

Preparation of Permselective Membranes by Means of a Radioinduced Grafting. I. Cation-Selective

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Synopsis

Permselective cationic membranes were prepared by a radioinduced grafting method of styrene onto PTFE, and a preirradiation technique was used. Some attempts were made to characterize the membranes. They show mechanical properties similar to the PTFE matrix, and good electrochemical behavior, i.e., good permselectivity, which, nevertheless, decreased with decreasing solutions concentration. Such behavior has been related to a larger swelling in diluted solutions. Swelling properties in aqueous solutions of KCl and some organic solvents are also reported.

The aim of the present work is the preparation of ion-exchanger membranes having good mechanical properties and interesting electrochemical characteristics (by means of graft copolymers).

Until recently,¹⁻⁵ many methods were used to prepare ion-exchanger membranes with some particular industrial features. The reproducibility of the properties of these membranes is not very good, even on taking care in the standardization of the preparation.

A few authors⁶⁻⁸ used radiochemical methods, but they left many variables uncontrolled during the preparation.

In a previous paper⁹ we pointed out the possibility of obtaining graft products with the required properties by using the preirradiation method of grafting, which did not affect the mechanical strength of the polymeric substrate at all.

Using the acquired experience in this direction, we prepared ion-exchange membranes that have both good electrochemical and mechanical properties.

EXPERIMENTAL

Materials

The polymeric matrix on which the active groups were grafted was PTFE DuPont obtained by polydispersion, in films of thickness: 0.2-0.1-0.075-0.05 mm.

Styrene used during the polymerization was commercial monomer purified by conventional techniques.

Chlorosulfonation has been carried out with HClSO_3 RP from Carlo Erba.

Experimental Technique

The graft polymerization has been carried out using the experimental technique reported in a previous paper,⁹ with exception of the irradiation, which was performed at room temperature.

It should be, however, pointed out that we tried with different temperatures and times of polymerization in order to get membranes having different characteristics, as we shall further describe.

Active sites like SO_3H were produced in the graft polymer using sulfonation, carried out as follows: square PTFE films, grafted with styrene, having 2×2 or 4×4 cm. size, were immersed in carbon tetrachloride at room temperature and allowed to swell a few minutes. The sample was then cooled to 10°C . and, drop by drop, under vigorous stirring, HClSO_3 was added until a concentration of 10% (volume) in HClSO_3 was reached. The temperature was then allowed to rise to 20°C . and the mixture was allowed to react for 3 hr.

The sulfonated film was then washed, first in CCl_4 and then in a water-alcohol 30% mixture. Sulfonic groups were hydrolized by leaving the sample for 24 hr. in a mixture of water and 10% alcohol. The film was then weighted, both dry and after it had reached the equilibrium humidity.

Experimental Results and Discussion

Using the technique briefly described above we have been able to prepare different kinds of membranes, i.e.: (1) membranes having a thoroughly homogeneous charge distribution; (2) membranes showing a decreasing concentration of charges from one side to the other. The latter have been obtained by calendering two PTFE sheets together and grafting the whole system.

The charge distribution was studied by dyeing the sulfonated grafted films with Rhodamine B and then by microscopical examination of sections 20μ thick.

Microdensitometric measurements, to study the SO_3H groups distribution, were also carried out. In Figure 1 microdensitometric curves of two different kinds of membranes are reported.

The experimental conditions used to obtain the two membranes are summarized in Table I.

TABLE I

Irradiation time, hr.	Polymerization temp., $^\circ\text{C}$.	Polymerization time, hr.	Membrane kind
12	50	48	Homogeneous
12	25	48	Not homogeneous

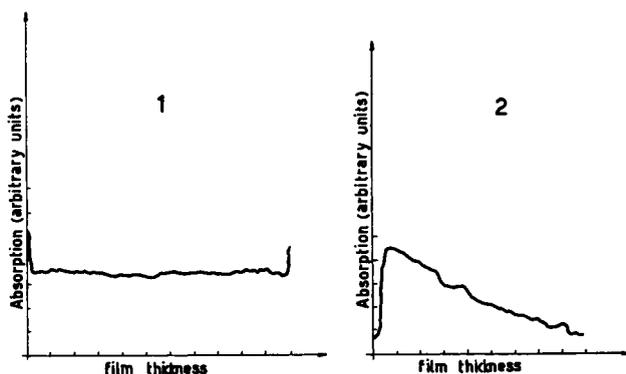


Fig. 1. Microdensitometric patterns for two kinds of membranes.

Complete sulfonation of a copolymer having 15% of grafted styrene is reached in about 3 hr. In such conditions we have 1.2 sulfonic groups on each benzene ring, and the amount of sulfonated groups does not increase even though the reaction is allowed to take place for 24 hr. After 3 hr. of chlorosulfonation the amount of sulfonic groups depends only upon the amount of grafted styrene.

Figure 2 plots the SO₃ per cent (calculated as increase in weight after the sulfonation) vs. the per cent of grafting (calculated as increase in weight after the grafting reaction). It also shows the per cent of water absorbed vs. the per cent of grafting.

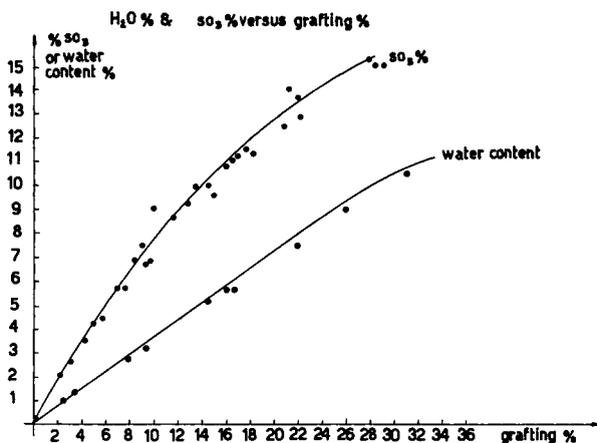


Fig. 2. Plot of SO₃ and water content per cent vs. grafting.

The experimental points refer to films having different thickness, reaction, and irradiation time; nevertheless they lay with a good approximation on a single curve; therefore the SO₃H per cent depends only on the grafted polymer amount.

An empirical equation can also be derived, with which, knowing the per cent of grafting, we can calculate the per cent of sulfonic groups:

$$\text{SO}_3\% = K(S_t)^{0.8}$$

where (S_t) is the per cent of grafted polymer related to the polymeric matrix.

Swelling Measurements

The swelling in water, salt solutions, and organic solvents was studied by means of length measurements on standard samples of membranes. Length measurements were then expressed as per cent volume increase, as done by other authors.¹⁰

These results are given in Figures 3, 4, and 5. Figure 3 shows the volume changes for membranes having different amounts of fixed charges, immersed in NaCl aqueous solutions at different concentrations. Swelling decreases with increasing concentrations of NaCl must be related to the SO_3^- ions affinity towards water.

The addition of Na^+ ions caused a decrease in solvation, because there is a saturation of polystyrene sulfonic acid groups, in the same way as happens in an ion-exchange resin.

Figure 4 shows the swelling of membranes with different amounts of charges in an organic solvent. The curves obtained in water-DMK mixtures show a maximum. This can be explained as follows: up to a certain DMK concentration, there is a swelling due to the hydrophobic chains of our copolymer and to the hydrophilic groups; at higher concentrations in DMK only the former effect is present, whereas with a less polar solvent, such as benzene, the swelling becomes negligible (Figs. 5 and 6).

Burst Strength Measurements

The burst strength of 0.1- and 0.05-mm. thick films were, respectively, about 6 and 3 atm. and, within the experimental error, were independent of the percentage of the grafted polymer.

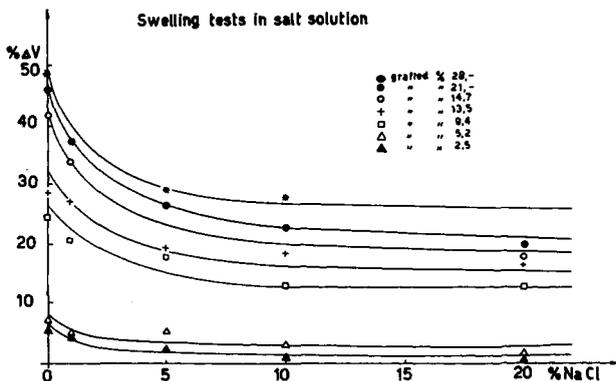


Fig. 3. Plot of vol.-% increase vs. salt (NaCl) concentration.

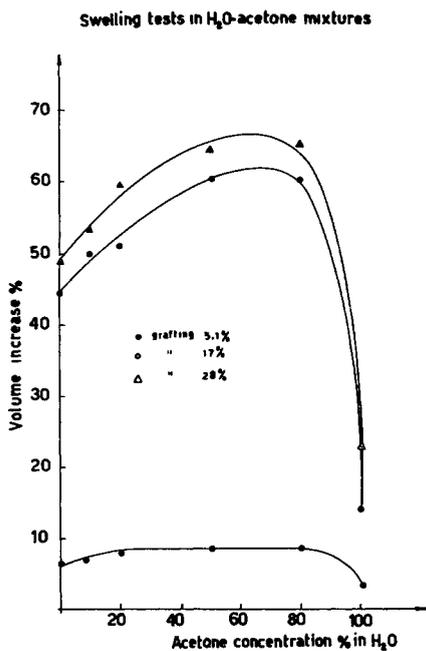


Fig. 4. Plot of vol.-% increase vs. acetone concentration in water.

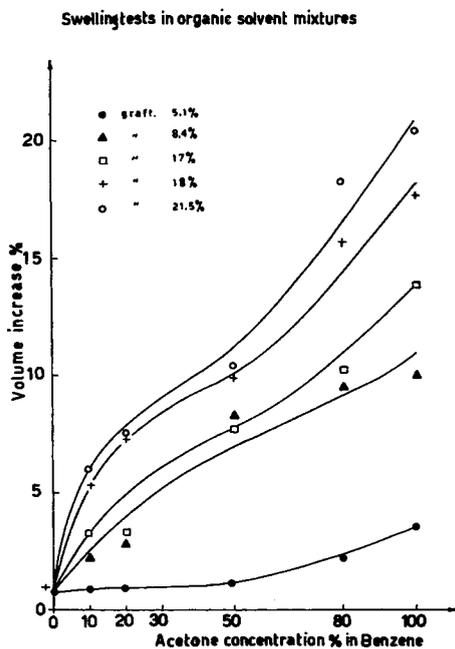


Fig. 5. Plot of vol.-% increase vs. acetone concentration in benzene.

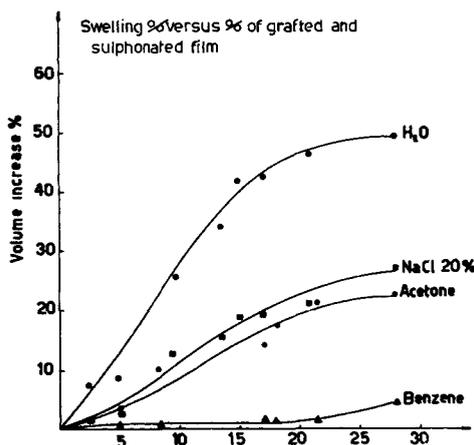


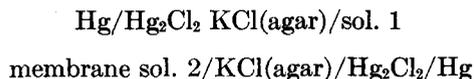
Fig. 6. Plot of vol.-% increase vs. sulfonated graft per cent in various solvents.

Up to 30% of grafted styrene no measurable change in mechanical properties of PTFE occurs. This is in good agreement with the elongation strength measurements on PTFE strips that had undergone the same process of grafting. These data will be reported elsewhere.

Dry and wet membranes were fixed between two stainless steel circular supports with a 1-cm.² hole and tested with an increasing pressure of N₂, controlled with a precision manometer.

Permselective Properties—Membrane Potential Measurements

Membrane potential measurements to determine permselectivity characteristics have been carried out, testing the membranes in a system that can be so schematized:



KCl solutions with normalities between 1 and 10⁻³ were used. Measurements with concentration ratio 2, 10, 500, 1000 have been performed.

The concentration potentials were 16.2, 14.3, and 14.0 mv., respectively, for concentration ratios 0.1N/0.05N, 0.2N/0.1N, 1N/0.5N, and within experimental error were independent of per cent SO₃ content. The amount of sulfonic groups was always more than 7%.

Using the relationship

$$E = (RT/F) (2t_+ - 1) \ln (a_1/a_2)$$

where t_+ = transference number of a cation, a_1 and a_2 = solution activity, it is possible to deduce the t_+ value, which represents effective transfer number, measuring the E in millivolts. We are able, therefore, to calculate permselectivity degree as:

$$P\% = [(t_+ - t_0)/(1 - t_0)] 100$$

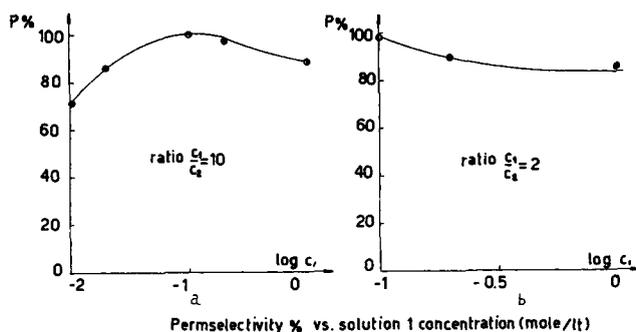


Fig. 7. Plot of membrane permselectivity vs. solution concentration at two different solution 1/solution 2 ratios.

where t_0 is the tabulated transfer number.

According to the plot of Figure 7, the permselectivity shows a drift with respect to usual behavior at very low concentrations.

While other kinds of membranes having sulfonic groups decrease their selectivity with increasing solution concentrations, these membranes show a maximum in the range studied.

This anomalous behavior can be explained by the results of the swelling measurements. At low concentration, though there is lower free diffusion, the permselectivity is decreased by the increased membrane swelling.

Homogeneous membranes having more than 7% of sulfonic groups, that is, at least 10% of grafted styrene, show permselectivity values close to 98%.

The membrane thickness, at least in our range (0.1–0.05 mm.) did not influence the results.

Because of the fast swelling in any solution, the conditioning was very rapid.

Conclusion

We shall summarize in Table II below the principal properties of a standard homogeneous membrane.

TABLE II

Properties	
Kind	Homogeneous
Thickness (dry)	0.1 mm.
Swelling H ₂ O (in volume)	20%
Elongation strength	2 kg./mm. ²
Burst strength (dry)	6 atm.
Burst strength (wet)	6 atm.
SO ₃ per cent	7%
Permselectivity (sols. ratio 1/0.5N KCl)	80%
Permselectivity (sols. ratio 0.1/0.05N KCl)	98%

Moreover, these membranes show a great resistance to any chemical agent such as concentrated NaOH, H₂SO₄, HCl, HNO₃, and HCl-HNO₃ mixtures, up to temperature above 100°C.

It is possible to store them in dry form; they do not need any conditioning before using; they have a great flexibility and mechanical resistance conferred from the PTFE matrix.

Finally, according to the aim of the present study, their properties are well reproducible.

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Résumé

Des membranes perméo-sélectives cationiques ont été préparées par greffage, induit par radiation du styrène sur du PTFE et on a utilisé la technique de pré-irradiation. Certains essais ont été effectués en vue de caractériser les membranes. Elles montraient des propriétés mécaniques similaires à la matrice TPFE, un bon comportement électrochimique, c'est-à-dire une bonne perméo-sélectivité qui néanmoins décroissait avec la diminution de la concentration des solutions. Un tel comportement a été lié au gonflement plus important dans les solutions diluées. Les propriétés de gonflement en solution aqueuse de KCl et de certains solvants organiques ont également été rapportées.

Zusammenfassung

Permeable Kationenmembranen wurden durch eine strahlungsinduzierte Aufpfropfung von Styrol auf PTFE nach einem Vorbestrahlungsverfahren hergestellt. Versuche zur Charakterisierung der Membranen wurden durchgeführt. Sie zeigen ähnliche mechanische Eigenschaften wie die PTFE-Matrix und gutes elektrochemisches Verhalten, nämlich gute Permeabilität, wobei diese aber mit fallender Konzentration der Lösung abnimmt. Ein solches Verhalten wurde mit einer stärkeren Quellung in verdünnten Lösungen in Verbindung gebracht. Quellungseigenschaften in wässrigen KCl-Lösungen und einigen organischen Lösungsmitteln werden beschrieben.

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