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Gas Transport in Electronically Conductive Polymers

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There has recently been a tremendous resurgence of interest in synthetic polymer films and membranes.[1–5] This resurgence is driven, in part, by the economic advantages inherent in membrane-based chemical separations[1–3] and by the recent development of polymeric materials with unique electronic[4] and optical[5] properties. We have been conducting research in both of these general areas, i.e., in developing new membranes for gas separations[3] and in exploring electronic conductivity in polymers.[4] It occurred to us that there might be some benefit in combining these seemingly divergent research areas, speicifically, in conducting fundamental investigations of gas transport in electronically conductive polymers (ECPs).

Our rationale is as follows: (1) We have found that polymers that contain high concentrations of fixed ionic sites can show exceptional gas-transport selectivity;[3b] the doped[4] forms of ECPs are exactly such polymers. (2) It is easy to synthesize thin films of ECPs;[4] this is important because flux of permeate is inversely proportional to film thickness in all membrane-based chemical separations. (3) ECPs can be reversibly "switched" between polyionic and neutral forms;[4] this raises the interesting prospect of reversibly "switching" the gas permeability of a film between two well-defined values.[6]

This correspondence describes results of the first fundamental investigations of rates and selectivities of gas transport in ECPs. We have focused our attention on the heterocyclic ECPs.[4] We will show that thin films of these polymers can exhibit extraordinary gas-transport properties.

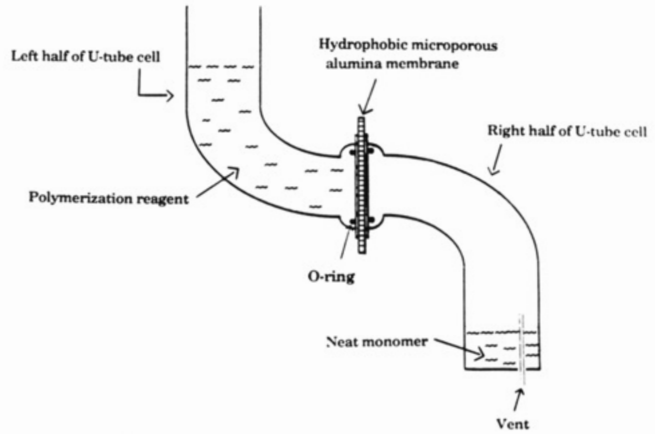

Figure 1. Schematic diagram of cell used to conduct interfacial polymerization of a thin conductive polymer film onto the surface of a microporous support membrane.

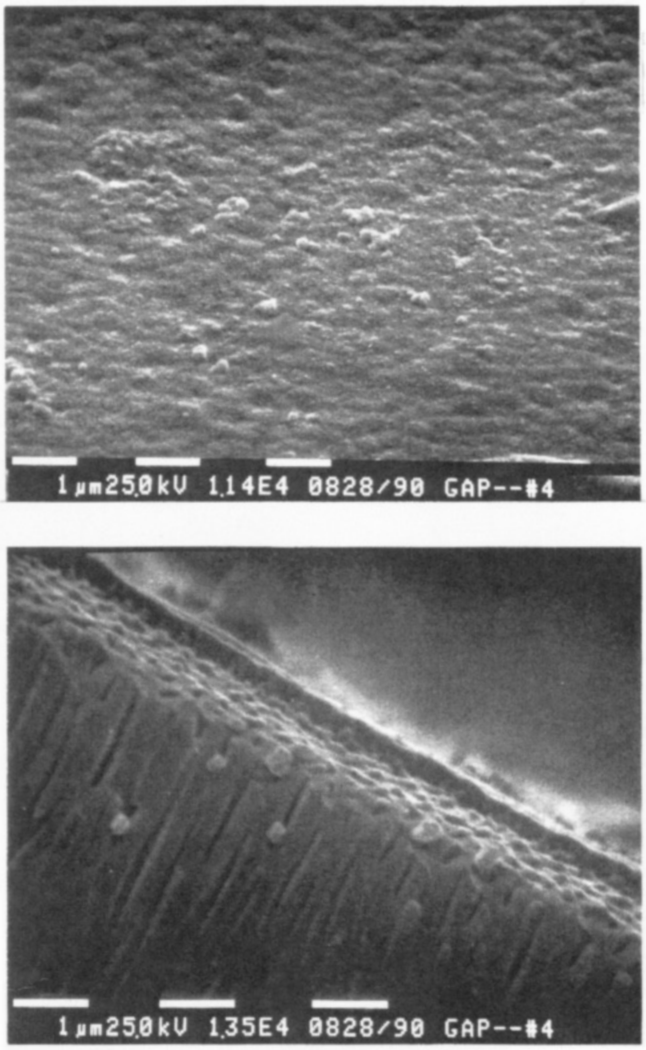

Figure 2. Scanning electron micrographs of top (upper) and cross section (bottom) of an Anopore/polypyrrole thin-film composite membrane.

We began our studies with free-standing films of the ECPs. We discovered, however, that these films were too brittle to be used in our gas-permeation cells.[7] We have, therefore, invented a new method for synthesizing thin-film composite membranes[2,3] based on ECPs. This method entails interfacial polymerization of an ECP film at the surface of a microporous alumina support membrane.[8] The surfaces of the membrane were first rendered hydrophobic by reacting with a silane derivative.[9] The membrane was then mounted in a cell (Figure 1) such that one surface[10] contacted an aqueous solution of the polymerization reagent (2.0 M $Fe(NO_3)_3$) and the other surface

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[6] Murray has demonstrated a similar concept involving "gated" ion-transport across an ECP film: Burgemayer, P.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 6139. To our knowledge, this concept has never been demonstrated for gas transport in a polymer film.

[7] Details of the gas-permeability apparatus can be found in: Liu, C. Ph.D. Dissertation, Texas A&M University, 1991.

[8] Obtained from Anotech, Ltd. These membranes have 200-nm-diameter pores that branch into 20-nm-diameter pores at one membrane surface. See ref 3.

[9] The Anopore was derivatized by using a solution 2% in hexadecyltrichlorosilane and 0.25% in dimethyldichlorosilane; the solvent was isopropyl alcohol. See: Brumlik, C. J.; Martin, C. R. *J. Am. Chem. Soc.* **1991**, *113*, 3174.

[10] The branched-pore surface (20-nm-diameter pores)[8] faced the Fe^{3+} solution.

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Table I. Permeability and Selectivity Coefficients for Various Gases in Polycationic (PMPy-NO_3) and Neutral[a] (PMPy) Poly(*N*-methylpyrrole) Films

polym	P_{O_2}[b]	P_{N_2}	α_{O_2/N_2}[c]	P_{CO_2}	P_{CH_4}	α_{CO_2/CH_4}
PMPy-NO_3	1.26	0.16	7.9	2.82	0.17	16.2
PMPy	2.04	0.33	6.2	6.90	0.22	31.9

[a] PMPy was prepared by treating PMPy-NO_3 with 0.005 M $NaBH_4$ in CH_3CN. [b] Permeability coefficients in Barrers = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg. Membrane area was 0.0792 cm^2. Pressure differential was 50 psi. Film thickness was 1.4 μm. [c] Ratio of permeability coefficients. See text.

contacted the equilibrium vapor associated with the neat monomer.

Because the membrane is hydrophobic,[9] the $Fe(NO_3)_3$ solution cannot flood the pores. Monomer vapor can, however, permeate the pores and react[4a,b] with the Fe^{3+} at the membrane/solution (opposite) interface (Figure 1). This caused a thin, strongly adherent film of the ECP to "grow" across the membrane surface. We have used this method to form Anopore/ECP composite membranes based on polypyrrole, polythiophene, poly(3-methylthiophene), and poly(*N*-methylpyrrole). A scanning electron micrograph of a typical composite membrane is shown in Figure 2. Film thickness can be conveniently controlled by varying the duration of the polymerization period.

The majority of our gas-transport data, to date, have been obtained on composites based on polypyrrole (PPy) and poly(*N*-methylpyrrole) (PMPy). Gas-transport data were obtained by using the single gas-permeation method.[7,11] This method provides the permeability coefficient (P_g) for the gas in the thin ECP film.[11] The permeability coefficients for two gases can then be ratioed to yield the selectivity coefficient (α).[11]

Table I shows P_g and α values for various gases in two PMPy films; the films were 1.4 μm thick. This table contains an enormous quantity of information. First, these data show that these thin films are essentially defect-free. If microscopic defects, or pores, were present in these films, gas would be transported through these defects via Knudson flow.[2] If this mechanism predominated, the O_2/N_2 selectivity coefficient ($\alpha_{O/N}$) would be 0.94; furthermore, even minute numbers of defects cause Knudson flow to predominate.[2] The high (vide infra) $\alpha_{O/N}$ values shown in Table I indicate that these thin PMPy films are essentially defect-free. This is extremely important to separations applications of such membranes because defects destroy chemical selectivity.[2] It is of interest to note that we have conducted analogous studies on PPy-NO_3 and these films show Knudson selectivity coefficients. Thus, in contrast to PMPy-NO_3, PPy-NO_3 appears to be porous.

Second, we raised the interesting possibility of using the polyionic to neutral-polymer transition[4] to reversibly alter the gas-transport properties of an ECP film. Table I indicates that this is an experimental reality. Note that the P_g values for all gases in the polycationic form of PMPy are lower than the P_g's for the neutral form of this polymer. It is well-known that introduction of ionic groups into a polymer lowers the available void volume.[12] This decrease in void volume is undoubtedly responsible for the diminution in the P_g values for PMPy-NO_3.

Finally, Table I shows that PMPy-NO_3 has extraordinary gas-transport characteristics. One of the highest $\alpha_{O/N}$ to be reported in the literature, to date, is a value of 8.0 for poly(*p*-hydroxystyrene).[11b] PMPy-NO_3 essentially matches this exceptional selectivity (Table I). However, the *P*s for O_2 and N_2 in PMPy-NO_3 are an *order of magnitude higher* than in poly(*p*-hydroxystyrene).[11b] Thus, PMPy-NO_3 provides both high selectivity and high flux. This is an important observation because enhanced selectivity in a polymer film can usually be achieved only at the expense of flux.[11b] PMPy-NO_3 appears to be an exception to this general rule and thus shows potential for use as a high-performance material in gas-separation systems.

We are currently attempting to elucidate the chemical basis for these extraordinary gas-transport characteristics. We have obtained analogous results from a highly sulfonated styrenic polymer.[3b] We believe, therefore, that the high ion content of these materials is a critical factor.[3b] Furthermore, ECPs provide a wealth of opportunities for fundamental investigations of the effects of molecular and supermolecular structure on gas transport in polymers. Polymers with a large variety of chemical structures and substituents can be easily synthesized,[13] and the counterion in the doped form can be changed, at will, via ion exchange. We are currently exploring these unique opportunities.

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Registry No. PPy, 30604-81-0; PMPy, 72945-66-5; NO_3, 14797-55-8; O_2, 7782-44-7; N_2, 7727-37-9; CO_2, 124-38-9; CH_4, 74-82-8; Anopore, 127361-04-0.

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Growth of Free-Standing Diamond Films on Glass

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The unique properties possessed by diamond make it extremely attractive for various materials applications.[1,2] In addition to being the hardest material available (Mohs hardness = 10) it also has the highest thermal conductivity (~20 W cm^{-1} K^{-1}) and a large optical bandgap (5.5 eV). The bandgap provides transparency in the high-frequency region of the spectrum. Hence free-standing films of di-

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