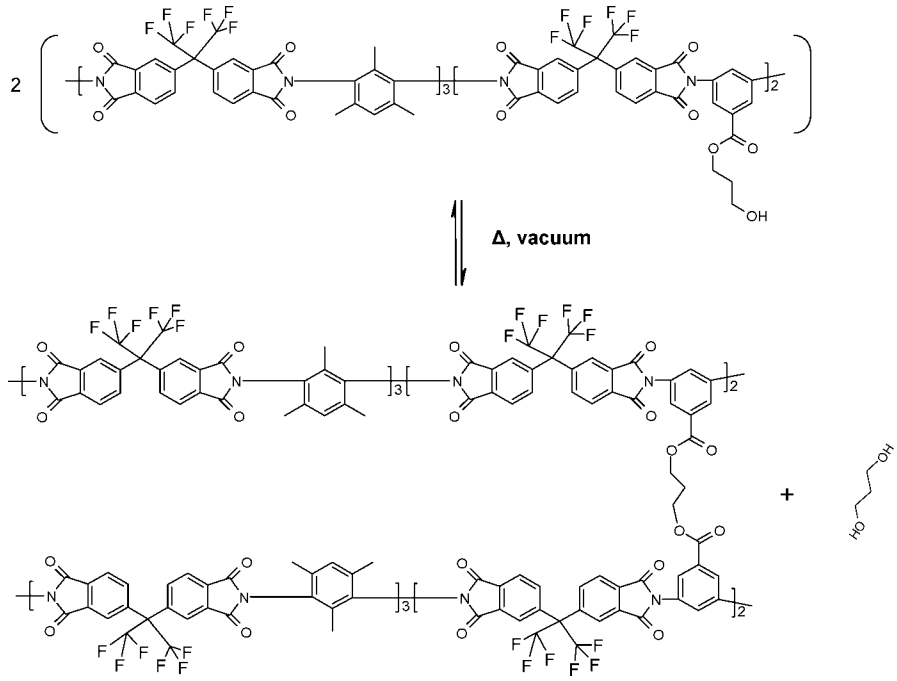

Figure 3. Cross-linking/transesterification reaction between two PDMC (3:2) polyimide chain segments.

investigated in this study since the focus was on developing the cross-linkable monoester, but some work has been done on this and can be found in the literature.[15] Once cross-linking occurs, the material becomes insoluble and more resistant to swelling by feed components that undermine intrinsic selectivity.

Molecular Weight Characterization. The molecular weight numbers are all weight-average molecular weight (M_w), measured by gel permeation chromatography (GPC) according to ASTM D5296-05. Estimated errors are about ±10%.

Membrane Formation: Hollow Fiber Spinning. The hollow fibers used in this research were made by a dry-jet/wet-quench method according to the framework developed by previous researchers.[14,21,26]

Results and Discussion

Monoesterification Effects on Polymer. In conventional monoesterification reactions for making the cross-linkable monoester polyimide, the importance of extremely rigorous dehydration of the reaction solution as the esters are formed was not stressed. This is partly because the monoesterification reaction occurs with an excess of the reactant diol, which drives the reaction forward to the formation of the ester product. Using conventional techniques, it was found that weight-average molecular weights drop to as low as 30% of the original unesterified polyimide. The cross-linkable monoesters made from the conventional technique were typically about 20 000−40 000 (M_w).[13,24] This caused films made from the polymer to be very brittle before and even after cross-linking, presumably due to dangling un-cross-linked chain ends. These un-cross-linked chain ends are defects in the ultimate cross-linked network resulting from shorter chains in the lower molecular weight polymer. Moreover, solutions made from the lower molecular weight cross-linkable polyimide were relatively low in viscosity and hard to process into hollow fibers by solution spinning. Solution ^{1}H NMR was carried out on the low molecular weight cross-linkable monoester polyimides to characterize the ester yields by the method described by Wind et al.[5] Typical "apparent ester yields" were close to 200%. The reason for the unusually high ester yields is explained in the next paragraph. A ^{1}H NMR spectrum from a low molecular weight monoester polyimide is shown in Figure 4, where the ester yield is about 160%.

From the unusually high ester yields and the huge drops in molecular weights, it was postulated that hydrolytic degradation was occurring at the imide rings as illustrated in the reaction sequence in Figure 4. Before the esterification reaction, imidization was confirmed by the reduction of the amide peaks from the polyamic acid precursor using IR and ^{1}H NMR until no change could be observed in the spectra. This corresponded to about 18−26 h of imidization at ∼190 °C during which the reaction distillate, which contains the water produced, was removed. These conditions complete the imidization reaction.[27] Amides can be seen at 1660 and 1550 cm $^{-1}$ on an IR spectrum,[28] which corresponds to the carbonyl (CONH) and C−NH groups, respectively. It is believed that although the water produced from the monoesterification reaction makes up a small fraction of the total reaction solution, the elimination of this water would help in reducing subsequent molecular weight loss. A hydrolyzed imide would cleave and form its polyamic acid precursor, which contains amide groups and carboxylic acid groups. In this case, these carboxylic acid groups are capable of participating in the monoesterification reaction, thus increasing the observed apparent ester yields relative to the theoretical limit at 100% conversion if no imide cleavage had taken place. Furthermore, it was hypothesized that if the reaction continues at the same condition, the amides that hold the chain together may also cleave by hydrolysis, thereby further increasing more esters and ultimately in a loss of molecular weight. To check for imide cleavage, IR was carried out on the low molecular weight monoester polyimide. As shown in Figure 5, the presence of amides was observed on the IR spectrum, indicating that imide cleavage had indeed occurred.

To alleviate this situation, a Dean−Stark trap fitted to a condenser was utilized for the monoesterification reaction. A Dean−Stark trap is conventionally used for the imidization reaction to remove the water distilled from the reaction solution, and the same idea was used for the monoesterification reaction. This helps in significantly reducing but not completely eliminating the water present, since water is intrinsically produced by the reaction. Since this measure was not sufficient to completely eliminate the loss in molecular weight typically seen after monoesterification, a balance appears to exist between imide/amide chain scissioning and enabling high levels of the ester

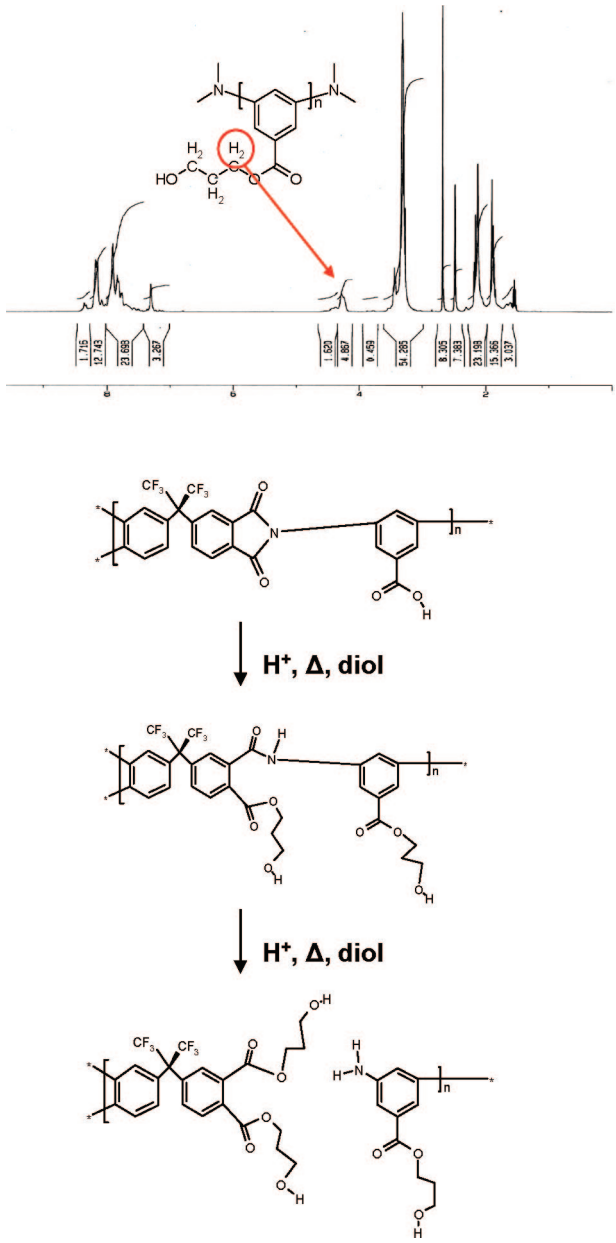

Figure 4. Solution ^{1}H NMR spectra of a PDMC (3:2) polyimide that experienced molecular weight loss (top) and reaction steps of a PDMC (3:2) chain segment undergoing chain scissioning on the imide ring (bottom).

yield to be reached during monoesterification. The method chosen to approach this balance was to reduce the catalyst concentration during the reaction. Typically, 5 mg or more of *p*-toluenesulfonic acid per gram polyimide is used to catalyze the reaction.[5−7,10,11,13] This amount was reduced to 2.5 mg of *p*-toluenesulfonic acid per gram polyimide. The reaction temperature was also lowered slightly from 140 to ∼130 °C. The effects of this change in the reaction conditions were monitored over the course of the reaction and were positive. The molecular weights and ester yields were obtained by analyzing the precipitated reaction products over time intervals of 4, 8, 12, 16, 18, and 22 h. The conditions used for the NMR analysis of ester yields and the GPC analysis of molecular weights were held constant to ensure consistency between the data. The plot in Figure 6 summarizes the results from this experiment.

From Figure 6, it can be seen that there was no molecular weight loss from using the dehydration conditions stated previously and by using a reduced amount of catalyst. The

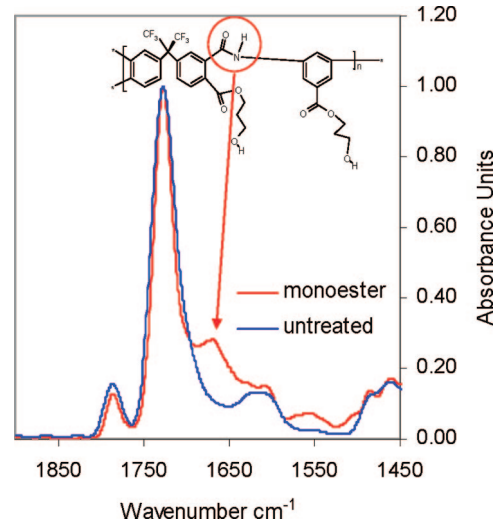

Figure 5. ATR-IR spectrum of a PDMC (3:2) polyimide that experienced molecular weight loss (red) and the precursor untreated/unesterified polyimide (blue).

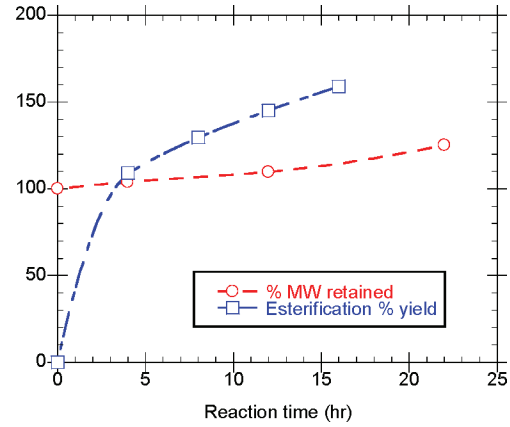

Figure 6. Monoesterification yield and weight-average molecular weight trends of a PDMC (3:2) polyimide, showing no molecular weight loss and high ester yields. Increased molecular weights indicate the addition of the esters on the polymer chain from the diol cross-linking agent.

molecular weight at 0 h was 103 000 (M_w) with a polydispersity of 3. The preservation of the molecular weight was an important objective. The ester yields were found to still be greater than the theoretical yield at 100% conversion if no imide cleavage had occurred. IR was carried out on these higher molecular weight polyimide batches obtained during the reaction to investigate the presence of amides. Figure 7 shows the spectra for this.

It can be seen from the spectra in Figure 7 that the amides had still appeared during the monoesterification reaction in the higher molecular weight cross-linkable monoester polyimides as well. This resurgence appeared to an extent even higher than that for the batch that experienced molecular weight loss shown in Figure 5. This suggests that more amides were present and may have been on the verge of leading to backbone scissioning if sufficiently activated or if excess moisture were present. However, even after 22 h of reaction under these modified monoesterification conditions, no molecular weight loss was observed.

Although ester yields were higher than normal, indicating imide ring opening, the molecular weight was preserved. Furthermore, IR analysis on the polyimide samples shows that the cleaved/ring-opened imides may be recyclized by annealing at high temperatures, at which cross-linking occurs simulta-

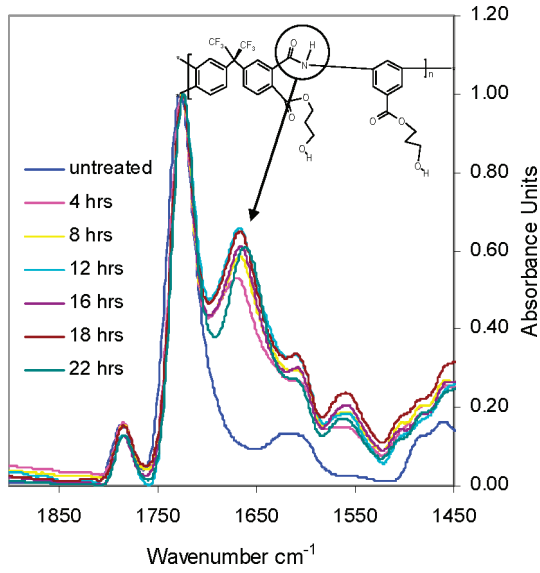

Figure 7. ATR-IR spectra of PDMC (3:2) polyimide samples that experienced no molecular weight loss but show the resurgence of amide peaks (top) and the precursor untreated/unesterified polyimide (bottom/blue).

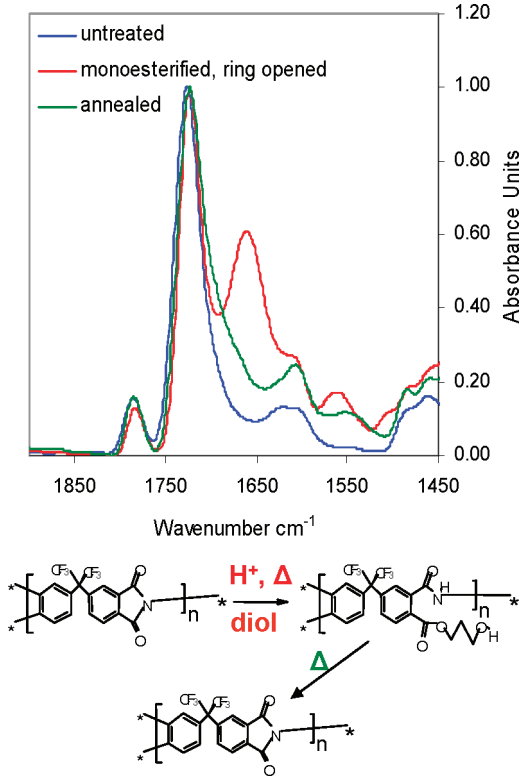

Figure 8. ATR-IR spectra of the precursor untreated/unesterified polyimide; a PDMC (3:2) polyimide (monoesterified) sample made from it that experienced no molecular weight loss but shows the resurgence of amide peaks; and an annealed/cross-linked polyimide showing recyclization of the imide ring.

neously. This can be seen in Figure 8, where the IR spectrum of an untreated/unesterified polyimide is plotted along with that for the esterified polyimide and its annealed version, where the temperature of annealing was ~245 °C.

Low molecular weight monoesters were also experienced when the catalyst concentration using *p*-toluenesulfonic acid was at 2.5 mg per gram of polyimide but without the use of dehydration. This suggests that both the removal of water and the lowering of the catalyst concentration were important in preserving the molecular weight of the cross-linkable monoester polyimide, while still obtaining high monoester yields.

Table 1. Hollow Fiber Spinning Conditions[a]

state no.	air-gap height (cm)	takeup rate (m/min)	dope extrusion rate (mL/h)	nominal draw ratio	fiber OD (μm)
1	10	50	180	15	~240
2	15	80	180	24	~200
3	15	122	180	37	~150
4	15	127	60	116	~80

[a] Spinneret temperature: 46−48 °C; aqueous quench bath temperature: 50−55 °C; bore fluid composition: 80/20 wt % NMP/H_20; bore fluid flow rate: 1/3 of dope extrusion rate.

Reaction Scale-up. To spin the cross-linkable polyimide in order to make hollow fibers for gas separations, the synthesis process was scaled up so that larger quantities (>100 g) of polymer could be made for hollow fiber production. The previous experiments were conducted in 100−500 mL reaction vessels used for making smaller quantities. In order to make such larger quantities of polymer, the reaction scale-up involved using a larger scale (~4 L) reactor. The surface area to volume ratio for the larger reactors are reduced compared to the smaller reactor vessels, and this reduces the efficiency for heating required for dehydrating the reaction solution. A one pot method was used for the monoesterification scale-up, where the *o*-DCB present in imidization was present for esterification. This not only reduced the synthesis steps, labor, and solvent consumption but also was geared to using the *o*-DCB dehydrating agent present to facilitate the removal of water during monoesterification, while catalyst levels were still lowered. The ester yield on a batch made using this technique was ~90%, most likely because a smaller amount of catalyst was used here (~1.75 mg of *p*-TSA per gram of polymer), and the weight-average molecular weight was 105 000. This batch was used for subsequent spinning and permeation tests. There is a plethora of literature on polyimide synthesis, useful in making the untreated polyimide at a high starting molecular weight, but the focus here is on the preservation of that molecular weight during the monoesterification reaction. Successive large batches have been made where using this technique enabled high molecular weights of the cross-linkable monoester, as high as 183 000, without molecular weight loss occurring on the precursor polyimide backbone.

Hollow Fiber Spinning. Hollow fibers were spun from the cross-linkable monoester, PDMC (3:2), under the conditions shown in Table 1. The polymer solution contained 35% polymer, 42% NMP, 8% $LiNO_3$, and 15% tetrahydrofuran (THF). The increased molecular weight cross-linkable polyimide was spun at nominal draw ratios as high as 116. This is an indication of the "spinnability" of the polymer. Previous attempts at spinning these cross-linkable polymers showed that draw ratios were at a maximum at 9, using lower molecular weight versions. The highest take-up rate tested in this study was 127 m/min, which was the maximum testable with the apparatus used. This produced fibers with outer diameters of about 80 μm as shown in Figure 9. The nominal draw ratios do not take into account the die swell that occurs as the polymer solution is extruded out of the spinneret. This is due to the fact that it is defined based on the ratio of the fiber takeup rate to extrusion rate. Nevertheless, the nominal draw ratios, as used here, do give a measure of the attenuation from fiber spinning.

Membrane Characterization. The hollow fibers were tested to measure the gas separation properties of the membrane. Before testing with the CO_2 containing feeds, the hollow fiber was cross-linked by heating the membrane at 200 °C in a vacuum oven for 1 h. This activated the transesterification reaction required to stabilize the membrane in the presence of

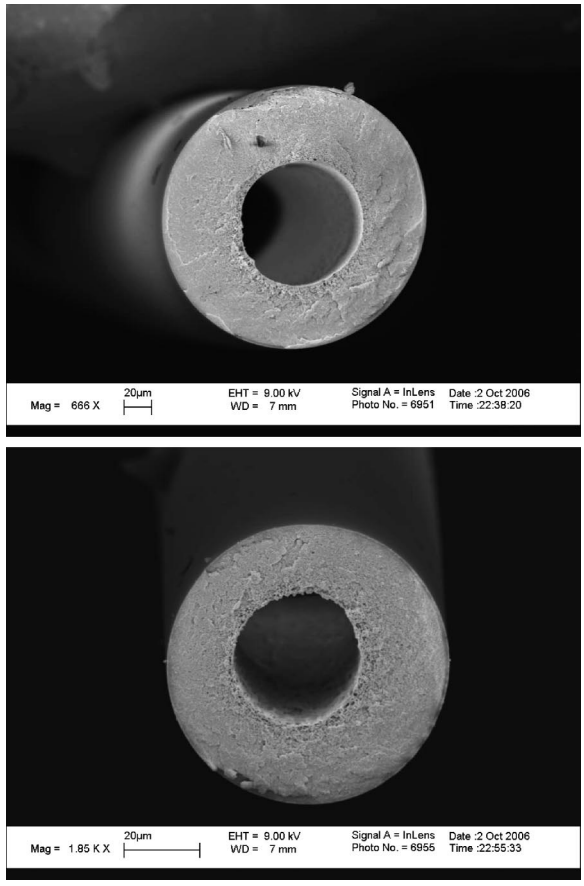

Figure 9. Scanning electron micrographs (SEM) of hollow fibers from states 2 (top) and 4 (bottom) of the PDMC (3:2) polyimide.

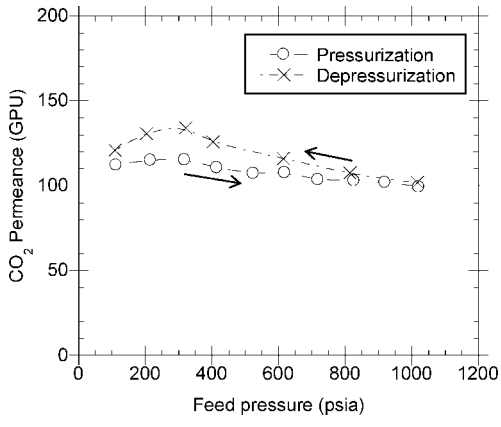

Figure 10. Mixed gas permeation using a 20/80 CO_2/CH_4 feed at 35 °C demonstrating the CO_2 permeance of a cross-linked PDMC (3:2) hollow fiber membrane at elevated feed pressures.

high-pressure CO_2 feeds. Subsequently, the cross-linked fibers were tested by pressurizing the membrane with a mixed gas CO_2/CH_4 feed with 20% CO_2 at 35 °C. For all the permeation experiments, the membrane was exposed to the feed for ~1 h to allow sufficient equilibration time for measurements to be recorded. Figures 10 and 11 show the permeation results from testing the membrane using this model natural gas mixture on the 200 μm OD fiber shown on the top of Figure 9. The uncertainty on the permeances is ±5%, while for the permselectivities is ±7%.

The high-pressure permeation data in Figure 10 show a CO_2 permeance ≥100 GPUs as the membrane was pressurized to about 1000 psia, which translates to a CO_2 partial pressure of 200 psia, and then depressurized. During pressurization, there

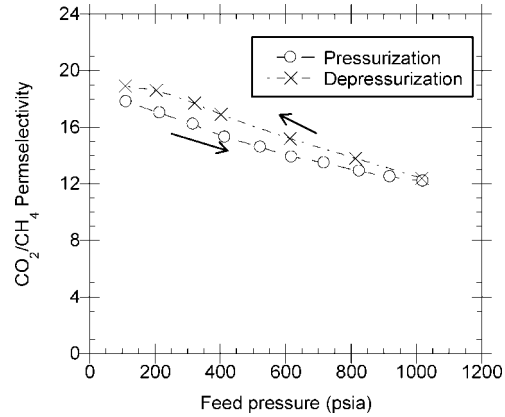

Figure 11. Mixed gas permeation using a 20/80 CO_2/CH_4 feed at 35 °C demonstrating the permselectivity of a cross-linked PDMC (3:2) hollow fiber membrane at elevated feed pressures.

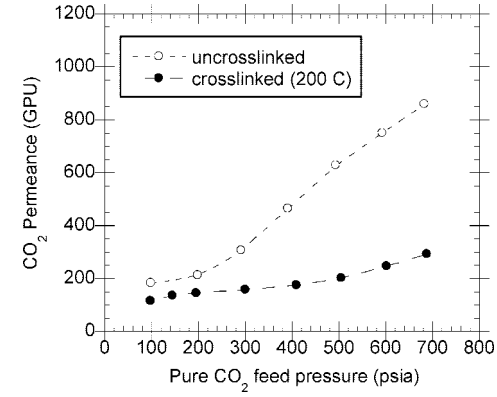

Figure 12. Plasticization curves for a cross-linked and un-cross-linked PDMC (3:2) polyimide. Test temperature was 35 °C.

is no increase in the permeances, indicating no plasticization. Instead, there is a decrease in the permeance of CO_2 and in the CO_2/CH_4 permselectivity, indicative of dual mode sorption effects. The CO_2 molecules have more of an advantage for sorption over CH_4, since CO_2 is more condensable. However, as the pressure is increased, the sorption advantage of CO_2 is reduced; thus, its permeance and permselectivity over CH_4 are decreased as the pressure is increased. The dual mode model describes this pressure dependence of the sorption and permeability for CO_2 and CH_4 in glassy polymers.[29,30] During the depressurization, a hysteresis was observed, which indicates that some swelling was occurring from CO_2, conditioning the membrane to a higher free volume state when it sorbed onto the polymer.[31] However, the swelling did not cause detrimental effects on the separation capability of the membrane due to the cross-linking, which stabilizes the matrix. This is evidenced by observing the permselectivities in Figure 11, which shows no loss in selectively permeating the gas molecules even as the membrane was conditioned during the depressurization process. In fact, the CO_2/CH_4 permselectivity increased as a result of the slight conditioning. This is an unusual trend in polymer membrane science because there is usually a tradeoff between a membrane's selectivity and permeability.[32,33] Presumably, CO_2 was able to compete successfully for any added free volume introduced by the conditioning process.

The cross-linked hollow fiber membrane was tested for its resistance to plasticization with pure CO_2 gas feeds at 35 °C and at elevated pressures and compared with the un-cross-linked version. The isotherms in Figure 12 show the results from this experiment, and it can be seen that the un-cross-linked fibers are unstable, evident by the huge increase in the CO_2 permeance.

On the other hand, the cross-linked fiber shows reasonably good stability even up to 700 psia of CO_2, although there is some creep in the isotherm as the pressure is increased. This illustrates the importance of cross-linking in stabilizing the hollow fiber membrane in the presence of plasticizing feeds.

The hollow fiber showed viability for separating the CO_2/CH_4 gas pair at high pressures, but the permselectivities shown in Figure 11 fall short of the intrinsic polymer permselectivity, which is about 45 at 65 psia and 35 °C.[7] This suggests the presence of minor skin defects in the membrane and/or inadequate resistance in the separating layer of the hollow fibers relative to the nonselective support layer. These problems may be alleviated by post-treating the membrane using common techniques[13,34−36] or could be avoided by adjusting the spinning process variables altogether to suit the desired separation properties. Post-treatment using a highly permeable silicone rubber coating has been shown to be an effective strategy in regaining a defective membrane's intrinsic permselectivity.[13] The post-treating process simply occurs by coating the membrane with a layer of a highly permeable polymer to reduce the nonselective flux contribution through the membrane. The cross-linked hollow fibers were post-treated using the technique described by Ekiner et al.,[35] also used by Husain et al.,[36] and the membrane was retested at 200 psia, with the 20/80 CO_2/CH_4 feed gas at 35 °C. The CO_2 permeance dropped to ∼22 GPU while the permselectivity rose to 44, which was typical for this polymer at this pressure, suggesting that the additional resistance from the silicone rubber coating was enough to reduce the effects of nonselective flow through the membrane.

Defect-Free Membranes. Previous studies show that silicone rubber post-treated hollow fiber membranes do not maintain their selectivity once exposed to aggressive feed streams.[15] Although post-treatment regains the membranes intrinsic permselectivity, it loses its benefit under harsh conditions and presents the need to create integrally skinned, defect-free membranes that do not require post-treatment to reach intrinsic polymer permselectivities. Hence, the PDMC polymer was spun into an integrally skinned, defect-free hollow fiber membrane from a solution containing 35% polymer, 8.5% ethanol, 35% NMP, 6.5% $LiNO_3$, and 15% tetrahydrofuran (THF) using the same spinning framework mentioned previously. The addition of ethanol (a volatile nonsolvent for the polymer) allowed a greater window of compositions to create the final spinning solution formulation than using stronger nonsolvents. The volatility of ethanol was also an advantage that determined its usage. The polymer used had a molecular weight of 183 500 (M_w). The solution was extruded at ∼70 °C at a rate of 180 mL/h out of a spinneret. The solution passed through a 33 cm air gap into an aqueous quench bath heated to 50 °C and was taken up on a rotating drum at a rate of 50 m/min. The bore fluid consisted of 80% NMP and 20% water and was coextruded at 60 mL/h with the polymer solution through the spinneret.

The advantage of using the higher molecular weight cross-linkable polymer is apparent from being able to extrude the solution at higher spinneret temperatures, while maintaining significant polymer chain entanglement in the air gap to form a dense skin layer. The elevated spinneret temperature allows evaporation of volatiles (particularly THF) in the solution, which promotes vitrification on the outer skin layer of the nascent hollow fiber membrane as it passes through the air gap. A polymer solution with a higher level of chain entanglement is believed to form a denser, defect-free skin layer once vitrification occurs. Once the hollow fiber is quenched, rapid phase separation causes the layer beneath the skin to become porous and rich in the polymer lean phase, while the skin layer remains dense. The hollow fiber membrane becomes vitrified into this state after phase separation occurs. Figure 13 shows pictures of the cross section of the skin layer and porous fiber wall.

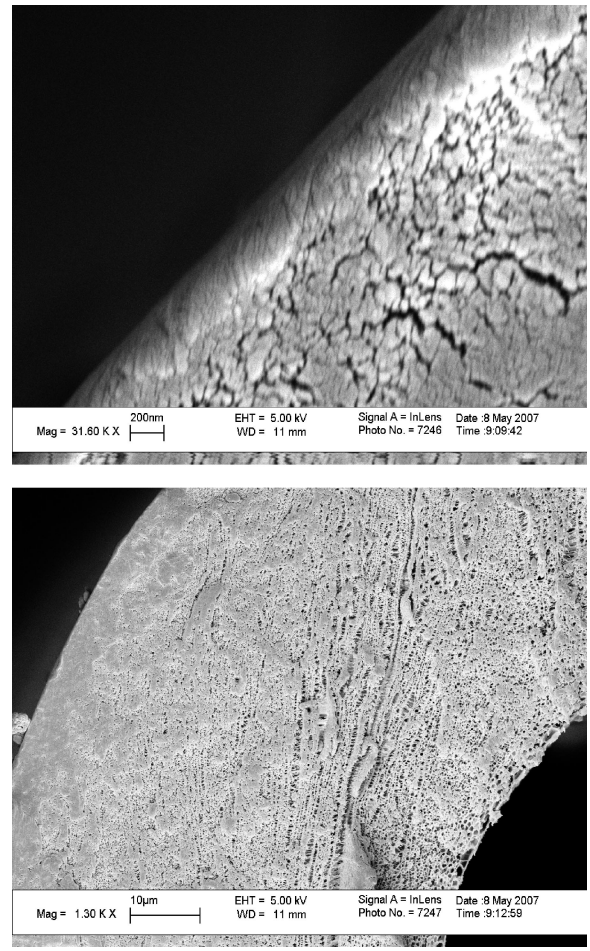

Figure 13. Scanning electron micrographs of a cross section of the PDMC hollow fiber, showing the skin layer (top) and the porous fiber wall (bottom) that acts mostly as a support for the skin layer.

The higher molecular weight PDMC polymer was cross-linked by annealing the hollow fiber membrane under vacuum at 200 °C for 2 h. The cross-linked hollow fiber membranes were tested for their gas separation properties. Using a feed gas mixture consisting of 20/80 CO_2/CH_4 at 35 °C (same feed mixture used previously), the cross-linked hollow fibers were tested with the feed at 200 psi, and the CO_2 permeance was ∼46 GPU while the CO_2/CH_4 permselectivity was recorded to be 43. The permselectivity at this pressure indicates the presence a defect-free skin layer in the hollow fiber membrane, thus requiring no further post-treatment. These defect-free PDMC hollow fibers made from the higher molecular weight polymer show permeances and selectivities higher than that for the lower molecular weight version, where the molecular weight was ∼29 000 (M_w).[15,24] The lower molecular weight version of the PDMC hollow fiber membrane showed a CO_2 permeance of ∼35 GPU and the CO_2/CH_4 permselectivity of 32[15] after cross-linking and under similar test conditions. After cross-linking, the polymer chains theoretically attain "infinite" molecular weight. Thus, the enhancement in the performance of the transport properties and mechanical properties (nonbrittleness) of the higher molecular weight polymer versus the lower molecular weight polymer after cross-linking suggests the presence of defects in the macromolecular cross-linked network that reduce the effect of the cross-linking on the lower molecular weight versions. The effect of high-pressure CO_2 on the defect-free fibers will be demonstrated in another study.

Conclusions

The cross-linkable monoester, PDMC (3:2), was synthesized successfully by intensively dehydrating the reaction solution during the monoesterification reaction and by lowering the *p*-toluenesulfonic acid catalyst by half the conventional amount. This prevented loss in the molecular weight of the cross-linkable polyimide (necessary for membrane formation) and also allowed high ester yields (necessary for achieving high cross-linking degrees in the membrane). The cross-linkable polyimide synthesis process leaves room for further research. There seems to be a balance in the reaction conditions necessary for promoting the ester yield while preserving cleavage at the imide/amide on the polymer. In this work, there was evidence of imide cleavage even though no loss in molecular weight occurred. Although this was not a major setback, better control of the reaction conditions to reduce the imide cleavage during the monoesterification reaction would be a next step in the right direction.

The monoesterification reaction was scaled up $>10\times$ by utilizing a one-pot synthesis method, where polymerization, imidization, and monoesterification occur in "one pot", without precipitation in between. During this procedure, the dehydrating agent, *o*-DCB, was used for both the imidization and monoesterification reactions in making larger quantities of the polyimide, and overall solvent consumption was reduced. It was shown that the cross-linkable polyimide could be spun at high takeup rates, up to 127 m/min, which translates to a draw ratio $\sim$116 under the conditions used. This demonstrates that the polymer was more spinnable than the lower molecular weight versions used previously. The cross-linkable polyimide could be cross-linked by heating the membrane under vacuum to activate a transesterification reaction, which was necessary for stabilizing the membrane in high-pressure CO_2 feeds. The cross-linked hollow fiber membrane could separate a model natural gas feed, a mixture of CO_2 and CH_4, at feed pressures as high as 1000 psi, without detrimental effects of plasticization occurring. The cross-linked hollow fiber membrane was also shown to be much more stable against plasticization compared to the un-cross-linked hollow fiber membrane using pure CO_2 feeds up to 700 psi.

A subsequent attempt at spinning the high molecular weight polymer was performed and was shown to produce defect-free fibers that did not require post-treatment using a silicone rubber caulking layer. The cross-linked hollow fiber membrane exhibited intrinsic polymer transport properties, with a CO_2/CH_4 permselectivity of 43 and a CO_2 permeance of 46 GPUs.

Acknowledgment. The authors acknowledge the financial support from Chevron Energy Technology Company and helpful contributions from Dr. John Wind. The financial support from DOE Basic Energy Sciences, DE-FG02-04ER15510, which built the foundation of this work, is also appreciated. The authors also thank Madhava Kosuri for help with SEM.

Supporting Information Available: The spinning process depicted in a schematic. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ohya, H.; Kudryavtsev, V. V.; Semenova, S. I. In *Polyimide Membranes: Applications, Fabrications, and Properties*; Gordon and Breach: Tokyo, 1996.
(2) Koros, W. J.; Staudt-Bickel, C. *J. Membr. Sci.* **1999**, *155*, 145–154.
(3) Wind, J. D.; Staudt-Bickel, C.; Paul, D. R.; Koros, W. J. *Ind. Eng. Chem. Res.* **2002**, *41*, 6139–6148.
(4) Kanehashi, S.; Nakagawa, T.; Nagai, K.; Duthie, X.; Kentish, S.; Stevens, G. *J. Membr. Sci.* **2007**, *298*, 147–155.
(5) Wind, J. D.; Staudt-Bickel, C.; Paul, D. R.; Koros, W. J. *Macromolecules* **2003**, *36*, 1882–1888.
(6) Wind, J. D.; Sirard, S. M.; Paul, D. R.; Green, P. F.; Johnston, K. P.; Koros, W. J. *Macromolecules* **2003**, *36*, 6433–6441.
(7) Hillock, A. M. W.; Koros, W. J. *Macromolecules* **2007**, *40*, 583–587.
(8) Wind, J. D.; Paul, D. R.; Koros, W. J. *J. Membr. Sci.* **2004**, *228*, 227–236.
(9) Wind, J. D.; Sirard, S. M.; Paul, D. R.; Green, P. F.; Johnston, K. P.; Koros, W. J. *Macromolecules* **2003**, *36*, 6442–6448.
(10) Kim, J. H.; Koros, W. J.; Paul, D. R. *J. Membr. Sci.* **2006**, *282*, 32–43.
(11) Wind, J. D. University of Texas at Austin, Austin, TX, **2002**.
(12) Hillock, A. M. W. Georgia Institute of Technology, Atlanta, GA, **2005**.
(13) Wallace, D. W. University of Texas at Austin, Austin, TX, **2004**.
(14) Wallace, D. W.; Staudt-Bickel, C.; Koros, W. J. *J. Membr. Sci.* **2006**, *278*, 92–104.
(15) Wallace, D. W.; Williams, J.; Staudt-Bickel, C.; Koros, W. J. *Polymer* **2006**, *47*, 1207–1216.
(16) Koros, W. J.; Wallace, D.; Wind, J. D.; Miller, S. J.; Staudt-Bickel, C.; Vu, D. Q. U.S. Pat. 6,755,900, **2004**.
(17) Koros, W. J.; Wallace, D.; Wind, J. D.; Miller, S. J.; Staudt-Bickel, C. U.S. Pat. 6,932,859, **2005**.
(18) Koros, W. J. *AIChE J.* **2004**, *50*, 2326.
(19) Baker, R. W. *Ind. Eng. Chem. Res.* **2002**, *41*, 1393–1411.
(20) Ekiner, O. M.; Vassilatos, G. J. U.S. Pat. 5,085,774, **1992**.
(21) McKelvey, S. A.; Clausi, D. T.; Koros, W. J. *J. Membr. Sci.* **1997**, *124*, 223–232.
(22) Baker, R. W. In *Membrane Technology and Applications*; John Wiley & Sons Ltd.: West Sussex, England, 2004.
(23) Carruthers, S. B.; Ramos, G. L.; Koros, W. J. *J. Appl. Polym. Sci.* **2003**, *90*, 399–411.
(24) Wallace, D. W. Personal communication, **2007**.
(25) Bruce, P. Y. In *Organic Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1995.
(26) Pesek, S. C.; Koros, W. J. *J. Membr. Sci.* **1994**, *88*, 1–19.
(27) Kim, Y. J.; Glass, T. E.; Lyle, G. D.; McGrath, J. E. *Macromolecules* **1993**, *26*, 1344–1358.
(28) Dunson, D. L. Virginia Polytechnic Institute and State University: Blacksburg, VA, 2000; p 21.
(29) Koros, W. J.; Chern, R. T.; Stannett, V.; Hopfenberg, H. B. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1981**, *19*, 1513–1530.
(30) Koros, W. J. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1980**, *18*, 981–992.
(31) Mohammed, A.; Koros, W. J. *J. Membr. Sci.* **2006**, *274*, 227–243.
(32) Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165–185.
(33) Robeson, L. M.; Burgoyne, W. F.; Langsam, M.; Savoca, A. C.; Tien, C. F. *Polymer* **1994**, *35*, 4970–4978.
(34) Henis, J. M. S.; Tripodi, M. K. *J. Membr. Sci.* **1981**, *8*, 233–246.
(35) Ekiner, O. M.; Hayes, R. A.; Manos, P. U.S. Pat. 4,863,496, **1989**.
(36) Husain, S. Georgia Institute of Technology, Atlanta, GA, **2004**.

MA800813W