Ion-Exchange Membranes by Sulfonation of Poly(vinylidene Fluoride) Films

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Synopsis

Attempted sulfonation of poly(vinylidene fluoride) film results predominantly in reaction at the surface of the film owing to lack of penetration by the reagents.   When the film is pre-swollen with a wide range of liquids, however, sulfonation with oleum proceeds smoothly through the body of the film, and a flexible membrane of low electrical resistance is produced.   The more important variables in the swelling and sulfonation steps have been investigated.   Side reactions during the sulfonation lead to the introduction of carbonyl and ethylenic groupings into the polymer molecule.   The latter grouping is assumed to be responsible for the lack of stability of the membrane towards oxidants.

INTRODUCTION

Certain fluorocarbon polymers are known to be particularly stable to chemical attack, and in the search for more chemically resistant ion-exchange membranes, these polymers have been used as base films for membrane preparation.   For example, polytetrafluorethylene film has been "grafted" with polystyrene which was subsequently sulfonated,[1] and polychlorotrifluorethylene has been similarly converted to ion-exchange membranes.[2]   Such an approach, however, introduces two sources of instability into the membrane: not all of the "grafted" polystyrene will be covalently linked to the base polymer and so the polyelectrolyte may slowly diffuse from the membrane over prolonged periods, and even the covalently linked polystyrene is a source of chemical instability, e.g., to oxidants.   In an attempt, therefore, to prepare chemically resistant ion-exchange membranes without the introduction of polystyrene, we have investigated the direct sulfonation of fluorocarbon polymer films.

Since the presence of a reasonably high proportion of C-H groups in the fluorocarbon polymer is a prerequisite for such an approach, we were limited to two commercially available films, viz., poly(vinyl fluoride) (Tedlar) and poly(vinylidene fluoride) (Kynar).   Tedlar was found to be particularly unstable to both sulfur trioxide and chlorosulfonic acid; the film blackened very rapidly, and it is assumed that hydrofluoric acid was eliminated.   All subsequent work was therefore carried out on Kynar film.

Ion-exchange membranes have previously been prepared by direct sulfonation of both polyethylene and poly(vinyl chloride),[3] and the sulfonation has been facilitated either by preswelling[5,7] or by use of a plasticized film.[3]

EXPERIMENTAL

Poly(vinylidene Fluoride) Film

Kynar sheet of ca. 2 mil thickness, for use in preliminary experiments, was kindly supplied by Pennsalt Chemicals Corporation, Philadelphia, and was unplasticized. Unless otherwise specified, however, the work described below was carried out on Kynar sheet of 7 mil thickness fabricated by Monosol Corporation, Gary, Indiana. The sheet contained a small amount of an unspecified plasticizer (probably an aromatic ester), showing absorption at 1640 cm.$^{-1}$. Infrared absorption at this frequency disappeared, however, when the film was treated with any of the swelling agents mentioned below, and a quantitative extraction of the sheet with acetone at 25°C. for 1 hr. resulted in a weight loss (dry weight) of 1%.

Swelling Measurements

A 0.1–0.2 g. sample of Kynar, immersed in 20 ml. of solvent was heated in a thermostat at the required temperature (±0.1°C.) and at intervals removed, lightly blotted between sheets of filter paper, and weighed in a stoppered bottle before being returned to the solvent.

Sulfonation of Kynar Film

In Chlorosulfonic Acid. A 0.1–0.2 g. sample of film (blotted as above, if preswollen) was immersed in 20 ml. chlorosulfonic acid in a thermostat (±0.1°C.) for a given time and temperature and then washed successively at room temperature for 1 hr. each in 1,2-dichloroethane, methanol, and water. The membrane was next heated in 1.0N sodium hydroxide solution at 60°C. for 1 hr., washed in 1.0N hydrochloric acid at room temperature for 1 hr. and then in water until free from acid.

In Oleum. A 0.1–0.2 g. sample of film (blotted as above, if preswollen) was immersed in 20 ml. of 20% oleum for a given time and temperature and then washed at room temperature with 96% sulfuric acid followed by water until free from acid.

In Sulfuryl Chloride. A 0.1–0.2 g. sample of Kynar film swollen with 35% acetophenone was immersed in 20 ml. sulfuryl chloride at 25°C. and irradiated with a 150-w. incandescent lamp at 2 in. for up to 24 hr. The films were subsequently washed successively in benzene, methanol, and water, hydrolyzed in 1.0N sodium hydroxide solution at room temperature for 20 hr., and washed with 1.0N hydrochloric acid (1 hr.) and with water until free from acid. Membranes prepared in this way had capacities <0.02 meq./g. and resistances >2000 ohm/cm.^{2}.

Membrane Characterization

Capacity. A 0.1–0.2 g. sample of membrane was washed with $1.0N$ hydrochloric acid at room temperature for 1 hr., then with water until free from acid, and immersed in 5 ml. of $0.1N$ sodium hydroxide in $1.25M$ sodium chloride solution for 1 hr. The membrane was then removed and the solution titrated with $0.1N$ hydrochloric acid. The results are expressed as milliequivalents of acid per gram dry weight of film, the dry weight being found by subsequent drying to constant weight at $40°C./5$ mm.

Gel Water. After titration as above, the membrane was lightly blotted between sheets of filter paper and weighed. The difference between this weight and the subsequent dry weight represents the gel water.

Resistance. Membrane resistance was measured in flowing $0.6N$ potassium chloride solution at $25°C.$ with the use of platinized platinum electrodes and a Wayne-Kerr B221 Universal bridge at 1592 cycles/sec.

Stability to Oxidant. A 0.1–0.2 g. sample of membrane was washed with acid as above and then with several changes of conductivity water until free from acid. The sample was next boiled 1 hr. under reflux with 50 ml. of 1.0% (w/v) hydrogen peroxide solution prepared by diluting 100 volumes Analar hydrogen peroxide with conductivity water. The resistance of the membrane was determined where possible, and its flexibility in the wet state tested by creasing under water.

RESULTS AND DISCUSSION

Sulfonation without Preswelling

With Oleum. Samples of Kynar film (0.1 g., 2 mil thick) were immersed in 20 ml. of 20% oleum at $75°C.$ for varying times and washed as described above. The results, which are tabulated in Table I, suggest that sulfonation takes place progressively from the surface of the film inwards, and the membrane resistance does not fall appreciably until the sulfonation zones meet. This has been confirmed by microscopic examination of cross sections of the film which showed a brown zone progressively penetrating the film from each surface with increasing time of sulfonation. This

TABLE I
Sulfonation of 2 mil Kynar Film in 20% Oleum at $75°C.$

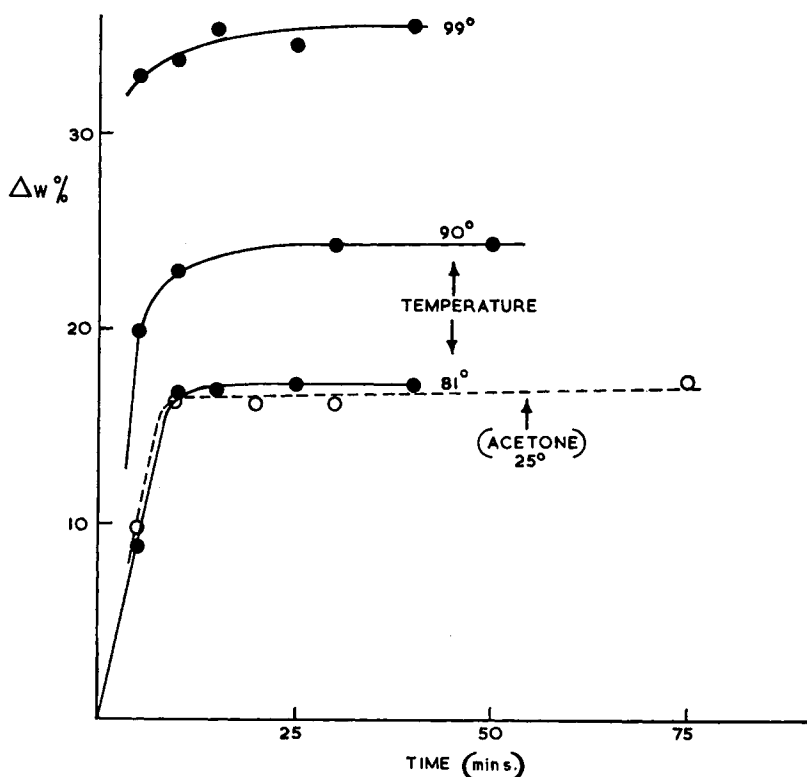| Sample	Sulfonation time, min.	Ion-exchange capacity, meq./g.	Membrane resistance, ohm/cm.^{2}
1	5	0.20	>20,000
2	10	0.35	>20,000
3	20	0.38	1,000
4	60	0.40	63
5	120	0.43	49

Fig. 1. Swelling behavior of poly(vinylidene fluoride) in acetophenone.

brown zone was selectively stained by methylene blue solution and apparently corresponds to the sulfonated part of the film.

The membranes sulfonated for 1 hr. or more were black, opaque, and brittle in the air-dry state.

With Chlorosulfonic Acid. Samples of Kynar film (0.1 g., 2 mil thick) were treated with 20 ml. chlorosulfonic acid for the times and temperatures shown in Table II. The results suggest that chlorosulfonic acid is rather more effective than oleum in penetrating Kynar film, but the membranes so produced were black, opaque, and brittle, even in the wet state.

TABLE II
Sulfonation of 2 mil Kynar Film in Chlorosulfonic Acid

Sample	Sulfonation time, min.	Sulfonation temperature, °C.	Ion-exchange capacity, meq./g.	Membrane resistance, ohm/cm.^{2}
6	4,000	25	0.05	>20,000
7	80	40–80	0.20	1,100
8	30	80	0.43	520
9	40	80	1.27	10

Swelling Behavior of Kynar Film

The isothermal swelling behavior of Kynar film in acetone and aceto-phenone at several temperatures is shown in Figure 1.   There is no indica-tion, on present evidence, as to whether the liquids penetrate the ordered regions of the polymer, or merely swell the amorphous regions.

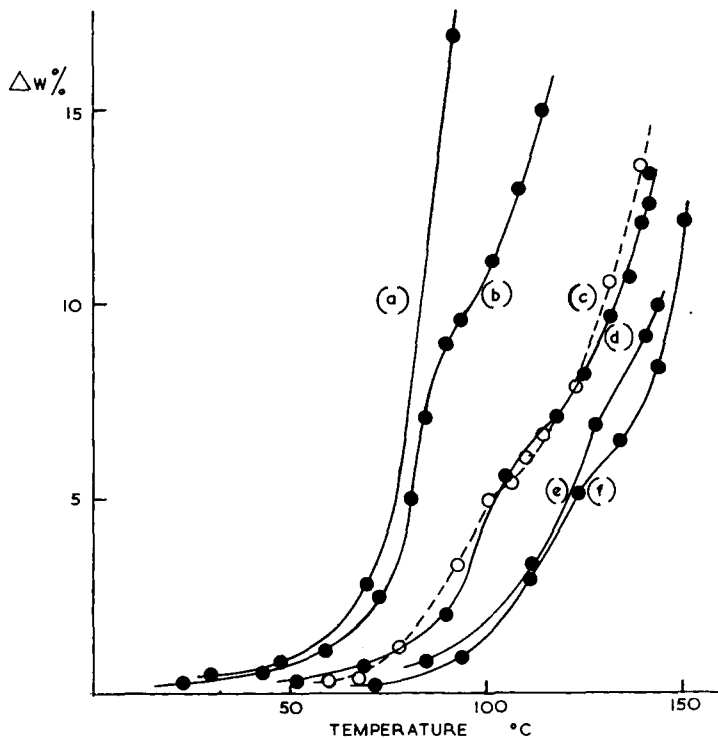Fig. 2. Swelling behavior of poly(vinylidene fluoride) with increasing temperature (1°C./min.): (a) acetophenone; (b) m-dimethoxybenzene; (c) benzyl chloride; (d) chlorobenzene; (e) xylene; (f) o-dichlorobenzene.

A wide range of liquids has been found to swell Kynar films at appropriate temperatures and the swelling curves for a constant rate of increase in temperature (ca. 1°C./min.) are shown in Figure 2 ($\Delta V = \Delta W$/density). The inflections in these curves suggest the occurrence of two transition temperatures in each case (with the exception of acetophenone), which may possibly be related to transitions in the amorphous and ordered regions, respectively.

Sulfonation of Kynar Film Swollen with Acetophenone

Samples of Kynar film (0.1–0.2 g.) were swollen in acetophenone at 99°C. for 30 min. ($\Delta W + 33\%$), blotted, and immersed in 20 ml. of 20% oleum at 60°C. for varying times before washing as described above.   The resultant
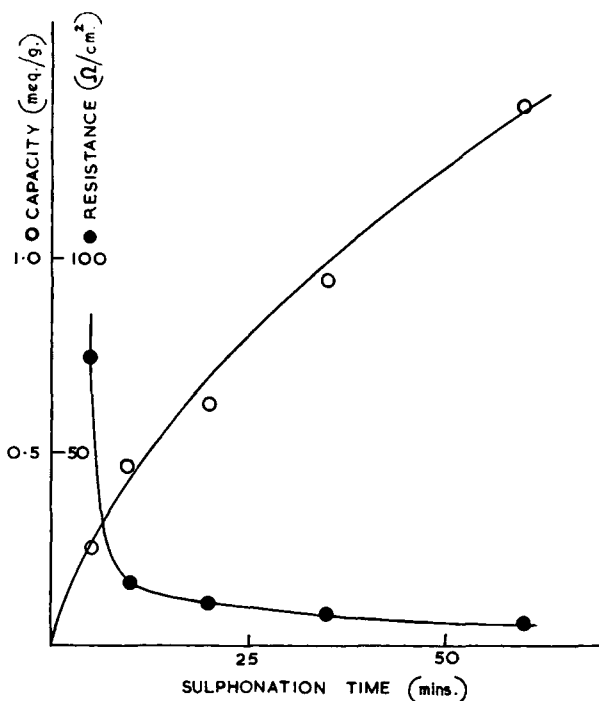
Fig. 3. Plots of (O) capacity and (●) resistance of poly(vinylidene fluoride) film swollen with acetophenone at 99° C., sulfonated in oleum at 60°C.

membrane properties are shown in Figure 3. In comparison with the results of Table I, the effect of swelling the film is to increase the rate of sulfonation and to decrease the membrane resistance for a given degree of sulfonation. These effects suggest that sulfonation is taking place throughout the film, probably simultaneously with the sulfonation and subsequent extraction of the acetophenone.

Kynar film was also swollen to varying extents by immersion for 30 min. in acetophenone at 81, 90, and 99°C., respectively and then sulfonated in 20% oleum at 60°C. for 60 min. The results, shown in Figure 4, show a linear dependence of ion-exchange capacity on extent of swelling. This fact might at first suggest that the acetophenone is being sulfonated and retained in the membrane (e.g., by sulfone crosslinking). However, the change in dry weight of the membrane (see Table III) during the above treatment shows that the weight increase is too small for the ion-exchange capacity to be due solely to sulfonated acetophenone, and it is concluded therefore that sulfonation of the Kynar is the predominant effect. This is confirmed by the preparation, described below, of membranes with swelling agents which are much less readily sulfonated than acetophenone.

The temperature of sulfonation in oleum has some effect in the relationship between ion-exchange capacity and membrane resistance. For
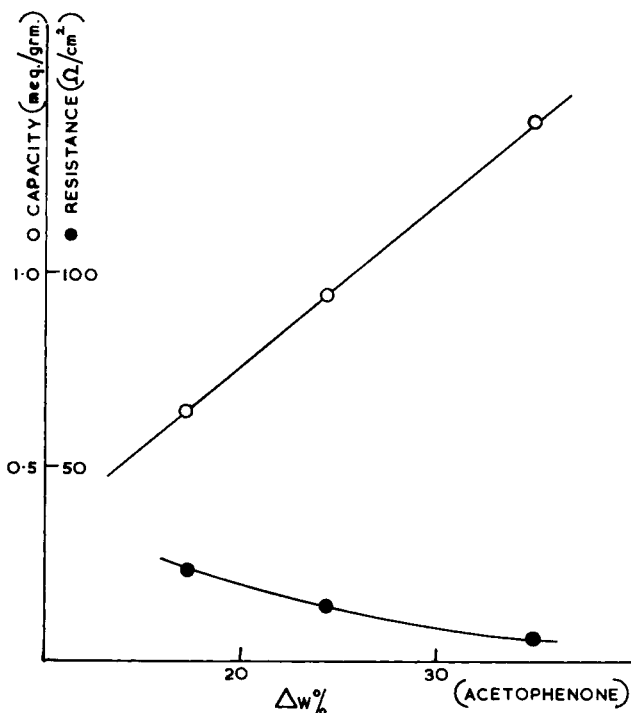
Fig. 4. Plots of (O) capacity and (●) resistance of poly(vinylidene fluoride) film swollen with acetophenone, sulfonated in oleum 1 hr at 60°C.

example, when Kynar was swollen with acetophenone at 100°C. for 30 min. (uptake 33%) and then sulfonated at 25°C. for varying times, the results shown in Figure 5 show that for a given ion-exchange capacity the mem-

TABLE III
Sulfonation of Kynar Film Preswollen with Acetophenone in Oleum at 60°C.

Sample	Aceto-phenone content, g./100 g. Kynar)	Sulfona-tion time, min.	Ion-exchange, capacity, meq./g.	Membrane resistance ohm/cm.²	Gel water, %	ΔW, %[a]
10	17	60	0.65	21	9	2.4
11	24	60	0.94	11	12	3.6
12	36	60	1.39	3	22	7.1
13	33	5	0.25	71	12	0 ± 0.2
14	32	10	0.46	13	13	1.4
15	33	20	0.62	8	15	2.9
16	33	35	0.94	5.5	16.5	7.4

[a] ΔW = percentage increase in membrane dry weight resulting from swelling, sulfonation, and washing.
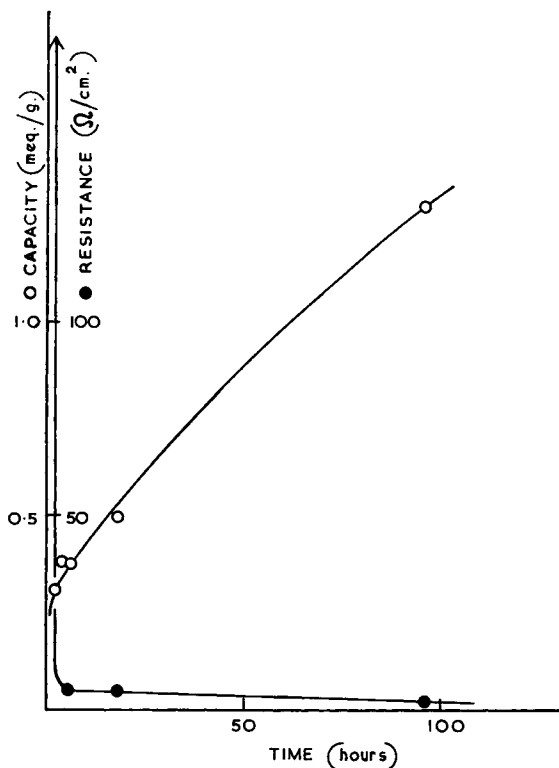
Fig. 5. Plots of (O) capacity and (●) resistance of poly(vinylidene fluoride) film swollen with acetophenone (+33%), sulfonated in oleum at 25°C.

brane resistance was significantly lower than in similar sulfonations at 60°C. (Fig. 3).

The membranes prepared by preswelling with acetophenone were brown and transparent, with the color increasing with the ion-exchange capacity. They were all flexible in the wet state, but in the air-dry state, flexibility adequate to withstand creasing was maintained only when the ion-exchange capacity was below 0.7 meq./g.

Sulfonation of Kynar Film after Various Preswelling Treatments

Samples of film (0.1–0.2 g.) were swollen, blotted, and then sulfonated in 20% oleum as indicated in Table IV. These results confirm the fact that increased swelling increases the rate of sulfonation, and they also show little difference in effectiveness between readily sulfonated swelling agents (e.g., acetophenone, dimethoxybenzene) and those more resistant to sulfonation (acetone, dimethyl sulfoxide).

A surprising effect is observed when the duration of preswelling treatment is varied. Thus with dimethoxybenzene at 118°C. and with dimethylsulfoxide at 25°C. an equilibrium uptake of swelling agent is rapidly

TABLE IV

Sulfonation of Kynar with 20% Oleum after Various Swelling Treatments

Sample	Swelling			Uptake of swelling agent, g./100 g. Kynar	Sulfonation		Gel water, %	Ion-exchange capacity, meq./g.	Resistance, ohm/cm.^{2}
	Agent[a]	Temp., °C	Time, min.		Temp., °C	Time, hr.			
17	Acetophenone	100	30	32	25	1	5	<0.1	23,000
18	"	100	30	33	25	2	5	0.31	710
19	"	100	30	32	25	4	15	0.38	6
20	"	100	30	33	25	6	14	0.38	5
21	"	100	30	27	25	18	15	0.50	5[b]
22	"	100	30	32	25	96	24	1.30	2[b]
23	DMB	125	10	37	60	1/2	29	0.72	15
24	"	125	10	37	60	1	30	1.1	15[b]
25	"	125	10	38	60	2	68	1.6	6[b]
26	"	125	10	34	60	3	21	1.7	3[b]
27	"	118	5	19	60	1	11	0.66	1800
28	"	118	10	20	60	1	11	0.70	220
29	"	118	20	20	60	1	13	0.64	87
30	"	118	40	21	60	1	12	0.69	25
31	Acetone	25	30	15	60	2	9	0.70	550[b]
32	"	"	"	15	60	3	10	0.82	140[b]
33	"	"	"	12	60	5	16	1.00	62[b]
34	DMSO	25	60	16	60	1	8	0.30	2500
35	"	25	1440	17	60	1	7	0.43	170

[a] DMB = *m*-dimethoxybenzene; DMSO = dimethyl sulfoxide.
[b] Brittle in air-dry state.

obtained, and more prolonged treatments with the swelling agents have negligible effect on the subsequent rate of sulfonation. These longer swelling treatments, however, produce membranes which, at a given level of sulfonation, have much lower resistances. The mechanism of this effect is not understood at present, but it is presumably associated with morphological changes in the polymer film during prolonged swelling.
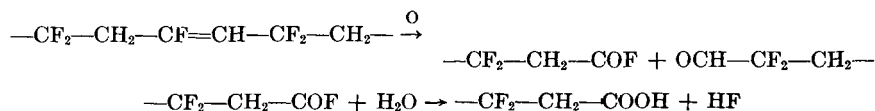
Infrared Studies of Sulfonated Kynar Film

The sulfonated film proved extremely difficult to grind to a small particle size. The spectra were therefore recorded directly from the sulfonated films with an unsulfonated sample of film of the same thickness in the reference beam. This reference sample was first extracted with acetone at 25 °C. for 1 hr. to remove plasticizer and then dried at 40 °C./5 mm.

All of the sulfonated films, both from oleum and chlorosulfonic acid sulfonations, showed absorption peaks at 1620 and 3450 cm.$^{-1}$ (strong), at 1720, 940, and 700 cm.$^{-1}$ (medium), and at 790 cm.$^{-1}$ (weak). The 1620 and 940 cm.$^{-1}$ peaks are attributed to C=C absorption, the 1720 cm.$^{-1}$ peak to C=O absorption, the 3450 cm.$^{-1}$ peak to O—H absorption, and the peaks at 700 and 790 cm.$^{-1}$ are unallocated.

When membrane sample 10 (Table III) was kept at 25 °C. for 20 hr. under a 5% aqueous solution of sodium borohydride, the 1720 cm.$^{-1}$ peak disappeared, and there was an increase in absorption at 3450 cm.$^{-1}$. This behavior is attributed to conversion of ketone to alcohol groups by the reducing agent.

When a similar sample of sulfonated film was boiled under reflux for 1 hr. with 1% hydrogen peroxide solution, the 1620 cm.$^{-1}$ peak was decreased, while the peak at 1720 cm.$^{-1}$ was increased. This behavior is attributed to partial conversion of C=C groups to carbonyl or carboxyl groups.

Side reactions resulting in formation of carbonyl groups during sulfonation are well known,[9] and this type of grouping is not likely to be particularly deleterious in respect of the chemical stability of the membrane. The ethylenic groups, however, which probably result from elimination of hydrofluoric acid, render the membrane labile to oxidants, since complete scission of the polymer chain is to be expected on oxidation of such a group, e.g.,

$$—CF_2—CH_2—CF=CH—CF_2—CH_2— \xrightarrow{O}$$
$$—CF_2—CH_2—COF + OCH—CF_2—CH_2—$$

$$—CF_2—CH_2—COF + H_2O \rightarrow —CF_2—CH_2—COOH + HF$$

Oxidation of Sulfonated Kynar Film

Samples of membrane (0.1 g.) were boiled under reflux for 1 hr. with 1% hydrogen peroxide solution and resistances measured. All samples became colorless during this treatment, and all became too brittle to fold in the wet state. For comparison, the same treatment was carried out on a commercial membrane C310 (from AMF Research & Development Division,

Springdale, Connecticut), prepared by polymerization of styrene in poly-chlorotrifluorethylene film and subsequent sulfonation. The C310 membrane could still be folded in the wet state after this treatment, and the effects on membrane resistance are shown in Table V.

TABLE V
Oxidation of Membranes with Hydrogen Peroxide

Membrane sample	Resistance, ohm/cm.^{2}	
	Before oxidation	After oxidation
10	21	1820
14	13	2900
13	71	6200
C310	7.5	492

The embrittlement of the sulfonated Kynar films on oxidation is probably due, at least in part, to the scission of the polymer molecule at ethylenic linkages (see above).

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Résumé

Des essais de sulfonation de film de poly-fluorure de vinylidène provoquent principale-ment une réaction à la surface du film sans pénétration du réactif dans le film. Cepen-dant quand le film est d'abord gonflé dans des liquides variés la sulfonation avec l'oléum a lieu lentement a travers le film et il se forme une membrane flexible de faible resistance électrique. On a étudié les plus importantes variables des étapes de gonflement et de sulfonation. Les réactions secondaires qui ont lieu pendant la sulfonation conduisent à l'introduction de groupements carbonyles et éthyléniques dans la molécule de polymère et ce dernier groupement est supposé être responsable du manque de stabilité de la membrane envers les oxydants.

Zusammenfassung

Sulfonierungsversuche an Polyvinylidenfluoridfilmen führen wegen des mangelnden Eindringens der Reagenzien hauptsächlich zu einer Reaktion an der Filmoberfläche. Hingegen verläuft die Sulfonierung mit Oleum nach Vorquellung des Films in einer grossen Zahl von Flüssigkeiten gleichmässig durch den ganzen Film, wobei eine biegsame Membrane mit niedrigem elektrischen Widerstand entsteht. Die wichtigeren Variablen für die Quellungs- und Sulfonierungsstufe wurden untersucht. Nebenreaktionen bei der Sulfonierung geben zur Einführung von Carbonyl- und Äthylengruppen in das Polymermolekül Anlass; es wird angenommen, dass letztere Gruppe für die mangelnde Stabilität der Membrane gegen Oxydationsmittel verantwortlich ist.