

Preparation and Properties of Cationic Membranes Obtained by Radiation Grafting of Methacrylic Acid onto PTFE Films

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Synopsis

Cationic membranes were prepared by direct radiation grafting of methacrylic acid (MAA) onto poly(tetrafluoroethylene) (PTFE) films followed by alkaline treatment to confer ionic character in the graft copolymer. The complete inhibition of homopolymerization of MAA by using ammonium ferrous sulfate (Mohr's salt) failed. However, the addition of 0.5 wt % FeCl_3 to the monomer solution effectively inhibited the homopolymerization process and higher grafting yield was obtained. It was found that the graft polymerization proceeded successfully in presence of methanol/water mixture (30/70 wt %), and much higher degrees of grafting were obtained as compared with those in the presence of other diluents used here. The influence of irradiation atmosphere (air, N_2 gas, and vacuum) on the grafting process was investigated. The dependence of the grafting rate on MAA concentration was found to be of orders 2.9 and 0.72 in the presence of 0.5 wt % Mohr's salt or 0.5 wt % FeCl_3 , respectively. This grafting system proceeds by the front mechanism. Investigation of mechanical properties, electrical conductivity, and swelling behavior of the grafted films revealed that such a copolymer could be acceptable in practical use as a cation-exchange membrane.

INTRODUCTION

Radiation grafting covers a very broad field of polymer chemistry with numerous potential applications of industrial interest. It is a well-known method for modification of the chemical and physical properties of polymers, and is of particular interest for achieving specifically desired properties.

A great deal of work was spent during the last 25 years for the development of the best possible membranes using almost every available polymeric materials.¹⁻¹² In previous studies, the preparation and selected properties of neutral,¹³⁻¹⁶ cationic,¹⁷⁻²¹ and anionic²²⁻²⁴ membranes obtained by radiation-induced grafting of some vinyl and acrylic monomers onto different polymeric substrates, using the direct and post-radiation techniques, were investigated. These grafted membranes showed great promise in practical applications as ion-exchange membranes and/or as reverse osmosis ones for the desalination of saline and brackish water.

In the present study, the preparation and some properties of cationic membranes obtained by direct radiation-induced graft polymerization of MAA solution onto PTFE films were investigated. The effect of grafting conditions on the grafting process and inhibition of homopolymerization was investi-

gated. The possibility of the practical use of such grafted films will be discussed.

EXPERIMENTAL

Materials

Polytetrafluoroethylene (Teflon) (PTEE) films, specific gravity 2.2 g/cm³, Nitto Co. Ltd., Japan, was used. Reagent grade methacrylic acid (MAA) of purity 99% (Merck), stabilized with 200 ppm hydroquinone, was used after purification by distillation in the presence of N₂ gas atmosphere. The other chemicals were reagent grade and were used without further purification.

Graft Polymerization

The direct radiation grafting method was used as a technique in which the polymer and monomer solution were subjected simultaneously to ionizing radiation at different atmospheres (in air, in nitrogen gas, and under vacuum).

The inhibitor was added to minimize the homopolymerization of MAA during irradiation. In the case of irradiation in nitrogen gas, the glass ampule containing the monomer solution and films was deaerated by bubbling nitrogen (commercial nitrogen gas which contains about 1.5% oxygen impurities was used) for 5–7 min and then sealed, while for irradiation under vacuum the glass ampule containing the reactants was frozen, degassed under reduced pressure less than 10⁻³ torr, and thawed. This process was repeated three times; then the glass ampule was sealed. The glass ampules were then subjected to Co-60 γ -rays at a dose rate that ranged from 0.22 to 0.31 Gy/s. The grafted films were washed thoroughly with hot distilled water and soaked overnight in water to extract the residual monomer and the homopolymer occluded in the film. The films were then dried in vacuum oven at 60°C for 24 h and weighed. The degree of grafting was determined by the percentage increase in weight as follows:

$$\text{degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

where W_0 and W_g represent the weights of initial and grafted films, respectively.

Swelling Measurements

The 80- μ m-thick PTFE film was immersed in the monomer solution for 24 h at constant temperature. Then, the film was removed, blotted quickly with absorbent paper to remove the liquid attached on its surface, and weighed quickly.

The degree of swelling was determined as follows:

$$\text{swelling (\%)} = \frac{W_s - W_0}{W_0} \times 100$$

where W_0 and W_s represent the weights of the initial and swelled films, respectively.

Electrical Conductivity Measurements

Conductivity measurements were carried out using Mega Ohm meter-MoM II (WTW instruments, FRG). The electrical resistance of the sample was measured, and the electrical conductivity (σ) was calculated as follows:

$$\sigma = \frac{1}{R} \cdot \frac{L}{a} \Omega^{-1} \text{ cm}^{-1}$$

where

L = thickness of the specimen (cm)

a = the area of the sample surface (cm²)

R = ohmic resistance (Ω)

Mechanical Properties Measurements

Dumbbell-shaped samples 50 mm long, with a neck of 28 mm and 4 mm wide, were used. Tensile strength and elongation percent at break were measured using an Instron (Model 1195, U.K.) at a crosshead speed of 50 mm/min.

RESULTS AND DISCUSSION

Effect of Solvent

Solvents are basically used in radiation grafting experiments to enhance the degree of accessibility of monomer to grafting sites within the polymer brought about by the great ability of the added solvent to swell the base polymer. But, in the case of PTFE, which scarcely swells in any common solvent, the grafting process occurred by the front mechanism.

Figure 1 shows the swelling percent for the trunk polymer (PTFE Teflon) as a function of MAA concentration (water and methanol/water mixture were used as a solvent of MAA). It can be seen that the absolute values of swelling for PTFE film are very small and it scarcely swells in such monomer solutions in the presence or absence of methanol at different temperatures (20 and 30°C).

Table I shows the effect of different solvents on the grafting of MAA onto PTFE films under different irradiation atmospheres. It was observed that the absence of inhibitor during radiation grafting process results in enhancement of homopolymerization and the grafting process is inhibited to some extent. The apparent high percentage grafting obtained in such a case may include homopolymer; therefore, it is not true grafting. Furthermore, the addition of small amount of inhibitor (0.25 wt %) results in enhancing the graft polymerization, but some homopolymer still formed. Meanwhile, among the different

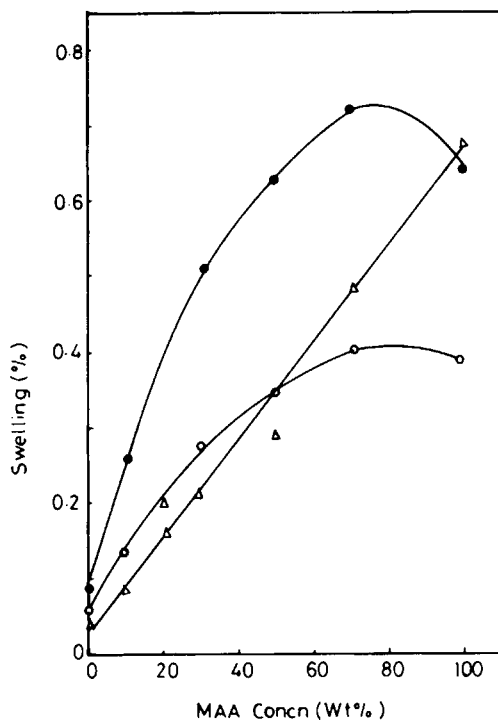


Fig. 1. Swelling percent vs. MAA concentration in different diluents: (○) distilled water at 20°C; (●) distilled water at 30°C; (Δ) methanol/water at 30°C, swelling time, 24 h. PTFE film thickness, 80 μ m.

TABLE I
Effect of Solvent on the Grafting of Methacrylic Acid onto PTFE Film
in Nitrogen Gas and Air Atmospheres^a

Solvent	MAA concentration (wt %)	Mohr's salt concentration (wt %)	Degree of grafting (%) irradiation atmosphere		Remarks
			Air	N ₂ gas	
Dist. water	50	—	5.0	7.5	Homopolymer Formation in all cases
Dist. water	50	0.25	6.8	8.7	
Methanol	50	—	8.1	7.9	Homopolymer Formation in all cases
(Methanol/water) (30/70)	50	—	12.6	19.7	
(Methanol/water) (30/70)	50	0.25	14.8	17.0	Homopolymer Formation in all cases
DMF	50	—	0.55	0.5	
DMF/water (50/50)	50	0.25	7.5	6.1	Homopolymer Formation in all cases
Isopropanol	50	—	0.6	1.2	

^aGrafting conditions: irradiation dose, 20 kGy; film thickness, 80 μ m.

solvents used as a diluent for MAA, it was found that distilled water and methanol/water mixture (30/70 wt %) are the most suitable diluents for this grafting system because the mixture swells the already grafted polymer.

Effect of Inhibitor

Methacrylic acid is highly polymerized during the radiation grafting process. The addition of inhibitor to the reaction medium is required to minimize the homopolymerization of such a water-soluble monomer. In this study, two inhibitors were used (Mohr's salt) and ferric chloride, and their effect on the graft polymerization of aqueous MAA in the presence and absence of organic solvent (methanol) were investigated under different irradiation atmospheres.

Figure 2 shows the effect of Mohr's salt concentration on the degree of grafting of aqueous MAA (50 wt %) onto PTFE films at different irradiation atmospheres (air, nitrogen gas, and vacuum). It is obvious that the degree of grafting increases with inhibitor concentration to reach a certain limiting value at higher inhibitor concentration under all irradiation atmospheres. However, at lower inhibitor concentration that ranged from 0 to 0.8 wt %, the highest degrees of grafting were obtained in N₂ gas atmosphere and the lowest degrees were obtained under vacuum irradiation. It was observed that the suitable concentration of Mohr's salt is about 0.5 wt % for the irradiation in N₂ gas and under vacuum; however, for the irradiation in air the suitable inhibitor concentration is shifted to higher value to be 1.0 wt % because oxygen enhances the homopolymerization process.

Effect of Mohr's salt on the grafting of MAA solution in a mixture of methanol and distilled water (30/70 wt %) is shown in Figure 3. It can be seen that higher degrees of grafting were obtained for all irradiation atmospheres,

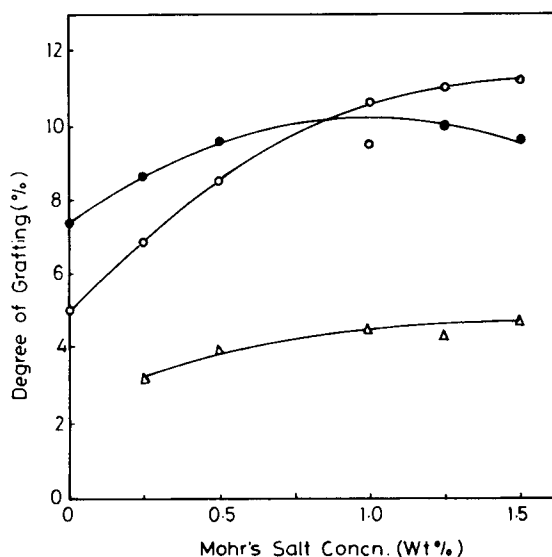


Fig. 2. Degree of grafting vs. inhibitor concentration at different irradiation atmospheres: (○) air; (●) nitrogen gas; (△) vacuum. Irradiation dose, 20 kGy; aqueous MAA concentration, 50 wt %; PTFE film thickness, 80 μ m.

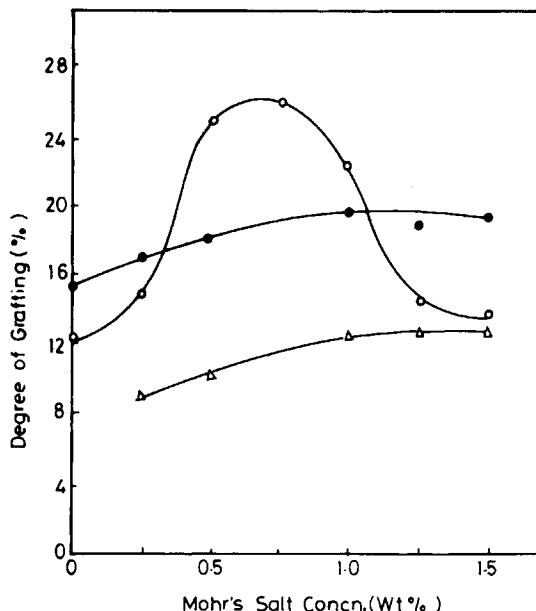


Fig. 3. Effect of inhibitor concentration on the degree of grafting of 50 wt % MAA in methanol/water mixture (30/70 wt %) at different irradiation atmospheres: (○) air; (●) nitrogen gas; (Δ) vacuum. PTFE film thickness, 80 μ m; irradiation dose, 20 kGy.

at a given inhibitor concentration, as compared with those obtained when MAA was diluted with distilled water only. It is also clear that, during irradiation in air (Fig. 3), there is an optimum concentration of Mohr's salt (0.75 wt %) at which the highest degree of grafting was obtained.

Generally, it can be concluded that the addition of inhibitor to the reaction medium is very necessary to achieve considerable grafting with minimum homopolymer formation of MAA. The addition of organic solvent such as methanol to the reaction medium results in enhancing the graft polymerization, and higher degrees of grafting were obtained at the given reaction conditions. The homopolymer formation was inhibited to some extent in the presence of Mohr's salt, but some homopolymer still formed specially in air and in N_2 gas irradiations.

Another trial was made to inhibit completely the homopolymerization of MAA solution during radiation grafting onto PTFE films. Table II shows the effect of $FeCl_3$ concentration on the grafting yield and homopolymer formation. It can be seen that the addition of 0.5 wt % $FeCl_3$ to the reaction medium inhibits effectively the homopolymerization of MAA solution, and reasonable degrees of grafting were obtained. Under such conditions, the grafting process occurred homogeneously and the films were smooth, flat, and easily extracted.

Effect of Monomer Concentration

The effect of MAA concentration in methanol/water mixture on the degree of grafting onto PTFE films at various irradiation times was investigated in the presence of Mohr's salt and also in $FeCl_3$, as shown in Figures 4 and 5,

TABLE II
Effect of FeCl_3 Concentration on the Grafting of MAA Solution (50 wt %) in Methanol/ H_2O (30/70 wt %) in N_2 Gas Atmosphere^a

FeCl_3 concentration (wt %)	Degree of grafting (%)	Remarks
0.1	9.8	Homopolymer formed
0.2	11.1	Little homopolymer
0.4	13.2	No homopolymer
0.5	15.8	No homopolymer
0.6	12.8	No homopolymer
0.7	11.5	No homopolymer

^aIrradiation dose, 20 kGy; PTFE film thickness, 80 μm .

respectively. It can be seen in Figure 4 that there is an induction period for initiation of the graft polymerization at the early stage of irradiation time. Such an induction period was probably due to oxygen impurities consumption, and the vacuum condition in the glass ampule may not be enough. Thereafter, the grafting begins, and the degree of grafting increases with irradiation time and then levels off at early doses, especially for the higher MAA concentrations. However, the higher the monomer concentration, the higher the initial grafting rate and degrees of grafting obtained.

The addition of Mohr's salt to the reaction medium did not inhibit completely the homopolymerization of MAA. Therefore, the grafting process levels off early at certain limiting values due to the hindrance of monomer diffusion in such viscous medium.

Figure 5 shows that the grafting process is enhanced in presence of FeCl_3 for all monomer concentrations, and higher degrees of grafting were obtained as compared with those observed in the presence of Mohr's salt. At lower

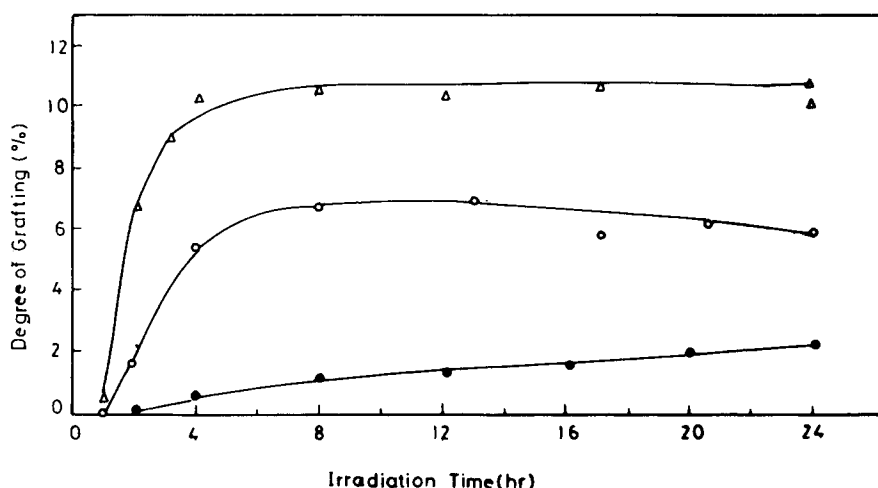


Fig. 4. Degree of grafting vs. irradiation time under vacuum for various MAA concentrations (wt %): (●) 20; (○) 40; (△) 60. Mohr's salt concentration, 0.5 wt %; diluent (methanol/water), 30/70 wt %; PTFE film thickness, 50 μm .

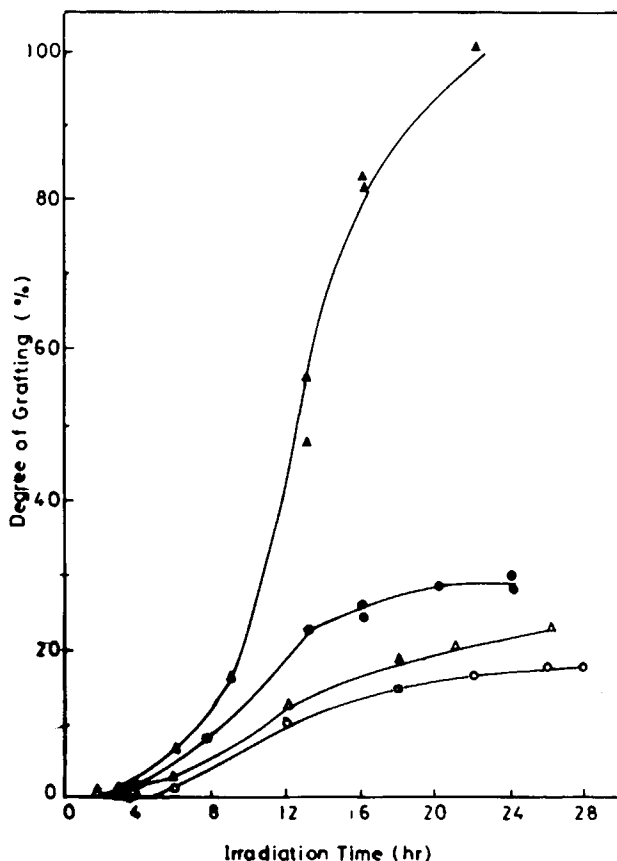


Fig. 5. Degree of grafting vs. irradiation time under vacuum for various MAA concentrations (wt %): (○) 15; (△) 30; (●) 50; (▲) 70. Grafting conditions are the same as in Figure 4, except that FeCl_3 concentration is 0.5 wt %.

MAA concentrations, the degree of grafting increases with irradiation time and it tends to level off at irradiation time higher than 20 h. However, at 70 wt % MAA solution, the degree of grafting sharply increases with irradiation time, and much higher grafting yield was achieved. No homopolymer was formed under such grafting conditions, even at higher MAA concentrations and also at higher irradiation dose.

The aforementioned results showed that FeCl_3 inhibited effectively the homopolymerization of MAA, and the grafting process was enhanced. The progressive diffusion of monomer in such a medium results in forming new growing chain radicals. Meanwhile, the monomer diffuses through the already grafted polymer; therefore, the higher the monomer concentration, the higher the grafting and diffusion of monomer.

The initial rate of grafting was calculated from Figures 4 and 5 and plotted logarithmically as a function of MAA concentration and shown in Figure 6. Such logarithmic plots give a linear relationship for both cases in the presence of Mohr's salt or in FeCl_3 . The dependence of the grafting rate on monomer

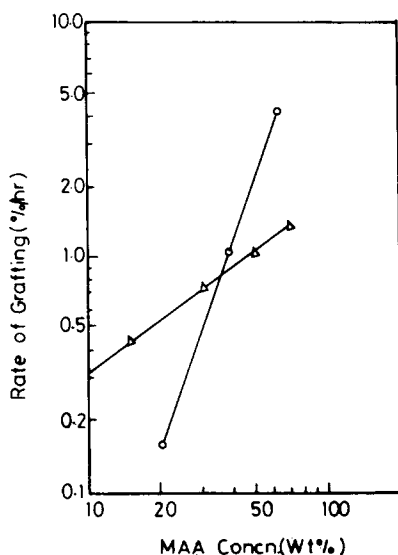


Fig. 6. Logarithmic plots of grafting rate of MAA onto 50 μm PTFE films vs. MAA concentration: (○) in the presence of 0.5 wt % Mohr's salt; (△) in the presence of 0.5 wt % FeCl_3 . Grafting conditions are the same as in Figures 4 and 5.

concentration in the presence of Mohr's salt was found to be of order 2.9. The very high dependence of the grafting rate on MAA concentration in the presence of Mohr's salt is due to the highly viscous medium occurring because of the homopolymerization of MAA. Consequently, the diffusion of monomer is hindered in such a viscous medium. On the other hand, no restriction of monomer diffusion in the presence of FeCl_3 ; therefore, the order dependence on MAA concentration is low.

It can be concluded that this grafting system proceeds by the front mechanism.

Properties of the Graft Copolymers

The grafting of hydrophilic monomers such as methacrylic acid onto hydrophobic polymers results in graft copolymers exhibiting hydrophilic properties as well as good swelling behavior. Moreover, in some cases, further modification of the graft copolymer is required to introduce easily ionizable groups, and, consequently, the swelling behavior and the electrochemical properties will improve as well. The alkaline treatment of poly(methacrylic acid) graft copolymer was carried out for the preparation of cation-exchange membranes.

Mechanical Properties of the Grafted Materials

It is very important that the grafted films show acceptable mechanical properties for their handling in the practical uses. Results given in Figure 7 show the variation of tensile strength (T_b) and percent elongation (E_b) at break for the PTFE-*g*-PMAA copolymer films with degree of grafting. It can

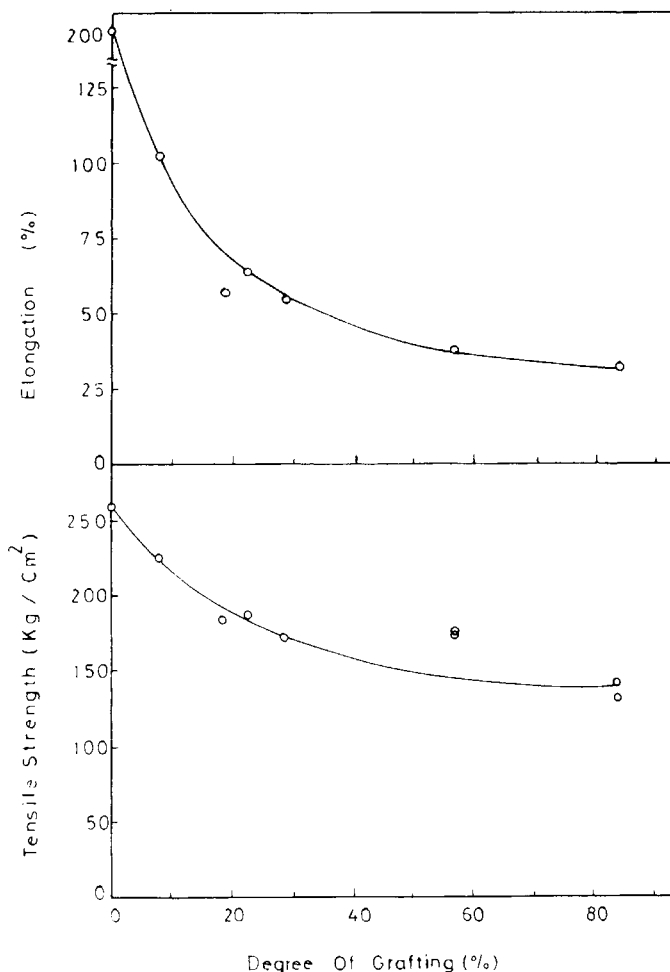


Fig. 7. Change in tensile strength and elongation percent with degree of grafting for PTFE-*g*-PMAA films.

be seen that E_b sharply decreases with increasing the degree of grafting. It is also noted that T_b gradually decreases as the degree of grafting increases. However, such grafted films show an acceptable tensile strength.

Generally, increasing the degree of grafting results in increasing the rigidity of some graft copolymers, especially if the grafted chains possess higher T_g . Consequently, a decrease in the elongation percent and an increase in the tensile strength are expected for such grafted films. In practical applications, it is important that the grafted films show good tensile strength, especially in the reverse osmosis desalination of sea water. That is because in this technique relatively high pressure is applied and the membrane must have a good tensile strength to be suitable for such purpose. From this point of view, it can be suggested that these grafted films show good tensile properties, which may make them acceptable for handling in some practical uses. It must be taken in account that, in most practical uses, the grafted films will be used in the wet form. Therefore, more elasticity and improvement in E_b will be expected due

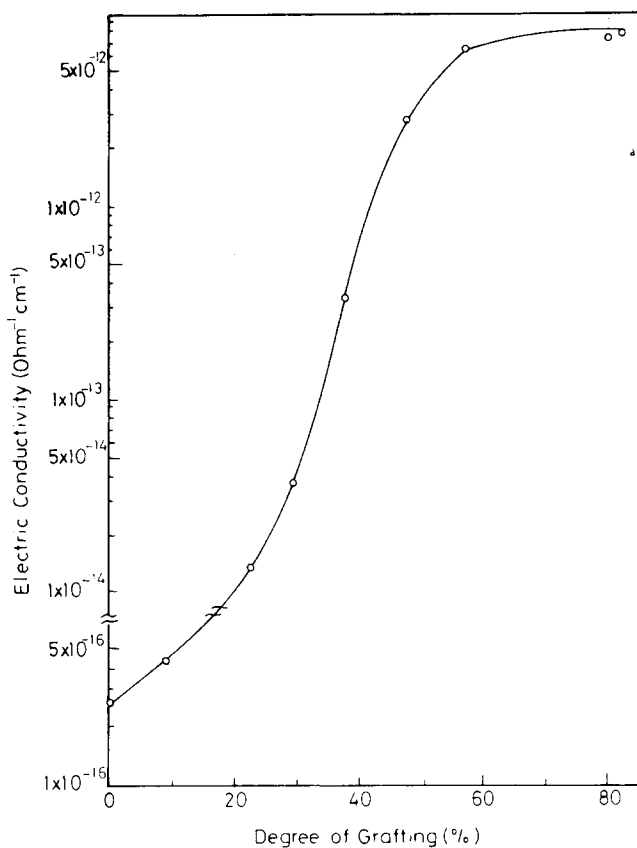


Fig. 8. Electrical conductivity for the alkali-untreated PTFE-*g*-PMAA films as a function of degree of grafting.

to the hydrophilic groups of such grafted films which swell in water and create more space for chain movement.

Electrical Conductivity of the Grafted Material

The methacrylic acid graft copolymers were expected to show higher electrical conductivity as compared to that of the trunk polymer. It is possible to introduce easily ionizable groups into such grafted copolymers by the alkaline treatments. The carboxylic acid groups were converted into their K salt by refluxing with KOH solution at 100°C.

Figures 8 and 9 show the electrical conductivity of the alkali-untreated and -treated PTFE-*g*-PMAA films. It is obvious that the electrical conductivity of the alkali-untreated grafted PTFE films sharply increases with the degree of grafting (Fig. 8). At higher degrees of grafting, above 60% the electrical conductivity tends to level off. The alkali-treated grafted PTFE films possess a much higher electrical conductivity as compared with that of alkali-untreated ones (Fig. 9). It can be seen from Figure 9 that the electrical conductivity gradually increases with degree of grafting. The electrolytic

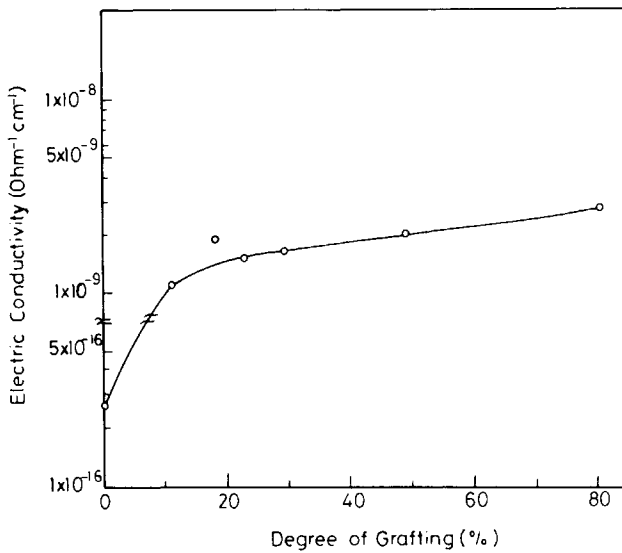


Fig. 9. Electrical conductivity for the alkali-treated PTFE-*g*-PMAA films as a function of degree of grafting.

groups introduced into the grafted films by the alkaline treatment result in an improvement of the electrochemical properties of such grafted materials.

Swelling Behavior of the PTFE-*g*-PMAA Films

Figure 10 shows the water uptake percent for the PTFE-*g*-PMAA films as a function of degree of grafting. Alkaline treatment of the graft chains was

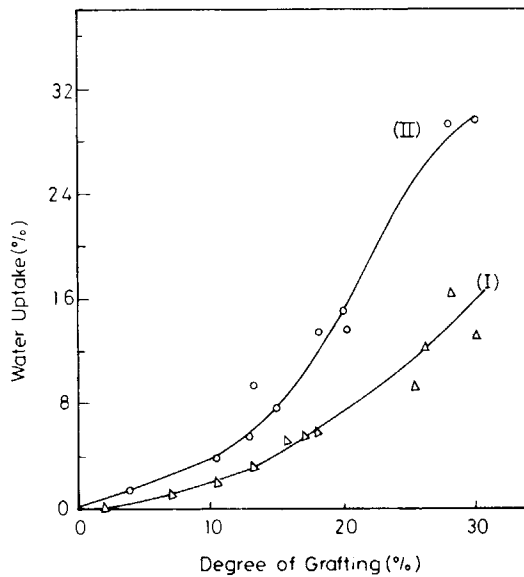


Fig. 10. Water uptake percent vs. degree of grafting for PTFE-*g*-PMAA films: (I) alkali-untreated; (II) alkali-treated.

carried out to confer a more ionic character in the graft copolymer, which may result in improving the hydrophilic properties of the films. It is obvious from Figure 10 that the water uptake percent increases with the degree of grafting for the alkali-untreated (I) and alkali-treated (II) grafted films. Meanwhile, the alkali-treated films possess higher hydrophilic properties than alkali-untreated ones.

This result is in a good agreement with that obtained for the fluorinated polymers-*g*-poly(acrylic acid) graft copolymers and reported in the literature.¹⁸ The water uptake for the alkali-treated and -untreated PTFE-*g*-PMAA films in the present study is much lower than that for PTFE-*g*-PAA, at a given degree of grafting.¹⁸ The methyl side group in methacrylic acid may have some steric hindrance, and this may retard the hydration of free-carboxylic groups and carboxylic salt as well. This may be the reason of lowering the hydrophilic properties of poly(methacrylic acid) graft copolymers as compared with that of poly(acrylic acid) graft ones. Shantora and Huang found also that acrylic acid-grafted membranes generally showed greater improvement in permeability than methacrylic grafted membranes.²⁵

This study was partially supported by the International Atomic Energy Agency (IAEA) under Research Contract No. 4127/RB.

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Received May 9, 1988

Accepted May 11, 1988