

## Composite Permselective Membrane by Deposition of an Ultrathin Coating from a Plasma

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### Synopsis

Permselectivity was vastly improved when ultrathin crosslinked coatings, of the order of 0.5 microns thick, were deposited from a plasma onto relatively permeable film substrates. In one example, the hydrogen-to-methane permeability ratio was increased from 0.87 to 33, and the hydrogen permeability was decreased by just 20% when benzonitrile was plasma deposited onto a silicone-carbonate copolymer film. In another example, the hydrogen-to-methane permeability ratio was increased to 297 when cyanogen bromide was plasma deposited onto a poly(phenylene oxide) film. Such coatings, while effective for the hydrogen/methane pair, had little effect on modifying film permselectivity for isobutene/butene-1, a pair nearly identical in molecular size and solubility. It appears therefore that the coatings can very effectively distinguish between molecules differing significantly in size. Also, since the coatings are so thin, the overall permeability of the coating-substrate composite can be high.

### INTRODUCTION

For industrial applications, membranes capable of high selectivity and permeability have been the goal of much research. When using unmodified, currently available polymer films for separations of interest, it very frequently occurs that, if the selectivity is at the desired level, the permeability is too low, and vice versa. This is not too surprising considering the polymer structural features associated with selectivity and permeability. Selectivity is increased with increasing differences in solubility in the membrane and when the spacing between polymer chains is small enough and restricted enough to distinguish between diffusing molecules of different sizes. The polymer structural features for high selectivity would then be inflexible polymer molecules that are further inhibited by crystallites, crosslinking or high van der Waals forces. However, these same structural features undesirably cause low permeability.

One approach to solving this dilemma is to take a film of high selectivity and fabricate it in a very thin gauge so that high diffusion rates may be achieved at reasonable pressure or concentration differences. This generally means thicknesses of the order of 0.5 microns; but practical fabrication methods cannot produce pinhole-free films much below 5 microns. Another approach, and one of the most successful to date, is the technique

developed by Loeb and Sourirajan.<sup>1</sup> In effect, the surface layer of a highly permeable porous film is collapsed into an ultrathin (0.3 microns), selective structure. Diffusion rates are high because the selective layer is so thin. Such membranes, frequently called asymmetric membranes, have played a major role in the development of water desalination by reverse osmosis.

In the present study, another technique was developed to fabricate improved membranes for separation applications. The method involves deposition, from a plasma, of a highly crosslinked, ultrathin coating onto a permeable substrate film. The plasma is formed by applying a voltage difference to a low-pressure chamber containing the monomer gas and the substrate to be coated. The gas molecules are ionized, and the electrons formed are thought to achieve a steady state where electrons lost by various means, including diffusion to the walls, are balanced by electrons formed on ionization of neutral molecules.<sup>2</sup> Low gas pressure, generally 0.1 to 10 torr, is necessary so that the mean free path is large enough for electrons to accelerate to sufficiently high energies to cause ionization on collision with a neutral gas molecule. In such plasmas, the gas temperature is characteristically low. It has been postulated<sup>3,4</sup> but not universally accepted that the ultrathin coating is formed on the substrate from adsorbed gas molecules which polymerize under electron bombardment. Free radicals and/or ions are thought to be formed on interaction of the electrons with the adsorbed gas or growing polymer, and highly crosslinked coatings can result. Experimentally, the ultrathin coatings have been found to be amorphous, crosslinked,<sup>3</sup> and pinhole free.<sup>5</sup>

Plasma deposition of coatings onto metals for capacitor applications have been reported by Bradley.<sup>6</sup> It is also known that polymer surfaces can be modified when treated in a plasma, but no data known to the authors have been reported on the effect of plasma-deposited coatings on gas permeability. Goodman<sup>7</sup> has studied the preparation and properties of a wide variety of ultrathin coatings made using the plasma technique. Recently, Buck and Davar<sup>8</sup> have applied plasma-deposited coatings to a microporous substrate and have tested the composite so formed in water desalination by reverse osmosis. They found that heavy coatings were necessary to bridge the micropores and consequently, the water diffusion rates were uneconomically low.

In the study reported here, the primary objective was to determine if the selectivity of relatively permeable substrate films could be improved by a plasma-deposited ultrathin coating.

## EXPERIMENTAL

The power for the plasma was supplied at the 100-watt level through two brass electrodes, each 6 in. square, connected to a 350-kHz capacitive generator (Lepel Model No. HFSG-4). The polymer film substrate to be coated (both sides) was also 6 in. square and was suspended midway

between the brass electrodes which were spaced 1 in. apart. The entire assembly was enclosed in a glass chamber, actually a desiccator whose top was replaced with a grease-fitted phenolic slab (Fig. 1). Gas entry and exit were provided through ports in the top. The exit port was connected to a vacuum pump, and the chamber pressure was controlled by feeding in vapors from a reservoir connected to the entry port. The reservoir, which was at room temperature, contained an organic liquid or solid sufficiently volatile to provide the vapors desired for deposition. Of the many organic materials used, three were solid: naphthalene, nicotinonitrile, and cyanogen bromide. The rest were liquids categorized as nitrile type, vinyl type, and aromatic. The polymer film substrates to be coated were poly(phenylene oxide), 0.83–0.96 mils thick; silicone-carbonate copolymer, 0.96–1.64 mils thick; and cellulose acetate butyrate, 1.2 mils thick, (Kodacel B298, Eastman Kodak). The poly(phenylene oxide) and the silicone-carbonate copolymer have moderate to high hydrogen permeability, and experimental film samples of each were provided through the courtesy of Dr. W. L. Robb at General Electric.

To determine the effect on selectivity, permeability measurements were made using plasma-treated and untreated films. In the apparatus employed, the volume of permeated gas was measured as a function of time in a precision-bore capillary tube. One end of the capillary tube was open to the atmosphere, and the volume of permeated gas was indicated by the position of mercury displaced in the tube (Fig. 2). Atmospheric pressure at the time of the permeability measurements was noted with a barometer. From the data, the steady-state volumetric rate  $J$  of gas permeating or diffusing through a film sample was determined and was corrected to standard temperature and pressure. The permeability  $P$  for the treated or untreated film was then calculated using the well-known<sup>9</sup> relationship that defines  $P$ :

$$P = \frac{J \cdot l}{\Delta p} \quad (1)$$

where  $l$  is the film thickness and  $\Delta p$  is the total pressure drop across the film.

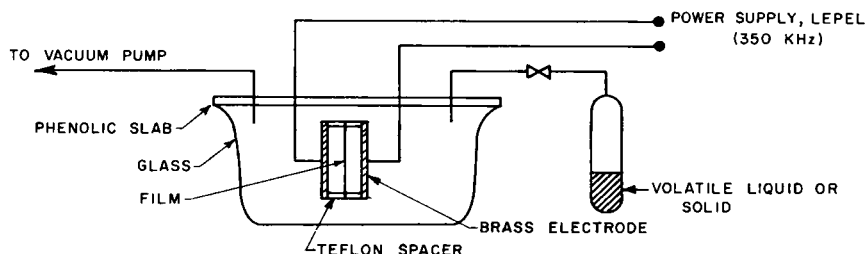


Fig. 1. Schematic of apparatus for film coating by plasma deposition.

Permeabilities, mostly at 25°C and some at 45–64°C, were measured for individual gases in each of two pairs: hydrogen/methane and isobutene/butene-1. The first pair was chosen as representative of separations where the molecules differ markedly in size, and the second pair was chosen because of their nearly identical molecular size. The measured permeabilities for the hydrogen methane pair should be largely independent of the pressure differential. This assumes that the solubilities of hydrogen and methane in the coating and in the substrate film are simply related to pressure by Henry's law and that the diffusivities of hydrogen and methane are independent of concentration. However, for the isobutene/butene-1 pair, these assumptions are not expected generally to hold because of the very high solubility that they can have, especially in the substrate film. Therefore, the pressure differentials used in the isobutene/butene-1 permeability measurements are listed with the tabulated data.

## RESULTS AND DISCUSSION

The plasma-deposited coatings were so thin that their thicknesses could not be readily measured; but an order-of-magnitude estimate was obtained by a crude method. Multiple internal reflectance (MIR) infrared was used to determine spectra of the plasma-deposited coating. With the design of the instrument employed (Perkin-Elmer infrared spectrophotometer with MIR accessory and KRS-5 45° internal reflecting plate), the thickness of the plasma-deposited coating would have to be 1 micron or greater for no reflections characteristic of the substrate to appear in the spectra. Therefore, if substrate reflections were noted, the thickness of

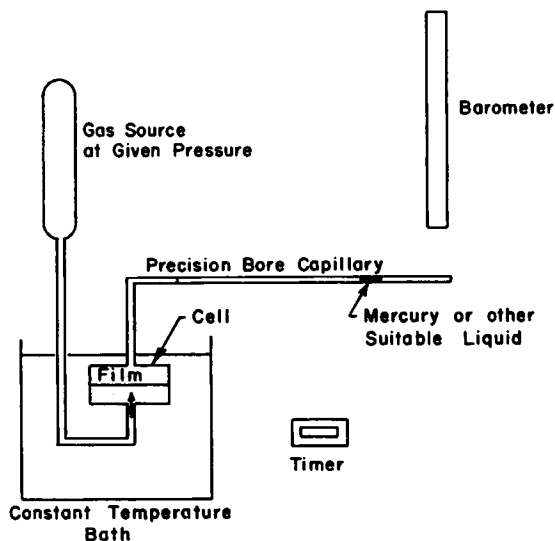


Fig. 2. Primary elements of system for gas permeability measurements.

the plasma-deposited coating could be assumed to be less than 1 micron. By this means, it was judged that the plasma-deposited coatings in this study were all no greater than 1 micron.

Silicone polymers were included in the substrates to be tested because they are characterized by high permeability and in this respect are desirable substrates for the plasma-deposited coatings. Initial studies and results with poly(dimethylsiloxane) were obscured by its apparent degradation on plasma treatment. A silicone-carbonate copolymer was much more stable. Many plasma coatings were deposited on this substrate and the coatings were found to markedly increase the hydrogen-to-methane permeability ratio. The ratio for the untreated silicone-carbonate film was 0.87, that is, the methane permeability was higher than the hydrogen permeability. After plasma treatment with benzonitrile monomer, the ratio was increased to 33 at just a 20% loss in hydrogen permeability (Table I). The ratio of less than unity for the untreated film apparently indicates that the greater size of the methane molecule tending toward lower permeability was more than compensated for by its higher level of dispersion forces favoring higher solubility. The average collision diameter is 3.8 Å for methane, compared to 2.9 Å for hydrogen,<sup>10</sup> but the methane shows 5 to 10 times the solubility of hydrogen in most organic solvents.<sup>11</sup>

TABLE I  
Hydrogen and Methane Permeabilities of Silicone-Carbonate  
Copolymer Plasma Treated with Various Monomers<sup>a</sup>

Monomer	Permeability $\times 10^7$ at 25°C, cc(S.T.P.)-cm/cm <sup>2</sup> -sec-atm		Permeability ratio H <sub>2</sub> /CH <sub>4</sub>
	H <sub>2</sub>	CH <sub>4</sub>	
None	9.2	10.5	0.87
Nitrile type			
Cyanogen bromide	2.74	0.075	36.6
Nicotinonitrile	3.96	0.11	36.0
Benzonitrile	7.26	0.22	33.0
3-Butenenitrile	8.87	0.39	21.7
Methacrylonitrile	9.04	0.55	16.4
Chloroacetonitrile	13.0	4.97	2.6
Acrylonitrile	15.3	4.37	3.5
Vinyl type			
Acrylic acid	8.15	0.33	24.5
Allyl bromide	8.37	0.66	12.6
Styrene	8.46	0.68	12.4
Divinylbenzene	9.85	1.33	7.0
Aromatic			
Naphthalene	8.1	0.44	18.4
Benzene	9.57	1.33	7.2
Mesitylene	9.43	1.72	5.5
1,3-Di(trifluoromethyl)- benzene	9.92	5.98	1.7

<sup>a</sup> Treatment time 1 min; pressure 1 torr.

The much higher selectivity to hydrogen permeation shown after plasma treatment of the silicone-carbonate copolymer, suggests that the plasma-deposited coatings are distinguishing between hydrogen and methane on a size basis. The effect of a particular plasma-deposited coating depends upon several factors, including coating thickness, degree of crosslinking in the coating, and coating integrity or freedom from pinholes. These effects, which are difficult to ascertain to a satisfactory degree, were not delineated in this study. However, the trend of the data (Table I) seems to indicate that the nitrile-type monomers perform best, which is not too surprising considering the reactivity of the carbon-nitrogen triple bond. The two exceptions are chloroacetonitrile and acrylonitrile. In these two cases, the silicone-carbonate copolymer substrate appeared to have undergone some degradation, which perhaps also may account for the higher hydrogen permeability after treatment than before treatment.

Next best to the nitriles were the vinyls, with acrylic acid, styrene, and allyl bromide particularly effective. In contrast, the aromatic-type monomers tested, except for naphthalene, were generally modest in their ability to modify the substrate selectivity. The aromatic monomers tried, in addition to naphthalene, were benzene, mesitylene, and 1,3-di(trifluoromethyl)benzene.

Another substrate tested was poly(phenylene oxide), PPO, characterized by a lower hydrogen permeability than the silicone-carbonate copolymer substrate but showing a much higher hydrogen/methane permeability ratio, 23.5, even when untreated. This ratio was increased to the extraordinarily high value of 297 when cyanogen bromide monomer was deposited at 0.5 torr over a 0.5-min time interval (Table II). The cyanogen

TABLE II  
Hydrogen and Methane Permeabilities of Poly(phenylene Oxide)  
Plasma Treated with Cyanogen Bromide and Benzonitrile

Monomer	Plasma treatment		Permeability $\times 10^7$ , cc(S.T.P.)-cm <sup>2</sup> -sec-atm			Permeabil- ity ratio H <sub>2</sub> /CH <sub>4</sub>
	Time, min	Pressure, torr	T, °C			
			H <sub>2</sub>	CH <sub>4</sub>	T, °C	
None	—	—	5.88	0.25	25	23.5
None	—	—	8.47	0.46	45	18.4
None	—	—	8.53	0.55	64	15.5
Cyanogen bromide	0.5	0.5	3.41	0.015	25	297
Cyanogen bromide	0.5	0.5	5.06	0.035	45	161
Cyanogen bromide	0.5	0.5	7.32	0.11	64	68
Benzonitrile	1.0	1.0	4.47	0.066	25	68

bromide was also used in plasma treatment of the silicone-carbonate copolymer substrate but its performance was not nearly as good. To contrast this difference in performance more clearly, the hydrogen-to-methane permeability ratio for the plasma coating alone can be calculated and compared, even though the individual permeabilities cannot be determined with the coating thickness unknown. It is first noted that the overall pressure drop  $\Delta p_0$  through the composite membrane is given by

$$\Delta p_0 = \Delta p_s + \Delta p_c \quad (2)$$

where 0, s and c subscripts refer to the overall composite, the substrate, and the coating, respectively. Next, substitution of eq. (1) into eq. (2) gives

$$\frac{l_0}{P_0} = \frac{l_s}{P_s} + \frac{l_c}{P_c} \quad (3)$$

and solving for  $P_c$  with the assumption that the coating is so thin that  $l_0 \sim l_s$ ,

$$P_c = \frac{l_c}{l_s \left( \frac{1}{P_0} - \frac{1}{P_s} \right)} \quad (4)$$

Therefore, the hydrogen-to-methane permeability ratio for the coating alone is

$$\frac{P_{c,H}}{P_{c,M}} = \frac{\left( \frac{1}{P_0} - \frac{1}{P_s} \right)_M}{\left( \frac{1}{P_0} - \frac{1}{P_s} \right)_H} \quad (5)$$

and is independent of coating thickness but depends upon the permeabilities of the treated film and untreated substrate.

Using eq. (5), the hydrogen-to-methane permeability ratio calculated for the cyanogen bromide coating alone when deposited on PPO was 490, while the cyanogen bromide deposited on the silicone-carbonate substrate was calculated to have a permeability ratio of 50. The reason for this difference is not clear. However, it does not seem likely that the cyanogen bromide coating would be more crosslinked for one substrate than for another.

The effect of temperature on hydrogen and methane permeability was also determined. Cyanogen bromide-treated and untreated PPO were compared at 25°C, 45°C, and 64°C. Permeabilities were found to increase with temperature, as is usually the case (Table II). Activation energies were determined from the data; and, as might be expected, the coating affects the activation energy for methane permeation (4.1 increased to 10.4 kcal/g-mole) much more than it affects the activation energy for hydrogen permeation (1.7 increased to 3.9 kcal/g-mole) (Fig. 3).

The only other monomer tried with the PPO substrate was benzonitrile, and it was found not as effective as the cyanogen bromide. The permeability ratio for the benzonitrile coating alone as calculated using eq. (5) was 210 compared to the 490 noted previously for the cyanogen bromide coating.

For comparative purposes with hydrogen and methane, data were obtained on an isomer pair, butene-1 and isobutene. These are very close in size, and their solubility parameters ( $\delta$ ) are nearly identical. Hildebrand<sup>11</sup> calculates a  $\delta$  of 6.7 for both, while Small's method<sup>12</sup> of additive molar

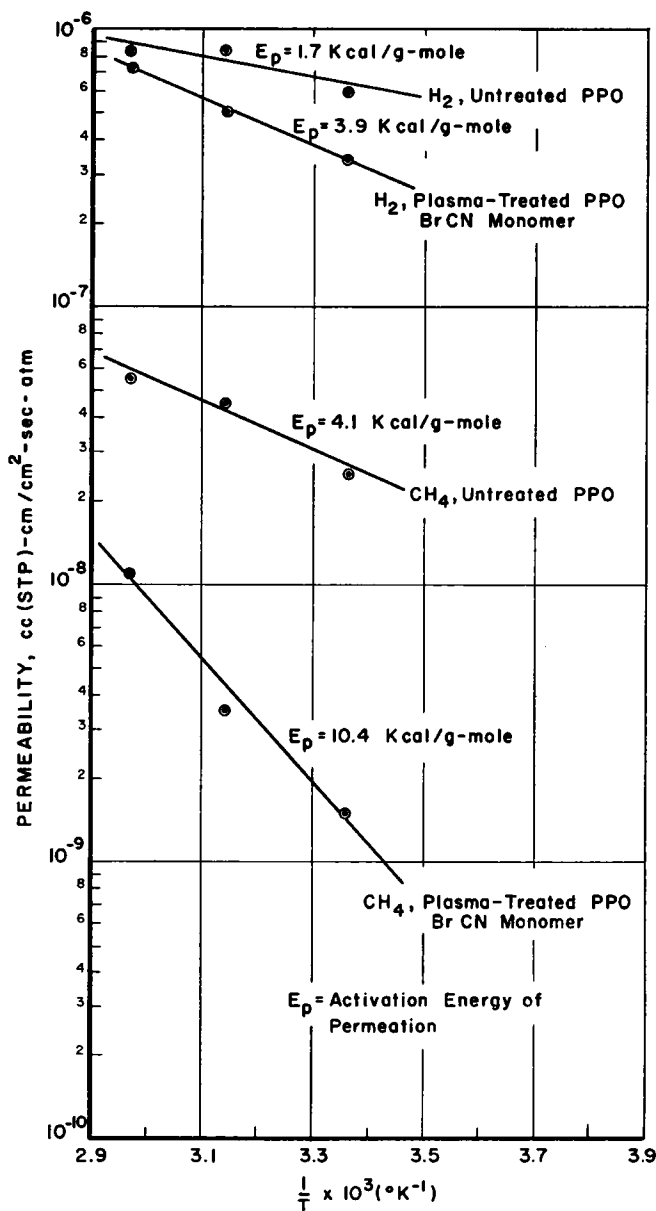


Fig. 3. Hydrogen and methane permeabilities of untreated and plasma-treated poly(phenylene oxide).

attraction constants gives 7.0 for butene-1 and 6.9 for isobutene. Therefore, these two molecules would generally be expected to have permeability ratios near unity, and plasma-deposited coatings would be judged a priori to have little effect on modifying membrane selectivity. The experimental results (Table III) are consistent with these views. Three different mono-



TABLE III  
Butene-1 and Isobutene Permeabilities as a Function of Substrate and Plasma Treatment<sup>a</sup>

Substrate	Monomer	Plasma treatment		Permeability $\times 10^7$ at 50°C, cc(S.T.P.)-cm/cm <sup>2</sup> -sec-atm				Permeability ratio Bu/i-Bu
		Time, min	Pressure, torr	Butene-1	$\Delta p$ , psi	Isobutene	$\Delta p$ , psi	
Poly(pbenylene oxide)	none	—	—	35.3	66	17.1	68	2.1
	styrene-BrCN	6.0	0.7	0.06	66	0.06	70	1.0
Silicone-carbonate copolymer	none	—	—	1330	67	1345	70	1.0
	benzotrile	0.5	0.7	20.5	65	18.3	67	1.1
Cellulose acetate	styrene-BrCN	2.0	0.7	29.1	67	22.0	69	1.3
	none	—	—	58.9	65	41.7	70	1.4
Butyrate	styrene	10.0	0.7	5.1	68	2.4	68	2.1

<sup>a</sup> The  $\Delta p$  values used in the permeability measurements are tabulated since the solubility of the butene-1/isobutene pair in the membrane can be very high and can cause permeability to vary with  $\Delta p$ .

mers, benzonitrile, styrene, and cyanogen bromide, and three membrane substrates, PPO, silicone-carbonate copolymer, and cellulose acetate butyrate, were used. In all cases, with and without plasma treatment, the permeability ratio of butene-1 to isobutene was near unity, with a maximum value of 2.1.

## CONCLUSIONS

Ultrathin, crosslinked, plasma-deposited coatings very effectively distinguish between molecules of different sizes and can vastly increase the permselectivity of substrate films. In addition, the overall permeability of the coating-substrate composite can be high since the coatings are so thin.

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