Preparation of Composite Reverse Osmosis Membranes by Plasma Polymerization of Organic Compounds. III. Plasma Polymers of Acetylene/CO/H₂O

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Synopsis

Reverse osmosis characteristics of composite membranes prepared by the plasma polymerization of acetylene/CO/H₂O mixtures with various ratios of components are investigated; porous film of cellulose nitrate–cellulose acetate is used as the substrate. This monomer system seems to have the following advantages: (1) A relatively short deposition time (1–2 min) is enough to produce reasonably good reverse osmosis membranes; and (2) good chemical stability of membranes can be obtained, especially in the case of chlorine resistance.

INTRODUCTION

As previously reported in the early parts of this series of studies, nearly all reverse osmosis membranes prepared by plasma polymerization which give reasonable reverse osmosis characteristics are nitrogen-containing polymers.[1] This is also the case with the results of other investigators. Buck and Davar[2] report that the best results are obtained with the plasma polymer of vinylene-carbonate-acrylonitrile and those obtained with vinylacetate–acrylonitrile are second best. They also note that not many monomers yield water-permeable membranes by plasma polymerization. The work done by Hollahan and Wydeven[3] and also by Bell, Wydeven, and Johnson[4] has been mainly with the plasma polymer of allylamine.

On the other hand, reverse osmosis membranes made of nitrogen-containing polymer, e.g., polyamide and aromatic polyamide, etc., seem to have the crucial weakness in chlorine resistance. Chlorine in the order of 10 ppm seems to virtually destroy otherwise excellent reverse osmosis characteristics of some membranes of this category. The weak chlorine resistance seems to negate the practical values of these membranes for the production of potable water, since the addition of chlorine is the most feasible practice to keep water potable.

Bell, Wydeven, and Johnson[4] report that composite reverse osmosis membranes prepared by plasma polymerization of allylamine have rather poor chemical stability and that their reverse osmosis characteristics deteriorate with time, particularly at elevated temperatures. This group of investigators did not examine chlorine resistance.

Reverse osmosis membranes of plasma polymers of acetylene/N_2/H_2O are found to be much more stable, and their chlorine resistance is far better than other reverse osmosis membranes made of nitrogen-containing polymers.[5] Nevertheless, a slight reduction in reverse osmosis characteristics after the membranes are treated with 0.5% NaOCl solution suggests that the nitrogen in the polymer could be a site of chlorine reaction and that the chlorine resistance of the membrane could be improved if the membrane is prepared with plasma polymers containing no nitrogen.

With this view as basis, copolymerization of acetylene/CO/H_2O is attempted for the preparation of reverse osmosis membranes, and some tentative results are presented in this paper.

EXPERIMENTAL METHOD

The apparatus and method used to prepare composite membranes by plasma polymerization are identical to those reported in the previous paper in this series of studies.[5] Porous film of cellulose nitrate–cellulose acetate (CNCA) (prepared by Gulf General Atomic, San Diego, Calif.) is used as the substrate. The average pore size of this substrate is approximately the same as that of porous polysulfone film; however, the thickness is considerably greater, and the gas perfusion rate is much smaller than that of porous polysulfone film.

Reverse osmosis characteristics are measured by using 3.5% NaCl solution at various applied pressures. The chlorine resistance of membranes is tested by treating membranes in the reverse osmosis test cells. In this procedure, a reverse osmosis test is carried out with a new membrane until salt rejection and water flux stabilize (in two to three days). Then the dependence of reverse osmosis performance on the applied pressure is measured by changing the pressure. After the pressure dependence is measured, the test cell is removed from the test loop and connected to a similar connector that allows water or chlorine solution to flow into the cell. After a brief washing by tap water, 0.5% NaOCl solution is introduced into the cell and kept for 30 min. After the chlorine treatment, the membrane surface is flushed by tap water for a period of from 5 hr to overnight. Before the cell is connected to the test loop, the membrane surface is washed with distilled water by flowing through approximately 200 ml of distilled water through the cell by means of a syringe. By this method, the effect of chlorine treatment can be observed with an identical membrane without removing the membrane from the test cell.

RESULTS AND DISCUSSION

Carbon monoxide is expected to copolymerize with acetylene in a manner similar to that in which nitrogen copolymerizes with acetylene, because of quite similar electronic structures. However, because of the general occurrence of oxygen in glow-discharge-produced polymers, it is necessary to look for indirect evidence of the incorporation of carbon monoxide. Such evidence can be found by monitoring the pressure changes in the acetylene/CO plasma systems as a function of relative partial pressures in the nonplasma monomer system. Acetylene alone displays almost complete polymerization
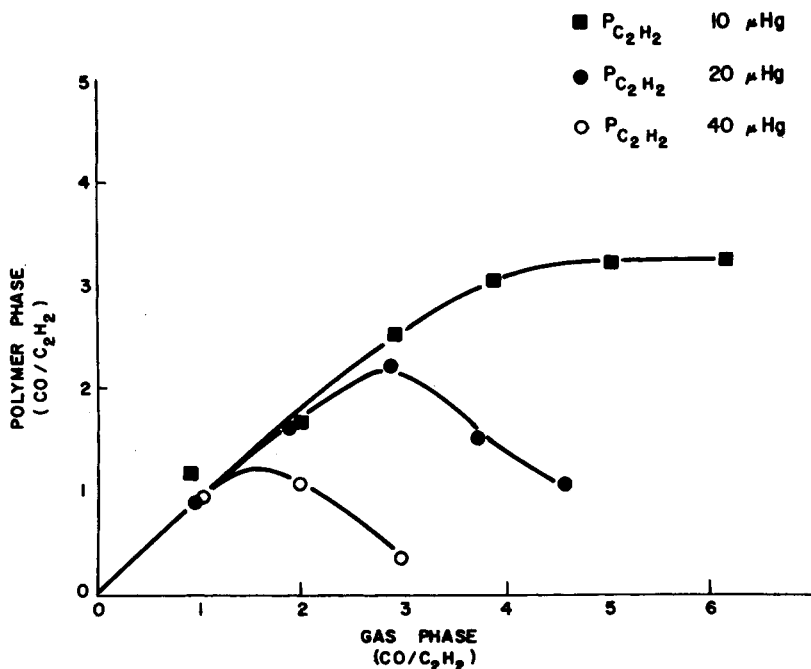
Fig. 1. The amount of CO incorporated into the polymer as a function of CO/C_2H_2 ratios.

with a drop to a very low (probably hydrogen) residual pressure. Carbon monoxide pressure is hardly affected by the presence of glow discharge; this indicates little self-polymerization, little attachment to reaction vessel walls, and little molecular breakdown. The drop in the pressure of the acetylene/CO system, however, is greater than what is expected according to the simple rule of additivity: and this implies the incorporation of the carbon monoxide
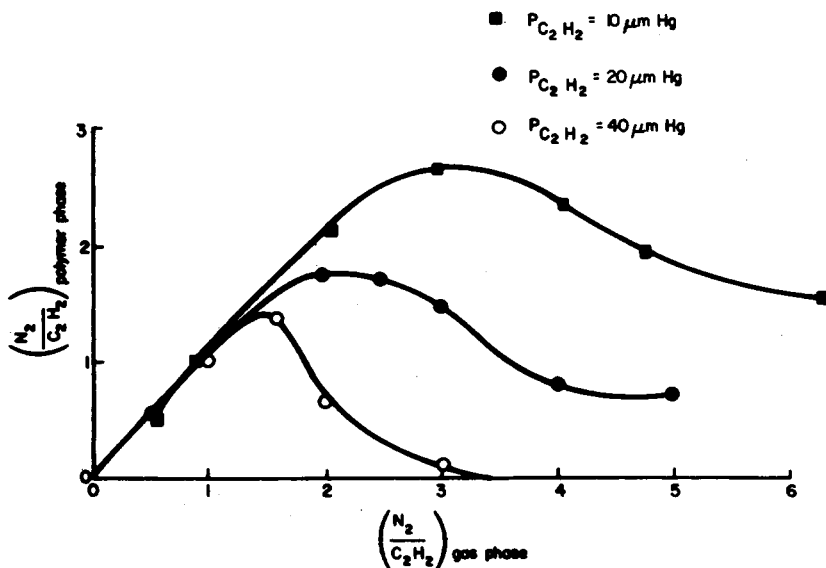

Fig. 2. The amount of N_2 incorporation into the polymer as a function of N_2/C_2H_2 ratios.

TABLE I
Reverse Osmosis Results of Membranes Prepared
from Acetylene/Carbon Monoxide System

Run no.	System	μHg	Time, min	Rs, %	Water flux, gal/ft^2 day
408	C_2H_2/CO	28/31	5.0	36.6	29.6
409	C_2H_2/CO	20/30	10.0	34.8	27.9
422	CO/C_2H_2	48/24	10.0	59.8	32.8

into the acetylene polymer. The details of these measurements can be seen in ref. 6.

Figure 1 plots carbon monoxide incorporation as a function of gas phase composition. In each of the three curves, the partial pressure of the acetylene is maintained constant and the gas phase composition is regulated by varying the partial pressure of the carbon monoxide. Figure 2 is another plot for the acetylene/N_2 system. The two systems behave in a similar fashion. With the acetylene/CO system, slightly higher polymer–phase ratios are obtained at given gas phase ratios. This indicates that carbon monoxide is more readily incorporated than is nitrogen. One possible explanation is that carbon monoxide–carbon monoxide interactions may not be completely unreactive. The complex nature of the plasma state allows for several different, and equally acceptable, explanations.

In an effort to preserve simplicity, the first membranes prepared used acetylene/CO on a CNCA substrate. Table I lists the reaction conditions and reverse osmosis performance of these membranes. The poor results were not encouraging; however, closer examination revealed the reasons: The dry membranes appeared stable to mechanical action; rubbing a finger across the surface produced no visible changes. When the membrane was immersed in water, however, visible changes became apparent. The deposited layer wrinkled up and seemed to separate from the substrate surface. Such a thin film was naturally destroyed if touched by a finger or other large object.

Table II lists the free-radical concentrations for several discharge polymers. The acetylene/CO polymer shows a high free-radical concentration (217×10^{19} spins/cm^3), which may account for its instability when exposed to

TABLE II
Free Radicals in Plasma Polymers of Acetylene with H_2O, N_2, and CO

Monomer and pressure, μHg	Spin concentration (spins/cm^3) $\times$ 10^{-18}
Acetylene	280
Acetylene/N_2 (30) (30)	180
Acetylene/N_2/H_2O (30) (10) (20)	9
Acetylene/H_2O (30) (20)	0
Acetylene/CO (30) (20)	217
Acetylene/CO/H_2O (30) (20) (15)	1.5

water. A free-radical-containing carbon should exhibit a bit more bond flexibility than its tetrahedrally oriented nonradical counterpart. This loss of flexibility when free radicals react with water is probably compounded by intramolecular hydrogen bonding of the hydroxyl groups in the highly branched polymer.

Whatever the cause, this instability is reminiscent of observations of the acetylene/N_2 glow-discharge polymer (which, incidentally, had a free-radical concentration of 180×10^{18} spins/cm^3). It was decided to add water to the plasma to improve stability. The acetylene/CO/H_2O system produces much more stable polymers, in that there are no visible changes when the membranes are immersed in water. It is interesting to note also that the free-radical concentration in the polymer is greatly reduced (1.5×10^{18} spins/cm^3) by the addition of water vapor.
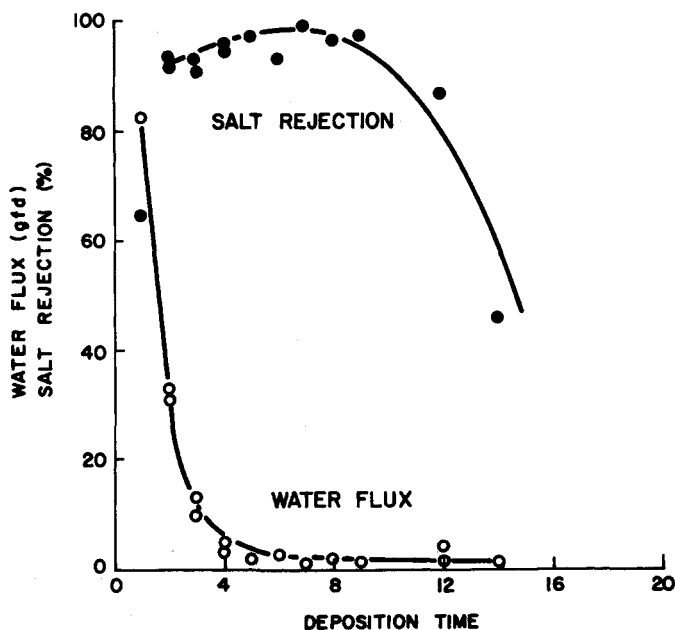

Fig. 3. Water flux and salt rejection as functions of deposition time, in minutes, for composite membranes of acetylene/CO/H_2O (CNCA porous membrane used as substrate).

Figure 3 plots water flux versus salt rejection for a series of acetylene/CO/H_2O discharge polymer membranes on CNCA. The reaction conditions are the same as for those membranes reported in Part II, except that carbon monoxide is substituted for nitrogen at an equal partial pressure. The results bear three important observations: First, good reverse osmosis membranes can be produced by CNCA without a nitrogen gas in the plasma. Second, much shorter deposition times are sufficient for the carbon monoxide system than for its nitrogen counterpart. This is primarily a reflection of the relative ease by which the carbon monoxide is incorporated. A deposition time of only 2 min, for instance, results in membranes with salt rejection around 94% and with water fluxes of 32 gal/ft^2 day. Lastly, extended plasma reaction times have negative effects on the salt-rejection properties of the

TABLE III
Reverse Osmosis Performance as a Function
of Relative Gas Phase Composition

Acetylene/H_2O/CO pressures	Rs, %	Flux, gal/ft^2 day
1. Effects of CO		
37.9/12.9/18.1	95.4	31.2
38.2/13.7/28.5	94.4	6.14
39.8/13.7/38.7	84.2	10.8
2. Effects of H_2O		
39.2/8.5/28.1	97.8	6.54
38.2/13.7/28.5	94.4	6.14
40.2/19.3/28.8	90.6	26.6
3. Effects of C_2H_2		
27.1/13.6/28.2	57.6	77.7
38.2/13.7/28.5	94.4	6.14
47.6/12.9/27.3	83.8	2.19

membrane. This is most likely the result of the degradative effects of ultraviolet radiation, details of which will be presented elsewhere.

Realizing the potential for good reverse osmosis membranes, we sought clues toward optimization of reaction conditions by perturbing the relative gas phase composition of the reactants. The results from the study are listed in Table III.

Perturbations in the acetylene partial pressure have the most drastic effects. Since acetylene must account for at least two thirds of the carbon in the polymer, this seems not unlikely. Decreasing the partial pressure of acetylene has effects similar to those of shorter deposition times; increasing the pressure is in effect similar to increasing deposition times.

The only alteration that gave both improved salt rejection and improved water flux was a decrease in the partial pressure of carbon monoxide.

Increasing the partial pressure of the water improves the water flux at the expense of salt rejection. This phenomenon may be a result of simply a slower deposition rate. The exact role of water in the plasma is complex and not entirely understood. Its presence results in carbonyl (and possibly hydroxyl) incorporation and in a tremendous decrease in the number of free radicals in the polymers. There are indications that the presence of water slows the rate of deposition. Direct evidence for this in the acetylene/CO system is found from deposition rates measured by weight increases.

Such a retarding effect by water readily explains the increased flux and decreased rejection observed when the partial pressure of water in the plasma is increased (at a fixed deposition time).

TABLE IV
Effects of Water on the Deposition Rates
of the Acetylene/Carbon Monoxide System

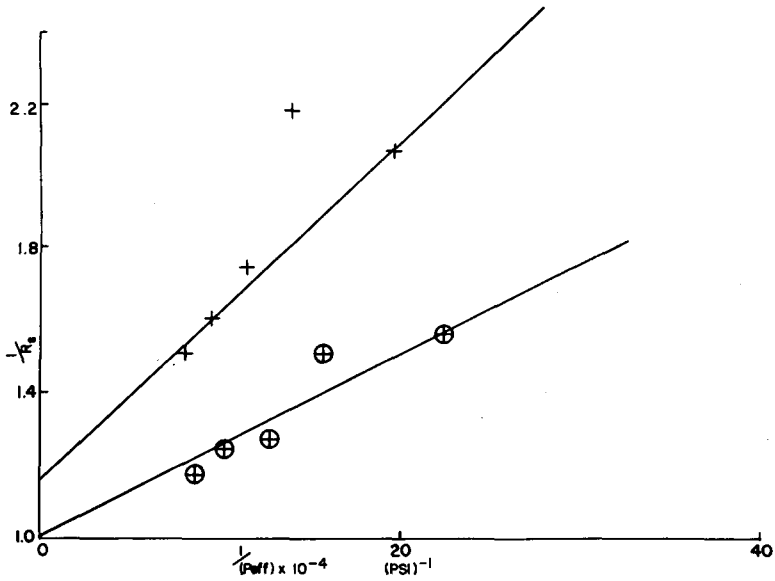| Monomer mixture	Pressures (μHg)	Deposition rate, A/min
CO/acetylene	20/30	320
CO/acetylene/H_2O	20/30/15	220

Fig. 4. The change of $1/R$ vs. $1/(\Delta p - \pi)$ dependence as result of chlorine treatment. Symbols: + for before; and ⊕ for after the chlorine treatment.

Since the acetylene/H_2O/CO glow-discharge polymer is without nitrogen functions, it was hoped that it would be resistant to reaction with chlorine. To test this idea, membranes were prepared and the reverse osmosis properties tested as usual. An 0.5% solution of NaOCl was then introduced into the test cell for one-half hour. The membrane was subsequently rinsed with tap water for 5 to 16 hr; this was followed by a final rise with deionized water. The performances of a single membrane before and after reaction with chlorine could then be compared. The reverse osmosis characteristics of mem-
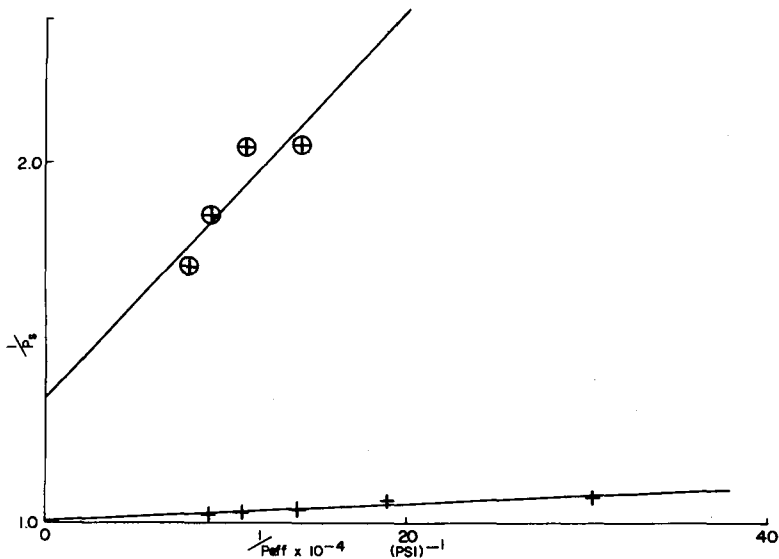

Fig. 5. The change of $1/R_s$ versus $1/(\Delta p - \Delta\pi)$ dependence as result of chlorine treatment. Symbols: + for before; and ⊕ for after the chlorine treatment.

TABLE V
Effects of Chlorine on Reverse Osmosis Performance
of Acetylene/H$_2$O/CO Glow-Discharge Membranes

	Regular—no treatment				Chlorine treatment			
No.	Rs, %	Flux, gal/ft^2 day	Inter-cept	Slope	Rs, %	Flux, gal/ft^2 day	Inter-cept	Slope
471	97.8	14.2	1.00	23.7	58.4	59.2	1.35	540
472	68.4	21.4	1.00	549	79.4	28.1	1.06	219
473	60.2	59.2	1.08	722	65.8	74.0	1.14	471
474	96.4	24.9	1.00	37.5	87.6	20.8	1.03	122
475	58.8	1.12	—	—	55.7	.98	—	—
476	58.4	.68	—	—	62.8	0.8	—	—
477	62.4	1.34	—	—	68.4	1.22	—	—
478	53.4	1.58	—	—	62.8	4.62	—	—
488	96.8	14.4	.97	74.9	68.4	32.2	.97	557
489	92.8	31.2	.99	109	58.8	51.8	.93	958
490	42.8	6.42	—	—	42.8	6.36	—	—
491	66.4	4.32	1.16	470	84.8	5.82	9.48	291
494	90.6	22.2	1.02	99.1	88.6	28.1	1.07	73.0
495	96.4	9.37	.991	66.0	95.8	16.4	1.02	26.1
496	52.8	78.8	—	—	34.8	119.8	—	—
514	36.2	32.6	—	—	35.4	29.6	—	—
515	87.2	50.3	1.16	14.5	39.4	96.2	—	—
517	83.8	29.6	1.03	202	75.6	46.8	1.14	223
526	75.6	54.8	1.01	383	74.8	49.3	1.13	234
540	72.0	29.6	—	—	48.4	51.8	—	—

branes before and after the chlorine treatment were investigated by the dependence of the salt rejection, Rs, on the applied pressure, as described in Part II of this series of studies. A typical case of improvement by the chlorine treatment is shown in Figure 4, and a typical case of deterioration by the chlorine treatment is shown in Figure 5. The results of these tests are included in Table V, where the value of intercepts and slopes of plots similar to Figures 4 and 5 are included. Out of 20 membranes, four showed little or no change in reverse osmosis properties, nine revealed detrimental effects, and seven were actually improved by reaction with the sodium hypochlorite solution. No satisfactory explanation of the varying effects of chlorine treatment has been found.

It was suggested that in cases of detrimental chlorine action, nitrogen had somehow been incorporated into the polymer. The source of such nitrogen would have been the CNCA substrate. Since plasma tends to liberate the nitrate groups, this idea was not unreasonable. Examination of the membrane surface by electron spectroscopy for chemical analysis (ESCA), however, indicated that the polymer coat contained no nitrogen. This explanation, therefore, had to be put aside. It should be recognized, in addition, that:

1. The chlorine-susceptibility of nitrogen-containing plasma polymers (e.g., acetylene/N$_2$/H$_2$O) is not really bad, considering an extremely severe condition used in the test. Note also that the incorporation of nitrogen at the interface of substrate and plasma polymer may be more detrimental to the chlorine resistance.
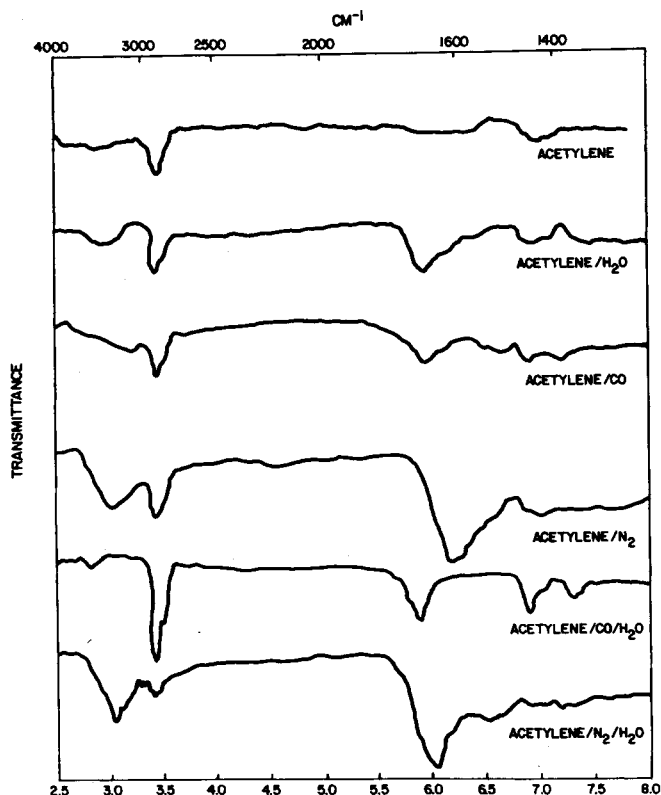
Fig. 6. IR spectra (4000 cm^{-1}–1250 cm^{-1}) of plasma copolymers of acetylene.

2. If nitrogen liberated from a CNCA substrate is incorporated in the early stage of polymer deposition, ESCA may not detect the existence of nitrogen, but it may reflect more sensitively in its chlorine susceptibility. In cases in which the reaction with chlorine improved membrane properties, an explanation involving nitrogen from the substrate is useless.

In order to gain more insight into the difference between plasma polymers of the CO series and those of the N$_2$ series, infrared (IR) spectra of polymers are taken by depositing polymers on NaCl crystals. IR spectra are compared in Figure 6. The details of analysis of IR spectra can be seen in ref. 6. The addition of carbon monoxide to the acetylene plasma apparently results in carbonyls in the polymer, but in no appreciable decrease in the free-radical

TABLE VI
General Character of Discharge Polymers from IR Data

Monomer system	Functional character of polymer
Acetylene	Hydroxyl
Acetylene/H$_2$O	Hydroxyl-carbonyl
Acetylene/CO	Carbonyl
Acetylene/N$_2$	Amine
Acetylene/CO/H$_2$O	Carbonyl
Acetylene/N$_2$/H$_2$O	Amide

concentration. The primary difference then between the acetylene/H_2O and the acetylene/CO polymer should be found in terms of stability. Conclusive evidence of this, however, has yet to be obtained.

Acetylene/CO/H_2O seems a likely enough hybrid of the preceding two. The hydrocarbon C—H stretching and bending signals are quite strong. The hydroxyl signal is very weak.

The addition of water, nitrogen, or carbon monoxide (or various combinations of these comonomers) to a glow-discharge polymerization of acetylene produces chemically distinct polymers. The characteristic nature of these poly mers may be summarized as given in Table VI. The polymers are, in general, highly branched and contain some form of oxygen subsequent to exposure to the atmosphere. The copolymerization of H_2O reduces the trapped free radicals in the plasma polymers in a remarkable manner and enhances the stability of the polymers.

The plasma polymers formed by copolymerization of acetylene/CO/H_2O therefore can be considered as mainly "carbonyl-type" polymers, whereas the plasma polymers of acetylene/N_2/H_2O are "amide type." This difference seems to be responsible for the difference in their chemical stabilities, as manifested by the effect of chlorine treatment of the membranes.

CONCLUSIONS

As concluding remarks, it should be pointed out that the following aspects found in this study are very significant in the preparation of composite reverse osmosis membranes by plasma polymerization. These aspects are:

1. Good reverse osmosis membranes can be prepared from monomer systems that do not contain nitrogen.

2. The deposition time necessary for the preparation of composite reverse osmosis membranes with some monomer systems (e.g., acetylene/CO/H_2O) is short enough so that the method can be utilized in a continuous manner in practical application.

3. Membranes with strong chlorine resistance (and probably high stability against other chemicals and severe conditions) can be prepared by selecting the proper combination of substrate and polymerization conditions.

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