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Conjugated Polymer Films for Gas Separations

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Permeabilities for a series of gases through free-standing films of the conjugated polymer polyaniline are reported. A remarkable selectivity has been achieved for important gas pairs including hydrogen-nitrogen, oxygen-nitrogen, and carbon dioxide-methane. The selectivity values of 3590 for H_2/N_2 , 30 for O_2/N_2 , and 336 for CO_2/CH_4 surpass the highest previously reported values of 313, 16, and 60 for the nonconjugated polymers poly(trifluorochloroethylene), cellulose nitrate, and a fluorinated polyimide, respectively. The process for tailoring gas selectivity of a polyaniline membrane involves first enhancing the permeabilities of gases with small diameters [<3.5 angstroms ($\text{\AA}$)] by doping and undoping the polymer film with counterions of an appropriate size. High selectivities are then achieved by decreasing the permeabilities of larger gases (>3.5 $\text{\AA}$ diameter) through controlled redoping of the polymer. The permanent morphological changes induced in this conjugated polymer system and others indicate the potential for development of universal membranes for gas separations.

THE ABILITY TO SEPARATE MIXTURES of gases is essential for a wide variety of industrial applications (1). In the manufacturing of chemicals, unreacted hydrogen can be recovered from waste gas streams and recycled. Low-grade natural gas can be purified by the removal of carbon dioxide and hydrogen sulfide to reduce pollution. Carbon dioxide can then be reused in tertiary oil recovery. Air can be separated into oxygen and nitrogen. Valuable nonrenewable resources such as helium can be recovered and recycled.

Membrane-based gas separations have tremendous potential as energy-efficient alternatives to cryogenic separations. Within the last decade a number of membrane systems have been introduced commercially (2, 3). The synthesis of new polymeric ma-

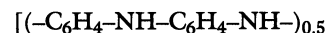
terials (4, 5) and the development of asymmetric membranes, in which a thin skin of polymer with high gas selectivity is grown on a porous structural support (1, 6-8), have made this possible. The thin polymer skin, which ranges in thickness from a few hundred to a few thousand angstroms, is crucial to any membrane separation process. Current membrane systems have limited applications because the morphology of a polymer film is difficult to predict prior to the manufacturing process and cannot be adjusted consistently once the film is formed. We report a new approach to gas membrane separators in which we use a class of polymers whose morphologies can be precisely controlled after synthesis to optimize a particular separation.

Dopable conjugated polymers, of which conducting polymers constitute a subgroup, form a relatively new class of organic materials that have been studied extensively for their electrical properties since the first doping experiments were reported on polyacet-

ylene in 1977 (9). Conducting polymers (including polypyrrole, polythiophene, polyparaphenylene, polyaniline, and their derivatives) have potential for use in a wide variety of electronic devices (10-13). Gas separation represents a new area of application for these materials. Although the features that predispose these polymers to being conductive may still be important, their electrical conductivity plays only an indirect role. The doping process that makes these materials conductive allows precise changes to be made in their morphology.

Polyaniline, $(C_6H_4NH)_x$, is a desirable membrane material because of its air stability in both neutral and doped forms, its excellent processability and rheological properties, and its simple acid-base doping chemistry in aqueous solution. The polymer powder is made directly from a relatively inexpensive monomer. Furthermore, conventional polymer processing techniques yield high-quality, mechanically robust films.

Polyaniline, in the emeraldine oxidation state,



is synthesized by chemical oxidation of aniline (14). The polymer powder was purified by successive wash cycles with aqueous acid (1.0 M HCl) and base (0.1 M NH_4OH), each cycle followed by filtration and vacuum drying. The emeraldine base was ground to a fine powder, swelled with tetrahydrofuran, and dissolved in *N*-methyl pyrrolidinone (NMP) (5.0% w/v). The films were formed by spreading the viscous, homogeneous solution onto glass plates with a casting bar. The polymer-coated plates were cured at 135°C for 1 to 3 hours in a drying oven. The resulting ~0.1-mm-thick films were separated from the glass plates by immersion in

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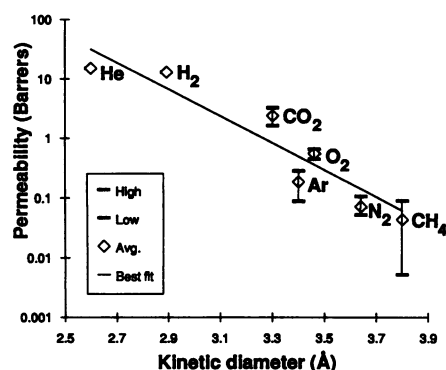


Fig. 1. Relation between the kinetic diameter of selected gases and their permeability through an as-cast polyaniline membrane. A size-dependent selectivity is apparent. Enhanced permeability of O₂ (relative to Ar) is probably due to the greater solubility of O₂ in polyaniline. The permeability data are based on six film samples with the He permeabilities normalized to 15 Barrers (20).

water and dried under dynamic vacuum for at least 24 hours prior to use. These "as-cast" films were tested for gas permeability to establish standard values for untreated polyaniline film. Samples of the as-cast film were doped in 4.0 M acid solutions for 15 hours, which yields a fully doped film, that is, 50 halide counterions per 100 ring nitrogens (15). The samples are tested and then undoped by treating with 1.0 M NH₄OH solution for 24 hours, which removes substantially all halogen from the film (16). The treated samples were redoped by immersion for 12 hours in a 0.0175 M solution of the same acid used for the initial doping, which yields a partially doped film, that is, 36 halide counterions per 100 ring nitrogens (17).

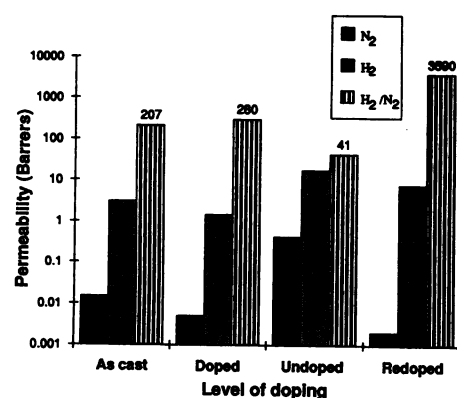


Fig. 2. The permeability of gases through a polyaniline membrane can be controlled by the doping process. The as-cast film has a size-dependent permeability and, therefore, a modest separation factor. Doping the polyaniline film decreases its permeability to both H₂ and N₂. Undoping the film increases the permeability of both gases. Redoping greatly decreases the permeability of N₂ while only slightly decreasing the permeability of H₂, which leads to a very high H₂/N₂ separation factor (24).

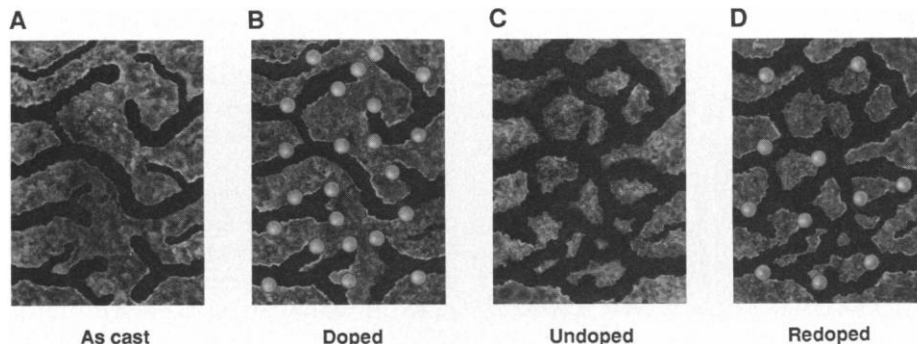


Fig. 3. A schematic representation of the effect of doping on the pore connectivity is shown in the above hypothetical cross section of a polymer membrane: (A) as cast with no dopant ions; (B) after heavily doping in a strong acid solution; (C) after undoping in a basic medium; and (D) after redoping in a mild acid solution. The as-cast film has some permeability to all gases which is size-dependent, leading to modest separation ratios. Heavy doping of the film reduces the permeability of all gases. Undoping the film increases the permeability of small gases relative to the as-cast film. Moderate redoping blocks the permeability of the larger gases and leads to very high separation ratios. Although this figure depicts dopant-induced changes in free volume to affect diffusion rates, solubility is also an important factor in obtaining such high separation ratios.

Treated and untreated film samples were mounted in the test cell and thoroughly degassed under high vacuum ($<10^{-6}$ torr) before they were used in permeability tests. In the test system an established manometric method (18) is used to measure the gas flux on the low-pressure side of the membrane. Pure gas permeabilities of He, H₂, CO₂, Ar, O₂, N₂, and CH₄ for all of the films were measured at 40 psi.

Standard values for gas permeabilities measured on as-cast polyaniline films are shown in Fig. 1. The kinetic diameters of the permeant gases (19) are well correlated with their permeabilities. Permeability is defined as the product of the diffusion rate of the permeant species and its solubility in the polymer (1) and is expressed in units of Barrers (20). The correlation of permeability of gases through the polyaniline membrane with their kinetic diameters indicates that the permeation rate is primarily influenced by diffusion and not by solubility (6, 21). However, the solubility component of the permeability appears to be non-negligible for O₂ and CO₂. Although the kinetic diameters of Ar and O₂ are similar, the O₂ permeability is greater (Fig. 1). This result indicates an enhancement most likely attributable to the solubility of O₂ in polyaniline.

The best gas separation membranes are polymer films near full density. Less dense films are porous to all gases and therefore have little or no selectivity. For example, polyacetylene films produced by Ziegler-Natta catalysis of acetylene possess a fibrillar morphology where the (CH)_x chains occupy only one-third of the film's total volume (22). Permeability tests revealed that these films are porous. Electrochemical polymerization also generally results in conjugated polymers having porous fibrillar morpholo-

gies (23). Tests on electrochemically grown polypyrrole and polyparaphenylene showed that they are unsuitable as gas separation membranes.

Solution casting is a direct method for producing dense films for gas separations. Polyaniline films cast from NMP solutions had a true (or matrix) density of 1.257 g/cm³ and an apparent (or bulk) density of 1.244 g/cm³. These values were determined from helium pycnometry and mass to volume ratio measurements, respectively. Comparison of these values indicates that the polyaniline films are near full density. Nitrogen gas adsorption experiments [BET (Brunauer-Emmett-Teller) method] indicated an average pore size of much less than 20 Å in diameter and a total surface area of 0.12 m²/g.

As shown in Fig. 1, the as-cast polyaniline films have an intrinsic ability to separate gases. The permeability of a new piece of polyaniline film was measured in order to determine the changes in permeability induced by doping, undoping, and redoping (cycling). Figure 2 shows results that compare H₂, a small permeant (kinetic diameter = 2.89 Å), to N₂, a large permeant (kinetic diameter = 3.64 Å). The as-cast film exhibited a H₂ permeability of 3.08 Barrers and a N₂ permeability of 0.014 Barrers, leading to a H₂/N₂ separation factor of 207. The permeabilities to both gases decreased after the sample was heavily doped in 4.0 M HCl solution (Fig. 2) (24). The decrease can be attributed to the presence of chloride dopant counterions, which fill much of the free volume in this near fully dense protonated polymer.

The protons and dopant counterions were completely removed by undoping the membrane in base solution, yet the polymer

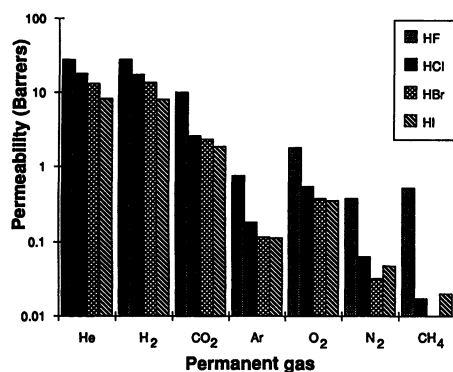


Fig. 4. The dependence of permeability on the size of the dopant is illustrated by comparing permeabilities of polyaniline films doped with the halogen acid series (at 4.0 M concentration) followed by undoping in base. The use of HF creates the largest or best connected pore network, or both, leading to the highest permeabilities for all gases. Pores of progressively smaller size or lower connectivity are formed with the use of HCl, HBr, and HI, respectively, and lead to a decreasing progression of permeabilities (24).

matrix retained its new expanded morphology as confirmed by an increase in H_2 permeability. The associated increase in N_2 permeability led to a decrease in H_2/N_2 selectivity to 41. The greater permeability suggests that the free volume in the membrane increases, which allowed for greater throughput of both H_2 and N_2 gases. The doping-undoping process thus has the effect of increasing free volume and creating channels through the polymer matrix. The final treatment of redoping the film in mild acid solution (0.0175 M HCl) reintroduces a moderate amount of dopant ions that partially fill the newly increased free volume. The diffusion of large gas molecules was more strongly affected by the redoping than the diffusion of small gases since fewer large pathways remained open. The reduced number of large channels led to a very high separation factor, as confirmed by a H_2/N_2 selectivity of 3590 observed for the redoped sample. Additional measurements made on the same sample several weeks apart showed less than 5% change in permeability, indicating that the doping process induced a permanent change in the polymer morphology. A schematic representation of the morphological changes induced in a hypothetical as-cast polyaniline film by cycling is given in Fig. 3.

The dopant cycling of polyaniline leads to one of the most selective polymer membranes known. This claim is supported by results from a sample of redoped (0.0175 M HCl) polyaniline film compared to the best published separation factors obtained with other polymers. These sources typically estimate separation factors from single gas measurements. The best reported results for

He/N_2 and H_2/N_2 separations are from the polymer poly(trifluorochloroethylene), which has a He/N_2 selectivity of 2200 and a H_2/N_2 selectivity of 313 (25). A cycled polyaniline film possessed selectivities of 4075 for He/N_2 and 3590 for H_2/N_2 .

Oxygen-nitrogen separations represent the greatest challenge for membrane systems since the kinetic diameters of these two gases differ by only a few tenths of an angstrom (3.46 Å for O_2 versus 3.64 Å for N_2). Cellulose nitrate has the best reported O_2/N_2 selectivity, which is 16 (25). The redoped polyaniline exhibits an O_2/N_2 separation factor of 30.

Carbon dioxide-methane separation is an area where specialty polymers have been successfully developed. A fluorinated polyimide has the highest CO_2/CH_4 selectivity of 60 (4). Cycled polyaniline film possesses a CO_2/CH_4 selectivity of 336. These results clearly indicate that the cycling process gives enormous versatility for tailoring specific gas separations. Moreover, additional samples of polyaniline membranes processed with other dopants and redoped to different concentrations display even greater separation factors. For example, a sample of film doped with 4.0 M HBr and undoped in base obtained a CO_2/CH_4 selectivity of 640. Additional experiments indicate that similar improvements are possible for the other gas pairs by controlling film formation parameters and the doping process (26).

Another important way to control the morphology of a conjugated polymer film is by changing the size of the dopant species. A group of samples cut from the same polyaniline film were each doped with one of the halogen acid series (HF, HCl, HBr, or HI) at a 4.0 M concentration and then undoped with 1.0 M aqueous base to remove essentially all of the halogen dopant species (16). A clear trend of decreasing permeability through the polyaniline doped with the following counterions, $F^- > Cl^- > Br^- > I^-$, is shown in Fig. 4. Since aqueous acid solutions are used for the doping, it is apparent that the size of the counterion solvation sphere is of primary importance. The size order of the solvated halogen counterions $F^-(aq) > Cl^-(aq) > Br^-(aq) \sim I^-(aq)$ is consistent with the permeability data observed and is opposite to the normal order of counterion sizes in a crystal lattice (27, 28).

This series of experiments again demonstrates that the permeability of the membrane to each gas generally decreases as the kinetic diameter of the gas increases. This trend is apparent in Fig. 4, in which the gases are given in order of increasing kinetic diameter. A deviation is observed for the increased permeability of O_2 relative to Ar

for all four dopants. This increased O_2 permeability is again likely due to the enhanced solubility of O_2 in the polyaniline membrane.

In addition to the large number of Bronsted acid dopants available for reaction with polyaniline, a number of Lewis acid dopants may be used. For example, doping-undoping with tosylic anhydride resulted in enhanced permeabilities for all of the gases tested. Many other conjugated polymers could possibly be modified by the cycling process. Recent tests indicate that poly(dimethoxyparaphenylenevinylene) shows an increase in gas permeabilities when doped with $FeCl_3$ and compensated with NH_4OH . However, not all conjugated polymers work so well. Permeability tests on poly(3-octylthiophene) and poly(thiophenevinylene) showed that they are nonselective. This result can be attributed to the non-fully dense structure of these polymers (29).

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A Room-Temperature Molecular/Organic-Based Magnet

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The reaction of bis(benzene)vanadium with tetracyanoethylene, TCNE, affords an insoluble amorphous black solid that exhibits field-dependent magnetization and hysteresis at room temperature. The critical temperature could not be estimated as it exceeds 350 kelvin, the thermal decomposition temperature of the sample. The empirical composition of the reported material is $\text{V}(\text{TCNE})_x \cdot \gamma(\text{CH}_2\text{Cl}_2)$ with $x \sim 2$ and $\gamma \sim 1/2$. On the basis of the available magnetic and infrared data, three-dimensional antiferromagnetic exchange of the donor and acceptor spins resulting in ferrimagnetic behavior appears to be the mode of magnetic coupling.

RECENTLY THERE HAS BEEN GROWING interest in the preparation and characterization of molecular/organic polymer-based materials that exhibit cooperative magnetic interactions (that is, ferro- and ferrimagnetic behavior) (1–6). The electron-transfer salt $[(\text{FeCp}^*)_2]^+ [\text{TCNE}]^-$ (Cp^* = pentamethylcyclopentadienide; TCNE = tetracyanoethylene) is a bulk ferromagnet with a Curie temperature T_c of 4.8 K (5, 6). Subsequently, $[\text{MnCp}^*_2]^+ [\text{TCNQ}]^-$ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) and $[\text{MnCp}^*_2]^+ [\text{TCNE}]^-$ were shown to have T_c 's of 6.2 (7) and 8.8 (8) K, respectively. These observed magnetic couplings and the trend in T_c are consistent, respectively, with the expectations of the extended-McConnell configurational admixture (9) and two-

spin-site mean-field Heisenberg models (10).

In addition to these electron-transfer ferromagnetic materials, the concept of having a large number of ferromagnetically coupled unpaired electrons in orthogonal orbitals was exploited by Day and co-workers in studies of (cation) $_2\text{CrCl}_4$. These compounds have extended network structures in two dimensions, T_c 's below 55 K, and are optically transparent (11). The ferrimagnetic coupling of differing spins sites has been promoted by Kahn's group, who used different metal ions (3) {for example, a Néel temperature, T_N , of 14 K for $\text{Cu}^{\text{II}}\text{Mn}^{\text{II}}(\text{obbz})\cdot\text{H}_2\text{O}$ [obbz = oxamidobis(benzoato)]} (12), and by the groups of Gatteschi and Rey, who used metal ions and nitroxide radicals in extended one-dimensional (1-D) network structures (4) [for example, 8.1 K T_N for $\text{Mn}^{\text{II}}(\text{hfac})_2\text{NITet}$ (hfac = hexafluoroacetylacetonate; NITet = ethyl nitronyl nitroxide)] (13). Other research groups have demonstrated the ferromagnetic coupling of spins in organic systems (2, 5, 14); however, bulk cooperative magnetic behavior has not been achieved. Thus, to date magnetic ordering temperatures for molecular/organic polymer-based materials are all below that acces-

sible by liquid nitrogen.

We have extended our research aimed at making high- T_c molecular-based magnets (5, 6, 9) to the reaction of $\text{V}(\text{C}_6\text{H}_6)_2$ (15) and TCNE (9). Like $[\text{Mn}^{\text{III}}\text{Cp}^*_2]^+$, $[\text{V}^{\text{I}}(\text{C}_6\text{H}_6)_2]^+$ is an $S = 1$ cation with a $^3E_{2g}$ ground state ($a_{1g}^1 e_{2g}^3$) (16, 17). The addition of $\text{V}(\text{C}_6\text{H}_6)_2$ to an excess of TCNE in dichloromethane at room temperature results in the precipitation of a black solid that is amorphous, as ascertained by powder x-ray diffraction. The empirical composition of this extremely air-sensitive material is $\text{V}(\text{TCNE})_x \cdot \gamma\text{CH}_2\text{Cl}_2$ (18), but because of the extreme insolubility of the precipitate and reactivity of the solvent, variations in composition as a function of preparation conditions have been observed. The first step in the reaction is electron transfer from $\text{V}(\text{C}_6\text{H}_6)_2$ to TCNE, which was followed unexpectedly by loss of the benzene ligands, as is evident from the infrared (IR) spectra, which lack $\nu_{\text{C-H}}$ absorptions in the 3060- to 3100- cm^{-1} region (19). All of the materials exhibit strong, broad absorptions at 2099 ± 5 and $2188 \pm 9 \text{ cm}^{-1}$, which are assigned to $\text{C}\equiv\text{N}$ ($\nu_{\text{C}\equiv\text{N}}$) or perhaps $\nu_{\text{N}=\text{C}=\text{C}}$ (Fig. 1) (19). The breadth of the $\nu_{\text{C}\equiv\text{N}}$ absorptions and relatively low frequency are consistent with the presence of reduced TCNE, with some N atoms bound to V.

TCNE has been reported to be a σ -N-bound ligand for several V and Mn complexes. $\text{V}^{\text{IV}}\text{X}(\text{C}_5\text{H}_5)_2(\text{TCNE})$ ($\text{X} = \text{Cl}, \text{Br}$, and I) (20) has $\nu_{\text{C}\equiv\text{N}}$ absorptions at 2118, 2152, 2192, and 2211 cm^{-1} . Likewise $\text{Mn}^{\text{II}}(\text{CO})_2(\text{C}_5\text{H}_5)(\text{TCNE})$ (21, 22) exhibits $\nu_{\text{C}\equiv\text{N}}$ absorptions at 2125m, 2205s, and 2230vw cm^{-1} (m, medium, s, strong, and vw, very weak). On the basis of the x-ray structures of these model compounds, the lower energy absorption is assigned to the $\text{M}\leftarrow\text{NC}$ interaction, whereas the higher energy absorption is attributed to the CN groups not bonded to M. With an increasing number of $\text{M}\leftarrow\text{NC}$ interactions per TCNE, the $\nu_{\text{C}\equiv\text{N}}$ absorptions shift to lower energy {that is, 2125m, 2160vw, and 2205vw cm^{-1} for $[\text{Mn}(\text{CO})_2(\text{C}_5\text{H}_5)]_2\cdot(\text{TCNE})$, 2105s and 2150m cm^{-1} for $[\text{Mn}(\text{CO})_2(\text{C}_5\text{H}_5)]_3(\text{TCNE})$, and 2110s and 2160m cm^{-1} for $[\text{Mn}(\text{CO})_2(\text{C}_5\text{H}_5)]_4\cdot(\text{TCNE})$ } (22). Additional model V-TCNE

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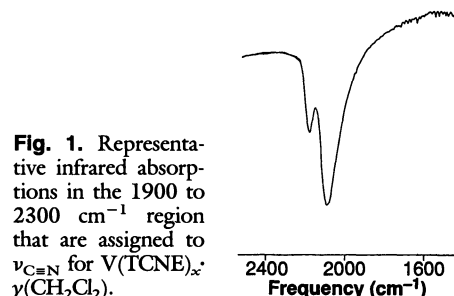


Fig. 1. Representative infrared absorptions in the 1900 to 2300 cm^{-1} region that are assigned to $\nu_{\text{C}\equiv\text{N}}$ for $\text{V}(\text{TCNE})_x \cdot \gamma(\text{CH}_2\text{Cl}_2)$.