Preparation of Ion-Exchange Membranes by Hydrolysis of Radiation-Grafted Polyethylene-*g*-Polyacrylamide Membranes

Bhuvanesh Gupta,[1] **Nishat Anjum**[1,2]

[1]*Department of Textile Technology, Indian Institute of Technology, New Delhi-16, India*
[2]*Department of Applied Chemistry, Delhi College of Engineering, Bawana Road, Delhi, India*

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ABSTRACT: Polyethylene-*g*-polyacrylamide membranes were prepared by graft polymerization of acrylamide onto polyethylene films using a preirradiation method. The ion-exchange membranes were obtained by the hydrolysis of grafted films so as to transform amide groups into carboxyl groups. The fraction of amide groups transformed into carboxyl groups was limited to ~0.5. The characterization and thermal behavior of membranes with different degrees of grafting were evaluated by FTIR, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) measurements. The heat of fusion and the crystallinity of polyethylene decreased considerably in the hydrolyzed membranes depending on the degree of grafting. It was found that the grafting of acrylamide led to the reduction in crystallinity due to disruption of the crystallites (crystal defects) and dilution of the inherent crystallinity (dilution effect). The contribution of the hydrolysis step to the crystallinity decrease was negligible. The thermal stability of the membranes as obtained from TGA showed considerable enhancement after hydrolysis. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 149–154, 2003

Key words: polyethylene (PE); membranes; radiation; grafting; hydrolysis

INTRODUCTION

The development of ion-exchange membranes by radiation-induced graft polymerization of acrylic monomers onto polymer films has generated considerable interest toward their utilization in various technologically important fields.[1–5] This method offers a versatile way to impart desirable properties into a polymer without much affecting its original characteristics. Moreover, the graft distribution may be achieved throughout the matrix because of the radiation activation of the film across its thickness. The modification may be achieved in a polymer already existing in the film form, which overcomes the rheological problems associated with the transformation of the grafted matrix into a thin foil.

Considerable efforts have been made to design and develop ion-exchange membranes by graft polymerization of vinyl and acrylic monomers of an ionic nature onto polymer films.[6–16] The most appropriate example of such a membrane preparation is the radiation grafting of acrylic acid onto polymer films of different natures.[7,15] Alternatively, a monomer may be grafted onto a film to provide a graft copolymer structure which is subsequently transformed into an ion-exchange membrane by suitable chemical reactions, such as sulfonation.[6,9] In recent studies, a mixture of monomers has been used to design a membrane with multiple functional groups to achieve efficient chelation of toxic metal ions from waste water.[17–21] However, our efforts have been to develop polyethylene (PE) membranes by grafting acrylamide onto the film and subsequently carrying out partial hydrolysis of the amide groups so that the membrane acquires both the carboxyl and amide functional groups for chelation with metal ions.

Recently, we reported the grafting of acrylamide onto PE films by a preirradiation method to develop membranes for the separation of toxic metals from textile waste water.[22,23] It was observed that the presence of a grafted PAAm component leads to significant changes in the surface morphology as well as to the bulk structure of membranes, which may subsequently influence the performance of these membranes in metal ion separation.[24,25] The membranes showed good chealation behavior toward the mercury ions and efficient ion separation was achieved by these membranes.[26] In the present investigation, the hydrolysis and the characterization of radiation-grafted polyethylene-*g*-polyacrylamide (PE-*g*-PAAm) membranes were investigated.

EXPERIMENTAL

Materials

PE-*g*-PAAm membranes with different degrees of grafting were synthesized by graft polymerization of

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Correspondence to: B. Gupta (bgupta@textile.iitd.ernet.in).

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acrylamide onto PE films (prepared from the chips of grade F-19010 and MFI 1.0) by a preirradiation method using a Co^{60} γ-ray source (900 Curies) as reported previously.[22,23] The γ-irradiation was carried out under air at a radiation dose rate of 0.36 kGy/h.

Graft polymerization was carried out on gamma-irradiated PE films under a nitrogen atmosphere in a glass tube containing a monomer solution of a desired concentration. Acetone–water was used as a medium for the grafting reaction. After the reaction, grafted films were extracted with hot water to remove traces of any homopolymer adhering to the film surface. The grafted films were dried under a vacuum and weighed. The degree of grafting of the PE films was calculated from the following equation:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100 \qquad (1)$$

where W_0 and W_g are the weights of ungrafted and grafted films, respectively.

Hydrolysis

The hydrolysis of the grafted membranes was carried out using a 10% sodium hydroxide solution at 50°C in a thermostated water bath for different time intervals. Subsequently, the membranes were taken out and washed thoroughly with double-distilled water. These membranes were placed in 2% hydrochloric acid for 2 h to transform them in the proton form. Finally, the membranes were washed with distilled water several times until the hydrochloric acid ceased to come out in the washings.

Ion-exchange capacity (IEC)

Membranes were placed in a 0.5*M* KCl solution for 6 h at ambient temperature. The solution was titrated against a 0.05*M* sodium hydroxide solution using a phenolphthalein indicator. The IEC was represented as the meq/g of the membrane.[27]

Fourier transform infrared (FTIR) spectroscopy

FTIR measurements on samples were recorded on Perkin–Elmer Spectrum 8X FTIR System. The membranes were vacuum-dried at 50°C before carrying out measurements and FTIR spectra were recorded in the absorbance mode.

Differential scanning calorimetry (DSC)

DSC studies on the samples were carried out using a Perkin–Elmer DSC-7 system. Samples were loaded into the DSC at 50°C and thermograms were run in the temperature range of 50–160°C under a nitrogen atmosphere at the heating rate of 10°C/min. The heat of fusion (ΔH_f) was obtained from the area under the thermogram. The crystallinity of the membranes was obtained using the following expression:

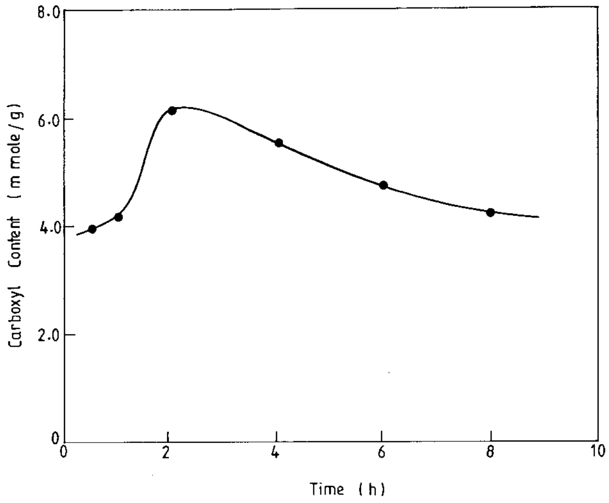


Figure 1 Variation of the carboxyl content with the time of hydrolysis in PE-*g*-PAAm membranes with 398% grafting. Sodium hydroxide, 10%; temperature, 50°C.

$$\text{Crystallinity (\%)} = \frac{\Delta H_f}{\Delta H_{f(\text{crys})}} \times 100 \qquad (2)$$

where $\Delta H_{f(\text{crys})}$ is the heat of fusion of 100% crystalline PE and was taken as 293 J/g.[28]

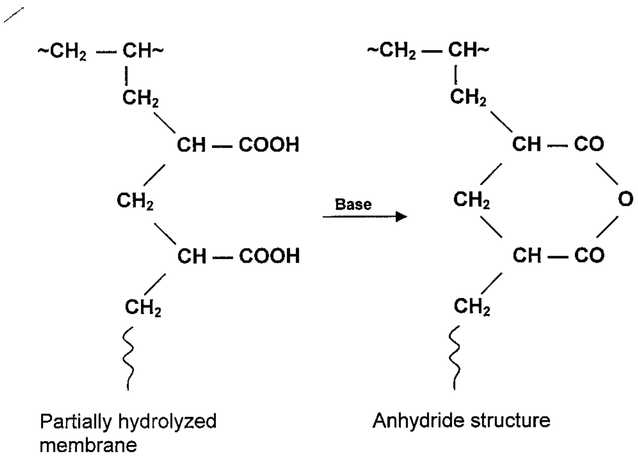
Thermogravimetric analysis (TGA)

TGA studies on the samples were carried out on a Perkin–Elmer DSC-7 system. The thermograms were obtained under a nitrogen atmosphere at a uniform heating rate of 10°C/min in the temperature range of 50–550°C. The relative thermal stability of the samples was evaluated in terms of decomposition temperature.

RESULTS AND DISCUSSION

Influence of hydrolysis conditions

The extent of hydrolysis was considerably affected by the time of the reaction. The results on the hydrolysis of the membrane with a degree of grafting of 398% are presented in Figure 1. The carboxyl content increases slowly with the time of hydrolysis and acceleration is observed beyond 1 h. A maximum in the carboxyl content is observed at 2 h followed by a slow decrease with a further increase in the reaction time. It is important to mention that the maximum conversion of amide groups into the carboxyl component (at 2 h of hydrolysis) was 56%. Our results are very much in



Scheme 1 Representation of cyclization during hydrolysis.

agreement with other workers who reported that the hydrolysis of polyacrylamide almost ceases near 40–50% conversion.[29,30] Such behavior has been interpreted in terms of the nearest mild effect due to the electrostatic repulsion between COO^- groups formed and hydroxyl ions catalyzing the reaction. This leads to the retardation and subsequent arrest of the hydrolysis process.

The decrease in the carboxyl content beyond 2 h of reaction suggests the partial deactivation of carboxyl groups during the course of hydrolysis. It seems that the carboxyl groups undergo a reaction with other carboxyl or amide groups from the same and adjacent chains. These reactions may be intermolecular and/or intramolecular; the latter leads to the cyclization along the polymer backbone (Scheme 1). The evidence for the cyclization during hydrolysis is evident from the FTIR in the form of the origin of the peak at 1787 cm^{-1} for the anhydride structure, as discussed in the subsequent section. The cyclization in polymers with such functional groups was reported by other workers as well.[30] It was reported that, under alkaline media, carboxylate ions in close proximity undergo cyclization to produce anhydride structures. The IEC of the hydrolyzed membranes with different degrees of grafting is presented in Figure 2. The IEC increases with increase in the degree of grafting. However, the increase in IEC is very fast initially up to 200% and then increases slowly. The increase in the IEC is an indication of the increase in the carboxyl content with the increase in the degree of grafting within the membrane matrix.

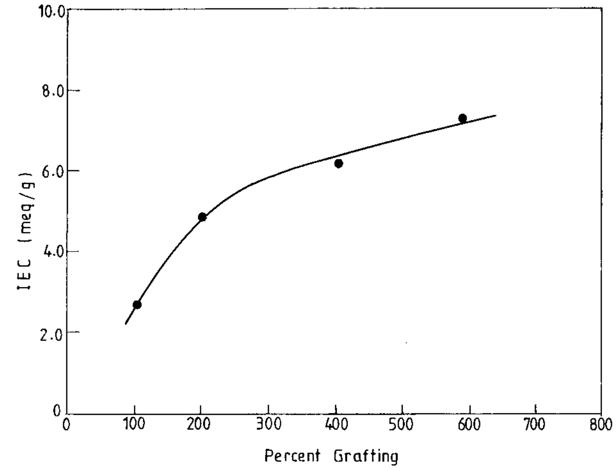


Figure 2 Variation of the ion-exchange capacity with the percent grafting in PE-*g*-PAAm membranes. Sodium hydroxide, 10%; temperature, 50°C.

FTIR

The FTIR of PE-*g*-PAAm membranes before and after hydrolysis are presented in Figure 3. The two regions between 3000 and 4000 cm^{-1} and 1600 and 1800 cm^{-1} show significant differences in the two spectra. The peaks that are evident in the grafted membrane diminish along with the origin of additional peak in the hydrolyzed membrane. In the grafted membranes, the peaks at 1645, 1666, and 1690 cm^{-1} are due to the —C=O stretching vibration of the amide groups. The merging of these amide peaks to one single peak at 1662 cm^{-1} after hydrolysis is an indication of the chemistry taking place during the reaction.

The diminishing of the peak at 1662 cm^{-1} along with the origin of an additional band at 1716 cm^{-1}

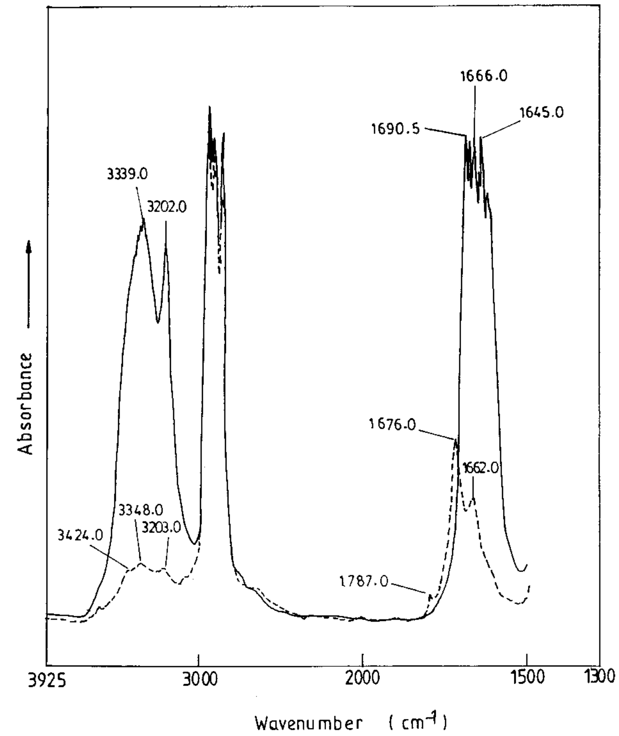


Figure 3 FTIR of the PE-*g*-PAAm membranes (—) before and (- - -) after hydrolysis. Degree of grafting, 30%.

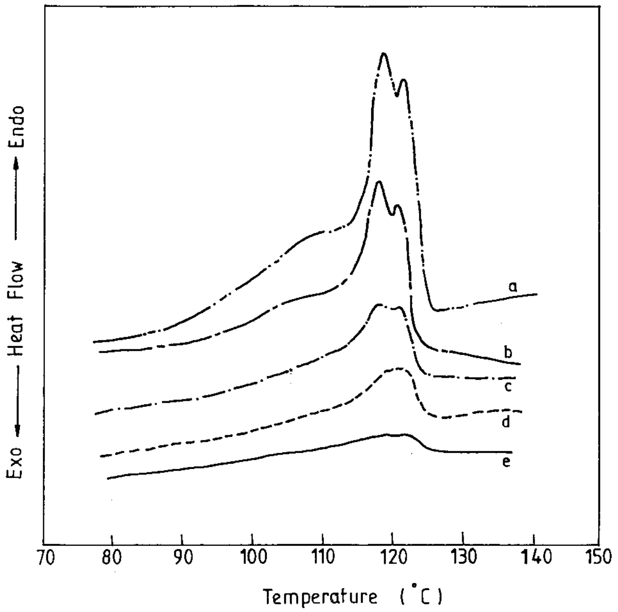


Figure 4 DSC thermograms of (a) ungrafted PE film and PE-*g*-PAAm membranes with (b) 100% grafting, (c) 198% grafting, (d) 398% grafting, and (e) 590% grafting.

(—C═O stretching) confirms the presence of carboxyl groups and the loss of amide groups during the hydrolysis of the membrane. The region 3000–4000 cm^{-1} also shows distinct changes in the two spectra. The two peaks at 3202 and 3339 cm^{-1} of the $—NH_2$ component in the amide groups diminish and an additional band at 3424 cm^{-1} originates, corresponding to the free —OH groups of carboxyl moiety.

Another interesting observation is in the form of origin of a band at 1787 cm^{-1} in the hydrolyzed membrane. This is characteristic of the anhydride structure along the chains, as has been observed for the poly(maleic anhydride) at 1782 cm^{-1}.[31,32] The formation of an anhydride structure originates from the dehydration reaction involving two carboxyl groups. These results strengthen the results in Figure 1, where a decrease in the ion-exchange capacity at longer hydrolysis periods is attributed to the deactivation of carboxyl groups. Probably, the carboxyl deactivation is much faster at higher hydrolysis periods as compared to the initial reaction. This, in turn, leads to the sharp decrease in the ion-exchange capacity beyond 2 h.

DSC

The DSC thermograms of virgin PE and hydrolyzed PE-*g*-PAAm membranes are presented in Figure 4. Both the area and intensity of the peaks decrease significantly with increase in the grafting. The dual mode of melting in the original PE is due to the inherent crystallization process that leads to crystallites with different spherulitic growth. This dual melting persists but diminishes with increase in the grafting. The heat of fusion, as obtained from the area under the thermogram, decreases considerably with increase in the degree of grafting. It is interesting to see that the heat of fusion values are almost identical to the ones prior to the hydrolysis. It may be stated that hydrolysis does not cause impedance to the existing crystalline structure of the grafted membrane (Fig. 5). While virgin PE possesses a crystallinity of 24.6%, the membranes show much lower crystallinity depending on the degree of grafting (Fig. 6). The membrane with a graft level of 590% shows virtually no crystallinity (1.2%). This suggests that the membrane structure undergoes severe crystalline deterioration during the preparation step.

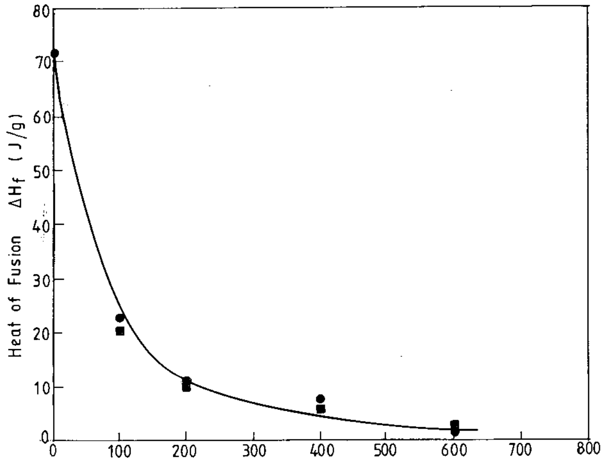


Figure 5 Variation of the heat of fusion in PE-*g*-PAAm membranes: (■) before hydrolysis; (●) after hydrolysis.

It is important to note that the grafting process itself leads to a considerable decrease in the heat of fusion of PE due to the cumulative effect of the dilution of the inherent crystallinity by the incorporation of amor-

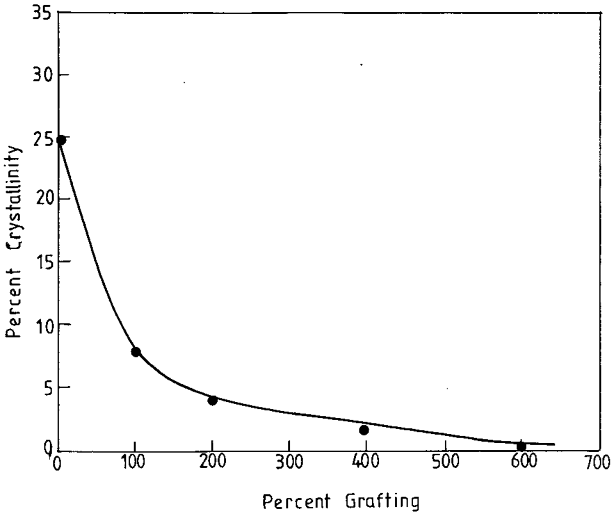


Figure 6 Variation of the percent crystallinity with the percent grafting.

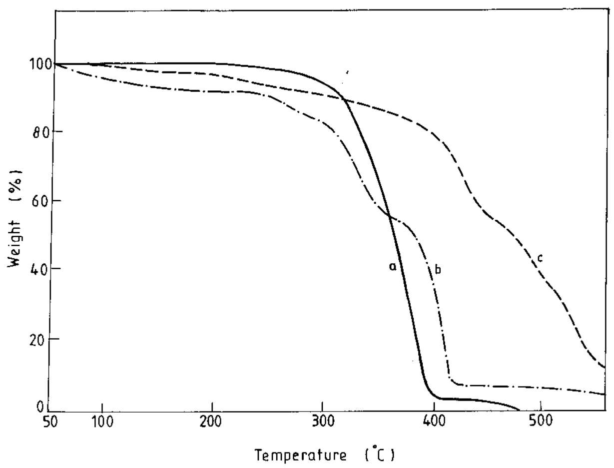


Figure 7 TGA thermograms of (a) ungrafted PE film, (b) PE-*g*-PAAm membrane (percent grafting 100%), and (c) hydrolyzed PE-*g*-PAAm-membrane (percent grafting 100%). Heating rate, 10°C/min; nitrogen atmosphere.

phous polyacrylamide grafts and the crystal distortion.[25] The identical heat of fusion values of the hydrolyzed membranes with the grafted ones suggests that hydrolysis does not cause any further deterioration in the crystallinity of the membranes and remains confined to the amorphous region only. In our studies on the preparation of FEP-*g*-poly(styrenesulfonic acid) membranes, the decrease in the crystallinity of the films in the grafting step was observed only due to the dilution effect of the incorporated polystyrene grafts. The sulfonation step also led to a further reduction in crystallinity by both the dilution effect and the crystal defect.[10] Both these studies suggest that the hydrophilicity-induced swelling and subsequent hydrophilic–hydrophobic strains may be responsible for the crystal distortions in addition to the dilution effect of the grafted component.

TGA

TGA thermograms of PE, PE-*g*-PAAm, and hydrolyzed PE-*g*-PAAm membranes are presented in Figure 7. The TGA thermogram of the grafted membrane shows a multistep degradation pattern which has been assigned to the dehydration, PE backbone degradation, and PAAm graft degradation.[25] The hydrolyzed membrane also shows multistep degradation similar to that of the grafted one. However, the thermal stability of the hydrolyzed membrane is much better than that of the grafted membrane. This indicates that some stable structures are formed *in situ* during the course of heating and introduces thermal stability in the structure. It appears that the carboxyl groups in the membrane undergo anhydride formation along the backbone, which are thermally stable structures and decompose at an elevated temperature (Scheme 1). In our earlier studies on methacrylic acid-grafted PE, we observed that the anhydride formation takes place at the temperature of 197°C and both intermolecular crosslinking and intramolecular cyclization take place during the course of heating.[33,34] This dehydrated structure, by virtue of a six-membered structure, becomes more stable and undergoes decomposition beyond 415°C. A similar mechanism may be assumed to be operating in our hydrolyzed membranes, which leads to a higher thermal stability of the membranes.

CONCLUSIONS

The radiation grafting of acrylamide onto PE films leads to PE-based graft copolymer membranes, which may be subsequently hydrolyzed to produce ion-exchange membranes. The hydrolysis shows an autocatalytic character but does not proceed beyond a 56% amide group conversion. This may lead to bifunctional membranes with both the carboxyl and amide groups. The membranes thus produced show ion-exchange behavior, which may be controlled by the proper variation in the degree of grafting. A maximum IEC of 7.2 meq/g was achieved for a graft level of 590%. It was interesting to observe that the ion-exchange membranes have very low crystallinity (1.2% at 590% grafting), which offers a more amorphous volume and better diffusion for the interaction with the metal ions. The investigation on metal ion sorption of these hydrolyzed membranes will be presented subsequently.[35]

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