Unusual Gas-Transport Selectivity in a Partially Oxidized Form of the Conductive Polymer Polypyrrole

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Received July 29, 1996. Revised Manuscript Received October 23, 1996⊗

Prior investigations have shown that polypyrrole has low gas-transport selectivity. This has been attributed to the microporous morphology obtained when thin films of this polymer are prepared by conventional synthetic methods. In this paper we show that polypyrrole with a dense (as opposed to microporous) morphology can be prepared by slowing down the rate of the polymerization reaction. We further demonstrate that a partially oxidized form of this material shows extraordinary gas-transport properties. When the volume percent of O_2 in the feed-gas stream was 100% (i.e., pure O_2), this partially oxidized form of polypyrrole showed an O_2 vs N_2 gas-transport selectivity coefficient of 18. This is one of the highest gas-transport selectivity coefficients to be reported to date for a polymeric material. The O_2 vs N_2 selectivity coefficient was found to increase with decreasing partial pressure of O_2 in the feed-gas stream. When the partial pressure of O_2 was 0.1% (99.9% N_2), the O_2 vs N_2 selectivity coefficient increased to 92. There is no precedent in the literature for selectivity coefficients of this magnitude for polymeric materials. The data are consistent with facilitated transport of O_2 in this unique partially oxidized form of polypyrrole.

Introduction

The possibility of using synthetic membranes for industrial gas separations has attracted considerable interest in recent years.[1−12] This interest is fueled by the potential economic advantages of membrane-separation technologies.[1−4] For membrane-based separations to gain wider commercial utilization, membranes with high transport selectivities and higher permeant fluxes will be required. Identifying new membrane materials for industrial gas separations is, therefore, an important research objective.[1−12]

We[7−9] and others[10−12] have found that a class of polymers, known collectively as electronically conductive polymers,[13] can show very high gas-transport selectivities. These are redox-active polymers that can exist in a fully reduced, a fully oxidized, or a partially oxidized form (Figure 1).[7−13] The fully reduced form is nonionic. The oxidized forms are polycationic, and these forms have been shown to have the highest gas-transport selectivities.[7−11] For example, partially oxidized polyaniline has an O_2 vs N_2 selectivity coefficient of ca. 15.[7,11] This is one of the highest O_2/N_2 selectivity coefficients obtained to date.

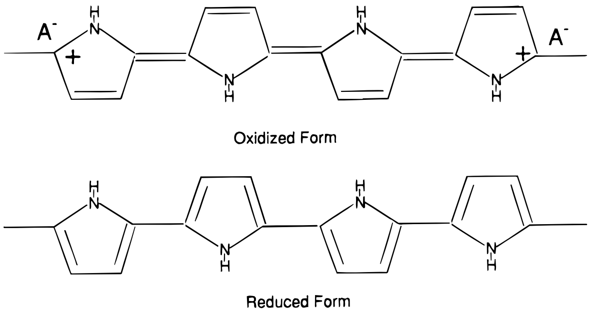

Figure 1. Representations of the chemical structures of the totally oxidized and totally reduced (or pristine) forms of polypyrrole. A^- is a charge-balancing counterion (e.g., Cl^-).

The gas-transport properties of polyaniline[7,10,11] and poly(*N*-methylpyrrole)[8] have been studied in some detail. Early on, we briefly investigated the gas-transport properties of another conductive polymer, polypyrrole (Figure 1).[8] We found that when prepared by conventional chemical synthetic methods, this polymer showed very low gas-transport selectivities.[8] This result has since been confirmed by another group.[14,15] Poor gas-transport selectivity is obtained because the conventional synthesis produces a polymer film with a microporous morphology.[16]

We have since discovered that if the rate of pyrrole polymerization is decreased, polypyrrole films with a dense (as opposed to microporous) morphology can be obtained. Treatment of such dense polypyrrole films

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⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1996.

(1) Spillman, R. W. *Chem. Eng. Prog.* **1989**, *85*, 41.

(2) U.S. Department of Energy Report No. DE90-01170 “Membrane separation systems- A research needs assessment”, U.S. Department of Energy, Washington, DC, April 1990.

(3) Hennis, J. M. S.; Tripodi, M. K. *Science* **1983**, *220*, 11.

(4) Abelson, P. H. *Science* **1989**, *224*, 1421.

(5) Koros, W. J.; Fleming, G. K. *J. Membr. Sci.* **1993**, *83*, 1.

(6) Liu, C.; Espencheid, M. W.; Chen, W.-J.; Martin, C. R. *J. Am. Chem. Soc.* **1990**, *112*, 2458.

(7) Kuwabata, S.; Martin, C. R. *J. Membr. Sci.* **1994**, *91*, 1.

(8) Liang, W.; Martin, C. R. *Chem. Mater.* **1991**, *3*, 390.

(9) Martin, C. R.; Liang, W.; Menon, V.; Parthasarathy, R.; Parthasarathy, A. *Synth. Met.* **1993**, *55−57*, 3766.

(10) Anderson, M. R.; Mattes, B. R.; Reiss, H.; Kaner, R. B. *Science* **1991**, *252*, 1412.

(11) Rebattet, L.; Escoubes, M.; Genies, E.; Pineri, M. *J. Appl. Polym. Sci.* **1995**, *57*, 1595.

(12) Hachisuka, H.; Ohara, T.; Ikeda, K.-I.; Matsumoto, K. *J. App. Polym. Sci.* **1995**, *56*, 1479.

(13) *Handbook of conducting polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986.

(14) Kamada, K.; Kamo, J.; Motonaga, A.; Iwasaki, T.; Hosokawa, H. *Polym. J.* **1994**, *26*, 141.

(15) Kamada, K.; Kamo, J.; Motonaga, A.; Iwasaki, T.; Hosokawa, H. *Polym. J.* **1994**, *26*, 833.

(16) Parthasarathy, R.; Martin, C. R. *Nature* **1994**, *369*, 298.

S0897-4756(96)00401-2 CCC: $14.00

with aqueous base yields a partially oxidized form of the polymer,[17-19] which can show extraordinary O_2 vs N_2 gas-transport selectivity at low O_2 partial pressures (O_2/N_2 selectivity coefficients in excess of 90 will be reported here). Furthermore, the O_2/N_2 selectivity coefficient was found to increase with decreasing partial pressure of O_2 in the feed-gas stream. This observation is consistent with, but does not prove, a facilitated transport mechanism[20,21] for O_2 in these polypyrrole films. These and related results are described here.

Experimental Section

Materials. Pyrrole was vacuum distilled prior to use. Ferrous and ferric chloride were used as received. Purified water was obtained by passing house-distilled water through a Milli-Q (Millipore) water purification system. Oxygen (99.9%), nitrogen (99.99%), and compressed air (80% nitrogen and 20% oxygen) were used for the routine gas-transport studies. In addition, gas tanks with O_2/N_2 volume percentages of 0.1% O_2/99.9% N_2, 1% O_2/99% N_2, 7.5% O_2/92.5% N_2, 50% O_2/50% N_2, and 90% O_2/10% N_2 were used to study the effect of O_2 partial pressure in the feed stream on the O_2/N_2 gas-transport selectivity coefficient. These were certified gas compositions; however, all gas compositions were confirmed in-house using the gas chromatographic method described below. All gases were obtained from General Air and were passed through a molecular sieve column (Scott Specialty Gases, Model No. 53-44R) prior to use to remove traces of water from the gas stream.

Synthesis of Polypyrrole/Polycarbonate Composite Membranes. The polypyrrole (PPy) was synthesized as ultrathin (200 ± 25 nm thick) films across both surfaces of a polycarbonate support membrane (Poretics). The support membrane was 6.0 μm in thickness and, in contrast to our prior work,[6-9,22,23] was nonporous. This ultrathin-film composite membrane approach was used because the gas permeabilities of the PPy films studied here are very low. Prior to the synthesis of the PPy layer, the membranes were etched in sodium hydroxide and then coated with a monolayer of polyvinylpyrrolidone (PVP) which improves adhesion of the PPy film. The latter was accomplished by simply immersing the membrane into a solution prepared by dissolving 0.58 g of PVP in 100 mL of methanol.

A 2.54 cm × 2.54 cm piece of the polycarbonate membrane was immersed into 10 mL of aqueous 0.2 M pyrrole. The membrane was ultrasonicated in the pyrrole solution for 2 min. An aqueous solution (10 mL) of ferrous chloride (0.4 M) and ferric chloride (0.5 M) were then added, and the membrane was ultrasonicated for an additional minute. Oxidative polymerization of pyrrole onto both surfaces of the polycarbonate membrane ensued. The polymerization was allowed to proceed for 30 min. After polymerization, the resulting PPy/polycarbonate/PPy composite membranes were thoroughly rinsed with water to remove excess monomer and oxidizing agent.

This synthesis yields the fully oxidized form of PPy (Figure 1). As will be discussed in detail below, we are interested in preparing a partially oxidized form of PPy. This was accomplished by treating the PPy/polycarbonate/PPy composite with aqueous base.[17-19] The composite membranes were immersed for 15 min into 500 mL of 1 mM aqueous NaOH, rinsed in water, and air-dried. After air drying, the membranes were heated in air for 15 min at 150 °C. This combination of exposure to base followed by heating is the standard postsynthesis treatment, and unless otherwise noted, gas-transport data were obtained on composite membranes that had been treated in this way.

Determination of the Thickness of the PPy Surface Films. The PPy film thickness was determined using scanning electron microscopy. As indicated above after PPy synthesis, the polycarbonate support membrane is sandwiched between two surface layers of PPy. One of these surface layers was removed by polishing with a laboratory tissue wetted with methanol. The other surface layer was not removed. The membrane was placed with the PPy-coated side down on an Anopore (Whatman) alumina filter in a vacuum filtration flask. Vacuum was applied to hold the PPy-coated polycarbonate membrane to the surface of the filter. The polycarbonate was then dissolved by filtering a large volume (50 mL) of chloroform followed by a large volume of dichloromethane through the filter. The PPy film is not soluble in these solvents and remains, intact, on the surface of the filter.

The filter with the PPy film on its upper surface was then immersed into liquid nitrogen and cracked to expose an edge of the PPy film. The exposed edge and surrounding surface was sputtered with ca. 20 nm of Au and then imaged using a Philips 505 scanning electron microscope. The thickness of the PPy film was determined from such images of the film edge. A value of 200 ± 25 nm was obtained. The standard deviation reflects measurements at four different places along the length of the PPy film.

Gas-Transport Apparatus. The gas-transport cell is described elsewhere.[24] Membrane samples were prepared by sandwiching the composite membrane between a piece of filter paper and a piece of Al-foil tape (All-foils, Inc.). A circular hole, of area between 0.5 and 2.0 cm^2, was punched into the Al foil tape; this hole defines the area of the membrane exposed to permeant gas(es). Gas flux from the feed half-cell, across the membrane, and into the permeant half-cell, was monitored using either a pressure transducer (for single gas-permeation experiments) or a gas chromatograph (for binary gas-transport experiments). All gas-transport data were obtained at 25 °C, the ambient laboratory temperature.

Single Gas Permeation Experiments. Prior to gas-transport measurement, both the feed and permeant half-cells were evacuated, and the sample was allowed to outgas until a flat baseline was obtained from the pressure transducer in the lower half-cell. The desired gas was introduced into the feed half-cell at a pressure of 50 psig (334.5 cm (Hg)). The gas flux across the membrane was monitored by recording the output of the pressure transducer on a strip chart recorder. The slope of the linear part of the resulting pressure–time transient provides the gas flux across the membrane. The permeability coefficient for the gas in the composite membrane (P_{com}) can be calculated via

$$dP/dt = P_{com} A \Delta P[(RT)/V]/I \qquad (1)$$

where dP/dt is the flux (cm(Hg)/s), A is the membrane area (cm^2), ΔP is the pressure differential across the membranes (cm (Hg)), I is the thickness of the composite membrane (cm), and $[RT/V]$ is the cell constant (cm (Hg)/cm^3(STP)). RT/V is obtained by calibrating the cell using a standard polystyrene membrane. The P_{com} values obtained from eq 1 have units of Barrers, where 1 Barrer = 10^{-10} cm^3(STP)cm/cm^2 s cm (Hg).[5-10]

P_{com} is the permeability coefficient for the desired gas in the composite membrane and includes contributions from both the polycarbonate support and the PPy surface layers. The permeability coefficient for the gas in the PPy surface layer (P_{PPy}) can be calculated using the following equation[25]

$$I_{com}/P_{com} = I_{pc}/P_{pc} + 2I_{PPy}/P_{PPy} \qquad (2)$$

where I_{com} is the thickness of the composite membrane, I_{PC} and P_{PC} are the thickness of and permeability coefficient for the gas in the polycarbonate support, and I_{PPy} is the thickness of the PPy surface layer. The thicknesses of the polycarbonate support and the PPy layers are known. P_{com} was determined as described above, and P_{pc} was determined from independent measurements of gas flux in the uncoated polycarbonate

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(17) Li, Y.; Qian, R. *Synth. Met.* **1988**, *26*, 139.

(18) Li, Y.; Qian, R. *J. Electroanal. Chem.* **1993**, *362*, 267.

(19) Li, Y.; Ouyang, J.; Yang, J. *Synth. Met.* **1995**, *74*, 49.

(20) Noble, R. D.; Koval, C. A.; Pellegrino, J. J. *Chem. Eng. Progr.* **1989**, *85*, 58.

(21) Nishide, H.; Suzuki, T.; Nakagawa, R.; Tsuchida, E. *J. Am. Chem. Soc.* **1994**, *116*, 4503.

(22) Liu, C.; Martin, C. R. *Nature* **1991**, *352*, 50.

(23) Ballarin, B.; Brumlik, C. J.; Lawson, D. R.; Liang, W.; Van Dyke, L. S.; Martin, C. R. *Anal. Chem.* **1992**, *64*, 2647.

(24) Liu, C. Ph.D. Dissertation, Texas A&M University, 1991.

Table 1. O_2 and N_2 Permeability Coefficients and α_{O_2/N_2}(ideal) Values from Single Gas-Permeation Experiments

	composite membrane	base/heat-treated PPy film[a]	polycarbonate support
P_{O_2}	0.0531	0.0036	0.80
P_{N_2}	0.0028	0.0002	0.13
α_{O_2/N_2}(ideal)	19	18	6.1

[a] Calculated via eq 2.

support (Table 1). Hence, all of the parameters in eq 2 are known except P_{PPy}, which can then be calculated. The standard deviation for the permeability coefficient measurement was found to be ±0.0008 Barrers. This number was obtained by making four replicate measurements on two different membranes.

Gas-transport selectivity coefficients are given the symbol α; e.g., the O_2 vs N_2 selectivity coefficient is α_{O_2/N_2}. We have used two different methods to obtain the α_{O_2/N_2} values reported here. The first method simply entails ratioing the permeability coefficients for O_2 and N_2 in the composite membrane. Selectivity coefficients determined in this way are often called "ideal" selectivity coefficients; in keeping with this tradition the term "α_{O_2/N_2} (ideal)" will be used here to designate selectivity coefficients determined using the single gas permeation method.

The standard deviation of ±0.0008 Barrers in the determination of the permeability coefficient results in rather large uncertainties for these α_{O_2/N_2} (ideal) values. For example, the α_{O_2/N_2} (ideal) values in Table 1 are good to, at best, two significant figures and, for the lower flux values, only one significant figure. This level of uncertainty simply reflects the low permeability coefficients for these PPy films. Because of these high uncertainties in the ideal selectivity coefficient values, an alternative approach based on a more precise gas chromatographic (GC) method (see below) was used to obtain the bulk of the selectivity data reported here.

Binary Gas-Transport Experiments. As indicated above, the level of uncertainty in the determination of the α_{O_2/N_2} (ideal) values is unacceptably high. For this reason, a more precise binary gas-transport experiment using a GC detector was employed. Selectivity coefficients determined in this way are often called "actual" selectivity coefficients. In keeping with this tradition, the term "α_{O_2/N_2} (actual)" will be used here to designate selectivity coefficients determined using the binary gas GC method. In addition to providing greater precision, this binary gas experiment allows for investigations of how the relative amounts of O_2 and N_2 in the feed gas affects the selectivity for O_2 vs N_2 transport across the composite membrane. Gas tanks containing various volume percentages of O_2 and N_2 (see Materials section) were obtained for these studies. In all cases, the total pressure of the feed gas mixture applied to the membrane was 50 psig.

The GC-based measurements were conducted as follows: As per the single gas-permeation experiment, prior to gas-transport measurement, both the feed and permeant half-cells were evacuated, and the sample was allowed to outgas. The desired O_2/N_2 gas mixture was then introduced into the feed half-cell at a total pressure of 50 psig (334.5 cmHg). The gas ran from the compressed gas tank through the molecular sieve column (to remove trace water, see above), directly to the feed half cell. Intially the permeant half-cell was maintained under dynamic vacuum which was applied for 2 h to ensure that steady-state gas flux had been achieved. (In fact, the single gas permeation measurement indicated that steady state is achieved in less than 10 min. However, we wanted to be absolutely certain that steady state had been achieved).

After steady state was achieved, the permeant half-cell was switched from dynamic to static vacuum. This allowed the permeant gas to be collected in the permeant half-cell. The permeant gas was collected until easily measurable quantities of both O_2 and N_2 were present in the permeant half-cell. Depending on the composition of the gas mixture, this required times ranging from 15 min to 3 days. When gas is being collected in this way, the GC sampling loop (volume = 500 mL) is connected directly to the end of the permeant half-cell. After the desired gas-collection period, the sampling loop is switched such that the GC's He carrier gas passes through it, sweeping the entire contents of the loop onto the GC column.

There are two important points to make with regard to this sampling protocol. First, the pressure of gas in the permeant half-cell never exceeded 0.1 psi. This very low pressure ensures that the pressure difference across the membrane remained constant throughout the course of the measurement. We proved this point by measuring α_{O_2/N_2} (actual) as a function of gas-collection time. Second, because the flux of gas across the membrane is low (and because the feed is essentially an inexhaustable supply from a compressed gas tank), the feed and retentate gases always had the same composition. This was proven by injecting the retentate gas mixture directly onto the GC column after the desired collection period.

A Hach Carle Series 500 CGC GC was used to determine the amount of O_2 and N_2 in the permeant gas mixture. The gas chromatograph used a molecular sieve column (80% 13×, 20% 5A, operating at a temperature of 70 °C) and a thermal conductivity detector (operating at 200 °C). The flow rate of He was 20 mL min^{-1}. The dead volume on the downstream side of the permeation cell was ~9 mL. The molecular sieve column provided baseline separation of the O_2 and N_2 peaks in ca. 8 s. The areas under these peaks were determined using an electronic integrator (Varian 4270). Since the thermal conductivities of oxygen and nitrogen are almost the same,[26] the ratio of the O_2 and N_2 peak areas is the ratio of the moles of O_2 and N_2 transported across the membrane.

If the partial pressures of O_2 and N_2 on the feed side of the membrane were the same (i.e., if the feed-gas mixture was 50 mol % O_2 and 50 mol % N_2), the ratio of the GC peak areas would be the α_{O_2/N_2} (actual) value for the composite membrane. However, for most experiments, the partial pressures of O_2 and N_2 in the feed gas were not the same. The following normalization procedure was used so that α_{O_2/N_2} (actual) for the composite membrane could be calculated from the chromatographic peak areas.

Assume that the feed-gas mixture contained 10 mol of N_2 and 1 mol of O_2. This means that the driving force for N_2 transport is 10 times higher than that for O_2 transport. The area for the N_2 peak can be normalized to the O_2 peak area by simply multiplying the N_2 peak area by 0.1. This normalization, in essence, corrects for the larger driving force for N_2 transport. The α_{O_2/N_2} (actual) value for the composite membrane would then be obtained by dividing the experimental O_2 peak area by the normalized (i.e., ×0.1) N_2 peak area.

Three replicate measurements on at least two different membranes, and on the same membrane over periods as long as 4 months, provided a standard deviation of ±0.6 for this GC-based determination of the α_{O_2/N_2} (actual). Finally, it is important to emphasize that two types of actual selectivity coefficients are reported here—the α_{O_2/N_2} (actual) value shown by the composite membrane and the α_{O_2/N_2} (actual) value shown by the PPy film, itself (obtained via eq 2).

Elemental Analysis. Elemental analyses were used to investigate the effects of thermal and base treatments on PPy. These analyses were conducted on bulk PPy powders that were synthesized under identical conditions as the PPy thin films. We have previously shown that the elemental composition of PPy grown in the pores of such polycarbonate membranes is identical to that of bulk powder samples synthesized under the same conditions.[27]

Spectroscopic Studies. FTIR and UV−visible−near-IR absorption spectroscopies were also used to explore the effects of base and thermal treatment on the PPy. Samples for the FTIR experiments were prepared by mixing measured quantities of the bulk PPy powders with KBr and pressing pellets at 10^4 atm. The pellets obtained were ca. 0.2 mm in thickness. Data were obtained using a Matson Galaxy FTIR spectrophotometer. The optical absorption data were obtained on the PPy/polycarbonate/PPy composite membranes using an Hitachi U3501 spectrometer. This necessitates subtraction of the

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(25) Ashworth, A. J. *J. Membr. Sci.* **1992**, *71*, 169.

(26) *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Lide, D. R., Eds.; CRC Press Inc.: Boca Raton, FL, 1989; p E-3.

(27) Parthasarathy, R.; Martin, C. R. Unpublished results, 1995.

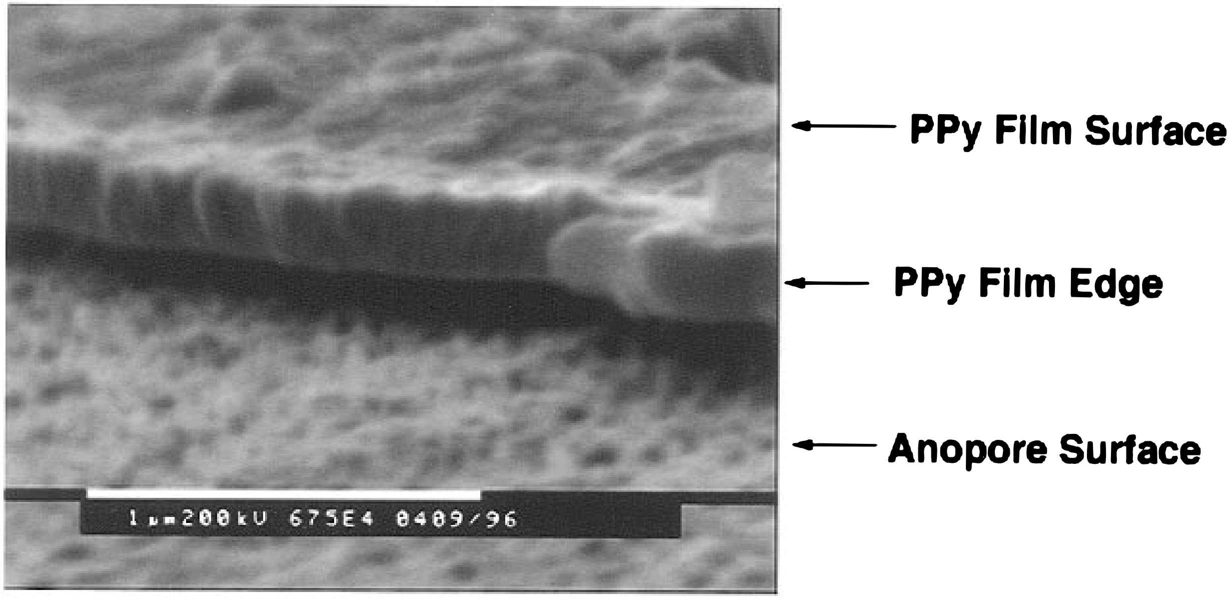

Figure 2. Scanning electron micrograph of the edge of a PPy film after isolation and collection on an alumina filtration membrane.

absorbance due to the polycarbonate. The methods used are described in refs 28–30.

Dc Conductivity. Conductivity data were obtained on the composite membranes using the standard four-probe conductivity method.[31]

Results and Discussion

Chemistry and Electrochemistry of PPy. Chemical representations of the totally reduced and totally oxidized forms of PPy are shown in Figure 1. The polymer is typically synthesized in the totally oxidized form. The totally reduced (sometimes called "pristine") polymer can be obtained by either chemical or electrochemical reduction.[32–34] PPy is unique among the electronically conductive polymers in that the pristine form is oxidized by molecular oxygen.[34] We have studied the interaction of O_2 with pristine PPy in some detail.[34] O_2 interacts with the pristine polymer by three mechanisms. The first entails partial electron transfer to O_2 to form a molecular-association complex. The second mechanism is identical with oxidation of the PPy and entails electron transfer to form partially oxidized PPy with the superoxide anion as the counterion. Finally, after long times, the superoxide anion deprotonates the polymer to yield an imine form of PPy. Details of these various types of chemical interactions can be found in our prior work.[34]

It occurred to us that the molecular-association[34] complex might provide a mechanism for facilitated transport[20] of O_2 through the PPy film. Such a facilitated transport mechanism would be expected to provide enhanced O_2 transport selectivity at low O_2 partial pressures. The problem with this concept is the irreversible electron-transfer and deprotonation chemistry discussed above. As a result of these chemistries the pristine material is not stable to O_2, an undesirable feature for an air-separation membrane. If, however, a partially oxidized form of the polymer could be obtained, the redox potential of this material might be too positive to allow for electron transfer to O_2. This might yield as PPy film that is still able to form the molecular association complex (i.e., partial electron transfer to O_2)[34] but is not irreversibly reactive to O_2. Since, treatment of doped PPy with base yields a partially oxidized material,[17–19] the gas-transport properties of base-treated PPy were studied.

Synthesis of the PPy Thin-Film Composite Membranes. We began our studies by synthesizing the PPy films across the surfaces of microporous polycarbonate filtration membranes. However, the porosities of these filters are so low and the PPy permeability coefficients are so small that the majority of the gas that is transported across the support permeates through the polycarbonate rather than through the pores. This is proven by the fact that composites made from porous and nonporous polycarbonate support membranes showed identical composite-membrane permeability coefficients. This led us to use nonporous versions of this membrane as the support since it is easier to model the gas flux (eq 2) when there is only one pathway through the support (the polycarbonate) as opposed to two (the polycarbonate and the pores).

The thickness of the PPy films synthesized across the surfaces of the support can be varied by controlling the polymerization time. A polymerization time of 30 min was used for the films investigated here. Scanning electron micrographs of cross sections of these films (Figure 2) yielded film thicknesses of 200 ± 25 nm. Thinner films (15 min polymerization time) gave higher gas fluxes; however, the flux data were not reproducible, suggesting that these thinner films were defective. Thicker films (2 h of polymerization time) showed immeasurably low gas fluxes.

As discussed in the Experimental Section, the key feature of the synthetic method used here is the addition of Fe^{2+} to the Fe^{3+}-based polymerization solution. Fe^{2+} was added to slow the rate of polymerization down in order to obtain a dense PPy film. Visual and electron microscopic examination of the films during synthesis showed that the rate of polymerization was, indeed, slower than when only Fe^{3+} was used[8,16] in the polym-

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(28) Menon, V. P.; Lei, J. T.; Martin, C. R. *Chem. Mater.*, in press.
(29) Cai, Z.; Lei, J.; Liang, W.; Menon, V.; Martin, C. R. *Chem. Mater.* **1991**, *3*, 960.
(30) Parthasarathy, R. V.; Martin, C. R. *Chem. Mater.* **1994**, *6*, 1627.
(31) Kim, H.; Laitinen, H. A. *J. Am. Ceram. Soc.* **1975**, *58*, 23.
(32) Lei, J.; Liang, W.; Martin, C. R. *Synth. Met.* **1992**, *48*, 301.
(33) Lei, J.; Martin, C. R. *Synth. Met.* **1992**, *48*, 331.
(34) Lei, J.; Martin, C. R. *Chem. Mater.* **1995**, *7*, 578.

erization solution. Furthermore, the extremely low gas fluxes and high gas-transport selectivities show that a dense (as opposed to microporous) film is achieved. Hence, the first interesting result of this study is that the morphology of PPy can be altered by varying the rate of polymerization.

Single Gas Permeation Experiments. Table 1 shows permeability coefficients and α_{O_2/N_2} (ideal) values for the following: (1) The composite membrane based on PPy films that had been subjected to the base/heat treatments. (2) The base/heat-treated PPy film itself. (3) The bare polycarbonate support membrane; to be consistant, this control membrane also received the base/heat treatments.

Note first that the permeability coefficients for the PPy film are over an order of magnitude lower than the permeability coefficients for the composite membrane. This shows that despite the fact that the PPy film is substantially thinner than polycarbonate support, the PPy film is predominantly responsible for the rate and selectivity of gas transport in the composite. This is further demonstrated by the fact that the α_{O_2/N_2} (ideal) value for the composite is very similar to the selectivity coefficient for the PPy film. The α_{O_2/N_2} (ideal) value for the polycarbonate support is substantially lower. It is worth noting that the polycarbonate permeability coefficient reported in Table 1 are somewhat lower than values typically found in the literature.[35] This is undoubtedly because the membranes used here are stretch-oriented, which increases polymer crystallinity.

The α_{O_2/N_2} (ideal) value for the base/heat-treated PPy film is, in fact, extraordinary. While claims have been made for higher selectivity coefficients in polyaniline,[10] these higher numbers have been difficult to reproduce.[7] Other than these disputed polyaniline data, the α_{O_2/N_2} (ideal) value of 18 reported here is, to our knowledge, the highest selectivity coefficient obtained for a polymeric material to date. There is a price to pay for this extraordinary selectivity—the O_2 permeability coefficient (PO_2) for the PPy film is extremely low, relative to PO_2 values for related polymers.[7,36] For example, polyaniline shows $P_{O_2} = 0.16$ Barrers and an α_{O_2/N_2} (ideal) of 14.8;[7] and a sulfonated polystyrene shows $P_{O_2} = 0.42$ Barrers and an α_{O_2/N_2} (ideal) of 11.7.[36] While these comparisons seem to indicate that this partially oxidized form of PPy is not a promising polymer for industrial gas separations, we will show below that dramatically higher α_{O_2/N_2} (actual) values are obtained at very low O_2 partial pressures.

Finally, it is of interest to note that PPy films that were heated but not treated with aqueous base showed even lower permeability coefficients. The O_2 permeability coefficient for such a film was 3×10^{-4} Barrers, an order of magnitude lower than that of the base/heat-treated PPy film (Table 1). The N_2 permeability coefficient for the heat-only-treated film was too low to measure with the pressure transducer. In addition, we made some measurements on the as-synthesized PPy films (i.e., no base or heat treatments). While these data were difficult to reproduce, such films showed substantially lower selectivity coefficients (α_{O_2/N_2} (ideal) ~ 10). In addition the gas flux increased (and α_{O_2/N_2} (ideal) decreased) as a function of measurement time.

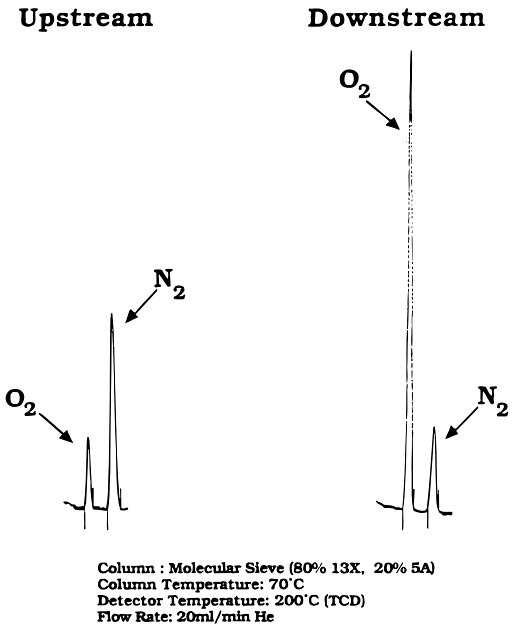

Figure 3. GC peaks for O_2 and N_2. The peaks labeled "upstream" are for the feed gas (compressed air). The peaks labeled "downstream" are for the permeant gas after passage through the PPy-based composite membrane.

Binary Gas Permeation Experiments. Figure 3 shows GC data for a PPy-based composite membrane when compressed air (80% N_2 and 20% O_2) was used as the feed gas. The dramatic enhancement in the relative height of the O_2 peak in the permeant gas clearly shows that this membrane is highly selective for O_2. In addition to allowing for binary mixtures to be used as the feed gas, the GC detector offers greater sensitivity and precision than the pressure transducer. This means that mixtures that contain low partial pressures of O_2 can be analyzed. However, the GC method only provides the selectivity coefficient for the composite membrane. That is, unlike the pressure transducer experiment, it is difficult to extract the selectivity coefficient for the PPy film itself using the GC detector. Since the composite selectivity coefficient is similar to (but slightly less than) the selectivity coefficient for the PPy film (Table 1), this is not a big problem.

It was important to ascertain that the GC-based method produces reliable selectivity coefficient data. As a first test of the reliability of this method, we did single gas permeation measurements on a PPy membrane using the GC as the detector. Since this experiment is analogous to the single gas permeation measurement done using the pressure transducer, a composite membrane selectivity coefficient of α_{O_2/N_2} (ideal) = 18 (Table 1) should be obtained. The GC detection method gave the identical value.

We were also concerned about the possibility, discussed in the Experimental Section, that the long gas collection times might cause a significant buildup of pressure on the low-pressure side of the membrane. This would result in a decreased driving force for permeation of the preferentially transported gas (O_2), which would yield spuriously low selectivity coefficient values. We obtained α_{O_2/N_2} (actual) values for a base/heat-treated membrane using compressed air at 50 psig as the feed gas for collection times of 4, 18, and 27 h. An α_{O_2/N_2} (actual) value = 18 was obtained for all three collection times.

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(35) Chen, W. J.; Martin, C. R. *J. Membr. Sci.* **1994**, *95*, 51.
(36) Reference 5, p 27.

Table 2. Effect of O_2/N_2 Binary Feed Gas Composition on the α_{O_2/N_2}(actual) Value Obtained for a Polycarbonate Composite Membrane[a]

	% O_2[b]					
	90	50	20	7.5	1	0.1
α_{O_2/N_2}(actual)	17	18	18	18	24	92

[a] The PPy film received the standard base/heat treatment. [b] The remainder of the gas was N_2.

Table 3. Elemental Analysis Data

sample	C	H	N	O	Cl	Na
as-synthesized PPy	3.97	3.83	1	0.67	0.25	trace
base-treated PPy	3.95	3.73	1	0.77	0.16	trace
base/heat-treated PPy	3.94	3.68	1	0.76	0.17	trace

Table 2 shows composite membrane α_{O_2/N_2} (actual) values obtained when binary gas mixtures having a wide range of partial pressures of O_2 and N_2 are used as the feed gas. If a simple dissolution/diffusion mechanism[37] for gas transport is operative in the PPy film, then the α_{O_2/N_2} (actual) values obtained from the single gas and binary gas-transport experiments should be the same. A comparison of the data in Tables 1 and 2 show that for O_2 percentages of 7.5% or higher this is essentially the case. This ability to obtain the same value of α_{O_2/N_2} using both the pressure transducer (Table 1) and GC (Table 2) detectors gives us further confidence that GC method produces reliable results.

The most interesting aspect of the data in Table 2 concerns the α_{O_2/N_2} (actual) values at very low O_2 partial pressures. We find that the selectivity coefficient increases dramatically at low O_2 partial pressures. There is no precedent in the literature for α_{O_2/N_2} (ideal or actual) values for polymeric materials as high as 90.[38] This suggests (but does not prove) that an unusual transport process occurs in this film at low O_2 partial pressures. It is worth reiterating that the highest value in Table 3 (α_{O_2/N_2} (actual) = 92) was obtained for three different measurements on two different composite membranes. Furthermore, the gas-collection system was tested for leaks by evacuating both the feed and permeant half-cells, maintaining this static vacuum for 3 days, and then injecting a sample of the permeant half-cell onto the GC column. Neither O_2 nor N_2 were detected. Furthermore, a leak would make α_{O_2/N_2} (actual) spuriously low, not spuriously high. This is because the gas that would have leaked into the apparatus would have been enriched in N_2 (i.e., air).

If, as suggested above, the molecular association complex[34] can facilitate the transport of O_2, a plot of α_{O_2/N_2} (actual) vs partial pressure of O_2 in the feed gas should show high selectivities at low partial pressures (region of facilitated transport), and selectivity should then decrease to a constant value at high O_2 partial pressure.[20,37] The data in Table 2 are clearly consistent with (but certainly do not prove) this facilitated transport mechanism. Put another way, the sites that form the molecular association complex with O_2 can be regarded as what Nobel et al. call "fixed-sites" along the polymer chain for facilitation of O_2 transport. The constant selectivity at high partial pressure is simply the inherent selectivity of the polymer itself, i.e., the selectivity obtained when all of these fixed-sites are saturated with O_2.[37]

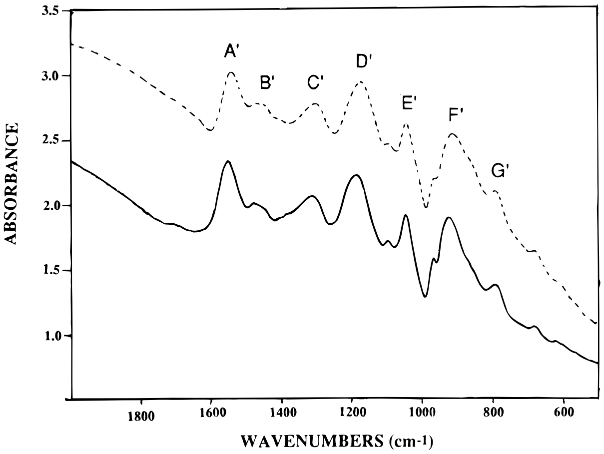

Figure 4. FTIR spectra for PPy that had received only heat treatment (upper/dashed curve) and for PPy that had received the standard base/heat treatment.

Elemental Analyses. Elemental analysis data were obtained on samples of as-synthesized, base-treated, and base/heat-treated PPy (Table 3). Consistent with previous investigations of this type,[39] base treatment causes a loss of Cl^- from the film. This could mean that Cl^- is simply being exchanged for OH^- from the base solution, in which case the extent of oxidation of the film would not be changed. If Cl^- is lost via ion exchange with OH^-, a concomitant increase in both the O and H content of the film would be expected. Table 3 shows, however, that while the O content does, indeed, increase, the H content decreases upon base treatment. Therefore, ion exchange does not appear to be the primary mechanism by which Cl^- is lost from the film.

The alternative possibility is that the base solution deprotonates the oxidized polymer, and HCl is lost from the film.[40] This would yield a partially oxidized imine form of the polymer,[41] which would explain the simultaneous loss of both Cl and H from the base-treated film (Table 3). Furthermore, the amount of Cl and H lost upon base treatment is essentially identical, which is also consistent with this model. (The further loss of H upon thermal treatment (Table 3) is undoubtedly due to thermally induced cross-linking of the polymer.) Loss of HCl to yield a partially oxidized form of the film is also consistent with the spectroscopic and conductivity data presented below. On the basis of all of these results, we propose that the base/heat treatment yields a partially oxidized imine form of PPy.[41] Finally, the increase in oxygen content upon base treatment (Table 3) is due to the formation of carbonyl defects.[41] This conclusion is also supported by the FTIR data.

FTIR Data. Infrared spectra for a PPy film that had been subjected to the standard base/heat treatment and for a film that received only heat treatment are shown in Figure 4. These spectra show a featureless absorption tail at energies above 1600 cm^{-1} and a series of bands below 1600 cm^{-1}. The featureless tail is due to free-carrier absorption and is a unique signature of the conductive state.[32] In accordance with Tian and Zerbi's nomenclature,[42,43] we have labeled the bands below 1600 cm^{-1} A′–G′.

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(37) Stern, S. A.; Trohalaki, S. In *Barrier Polymers and Structures*; Koros, W. J., Ed.; American Chemical Society: Washington, DC, 1990.

(38) Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165.

(39) Van Dyke, L. S.; Martin, C. R. *Langmuir* **1990**, *6*, 1118.

(40) Inganas, O.; Erlandsson, R.; Nylander, C.; Lundstrom, I. *J. Phys. Chem. Solids* **1984**, *45*, 427.

(41) Lei, J. T.; Cai, Z.; Martin, C. R. *Synth. Met.* **1992**, *46*, 53.

(42) Tian, B.; Zerbi, G. *J. Chem. Phys.* **1990**, *92*, 3892.

(43) Tian, B.; Zerbi, G. *J. Chem. Phys.* **1990**, *92*, 3886.

Table 4. $I_{A'}/I_{B'}$ **Ratio (See Text) and the dc (4-point) Conductivity Data for the Various PPy Samples**

sample	$I_{A'}/I_{B'}$	conductivity (S cm^{-1})
as-synthesized PPy	2.1	112
heat-treated PPy	2.3	26
base-treated PPy	2.5	0.43
base/heat-treated PPy	2.9	0.01

Rabolt et al. have shown that the so-called "doping-induced bands" (D′ and F′) blue-shift upon conversion of fully oxidized PPy to a partially oxidized form.[44,45] The D′ and F′ bands in the as-synthesized PPy are at 1169 and 906 cm^{-1}, respectively. We have found that while heating, alone, does not affect the position of the D′ and F′ bands, treatment with base followed by heating causes these bands to blueshift (to 1180 and 914 cm^{-1}, respectively). This indicates that base/heat treatment yields a partial oxidized PPy. This is consistent with the elemental analysis data discussed above.

Another interesting feature to be noted in the sample that received the base treatment is a very weak band at 1705 cm^{-1} (Figure 4). This band is not observed in the sample that had not been exposed to base. This can be attributed to the introduction of carbonyl defect sites upon exposure to base.[41] Again, this conclusion is supported by the elemental analysis data, where it was noted that base treatment causes an increase in O content in the PPy (but no concomitant increase in H).

We have established that base treatment of PPy introduces both imine and carbonyl defect sites. These defects sites would be expected to interrupt conjugation, and the conjugation length of the base-treated polymer should be diminished.[41] To verify this, we have used a previously described[41] FTIR method to assess the relative conjugation before and after base and heat treatment. According to this method, the conjugation length in PPy is inversely proportional to the ratio of the integrated absorption intensities of the A′ and B′ FTIR bands (Figure 4).[41] We call this ratio $I_{A'}/I_{B'}$, where I indicates the integrated absorption intensity of the indicated FTIR peak. Table 4 shows this $I_{A'}/I_{B'}$ ratio for the various PPy samples studied here. We find that the conjugation length does, indeed, decrease upon base/heat treatment of the polymer.

Optical Spectroscopy. Optical spectra of heat-treated and base/heat-treated PPy are shown in Figure 5. In agreement with previous studies,[46-48] two broad bands are observed—one centered approximately at 450 nm and the other centered at around 900 nm. Bredas and Street[46] and Bredas et al.[47,48] have explained the spectra of PPy on the basis of a simplified band approach. According to them, the 450 and 900 nm peaks correspond to transitions between the valence band and antibipolaron band and the valence and bipolaron band, respectively. As seen in Figure 5, base/heat treatment causes a blue-shift in both of these bands relative to the material that was not treated with base. This indicates that the bandgap has increased, which is completely consistent with the decrease in conjugation length reported by the FTIR method.

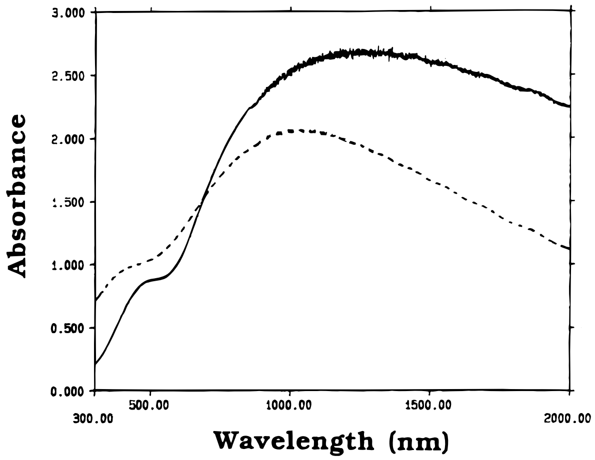

Figure 5. Optical absorption spectra for PPy that had received only heat treatment (upper/solid curve) and for PPy that had received the standard base/heat treatment.

Note further that the intensity of the broad near-IR absorption is lower for the base-treated film (Figure 5). Since the absorption intensity in this region is related to the number and mobility of free charge carriers,[32] these data suggest that the base-treated material is less conductive. This would, of course, be the expected result given the fact that the base/heat-treated material (1) is only partially oxidized, (2) has higher concentrations of imine and carbonyl defect sites, and (3) has attenuated conjugation. Furthermore, lower conductivity is confirmed by the dc conductivity data presented below. It is gratifying that all of the various methods used to investigate these samples tell a coherent story about these materials.

Conductivity Data. Four-probe conductivity data are shown in Table 4. As would be anticipated from all of the preceding analyses, the base and base/heat-treated films have dramatically lower conductivities than the as-synthesized PPy.

Conclusions

Our prior investigations of the interactions of O_2 with undoped polypyrrole[34] suggested that a partially oxidized form of the polymer might be able to provide a route for facilitated O_2 transport. To test this premise, we studied gas transport in base/heat-treated PPy films. (Careful elemental and spectroscopic analyses confirmed that this treatment did, indeed, yield a partially oxidized material). The gas-transport data are qualitatively consistent with a facilitated model. Furthermore, the O_2/N_2 selectivity coefficients (actual) obtained at low partial pressures are extraordinarily large for a polymeric material. However, further study of this interesting chemical system must be done before definitive conclusions about the transport mechanism can be drawn.

Acknowledgment. This work was supported by the Dow Chemical Co. and the National Science Foundation.

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(44) Rabolt, J. F.; Clarke, T. C.; Street, G. B. *J. Chem. Phys.* **1979**, *71*, 4614.

(45) Rabolt, J. F.; Clarke, T. C.; Street, G. B. *J. Chem. Phys.* **1982**, *76*, 5681.

(46) Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309.

(47) Bredas, J. L.; Scott, J. C.; Yakushi, K.; Street, G. B. *Phys. Rev.* **1984**, *30*, 1023.

(48) Bredas, J. L.; Quattrocchi, C.; Libert, J.; MacDiarmid, A. G.; Ginder, J. M.; Epstein, A. J. *Phys. Rev.* **1991**, *B26*, 4859.