

# Development of Membranes by Radiation Grafting of Acrylamide into Polyethylene Films: Characterization and Thermal Investigations

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**ABSTRACT:** Polyethylene-*g*-polyacrylamide membranes were prepared by graft polymerization of acrylamide into polyethylene films by preirradiation technique. The characterization and thermal behavior of membranes with different degrees of grafting were evaluated by density, X-ray diffraction, thermogravimetric analysis, and differential scanning calorimetry measurements. Grafting led to considerable changes in the structure of polyethylene membranes. The density of the polyethylene film increased with the increase in the degree of grafting, although the increase beyond 100% grafting was less pronounced than at lower graft levels. The heat of fusion and the crystallinity of polyethylene decreased with the increase in the degree of grafting. The decrease in crystallinity is because of the cumulative effect of the dilution of inherent crystallinity by the incorporation of amorphous polyacrylamide grafts within the noncrystalline region of polyethylene (dilution effect) and partial disruption of the crystallites (crystal defects). X-ray diffraction measurements also revealed a decrease in the crystallinity in grafted films. Membranes behaved as a two-component system where polyethylene and polyacrylamide components underwent independent degradation irrespective of the graft levels. In general, the thermal stability of polyethylene in membranes was markedly improved by the grafting of acrylamide monomer as evident from the initial decomposition temperature increasing from 311°C for virgin PE to 390°C in grafted membranes. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2629–2635, 2001

**Keywords:** Polyethylene; acrylamide; membrane; radiation grafting

## INTRODUCTION

Radiation-induced graft polymerization of vinyl and acrylic monomers into polymer films has generated considerable interest towards the development of membranes for various technologically important fields.<sup>1–7</sup> This procedure offers a versatile way to impart desirable properties into the

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.<sup>8,9</sup> The modification may be achieved with a polymer already existing in the film form, which overcomes the rheological problems associated with transforming the grafted matrix into a thin foil.

The structure of a membrane may undergo considerable changes at different steps of its preparation depending on the nature and the amount of

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the monomer being grafted. These changes may be in the form of thermal stability, crystallinity, glass transition temperature, melting behavior, and the compatibility of the grafted component with the backbone polymer.<sup>10–13</sup> Lodesova et al.<sup>14</sup> have shown that the thermal decomposition temperature of polypropylene films grafted with acrylamide monomer increased and reached the range 298–423°C. Similarly, Sundardi<sup>15</sup> has reported that the grafting of vinylpyrrolidone, acrylonitrile, acrylamide, and acrylic acid results in an improvement in the melting behavior of the polypropylene fiber. A multistep degradation becomes evident when polar moieties like polystyrenesulfonic acid or methacrylic acid are present as the grafted components in a polymer.<sup>16,17</sup>

The grafting of acrylic monomers into polyethylene (PE) films to produce membranes has been reported by several workers.<sup>18–21</sup> These membranes are very effective in separating different ions from the waste water. Recently, we carried out the grafting of acrylamide into PE films to develop membranes for the separation of toxic metals from textile waste water.<sup>22,23</sup> These membranes undergo considerable changes in the surface morphology as a function of the grafted polyacrylamide (PAAm) component.<sup>24</sup> However, the presence of the grafted PAAm component may also lead to significant changes in the bulk structure of membranes, which may subsequently influence the performance of these membranes in metal ion separation. In the present study, the characterization and thermal behavior of radiation grafted polyethylene-*g*-polyacrylamide (PE-*g*-PAAm) membranes is investigated.

## EXPERIMENTAL

### Materials

Polyethylene-*g*-polyacrylamide (PE-*g*-PAAm) membranes with different degrees of grafting were prepared by graft polymerization of acrylamide onto polyethylene (PE) films (prepared from chips of grade F-19010 and MFI 1.0) by a preirradiation method using a  $\gamma$ -ray source (900 Curies) as reported previously.<sup>22,23</sup> The  $\gamma$ -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 nitrogen atmosphere in a glass tube containing monomer solution of desired concentration. Acetone was used as a me-

dium 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 vacuum and weighed. The degree of grafting in PE films was calculated from 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 ungrafted and grafted films, respectively.

### Density Measurement

Density measurements of original PE and grafted membranes were carried out using a Davenport density gradient column.<sup>25</sup> The column was prepared using carbontetrachloride ( $d$ , 1.59 g/cm<sup>3</sup>) and ethanol ( $d$ , 0.79 g/cm<sup>3</sup>).

### X-ray Diffraction

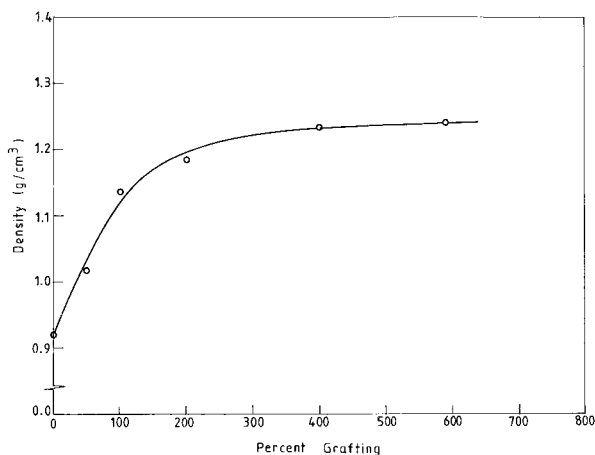
X-ray diffraction (XRD) patterns of original PE and grafted membrane were recorded on a Philips X-ray diffractometer equipped with a scintillation counter. CuK $\alpha$  radiation (wavelength, 1.54 Å) was used for the diffraction measurements in the  $2\theta$  range 10–35° according to the method reported earlier.<sup>25</sup>

### Thermogravimetric Analysis (TGA)

TGA studies on samples were carried out on Perkin Elmer DSC-7 system. The thermograms were obtained under nitrogen atmosphere at a uniform heating rate of 10°C/min in the temperature range 50–600°C. Relative thermal stability of the samples was evaluated in terms of initial decomposition temperature (IDT).

### Differential Scanning Calorimetry (DSC)

DSC studies on samples were carried out using a Perkin Elmer DSC-7 system. Samples were loaded into the DSC system at 50°C, and thermograms were run in the temperature range 50–160°C under nitrogen atmosphere at the heating rate of 10°C/min. The heat of fusion ( $\Delta H_f$ ) and heat of crystallization ( $\Delta H_c$ ) were obtained from the area under the thermogram and were related to the weight fraction of PAAm ( $W_{\text{PAAm}}$ ) in the grafted sample by the following equation<sup>12</sup>:



**Figure 1** Variation of the density with the percent grafting in PE-g-PAAm membranes.

$$W_{\text{PAAm}} = \frac{G}{1 + G} \quad (2)$$

where  $W_{\text{PAAm}}$  is the weight fraction of PAAm in the grafted sample and  $G$  is the graft content. The crystallinity in membranes was obtained by the following expression:

$$\text{Crystallinity}(\%) = \frac{\Delta H_f}{\Delta H_{f(\text{crys})}} \times 100 \quad (3)$$

where  $\Delta H_{f(\text{crys})}$  is the heat of fusion of 100% crystalline PE and was taken as 293 J/g.<sup>26</sup>

## RESULTS AND DISCUSSION

The grafting of acrylamide into PE films led to the PE-g-PAAm membranes containing different degrees of grafting. The characterization and thermal properties of the ungrafted PE film and grafted membranes with graft levels in the range 54–590% were evaluated by density, X-ray, TGA, and DSC measurements.

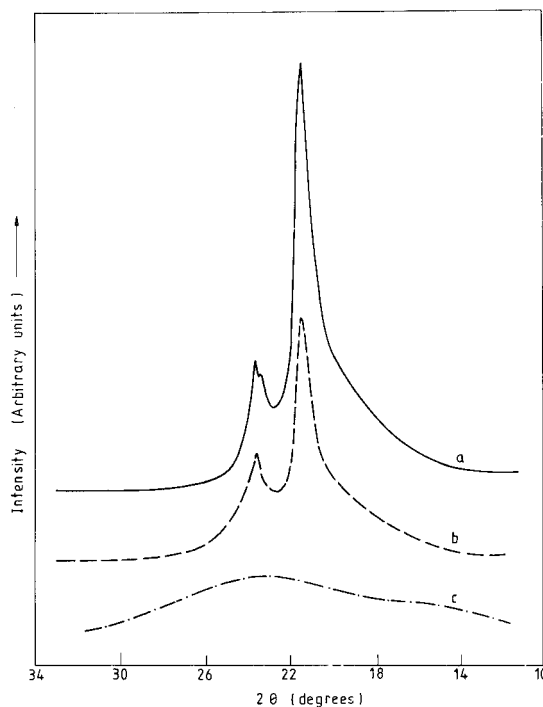
### Density Measurements

Density of original PE and grafted membranes as a function of degree of grafting is presented in Figure 1. Density increases with the increase in the degree of grafting in membranes. The density of virgin PE was measured to be 0.918 g/cm<sup>3</sup>, which increases to 1.23 g/cm<sup>3</sup> for a graft level of 590%. The increase in density in membranes may

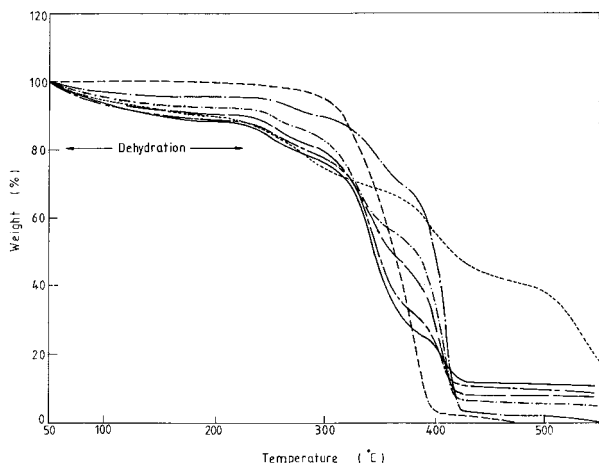
be attributed to the higher density of PAAm component ( $d = 1.302 \text{ g/cm}^3$ ) that is incorporated within the film.<sup>27</sup> The PAAm grafts may be considered as the microdomains within the PE matrix. A sharp increase in the density at low graft levels suggests that the initial grafted microdomains are incorporated within the voids in amorphous region of the matrix. At higher graft levels, the PAAm domains increase in size and PE chains are pushed apart to accommodate these large grafted structures. This phenomenon is evident from the large increase in the dimensions of the PE film at higher graft levels. The density, as a result, shows a little change at higher graft levels.

### X-ray Diffraction

The XRD patterns of PAAm homopolymer, ungrafted PE, and the membrane with 100% degree of grafting are presented in Figure 2. PE film shows a crystalline diffraction pattern that suggests the semicrystalline nature of the film. However, in grafted sample, the crystalline peak intensity decreases considerably. These results lead to the conclusion that the inherent crystallinity of PE film decreases on acrylamide grafting. It may



**Figure 2** X-ray diffraction patterns of (a) original PE, (b) PE-g-PAAm membranes, and (c) PAAm homopolymer.



**Figure 3** TGA thermograms of (---) original PE and PE-*g*-PAAm membranes, (— · —) 54% grafting, (- · -) 100% grafting, (— —) 198% grafting, (— · · —) 398% grafting, (—) 590% grafting, and (—) PAAm homopolymer.

be seen from the figure that PAAm does not show any crystalline diffraction; instead, a diffuse amorphous pattern is obtained. It may be assumed that the incorporation of amorphous PAAm chains within PE film may be one of the reasons for the decrease in the inherent crystallinity of the membrane. Similar observations have been made in our earlier studies on the grafting of methacrylic acid and acrylonitrile into polypropylene.<sup>11,17</sup>

### Thermogravimetric Analysis (TGA)

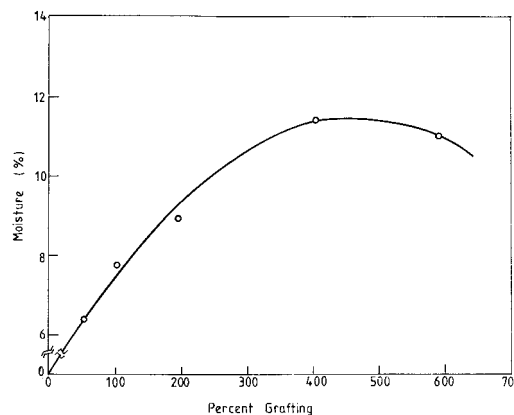
Primary thermograms of ungrafted PE, PAAm homopolymer, and PE-*g*-PAAm membranes with various degrees of grafting are presented in Figure 3. The thermogram of PE shows a clean single-step degradation with initial decomposition temperature (IDT-II) of 311°C. However, the thermograms of acrylamide-grafted PE membranes show a multistep degradation pattern that may be divided into three distinct steps (i.e., dehydration, PAAm degradation, and PE main chain decomposition). Unlike PE, all samples show residue at the end of the thermogram, which increases with the increase in the degree of grafting. It is interesting to see that the PE and PAAm components in membranes undergo degradation independently irrespective of the degree of grafting. The degradation of PAAm in membranes follows a multistep pattern similar to that of the PAAm homopolymer. This result suggests that the copolymer behaves as a two-component sys-

tem where PAAm forms a microdomain within the PE matrix. This result may be because of the incompatibility of the hydrophilic PAAm moiety with the hydrophobic PE component.

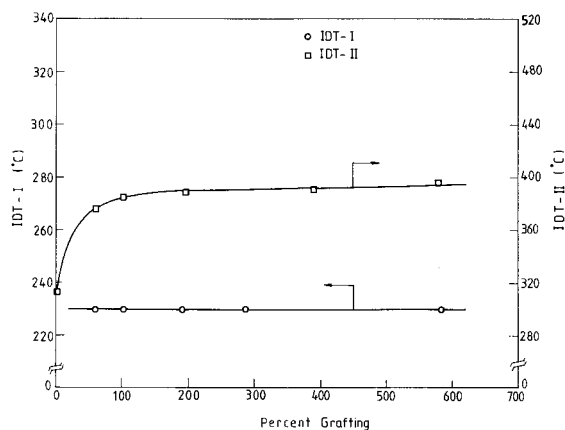
The PAAm-grafted PE membranes are hydrophilic in nature and contain certain amount of water as moisture. As a result of dehydration, membranes undergo loss of water in the range 50–180°C. A similar dehydration step has been reported in our earlier studies on FEP-*g*-polystyrenesulfonic acid membranes.<sup>28</sup> The variation in the moisture content (as obtained from the dehydration step) with the degree of grafting is presented in Figure 4. The moisture content increases with the increase in the PAAm content up to 400%, beyond which it tends to decrease. It seems that at higher graft levels, PAAm domains form a compact structure within the PE matrix in such a way that a fraction of amide groups is not available for interaction with the moisture.

The initial decomposition temperatures of the PAAm component (IDT-I) and the PE component (IDT-II) as a function of the degree of grafting are presented in Figure 5. The IDT-I remains identical for the whole range of graft levels. However, IDT-II increases with the increase in the degree of grafting up to 100% and then remains constant. These results suggest that the thermal stability of PE backbone in membranes is enhanced by PAAm grafting.

This increase in the thermal stability of the PE moiety in the grafted matrix may be attributed to two factors: the abstraction of hydrogen from a carbon atom, followed by the grafting of PAAm chain at the site generated and the cyclization reaction involving the PAAm moieties, which takes place during the course of heating. The



**Figure 4** Variation of moisture content with the percent grafting in PE-*g*-PAAm membranes.

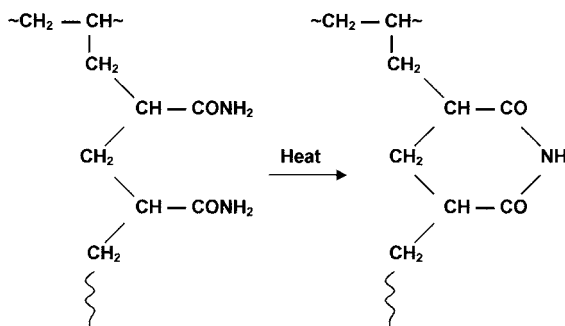


**Figure 5** Variation of IDT-I and IDT-II with the percent grafting in PE-g-PAAm membranes.

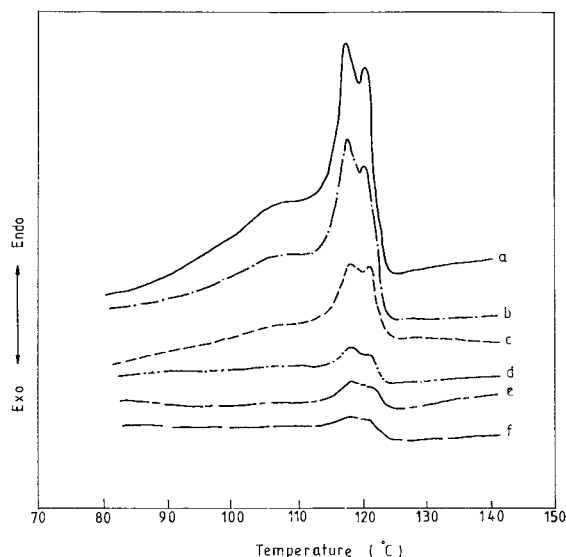
latter leads to the formation of six-membered PAAm anhydride rings of increased thermal stability. The schematic representation of cyclization is shown in Scheme 1.<sup>29</sup>

#### Differential Scanning Calorimetry (DSC)

DSC thermograms of virgin PE film and PE-g-PAAm membranes are presented in Figure 6. Although, the shape of the thermograms in all samples remains almost identical, the intensity of peaks decreases with the increase in the degree of grafting. As a result, the heat of fusion of membranes as obtained from the area under thermogram decreases. The variations in heat of fusion ( $\Delta H_f$ ) and heat of crystallization ( $\Delta H_c$ ) with the degree of grafting are presented in Figure 7. Both the heat of fusion and heat of crystallization show considerable decrease with the increase in the degree of grafting up to 198%, beyond which the decrease is very little. In our earlier studies on the grafting of methacrylic acid and 2-hydroxy-

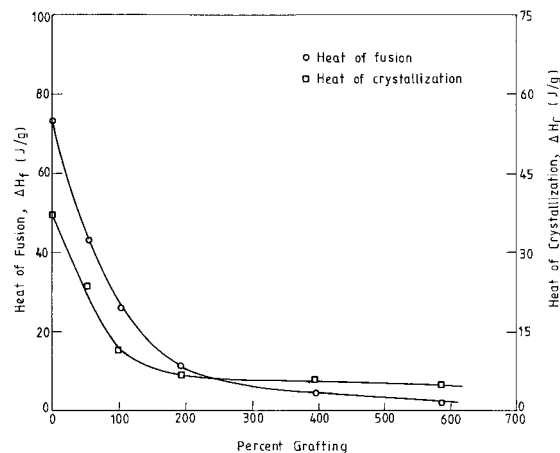


**Scheme 1** Thermal cyclization of PE-g-PAAm membrane.

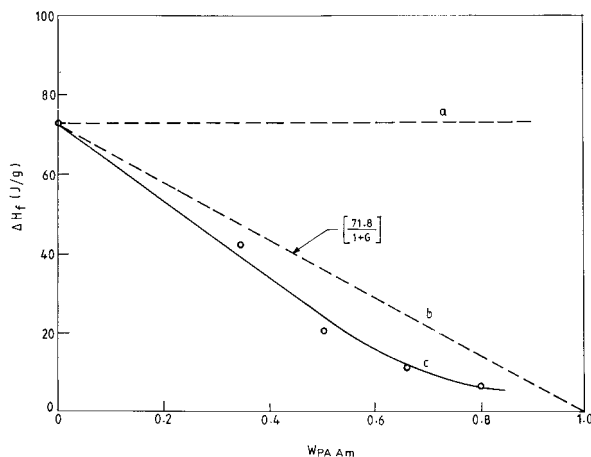


**Figure 6** DSC thermograms of original PE (a) and PE-g-PAAm membranes with different degrees of grafting: (b) 54%, (c) 100%, (d) 198%, (e) 398%, and (f) 590%.

ethylmethacrylate into polypropylene, the heat of fusion decreased as a function of the polypropylene fraction in the copolymer.<sup>25,28</sup> It was found that the grafting takes place in the noncrystalline region of the base polymer, thereby exerting a dilution effect on the inherent crystallinity. The XRD pattern, as discussed earlier, suggests that the PAAm grafts are amorphous in nature. Hence, it is important to correlate the inherent heat of fusion,  $\Delta H_{f(\text{inh})}$  values with the PE fraction  $[1/(1 + G)]$  in membranes as follows:



**Figure 7** Variation of the heat of fusion and the heat of crystallization with the degree of grafting in PE-g-PAAm membranes.

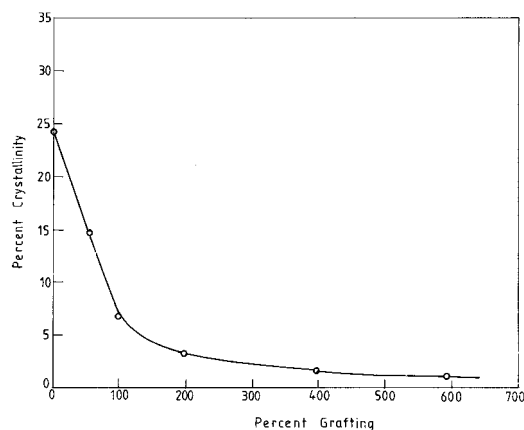


**Figure 8** Variation of the heat of fusion with the weight fraction of acrylamide,  $W_{\text{PAAm}}$ , in PE-*g*-PAAM membranes.

$$\Delta H_{f(\text{inh})} = \frac{71.8}{[1 + G]} \quad (4)$$

Considering the amorphous nature of the PAAm, the heat of fusion of membranes is expected to follow the trend reported by plot b in Figure 8. Hence, the decrease in the heat of fusion from a to b would be due to the dilution effect of amorphous PAAm domain present in membranes. However, the heat of fusion values deviate significantly from plot b and fall on plot c. The decrease in the heat of fusion from plot b to c may therefore be attributed to the disruption of inherent crystallites. It may be stated that the decrease in the heat of fusion in membranes is due to the cumulative effect of the dilution effect and the crystal distortion within the membrane.<sup>10</sup> It may be assumed that during grafting, some of the chains grow from the crystallite surface as well. When the membrane absorbs water, strain is created between hydrophilic PAAm and the hydrophobic PE backbone. As a result, some of these chains are cleaved off, leading to the crystal disruption.

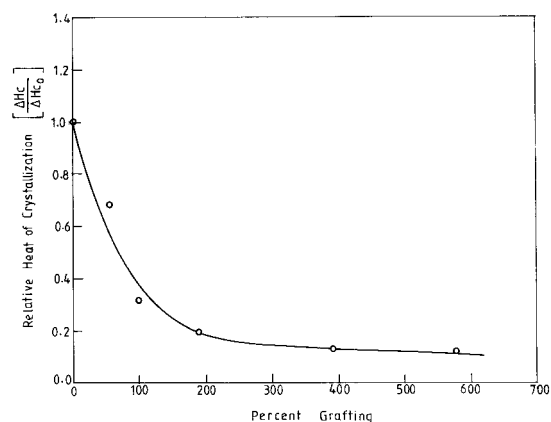
Heat of fusion is the direct measure of the crystallinity in a polymer. The crystallinity of membranes, as obtained from eq. 3, as a function of the degree of grafting is presented in Figure 9. Crystallinity shows a sharp decreasing trend up to 198% grafting and then slows down. This pattern is the result of the incorporation of amorphous PAAm within the noncrystalline region of the film and partial disruption of the crystallites, as discussed earlier. It is interesting to see that the membranes with degree of grafting as high as



**Figure 9** Variation of the percent crystallinity with the percent grafting in PE-*g*-PAAM membranes.

590% are left behind with very little crystallinity, which leads to a highly amorphous structure.

A relative change in the heat of crystallization of backbone polymer,  $(\Delta H_c / \Delta H_{c0})$ , where  $\Delta H_c$  and  $\Delta H_{c0}$  are heat of crystallization values of the grafted and original polyethylene films, respectively) against percent grafting is presented in Figure 10. The results show that the heat of crystallization does not follow a linear relationship with PAAm content. Instead, it decreases initially and then remains almost unchanged with the further increase in the percent graft. It appears that the grafted PAAm branches fill in the amorphous region of PE. After the grafted samples are melted, the amorphous PAAm chains have considerable mobility within the molten PE matrix and interfere with the growth of crystals.<sup>20</sup> It seems that the incorporation of 198% PAAm as the graft is sufficient to cause hindrance



**Figure 10** Relative change in the heat of crystallization with the percent grafting in PE-*g*-PAAM membranes.

during crystallization of grafted samples, and further grafting does not impede crystallization any more.

## CONCLUSIONS

The graft polymerization of acrylamide into PE films leads to membranes that behave as two-component system. Both the PE and PAAm moieties in the membrane undergo independent degradation, irrespective of the degree of grafting. All the membranes show a multistep degradation pattern that may be attributed to the dehydration, PAAm degradation, and PE backbone degradation. Initially, PAAm grafts are introduced into the voids within the membrane leading to the increase in the density with the increase in the degree of grafting up to 200%, beyond which the increase is very slow. The grafting leads to considerable decrease in the heat of fusion and crystallinity of PE membranes because of the cumulative impact of the dilution effect of the grafted PAAm chains and the crystal distortion by amorphous PAAm chains. PAAm grafts are amorphous in nature and are incorporated within the non-crystalline region of the PE film, which leads to the dilution of the inherent crystallinity. At the same time, some of the grafted PAAm chains that originate at the crystal surface experience stress due to the strong hydrophilic and hydrophobic interaction. This stress may lead to the cleavage of some of these chains and then to the crystal disruption. It may be proposed that the grafting leads to membranes with very high amorphous volume for better water permeation characteristics for our subsequent studies on toxic metal ion separation.<sup>30</sup>

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