

# Preparation of Ion-Exchange Membranes by the Hydrolysis of Radiation-Grafted Polyethylene-g-Polyacrylamide Films: Properties and Metal-Ion Separation

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**ABSTRACT:** Ion-exchange membranes were prepared by the alkaline hydrolysis of radiation-grafted polyethylene-g-polyacrylamide membranes. The hydrolyzed membranes showed a good water uptake of approximately 1060 for a graft level of 590%. The electrical resistance of the membranes decreased with an increase in the degree of grafting up to 200% and then stabilized with further increases in the graft level. The membranes had an excellent binding capacity for mercury ions. The metal-binding capacity increased with an increase in the degree of grafting in the membranes. A binding capacity as high as 7.2 mmol/g in a membrane

with 590% grafting was achieved. The pH of the metal solution had a significant influence on the binding ability of the membranes. The partial hydrolysis of the grafted membranes contributed to the higher binding because of the expansion of the bulk structure by ionized carboxyl groups and the better accessibility of mercury to amide groups. The mercury-loaded membranes showed thermal stability inferior to that of membranes without metal binding. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3747–3752, 2003

**Key words:** polyethylene (PE); membranes; radiation

## INTRODUCTION

Water contamination is a universal problem, with toxic materials from industrial effluents contributing to the ecological degradation.<sup>1</sup> Textile chemical processing is one of the major industries responsible for enormous water contamination.<sup>2</sup> Therefore, it has become necessary to remove toxic metals from the effluents before they are discharged into drains. One of the approaches for such environmental care requires the separation and recovery of these metal ions from heavy-metal-contaminated wastewater via the chelating ability of polymeric materials.<sup>3</sup> Efforts are being made to develop ways of achieving this task by the proper design of polymeric structures by chemical means in such a way that they can perform chelating functions for specific metal ions.<sup>4–7</sup>

Membrane-based separation is one unique approach for water purification. The radiation-induced graft polymerization of vinyl and acrylic monomers into polymer films has generated considerable interest in the development of membranes for various technologically important fields.<sup>8–14</sup> It offers a versatile way of imparting desirable properties to a polymer without the original characteristics being affected much. Moreover, graft distribution may be achieved

throughout the matrix because of the radiation activation of films across the thickness.<sup>9</sup> The modification may be achieved for a polymer already existing in a film form; this overcomes the rheological problems associated with the transformation of a grafted matrix into a thin foil.

The radiation grafting of acrylic monomers into polyethylene (PE) films to produce membranes has been reported by several workers.<sup>15–18</sup> Recently, we carried out the grafting of acrylamide onto PE films to develop membranes for the separation of toxic metals from textile wastewater.<sup>19–22</sup> These membranes underwent considerable changes in the surface morphology and the bulk structure as a function of the grafted polyacrylamide (PAAm) component.<sup>21,22</sup> These membranes, by virtue of the amide group in the grafted chain, performed as binding sites for mercury ions.<sup>23</sup> However, it has been found that membranes with more than one functionality may perform better for metal-ion sorption. In an effort to develop membranes with a dual functionality of amide groups and carboxyl groups, the hydrolysis of these membranes was carried out. Although hydrolysis was achieved within a reaction period of 2 h, the reaction for mercury separation was carried out for 15 min to ensure the partial conversion of amide groups into carboxyl groups. The influence of the hydrolysis conditions on the carboxyl content and the physical structure of the membranes was reported in a previous article.<sup>24</sup> In this article, physical properties, such as swelling, elec-

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trical resistance, and mercury binding, of these hydrolyzed polyethylene-*g*-polyacrylamide (PE-*g*-PAAm) membranes with different degrees of grafting are reported.

## EXPERIMENTAL

### Materials

PE films (40  $\mu\text{m}$ ) were received from Reliance Industries (India). A  $^{60}\text{Co}$   $\gamma$ -radiation chamber (900 Ci), supplied by Bhabha Atomic Research Center (Mumbai, India), was used for the irradiation of the films.

Acrylamide (Sisco, India) was used as received without any further purification. Mercuric acetate was received from Loba Chemie (India). Glaxo (India) supplied potassium chloride and sodium hydroxide. Hydrochloric acid was received from Merck (India). Double-distilled water was used for all experiments.

### Graft polymerization

PE-*g*-PAAm membranes with different degrees of grafting were prepared by the graft polymerization of acrylamide into PE films by a preirradiation method.<sup>19,20</sup> The  $\gamma$  irradiation of the PE films was carried out under air at a radiation dose rate of 0.36 kGy/h.

The graft polymerization was carried out on  $\gamma$ -irradiated PE films under a nitrogen atmosphere in a glass tube containing a monomer solution of the desired concentration. An acetone-water mixture was used as a medium for the grafting reaction. After the reaction, grafted films were extracted with hot water for the removal of traces of any homopolymer adhering to the film surface. The grafted films were dried *in vacuo* and weighed. The degree of grafting in PE films was calculated with the following equation:

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

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

### Hydrolysis of the membranes

The hydrolysis of the membranes was carried out under an alkaline medium at a temperature of 50°C. The sodium hydroxide concentration was maintained at 10%, and the reaction was carried out up to 2 h.<sup>24</sup>

### Water uptake measurements

The equilibrium water uptake of the membranes was measured in distilled water as reported earlier.<sup>16</sup> Dried membranes were immersed in water for 24 h under ambient conditions ( $\sim 30^\circ\text{C}$ ). After the removal

of the membranes from water, the excess water adhering to the surface was removed via blotting with adsorbent paper and was weighed quickly. The water uptake (%) was measured from the increase in the weight of the membranes as follows:

$$\text{Water uptake (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where  $W_d$  and  $W_s$  are the weights of the dry and wet membranes, respectively.

### Electrical resistance measurements

The electrical resistance of the membranes was measured after they were conditioned in a 0.5M KCl solution for 24 h, as reported earlier.<sup>16</sup>

### Mercury uptake measurements

The mercury uptake of the membranes (hydrolyzed for 15 min) was studied with an MA 5800E mercury analyzer supplied by Electronics Corp. of India, Ltd. A calibration plot of the optical density versus the mercuric acetate concentration was made, and the  $\text{Hg}^{2+}$  concentration of the unknown solution was obtained from this calibration plot.

For the metal-ion separation, the mercuric acetate solution was prepared by its dissolution in distilled water, and the desired pH was adjusted with acetic acid or sodium hydroxide solutions. The mercuric acetate concentration was 10,000 ppm, and the liquor ratio was maintained at 1:500. The membranes were immersed in the metal-ion solution for 2 h with stirring. The membranes were subsequently removed from the solution, and the remaining solution was analyzed for the metal-ion concentration.

The regeneration of the metal-ion-loaded membranes was studied by elution in 1M hydrochloric acid. The supernatant liquid was then analyzed for mercury ions. The regenerated membrane was reused for mercury chelation in three repeated cycles at a  $\text{Hg}^{2+}$  concentration of 10,000 ppm and at pH 4.6. The liquor ratio was kept at 1:500.

### Thermogravimetric analysis (TGA)

TGA studies were carried out with a PerkinElmer DSC-7 system. The thermograms were obtained under a nitrogen atmosphere at a uniform heating rate of 10°C/min from 50 to 550°C.

### Fourier transform infrared (FTIR) spectroscopy

The FTIR measurements were recorded on a Jasco micro-FTIR (Japan) instrument. The membranes were vac-

**TABLE I**  
**Variation of Water Uptake, Specific Resistivity, with the Degree of Grafting in Membranes**

Percentage grafting	Water uptake (%) <sup>a</sup>	Specific resistivity ( $\Omega \text{ cm } 10^{-3}$ ) <sup>b</sup>	
		NHM	HM
100	222	200	186
198	570	109	65
390	912	68	40
590	1060	37	17

NHM = nonhydrolyzed membrane; HM = hydrolyzed membrane.

<sup>a</sup> In sodium form.

<sup>b</sup> In 0.5M KCl solution.

uum-dried at 50°C before the measurements were carried out, and the FTIR spectra were recorded in the absorbance mode.<sup>25</sup>

## RESULTS AND DISCUSSION

### Water uptake

The variation of the water uptake with the degree of grafting is presented in Table I. The water uptake increased with the increase in the degree of grafting in the membranes, and a maximum of 1060 for a graft level of 590% was achieved. The uptake of the same membranes before hydrolysis (i.e., in  $-\text{CONH}_2$  form) was much lower (230%).<sup>24</sup> The hydrolysis lead to an almost fourfold increase in the uptake of the membranes. Even in the nonhydrolyzed form, the membranes acquired hydrophilicity because of the presence of PAAm-grafted domains. The hydrophilicity of the membranes increased because of the presence of carboxyl groups, which were in the ionized state as sodium salt, and was reflected in an increase in the water uptake. Almost half of the amide groups were hydrolyzed into carboxyl groups under our experimental conditions.<sup>24</sup> These ionized carboxylic groups enhance the water uptake. Similar observations of swelling behavior were made by Dessouki et al.<sup>26</sup> for the hydrolysis of acrylamide-grafted PE films. They found that a sodium hydroxide treatment led to much higher water uptake than a potassium hydroxide treatment.

The importance and contribution of physicochemical changes to water uptake were previously discussed for poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP)-*g*-poly(styrene sulfonic acid) membranes.<sup>12</sup> It was proposed that the ionic effect, hydrophilicity, and crystallinity influenced the water uptake independently. Similar observations were made by Dessouki et al.<sup>26</sup> for acrylamide-grafted PE membranes. However, in this study, the degree of swelling was much higher than what they observed.

The structure of the membranes developed in our system was probably more amenable to water uptake because of the sharp decrease in the crystallinity by grafting.<sup>24</sup> As a result, large amorphous volumes may have been available for water penetration within the membranes.

### Electrical resistivity

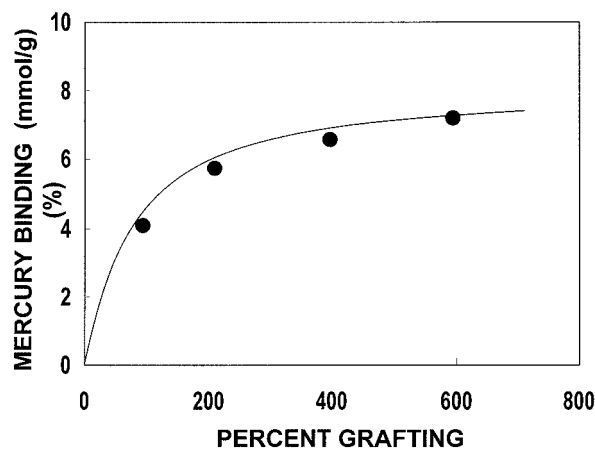
The electrical resistance of the membranes as a function of the degree of grafting is presented in Table I. The resistance decreased with an increase in the degree of grafting, and a minimum of  $17 \times 10^3 \Omega \text{ cm}$  was achieved for a graft level of 590%. The hydrolyzed membranes showed lower resistivity than the nonhydrolyzed membranes, probably because of the higher water uptake. A similar trend in the resistance of poly(acrylic acid)-grafted PE membranes was observed in our earlier studies as well.<sup>16</sup> However, the absolute values of the membrane resistance in this work were much higher than those observed earlier. The initial grafting took place at the film surface only and proceeded further by the progressive diffusion of the monomer within the films through the water-swollen grafted domains. The high resistance at low grafting levels was due to the nonhomogeneity in the graft distribution in which very few grafted chains were present, and this middle portion offered high resistance in the membrane. At higher grafting levels of 200% or more, films appeared thoroughly grafted as well as homogeneous and showed the least resistance.<sup>12</sup> A slow decrease in the electrical resistance even after 200% grafting was due to efficient water management within the membranes at higher graft levels.<sup>27</sup>

### Mercury separation

The variation of the metal-binding capacity of the membranes (hydrolyzed for 15 min) with the degree of grafting is presented in Figure 1. The mercury-binding capacity increased with the increase in the degree of grafting. The hydrolyzed membranes showed slightly better mercury binding than the nonhydrolyzed one reported earlier.<sup>23</sup>

The influence of the pH on metal binding by membranes with a 398% degree of grafting is presented in Figure 2. The metal uptake by the membranes was considerably influenced by the pH of the medium. The higher the pH was, the higher the metal binding was. This behavior in the hydrolyzed membranes was in contrast to the observations for the nonhydrolyzed membranes, for which the pH variation did not influence the metal uptake.<sup>23</sup>

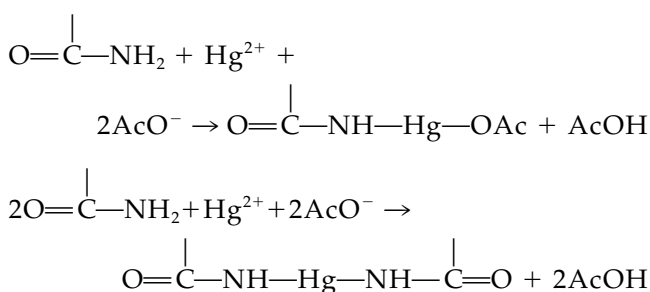
Interestingly, pH played an important role in the mercury binding. At a lower pH, the  $\text{Ac}_2\text{O}^-$  nucleophile could be protonated from the medium instead of



**Figure 1** Variation of the mercury-binding capacity with the degree of grafting (time = 2 h;  $\text{Hg}^{+2}$  concentration = 10,000 ppm; liquor ratio = 1:500; pH = 4.6).

abstraction from the  $\text{NH}_2$  group. At the same time, the ionization of carboxyl groups was suppressed at a lower pH. The dissociation of carboxyl was facilitated at pH 4.2. This was the reason that grafted chains were expanded at this pH, and it facilitated the accessibility of the mercury ions. A similar pH dependence of metal ions in graft copolymers was reported by Saliba et al.,<sup>5</sup> El-Rehim et al.,<sup>15</sup> Sreedhar and Anirudhan,<sup>28</sup> and Hegazy et al.<sup>29</sup>

Bicak et al.<sup>30</sup> reported mercury binding on cellulose-g-polyacrylamide graft copolymers. It was proposed that the major fraction (90%) of mercury was attached to amide groups as the monoacetate form, whereas the rest was bonded from both sides.

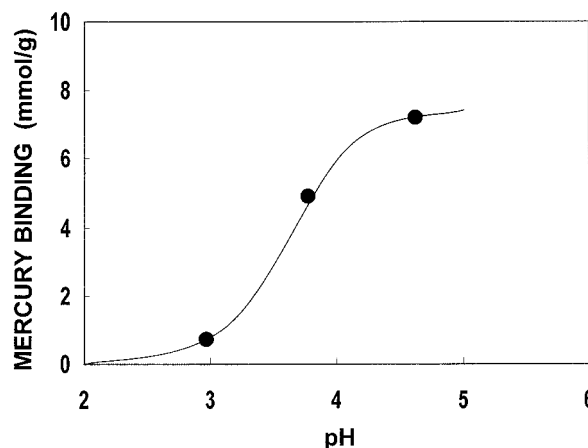


On the basis of the functionality of this membrane with a degree of grafting of 398% and an ion exchange capacity (IEC) of 11.26 mequiv/g, the carboxyl content was estimated to be 2.14 mmol/g. This left 9.12 mmol/g of amide groups for the interaction with mercury. However, the mercury binding was confined to be 6.62 mmol/g, which suggested that a large number of the amide groups were bonded as monoacetate. The nonhydrolyzed membranes showed a mercury binding of 6.22 mmol/g.<sup>23</sup> The hydrolysis actually enhanced the mercury binding in the membranes. Because the amide groups were specific for mercury binding, a

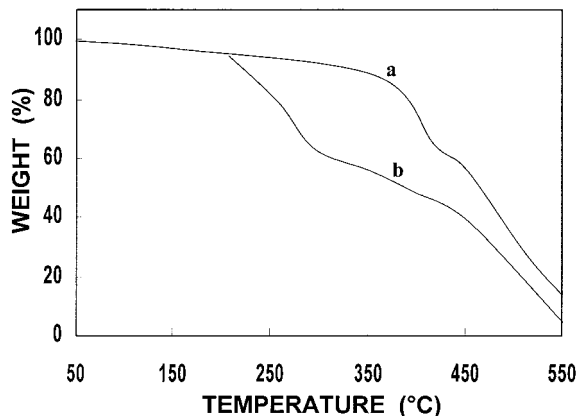
decrease in the amide fraction due to partial conversion into carboxyl groups could have led to a loss in the mercury-binding capacity of the membranes. These results may be understood by the fact that in nonhydrolyzed membranes, 11.26 mmol/g amide groups bound only 6.2 mmol/g mercury ions. This indicated that a significant fraction of the amide groups was not accessible to the mercury ions because of the compact structure of the PAAm grafts within the membranes. Once the membranes were hydrolyzed, the carboxyl groups due to their ionized form exerted repulsive forces, and the grafted chains expanded and were pulled apart (this was evident from the large increases in the swelling of the membranes on hydrolysis). The accessibility of the amide groups to mercury ions was enhanced in the expanded form of the membranes and led to enhanced mercury binding, despite the decrease in the amide content in the membranes.

#### TGA

The TGA thermograms of the membranes with and without mercury loading are presented in Figure 3. The metal-bonded membranes showed lower thermal stability than the original membranes. The degradation was more severe in mercury-loaded membranes initiated at a temperature of 200°C. The results may be understood by the fact that the membranes contained carboxyl and amide groups along the backbone. These groups underwent cyclization during the course of heating; this led to the formation of six-membered anhydride structures and imparted thermal stability to the membranes (Fig. 4). In the mercury-bonded membranes, the cyclization step was probably not very significant, and the resultant membranes did not



**Figure 2** Variation of the mercury-binding capacity with the pH of the medium (grafting percentage = 398; time = 2 h;  $\text{Hg}^{+2}$  concentration = 10,000 ppm; liquor ratio = 1:500).

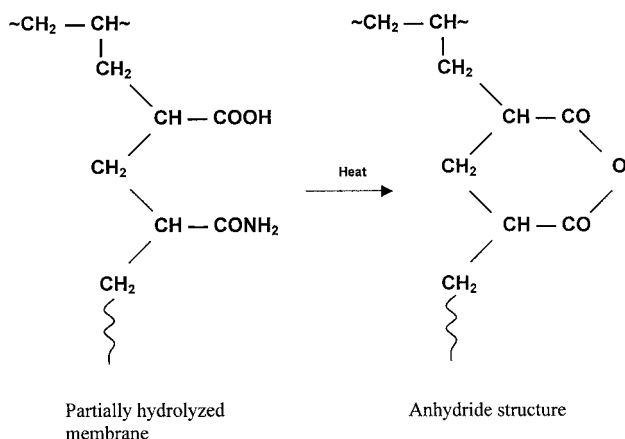


**Figure 3** TGA thermograms of (a) PE-g-PAAm (grafting percentage = 100) and (b) PE-g-PAAm-Hg membranes (grafting percentage = 100). The heating rate was 10°C/min, and the atmosphere was N<sub>2</sub>.

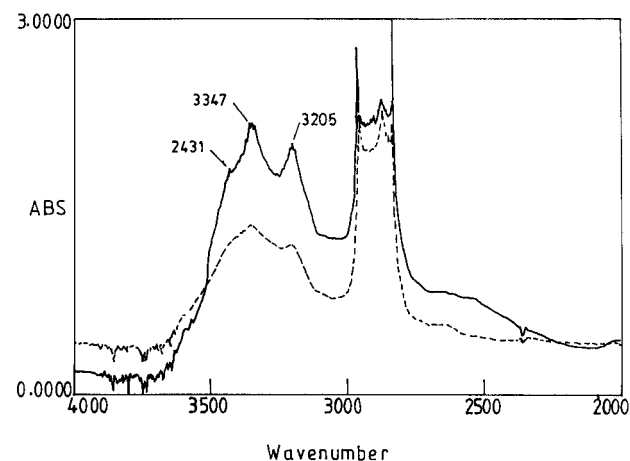
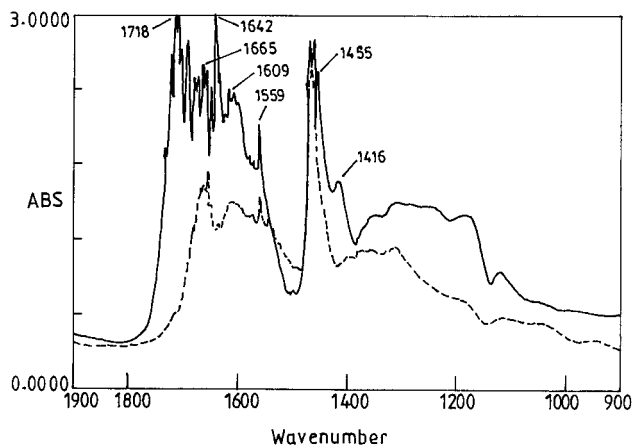
contain thermally stable cyclized structures. This may have led to the earlier degradation of the membranes.

**FTIR spectroscopy**

The FTIR spectra of membranes with or without mercury loading are presented in Figure 5. Mercury loading led to distinct changes in the spectra of the membranes. The membranes showed peaks at 3431, 3347, and 3205 cm<sup>-1</sup>, which could be assigned to the presence of —OH groups and —NH<sub>2</sub> groups. The presence of peaks at lower wave numbers of 3205 and 3347 cm<sup>-1</sup>, in comparison with normal peak positions, was an indication of hydrogen bonding among the functional groups. However, in the mercury-loaded sample, these peaks tended to vanish, and a broad peak at 3000–3600 cm<sup>-1</sup> was almost observed; this indicated the loss of hydrogen bonding among carboxyl and amide groups and the involvement of these groups



**Figure 4** Representation of cyclization in PE-g-PAAm membranes.



**Figure 5** FTIR spectra of PE-g-PAAm membranes (—) without and (---) with mercury loading (grafting percentage = 100).

with mercury ions. The region in the lower wavenumber range also showed distinct changes in the spectra of the loaded sample. The peak at 1718 cm<sup>-1</sup> for the membrane indicated the presence of carboxyl groups. However, this peak, along with other characteristic peaks of amide groups, was lost in the mercury-loaded sample, and this suggested that the carboxyl groups had strong interactions with the mercury ions. Moreover, the peaks at 1609 and 1559 cm<sup>-1</sup> decreased considerably, and this indicated the interaction of these functional groups with mercury.

**Regeneration of the membranes**

The mercury-loaded membranes showed excellent regeneration with acid treatment. Almost complete regeneration of the membranes took place (Table II). The rebinding efficiency of these hydrolyzed membranes was almost identical to that of the nonhydrolyzed membranes, as reported earlier.<sup>23</sup> A similar behavior for membranes containing carboxylic and sulfonic acid groups was reported by Choi and Nho<sup>31</sup> and

**TABLE II**  
**Adsorption and Desorption of Mercury Ions by a Hydrolyzed PE-g-PAAM Membrane with a 398% Degree of Grafting**

Repeat cycle	Hg <sup>2+</sup> adsorption (mmol/g)	Hg <sup>2+</sup> desorption (mmol/g)	Recovery (%)
I	6.62	6.54	98.8
II	6.42	6.34	98.7
III	6.40	6.30	98.4

Hg<sup>2+</sup> = 10,000 ppm; pH = 4.6; liquor ratio, 1 : 500.

Zhang et al.<sup>32</sup> Choi and Nho determined the membrane regeneration as a function of the acid concentration. At higher acid concentrations, the rate of desorption was much higher, but the final desorption quantity of Co<sup>2+</sup> was the same, regardless of the acid concentration.

### CONCLUSIONS

The graft polymerization of acrylamide into PE films and subsequent hydrolysis led to ion-exchange membranes, which showed good water uptake. Membranes with low resistivity of approximately  $17 \times 10^3 \Omega \text{ cm}$  were obtained for graft levels of 590%. The membranes had an excellent ability to bind mercury ions from aqueous solutions. The mercury-binding capacity of the membranes strongly depended on the degree of grafting. The higher the degree of grafting was, the higher the mercury uptake was achieved. A mercury uptake as high as 7.2 mmol/g was achieved for a membrane with a 590% degree of grafting. The metal-binding capacity of the membranes was considerably affected by pH variation in the range of 3.0–4.6. At pH 4.6, the ionization of —COOH groups was favored. This exerted repulsive forces, expanded grafted chains apart, and contributed to mercury accessibility to the amide groups. This was the reason that, despite lowering in amide groups, the mercury binding in hydrolyzed membranes was enhanced in comparison with that of the nonhydrolyzed membrane. The mercury-loaded membranes showed lower thermal stability than the unloaded membranes. This may be an outcome of the inhibition of cyclization involving carboxyl and acrylamide due to the involvement of these sites in mercury binding.

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