Grafting of Acrylamide to Nylon-6 by Electron Beam Preirradiation. IV. Sorption of Water in Nylon Grafted Acrylamide Membranes

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Synopsis

Membranes prepared by extensive grafting of acrylamide onto nylon-6 films exhibit high water sorption capacity. Swelling of the membranes increases after treatment with aqueous solutions of formic acid. Sorption of water into these annealed membranes reaches values of ca. 25 moles of water per mole of grafted acrylamide. The sorption characteristics of the swollen membrane-gels crosslinked with *bis*-acrylamide were explored. Membranes grafted with acrylamide, crosslinked with *bis*-acrylamide and annealed with formic acid reach the maximum swelling capacity at low graft yields.

INTRODUCTION

The sorption of water into polymeric films grafted with hydrophilic monomers was investigated by several authors.[1-5] Nylon-6 itself is a polymer having moderate water uptake capacity: up to 9.5% add-on, compared with 40-120% in cellulose and less than 0.02% in polyethylene.[6-8] Grafting of nylon-6 with hydrophilic monomers such as acrylic acid or acrylamide was reported to have slight effect on the water sorption capacity of the graft-copolymer.[1-5] Hayakawa[9] et al. reported a 12-fold increase of the water sorption capacity of nylon-6 film due to grafting with *N*-vinyl pyridine (400% graft). Recently, Takigami and co-workers reported similar effects in nylon-6 films grafted with acrylic acid and acrylamide[10] (at ca. 400% graft yield). Hoffman et al. have recently demonstrated the role of water sorption into grafted hydrogels[11] in the biocompatability of such grafts with blood, tissue, etc. It is of interest, therefore, to try to evaluate the amount of water that grafted polymeric matrix can absorb, when formed under various experimental conditions.

In our previous papers[12-14] we reported that nylon membranes grafted with acrylamide (NYgAM) are highly permeable to water and solutes. We also reported a sudden increase of the permeability to water at a certain "critical" degree of swelling. This observation was accounted for in terms of the existence of at least two classes of water structures in the grafted polymer. In the present paper, parameters which influence the sorption of water into the NYgAM membranes are investigated, such as polyacrylamide (PAM) content, crosslinking of the graft, and the pretreatment of the nylon substrate. Influence of the annealing treatment of the grafted membranes with aqueous

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solutions of formic acid on the water sorption capacity of the graft was also investigated.

EXPERIMENTAL

The grafted membranes were prepared by immersion of preirradiated nylon-6 film in deaerated aqueous solution of the monomer for the appropriate period of time. The membranes were annealed by a 5 min immersion in 65% aqueous solution of formic acid. Detailed description of the procedures for membrane preparation and annealing were previously described.[13,14]

Water Uptake Measurements

The sorption capacity of the membranes was measured by immersing the membrane samples in water in a thermostatted vessel for at least three days. After wiping with a cleansing tissue, the membranes were weighted as quickly as possible. This procedure was repeated 10–20 times until satisfactory reproducibility was achieved. The samples were then dried in a heated vacuum oven (50°C, 25 mmHg) to a constant weight. The water uptake Δ onto a dry membrane and the water solubility S in the wet membrane were calculated according to:

$$\Delta(\%) = (W_w/W_O - 1) \times 100\% \qquad (1)$$

$$S(\%) = (1 - W_O/W_w) \times 100\% \qquad (2)$$

where W_O and W_w are the weights of the dry and wet membranes, respectively. The water absorption into the grafted polyacrylamide (PAM) in the membranes was calculated using the value of 7.4% previously found for the absorption of water onto the nylon substrate film, according to the following equations:

$$\Delta_1(\%) = (\Delta \times (100 + G) - 740)/G \qquad (3)$$

$$S_1(\%) = \Delta_1/(100 + \Delta_1) \qquad (4)$$

where G is the graft yield percentage.

RESULTS AND DISCUSSION

Water Sorption onto Nylon-Grafted Acrylamide (NYgAM) Membranes

The sorption of water onto the polyacrylamide in the NYgAM membranes vs. the PAM content in membranes prepared under various experimental conditions is shown in Figure 1. The relationship between water sorption capacity and PAM content shown in the figure clearly indicates that variation of the experimental parameters of the grafting process has no effect on water uptake. The water uptake appears to reflect predominantly the percentage of PAM in the membranes. Figure 2 shows the water sorption capacity of PAM (see Experimental for details) in NYgAM membranes vs. PAM content before

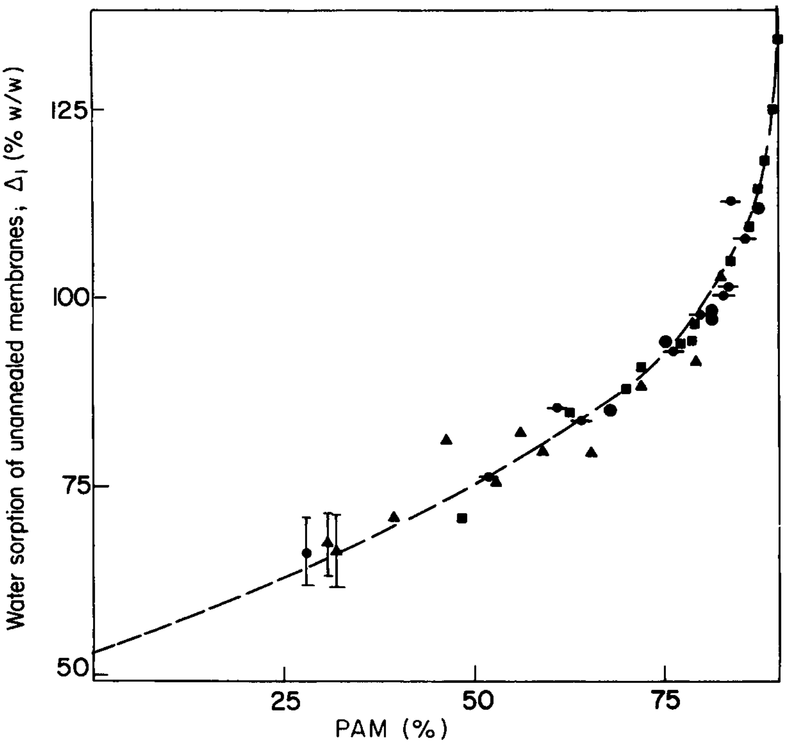

Fig. 1. Water sorption at 37°C into PAM in NYgAM membranes prepared under various grafting conditions. Δ_1 = water sorption capacity; Grafting conditions: (■) 12 Mrad, 10% AM; (▲) 12 Mrad, 5% AM; (●) 8.4 Mrad, 10% AM; (-●-) 4.8 Mrad, 10% AM; grafting temp 50°C.

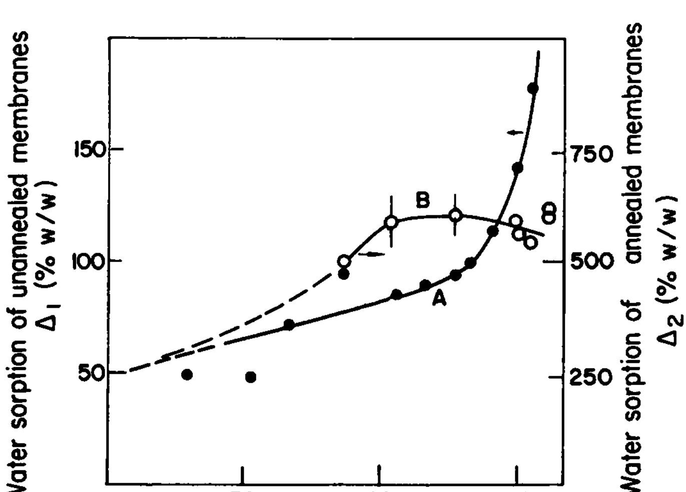

Fig. 2. Water sorption at 37°C into the PAM in NYgAM membranes. Grafting conditions: 12 Mrad, 10% AM solution at 50°C, Δ_1, Δ_2 = water sorption capacity of PAM in nonannealed (●) and annealed (○) membranes, respectively; annealing procedure: 5 min swelling in 65% aqueous formic acid.

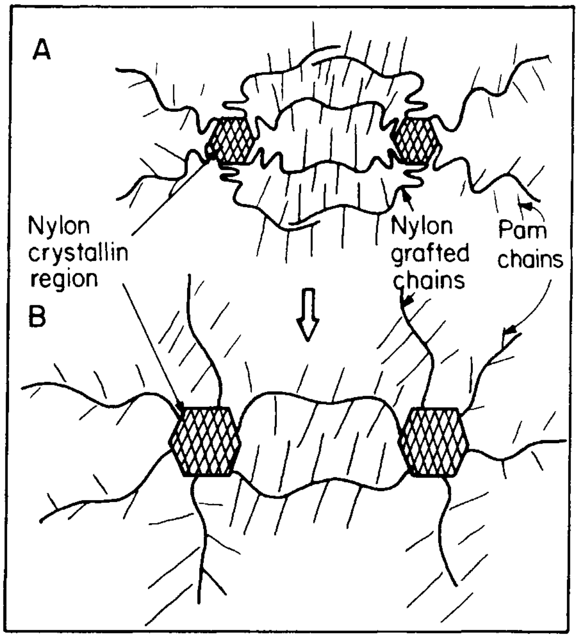

Fig. 3. Schematic description of the processes occurring in the NYgAM matrix during swelling in formic acid solution: (A) before swelling (B) after swelling. Thick and thin lines denote nylon and PAM chains, respectively. Hexagon denotes nylon crystallite.

and after annealing[14] with formic acid solution (5 min in 65% acqueous solution of formic acid). The extrapolated lower limit of the amount of sorbed water onto the nonannealed membranes is estimated to be ca. 50% (w/w) which is equivalent to ca. 2 moles of water per mole of grafted PAM. At high PAM content in the membranes the water sorption capacity rises and at PAM content of 93% (1300% graft yield) a molar ratio (water/PAM) of ca. 7 is observed. The PAM grafted onto the nylon can be related to as a matrix which is crosslinked by the nylon backbone. Thus, at low graft yields (or at high nylon content) the nylon backbone constrains the swelling of PAM. The rise in water sorption capacity of the highly grafted membranes probably reflects the fact that the constraining effect of the nylon on the swelling of PAM becomes of marginal importance at low nylon content.

Turning our attention to the swelling capacity of membranes annealed with formic acid (Fig. 2, curve B), we notice two main phenomena. The first is the much higher swelling capacity of the annealed membranes than that of the nonannealed ones. This observation can be attributed most probably to phase separation between the PAM and the nylon matrix, which occurs while the grafted copolymer is swollen in the formic acid solution. Such a phase separation process probably results from the enlargement and the perfection of the crystalline regions of the nylon substrate matrix[14] which leads to disentanglement between the PAM chains and grafted nylon chains, as described schematically in Figure 3. The latter process may loosen the connection between neighboring crystalline regions, which act as junction points of the grafted matrix. This process leads to less constraints of the PAM which is manifested by a higher degree of swelling, as shown in curve B of Figure 2.

The second phenomenon seen in Figure 2 is the existence of a maximum in the water sorption capacity, of ca. 25 moles of water per mole of PAM. This maximum, occurring (at a PAM content range of 67–75%) probably reflects two factors: at low graft yields the predominant factor is the content of nylon backbone which constrains the swelling of PAM, although to a lesser extent than before annealing. At very high graft yields the long PAM chains form entanglements which are less affected during the formic acid annealing treatment thus constraining the swelling of PAM in water.

Water Sorption onto Nylon Grafted with Acrylamide + *Bis*-acrylamide (NYgAM + *bis*-AM)

Thus far, we have considered the swelling characteristics of PAM which is constrained by the nylon matrix only. An effort was made to establish the effect of crosslinking the PAM with *bis*-acrylamide (added to the grafting solution) on the sorption capacity of the membranes, both in the annealed and nonannealed forms. As shown in Figure 4, crosslinking PAM with *bis*-AM causes considerable decrease in the swelling capability in water of PAM in the nonannealed membranes. This decrease is most likely caused by the further constriction of the mobility of the PAM chains due to the additional crosslinking (Fig. 4, curves A and A′). As expected, the higher the crosslinking-monomer concentration in the feed solution is, the lower the sorption capacity of the grafted PAM.

The annealing treatment with formic acid solution increases the sorption capacity of the PAM in the NYg(AM + *bis*-AM) membranes (Fig. 4., curves B and B′). We expected the general features of the sorption vs. graft yield of the annealed crosslinked membranes to be similar to those of the annealed noncrosslinked (NYgAM) membranes. (Compare Fig. 2, curve B with Fig. 4

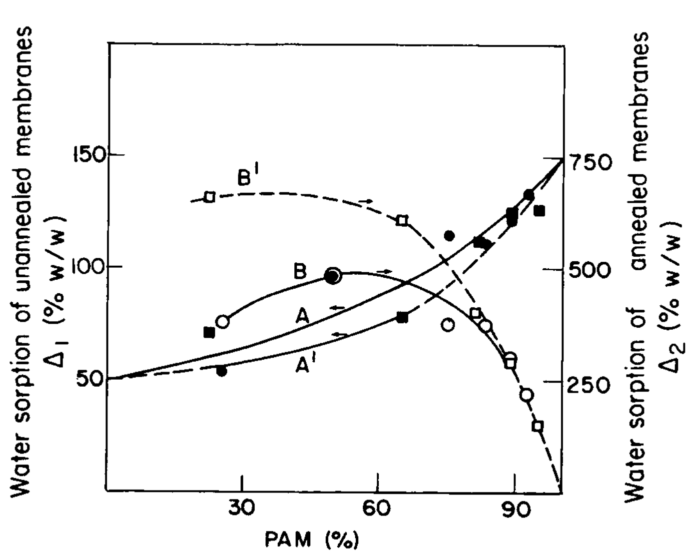

Fig. 4. Water sorption into the PAM in NYg(AM + *bis*-AM) membranes (prepared at 12 Mrad), at 37°C. Δ_1, Δ_2 = water sorption capacity of PAM in nonannealed (●,■) and annealed (○,□) membranes, respectively. Annealing procedure: 5 min swelling in 65% aqueous formic acid solution. The weight ratio of AM to *bis*-AM is 19:1 (○,●) and 9:1 (□,■), respectively.

curves B, B′.) However, in the latter the existence of a maximum in the sorption capacity at an "optimal" range of graft yields reflects mainly the effect of the *bis*-AM crosslinking upon PAM swelling capability. This finding can be rationalized as follows: since the relatively large *bis*-AM monomer diffuses into the nylon matrix more slowly than AM, the concentration of the crosslinking monomer *bis*-AM is lower in the graft than in the free monomer solution. At high PAM content (ca. 90%) the grafted film is highly swollen by the monomer solution, hence the crosslinking monomer can penetrate and graft onto the film at an increasing rate.

Thus, the existence of a maximum of the sorption capacity in the annealed crosslinked membranes reflects the interplay between two factors: on one hand, an increase in the content of PAM favors water sorption capacity and on the other , a high PAM content leads to an increase in the concentration of the crosslinks due to a higher uptake of *bis*-AM into the membranes, which affects the water uptake adversely. The fact that the "optimal" PAM content (in which the highest water sorption capacity is attained) shifts from ca. 70% in the NYgAM membranes to ca. 52% and 35% in the NYg(AM + *bis*-AM) membranes (in which the concentration of the bis-AM in the monomer in the feed solution is 5% and 10%, respectively), is in agreement with this explanation.

It is noteworthy that among the annealed membranes, the highest sorption capacity is attained for the NYg(AM + *bis*-AM) membranes (10% *bis*-AM in AM), while somewhat lower values are observed for the NYgAM and NYg(AM + *bis*-AM-5%) membranes. In these membranes the water-to-PAM molar ratio is ca. 26, 25, and 20, respectively. These findings may reflect constructional stabilization of the gel against collapsing, during and after the swelling in formic acid, which is imparted by the *bis*-AM crosslinks.

This dual effect on sorption of the crosslinking by *bis*-AM is similar to that of the "crosslinking" by the nylon matrix. However, one must bear in mind that as the graft yield rises, the concentration of the nylon in the membrane decreases, while conversely, the concentration of *bis*-AM crosslinks significantly increases. It is also noteworthy that the partial prevention of the annealing of the grafted membranes in formic acid due to the *bis*-AM crosslinking is consistent with the measurements of the crystallinity of the nylon matrix present in these membranes by differential scanning calorimetry (DSC):[14] Swelling in formic acid was found to have less of an effect on the apparent crystallinity of NYg(AM + *bis*-AM) membranes than NYgAM membranes.

Water sorption onto Preannealed AM-Grafted Nylon (NY-RgAM)

In the former sections we considered the swelling characteristics of grafted membranes before and after annealing treatment by swelling in formic acid solution. Figure 5 shows the swelling capacity vs. PAM content, of the PAM in membranes which were prepared by grafting AM onto preannealed nylon substrate films annealed (1 hour in 65% formic acid solution) prior to the radiation-induced grafting (NY-RgAM). These NY-RgAM membranes exhibit water sorption capacity which is about 50% higher than in the NYgAM membranes (compare curve A in Figs. 5 and 2). This phenomenon probably reflects the fact that the "crosslinking" effect of the nylon matrix upon the

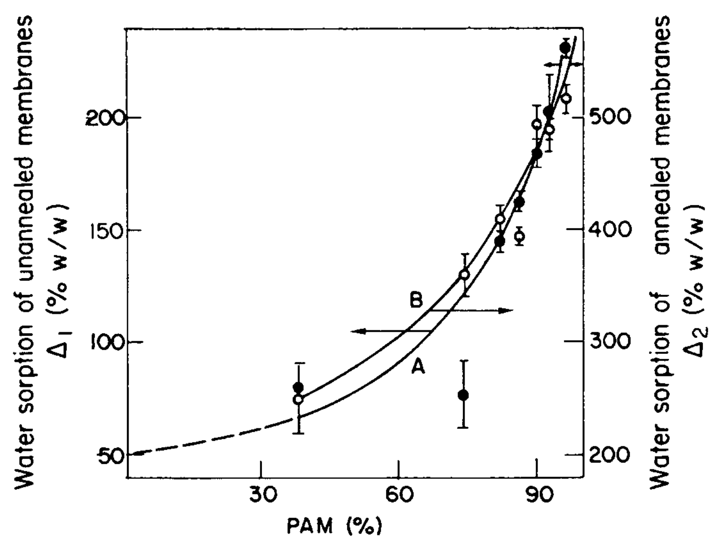

Fig. 5. Water sorption into PAM in preannealed AM-grafted nylon NY-RgAM membranes. Grafting conditions, Δ_1, Δ_2 = same as in Fig. 2.

grafted PAM, in the preannealed membranes, is considerably smaller as compared with that in the NYgAM membranes. This observation is in agreement with our X-ray and DSC findings that the preannealed nylon films contain higher fractions of crystalline regions. Therefore, the PAM chains which are grafted onto the amorphous fraction of the nylon[14] are anchored to a smaller portion of the nylon matrix. Hence, the local PAM concentration in the grafted regions in the NY-RgAM membranes is higher than in the NYgAM ones, and consequently the water sorption capacity is also higher.
contain higher fractions of crystalline regions. Therefore, the PAM chains which are grafted onto the amorphous fraction of the nylon[14] are anchored to a smaller portion of the nylon matrix. Hence, the local PAM concentration in the grafted regions in the NY-RgAM membranes is higher than in the NYgAM ones, and consequently the water sorption capacity is also higher.

Further annealing of the membranes prepared from preannealed nylon leads to only a slight increase in the water sorption capacity, resulting, most likely, from the fact that in these membranes the nylon has already reached the maximum degree of crystallinity. The only variation that may be caused by a second annealing treatment could be a partial disentanglement between PAM and nylon chains, which has little effect upon the water sorption capacity.

It is also noteworthy that the swelling capacity of the reannealed NY-RgAM membranes discussed here (curve B in Fig. 5) continues to rise even at high graft yields, as opposed to the annealed NYgAM and NYg(AM + *bis*-AM) membranes (cf. Figs. 2 and 4, curves B and B′). This finding is consistent with the fact that the reannealing of the NY-RgAM membranes causes only minor changes in the morphology of these membranes and therefore the water sorption characteristics of the membranes, before and after annealing, are similar.

It should be mentioned that at high irradiation dose the nylon matrix may undergo a significant extent of crosslinking prior to the grafting process. In spite of this, no difference in water sorption capacity at similar graft yields was observed in membranes prepared from nylon samples irradiated to 50 or 12 Mrad. However, the effect of annealing with formic acid on the sorption capacity was much more pronounced in the membranes prepared from 12 Mrad-irradiated nylon. This observation probably reflects the fact that when the nylon matrix is highly crosslinked, the annealing by swelling in formic acid solution is less effective and the nylon and PAM chains are separated to a lesser extent.

CONCLUSIONS

Water sorption capacity of grafted nylon membranes depends predominantly upon the PAM content. The second main factor is the extent of crosslinking, mainly in the grafted copolymer and to a lesser extent in the host nylon matrix. In addition to crosslinking of the grafted copolymer via chemical bonds one has to consider also the crosslinking via hydrogen bonds and entanglements. The crystalline regions of the nylon can be viewed as junction points in the nylon matrix which connect the grafted nylon chains of the gel network. Part of the physical crosslinking diminishes during the annealing treatments with formic acid, thus increasing the water sorption capacity. The highest water sorption capacity has been attained by using the combination of moderate PAM content (ca. 35%), with monomer containing 10% of *bis*-AM, followed by annealing treatment with formic acid solution.

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