

# Grafting of Acrylamide to Nylon-6 by the Electron Beam Preirradiation Technique. V. Permeability and Selectivity of the Grafted Membranes to Ionic Solutes and Metabolites\*

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## Synopsis

Nylon-6-grafted polyacrylamide (NYgAM) membranes were modified by crosslinking and/or annealing with 65% aqueous solution of formic acid at room temperature. The permselectivity properties of the treated NYgAM membranes to a number of ionic solutes of varying molecular size ranging from HBr to tetrabutylammoniumbromide ( $\text{Bu}_4\text{NBr}$ ) were studied in the temperature range of 27–47°C. The temperature dependence of the permeation coefficients through the cross linked membranes indicates an apparent energy of activation of 6.6 and 11.3 kcal/mol for HBr and  $\text{Bu}_4\text{NBr}$ , respectively. In the crosslinked and annealed membranes the corresponding activation energy values were found to range from 4.4 to 5.6 kcal/mol, reflecting the increased water uptake of the annealed membranes. The flux of water and bromide solutes through the 135  $\mu\text{m}$  thick crosslinked and annealed NYgAM membranes at 332% graft yield was found to be approximately equal to that of 18  $\mu\text{m}$  thick cellophane films. The permeability coefficients of urea, uric acid, raffinose, and inulin through the crosslinked annealed NYgAM membranes were determined in order to establish the potential applicability of the modified membranes to clinical separation of metabolites. The flux of all four solutes, especially that of uric acid, through the modified NYgAM membranes at 100% graft yield was found to be higher than through the cellophane films. In addition, the flux of inulin was found to be strongly affected by variation in graft yields.

## INTRODUCTION

Synthetic membranes, which display a strong interaction between solvent (typically water) and the membrane matrix that leads to swelling of the membrane, are permeable to both ionic and neutral solutes.<sup>1–9</sup> The flux of solutes into and through the membrane network is an important characteristic which governs the possible assignment of membranes to processes and products, such as battery separators,<sup>3</sup> desalination,<sup>4</sup> dialysis,<sup>5</sup> catalyst support,<sup>6</sup> etc. In addition to favorable transport characteristics, durability and

\*Dedicated to Professor T. Gaumann, Institute de Chimie-Physique EPFL, Switzerland, on the occasion of his 60th birthday.

high permselectivity of the membranes toward different solutes are properties of importance in biological and biomedical separation processes.

In a previous communication we have shown<sup>7</sup> that electron beam-induced grafting of acrylamide onto nylon films imparts to the graft copolymer films (NYgAM), at ca. 100% graft yield, water permeation rates similar to those of commercial poly(vinyl alcohol) (PVA) and dialysis-grade cellophane films of comparable thickness. In a subsequent study,<sup>8</sup> the effect of graft yield in NYgAM membranes, prepared from 13  $\mu\text{m}$  thick biaxially oriented nylon-6 films, on the permeation of water and a number of ionic solutes of increasing size, namely HBr,  $\text{NH}_4\text{Br}$ , KBr, NaBr,  $\text{Me}_4\text{NBr}$ ,  $\text{Et}_4\text{NBr}$ ,  $\text{Pr}_4\text{NBr}$ , and  $\text{Bu}_4\text{NBr}$  was studied.<sup>8</sup> In that study it was found that the permeation rates of all the ions increase with the growth in graft yields. This increase most likely reflects the increase in water uptake upon increase in graft yield. However, the selectivity parameter which defines the ratio of the flux of HBr to that of the largest ion, namely  $\text{Bu}_4\text{NBr}$ , was found to decrease upon increase in graft yield above 250%. At 250% graft yield the selectivity parameter of the NYgAM films is about 20 times higher than that of cellophane. The enhanced selectivity of the NYgAM membranes, at 250% graft yield, toward the solutes was accompanied by a decrease, by a factor of about 4, in the flux of HTO and HBr, as compared with cellophane.

It is well known that the transmission of water and solutes through a membrane can be modified by varying its water sorption capacity. We have recently shown<sup>10</sup> that the swelling-annealing of the NYgAM membranes, by a 5 min immersion in 65% w/w aqueous solution of formic acid, leads to an increase in the water sorption capacity of the membranes. It should be stressed that the borrowed terminology "annealing" refers to relaxation effects attained by applying the swelling treatment process only (as described in the experimental part) and not to a heat treatment process, because thermal annealing of the NYgAM membranes is not applicable, since the grafted polyacrylamide (PAM) decomposes at the temperatures required for the annealing of nylon-6. The highest water uptake, which corresponds to an eightfold increase in the hydration of the grafted PAM, was observed at ca. 250% graft yield. This enhancement in the grafted membrane hydration, following annealing, was attributed to phase separation between the enlarged crystalline regions of the nylon substrate, which serve as junction points of the grafted PAM, and the amorphous regions of the grafted PAM, accompanied by disentanglement of the grafted PAM chains.<sup>9</sup>

A similar increase in water swelling capacity, following annealing, was observed in NYgAM films in which the constraint on the mobility of the PAM chains was increased by incorporating *bis*-acrylamide (*bis*-AM) in the monomer feed solution<sup>10</sup> (see experimental). In the annealed crosslinked membranes (NYgAM + *bis*-AMa), a maximum in the water sorption capacity, equivalent to that displayed by similarly annealed NYgAM membranes at 250% graft yield, was observed at 55% and 110% graft yields, for membranes prepared with monomer feed solutions at AM/*bis*-AM w/w ratios of 9 and 19, respectively.

In the present study we have focused our attention on the effect of morphological changes induced in NYgAM membranes by modification of the

crosslinks density and by annealing, on the permselectivity characteristics of the membranes, with respect to the transport of ionic solutes and metabolites.

## EXPERIMENTAL

The grafted membranes were prepared by immersion of preirradiated nylon-6 films in deaerated aqueous solution of the monomer: 10% AM or 9.5% AM + 0.5% *bis*-AM, at 30–50°C, for the appropriate period of time. The grafted membranes were annealed by a 5 min immersion in 65% aqueous solution of formic acid. The detailed procedures for the preparation and modification of the membranes and for the determination of the permeation rates of water and the ionic solutes have been described previously.<sup>8-10</sup> The permeation rates of the metabolites were determined by liquid scintillation spectroscopy with labeled compounds, using Packard Insta-Gel Liquid Scintillator No. 6013009, in the Packard Tri-Carb Liquid Scintillation Spectrometer Model 3320. Urea, uric acid, and inulin were labeled with <sup>14</sup>C and water and raffinose with <sup>3</sup>H.

## RESULTS AND DISCUSSION

### Permselectivity Features of Formic Acid Annealed NYgAM Membranes

The effect of 5 min exposure of NYgAM films to 65% aqueous solution of formic acid on the permselectivity characteristics of the membranes is shown in Table I. These data indicate the strong rise in the permeability coefficients of the solvent (water) and all the bromide solutes through the annealed membranes. The annealing treatment effect is most pronounced in the transport of the relatively large solutes. The accompanying result is the loss of selectivity which can be best appreciated by comparing the performance of nonannealed and annealed NYgAM membranes at 249% graft yield. At this grafting level the selectivity parameter, which is defined as the ratio of the flux of HBr to that of Bu<sub>4</sub>NBr, is lower for the annealed NYgAM membrane by a factor of about 26 than that of the nonannealed membrane. At other graft yields the selectivity decrease is less pronounced. Another notable feature of the annealed NYgAM membranes is the relatively small effect of the extent of grafting on the permeability coefficients of the solvent and the solutes. This observation is to be contrasted with the permselectivity characteristics of the nonannealed NYgAM membranes which exhibit a strong rise in the permeability coefficients with increase in graft yield. This increase in the permeability coefficients was attributed by us<sup>8</sup> to a concomitant rise in water uptake.

In light of the above arguments, it appears that the changes incurred in the permselectivity properties of the annealed NYgAM membranes can be attributed predominantly to an enhanced hydration of the polymer network. This increase in swelling, which is pronounced at all graft levels, manifests itself by growth in the thickness of the annealed NYgAM membranes (see the 3rd column in Table I). The higher water uptake of the annealed membranes creates a pore distribution which permits a relatively uninhibited passage of

TABLE I  
Permeability and Selectivity of NYgAMa<sup>a</sup> Membranes to Water and Solutes<sup>b</sup>

No	Graft yield (%)	Wet thickness (μm)	Permeant <sup>c</sup> Stokes radius of cation (Å) <sup>d</sup>	Permeability ( $P$ ) × 10 <sup>7</sup> (cm <sup>2</sup> s <sup>-1</sup> )							Flux (HBr)		Selectivity		Performance Flux <sub>HBr</sub> × Selectivity
				HTO	Bu	Pr	Et	Me	H	HBr	P(HBr)	Thickness	P(HBr)	P(Bu)	
1	181 (204)	68 ± 2 48	80 ± 8 10	10 ± 1 0.07	—	23 ± 2 0.16	24 ± 3 0.26	39 ± 3 1.0	66 ± 5 3.9	97 ± 4 8	6.7 ± 0.7 59	650 ± 60 470)			
2	249 (249)	95 ± 2 57	70 ± 9 —	16 ± 1 0.11	23 ± 3 0.19	28 ± 3 0.42	37 ± 4 0.65	48 ± 5 2.8	58 ± 6 10.2	61 ± 5 18	3.6 ± 0.5 93	220 ± 40 1670)			
3	584 (582)	135 ± 5 92	77 ± 7 16	16 ± 1 0.71	28 ± 3 1.08	33 ± 3 2.3	36 ± 4 3.6	41 ± 9 12	53 ± 5 24	39 ± 2 26	3.3 ± 0.3 34	130 ± 10 880)			
4	856 (856)	152 ± 3 125	79 ± 6 50	11 ± 1 1.2	—	25 ± 1 4.2	32 ± 2 5.9	51 ± 4 18	100 ± 10 39	66 ± 4 31	9 ± 2 33	590 ± 150 1020)			
5	1270 (1270)	160 ± 5 140	45 ± 5 116	15 ± 2 1.8	—	—	—	61 ± 6 23	97 ± 8 51	61 ± 3 36	6.5 ± 1.1 28	400 ± 60 1010)			
Cellophane	18	16	16	2.6	3.1	5.2	6.4	11	13	73	5	365			

<sup>a</sup>5 min annealing in 65% aqueous solution of formic acid.

<sup>b</sup>The data in parentheses refer to nonannealed membranes of similar graft yields, taken from Ref. 8.

<sup>c</sup>Bu = Bu<sub>4</sub>NBr; Pr = Pr<sub>4</sub>NBr; Et = Et<sub>4</sub>NBr; Me = Me<sub>4</sub>NBr; H = H<sub>4</sub>NBr

<sup>d</sup>Data taken from Ref. 11.

<sup>e</sup>Proton-jump transport,  $r_{Br}$  = 1.95 Å.

ions having Stokes' radius as high as 4.7 Å. It should also be mentioned that the 5 min exposure of the NYgAM membranes to the formic acid solution results in a significant decrease in the wet strength of the membranes, which tend to deteriorate after several weeks of immersion in aqueous solutions.

### The Permselectivity Properties of Chemically Crosslinked and Annealed NYgAM + *bis*-AM Membranes

In a further attempt to explore the potential of modification of the permselectivity properties of the grafted copolymer membranes by the annealing procedure, chemical crosslinking of the PAM grafted onto the nylon via the *bis*-AM monomer was attempted, followed by the formic acid treatment. In the first stage of the grafting process, which involves the electron beam irradiation of the nylon backbone, a certain extent of crosslinking may occur within the host matrix. However, practically no crosslinking is expected to occur between the PAM chains which are formed during the exposure of the preirradiated nylon film to the aqueous solution of AM. Incorporation of the *N,N'*-methylene *bis*-acrylamide monomer (*bis*-AM) on the monomer feed solution, in an AM/*bis*-AM w/w ratio of 19 : 1 would be expected to result in a significant amount of crosslinks between the grafted PAM chains. The ensuing crosslinked network should be able to withstand the disruptive effect of the formic acid annealing treatment. At the same time it would impose a more tortuous path for the diffusion of solutes through the membrane, leading to somewhat reduced permeability and enhanced selectivity.

The data in Table II provides a summary of the permselectivity properties of the NYgAM + *bis*-AM membranes in the temperature range 27–47° C. We shall first consider the effect of crosslinking (without annealing) on the permselectivity characteristics of the NYgAM + *bis*-AM membranes. The findings can be summarized as follows.

a. For membranes grafted to 500–1200% graft yield, the permeability coefficients of the bromide solutes at 37°C are lower by about 15–30% for crosslinked than for noncrosslinked NYgAM membranes at comparable graft yields.

b. The selectivities and the overall performance factors (defined as the flux of HBr multiplied by the selectivity) of the NYgAM + *bis*-AM membranes are almost constant, within the range of 330–1200% graft yields, the average performance factor of the crosslinked membranes being lower by about 20% than the highest value observed in the NYgAM membranes, at 249% graft yield.

c. The permeability coefficients of the bromide solutes through the NYgAM + *bis*-AM membranes increase, on the average, on going from 27°C to 47°C, by a factor varying from 2 to 3.2 for HBr and Bu<sub>4</sub>NBr, respectively. This temperature dependence implies an overall activation energy of solutes permeation through the membranes in the range of 6.6–11.3 kcal/mol.

Now let us consider the combined effect of crosslinking and annealing. Unlike in the case of the NYgAM membranes, the annealing treatment of the NYgAM + *bis*-AM membranes with formic acid solution (NYgAM + *bis*-AMa) did not lead to a significant loss of the wet strength properties of the membranes. From the data in Table II we can deduce the following.

TABLE II  
Permeability and Selectivity of Crosslinked NYgAM + bis-AM<sup>a</sup> Membranes to Water and Solutes  
in the Temperature Range 27–47°C

No.	Annealing <sup>d</sup>	Temperature (°C)	Graft yield (%)	Wet thickness (μm)	Permeant <sup>b</sup> Stokes radius of cation (Å) <sup>c</sup>	Permeability (P) × 10 <sup>7</sup> (cm <sup>2</sup> s <sup>-1</sup> )						Flux		Selectivity Performance			
						HTO	Bu	Et	Me	H	HBr	P(HBr)	P(HBr) Thickness	P(Bu)	P(Bu) Thickness	Flux <sub>HBr</sub> ×	Selectivity
					1.13	4.71	2.81	2.04	1.25	e							
6	(na)	27	332	65 ± 8		0.12 ± 0.02	0.42 ± 0.09	0.82 ± 0.16	3.4 ± 0.6	7.4 ± 1.2	11.4 ± 0.4	62 ± 4	710 ± 70				
		37			17 ± 2	0.21 ± 0.03	1.1 ± 0.2	3.3 ± 0.4	5.1 ± 0.7	12 ± 1	18 ± 1	57 ± 2	1030 ± 90				
		47				0.45 ± 0.7	1.5 ± 0.2	2.6 ± 0.4	7.9 ± 1.4	18 ± 3	28 ± 1	40 ± 1	1120 ± 70				
6	(a)	27	332	135 ± 5		8.9 ± 0.6	25 ± 2	27 ± 2	65 ± 6	86 ± 7	64 ± 2	9.7 ± 0.3	620 ± 40				
		37			123 ± 9	19 ± 1	44 ± 4	53 ± 5	78 ± 8	123 ± 15	91 ± 3	6.5 ± 0.4	500 ± 60				
		47				17 ± 1	42 ± 5	52 ± 5	80 ± 8	135 ± 12	100 ± 5	7.9 ± 0.3	790 ± 70				
7	(na)	27	506	92 ± 5		0.34 ± 0.04	1.1 ± 0.1	1.1 ± 0.1	6.2 ± 0.8	14.3 ± 1.3	15.5 ± 0.6	42 ± 2	650 ± 60				
		37				0.41 ± 0.02	1.5 ± 0.2	2.7 ± 0.2	8.2 ± 0.7	21 ± 1	23.0 ± 0.9	51 ± 7	1170 ± 100				
		47				0.85 ± 0.05	3.0 ± 0.2	4.3 ± 0.3	14.0 ± 0.9	26 ± 2	29 ± 1	30.6 ± 0.5	890 ± 40				
7	(a)	27	506	135 ± 5		9.9 ± 0.8	22 ± 2	31 ± 3	51 ± 4	94 ± 7	70 ± 2	9.5 ± 0.2	680 ± 20				
		37				14 ± 1	31 ± 2	44 ± 4	67 ± 6	113 ± 9	84 ± 3	8.1 ± 0.2	680 ± 40				
		47				16 ± 2	34 ± 3	54 ± 5	78 ± 7	136 ± 10	101 ± 3	8.5 ± 0.5	850 ± 90				

8	(na)	804	107 ± 5	27	0.18 ± 0.05	0.39 ± 0.05	1.15 ± 0.09	6.6 ± 0.6	14.7 ± 1.2	13.7 ± 0.5	82 ± 7	1120 ± 140	
				37	0.60 ± 0.08	2.0 ± 0.2	3.4 ± 0.3	13 ± 1	29 ± 3	27 ± 2	48 ± 3	1300 ± 180	
				47	0.47 ± 0.04	2.2 ± 0.2	4.7 ± 0.5	16 ± 2	31 ± 2	29 ± 0.5	66 ± 2	1910 ± 100	
8	(a)	804	145 ± 5	27	6.9 ± 0.5	22 ± 1	31 ± 2	58 ± 4	97 ± 5	67 ± 1	14.1 ± 0.5	940 ± 50	
				37	88 ± 6	10.3 ± 0.7	36 ± 4	48 ± 4	70 ± 7	125 ± 18	86 ± 9	12.1 ± 1.2	1040 ± 220
				47	12 ± 1	36 ± 2	47 ± 4	78 ± 7	133 ± 10	92 ± 3	11.1 ± 0.8	1020 ± 110	
9	(na)	1194	145 ± 5	27	0.34 ± 0.03	1.6 ± 0.1	3.4 ± 0.3	13 ± 1	24 ± 2	16.6 ± 0.7	71 ± 5	1180 ± 130	
				37	0.77 ± 0.06	3.2 ± 0.3	5.3 ± 0.4	19 ± 2	36 ± 3	25 ± 1	47 ± 1	1180 ± 70	
				47	1.4 ± 0.1	6.6 ± 0.5	9.2 ± 0.7	27 ± 2	48 ± 4	33 ± 2	34 ± 2	1120 ± 140	
9	(a)	1194	165 ± 5	27	5.0 ± 0.5	15 ± 1	23 ± 1	43 ± 3	71 ± 5	43 ± 2	14.2 ± 1.0	610 ± 70	
				37	4.6 ± 0.4	12 ± 1	18 ± 2	54 ± 4	88 ± 7	53 ± 3	19 ± 1	1000 ± 120	
				47	9.0 ± 1.0	25 ± 2	24 ± 2	67 ± 5	101 ± 7	61 ± 3	11.2 ± 0.7	710 ± 50	
Cellophane				27	1.4 ± 0.1	3.6 ± 0.3	5.6 ± 0.5	8.8 ± 0.9	13 ± 1	72 ± 7	9.3 ± 0.5	670 ± 100	
				37	1.9 ± 0.2	4.9 ± 0.5	6.9 ± 0.7	11 ± 1	18 ± 2	100 ± 6	9.5 ± 0.3	950 ± 90	
				47	2.5 ± 3	6.1 ± 0.6	7.6 ± 0.9	14 ± 1	20 ± 2	111 ± 6	8.0 ± 0.2	890 ± 80	

<sup>a</sup> The ratio bisAM/AM in the monomer feed solution is 5%.

<sup>b</sup> Bu = Bu<sub>4</sub>NBr; Et = Et<sub>4</sub>NBr; Me = Me<sub>4</sub>NBr; H = H<sub>4</sub>NBr.

<sup>c</sup> Data taken from Ref. 11.

<sup>d</sup> (a) and (na) denote annealed or nonannealed membranes, respectively.

<sup>e</sup> Proton-jump transport, r<sub>Br</sub> = 1.95 Å.

a. The swelling-annealing treatment results in a significant increase in the permeability coefficients and flux values of HTO and the bromide solutes through the NYgAM + *bis*-AMa membranes. In the case of HTO and HBr at 332% graft yield, the permeability coefficients at 37°C are higher by a factor of 7 and 10, respectively, than through the NYgAM + *bis*-AM membranes. The increase in the transport of the heavier solutes is even more prominent. Thus, at 332% graft yield the annealing treatment leads to an increase in the permeability coefficient of Bu<sub>4</sub>NBr by a factor of about 90. It should be noted that the increase in the corresponding flux value is less pronounced, due to thickening of the membranes following the annealing treatment. The effect of annealing on the increase in the transport properties of HTO and the bromide solutes, especially those of higher molecular weight, becomes smaller when the graft yield is increased. Thus, on going from 332% to 1194% graft yield, the permeability coefficients of HBr and Bu<sub>4</sub>NBr are reduced by about 30% and 75%, respectively, and the corresponding selectivity factors are increased from 6.5 to 19. These changes result in a twofold increase in the overall performance factors of the more highly grafted membranes.

b. In the temperature range of 27–47°C, the permeation coefficients of HBr and Bu<sub>4</sub>NBr increase, on the average, by a factor of 1.44 and 1.76, respectively. These variations in the permeation coefficients imply activation energies of the bromide solutes permeation in the ranges of 4.4 and 5.6 kcal/mol. The latter values, which are significantly lower than the corresponding values of 6.6 and 11.3 kcal/mol derived in NYgAM + *bis*-AM membranes, most likely reflect the shift of the pore size distribution in the highly swollen annealed membranes toward larger pore sizes.

In conclusion, it appears that the structural modifications imposed on the NYgAM membranes by a combination of crosslinking and annealing treatments, lead mainly to an increase in the flux values of water and the bromide solutes. Unfortunately, the improved transport properties of the modified membranes are counterbalanced by a loss in the selectivity parameters. It would thus appear that insofar as separation of ionic solutes in the molecular weight range of 81–332 is concerned, the unmodified NYgAM membrane remains superior to the NYgAM + *bis*-AMa one. It is, however, of particular interest to note that the selectivity parameters and the flux values of water and the bromide solutes through the 135 μm thick annealed crosslinked NYgAM + *bis*-AMa membrane, at 332% graft yield, are almost identical to those observed through the 18 μm thick cellophane film. This observation served as a rationale to evaluate the effectiveness of the modified NYgAM membranes toward the separation of metabolites.

#### **Permselectivity Features of the Annealed Crosslinked NYgAM + *bis*-AMa Membranes Toward Metabolites**

In order to evaluate the potential applicability of the annealed crosslinked NYgAM + *bis*-AMa membranes to clinical devices, the permeabilities of urea, uric acid, raffinose, and inulin through the membranes were determined. The molecular weight distribution of these test metabolites ranges from 60 to 5200. Urea and uric acid represent typical low molecular weight uremic toxins, while



inulin can be classified in biomedical terms as a middle molecular weight metabolite.

The transport data of these solutes through the modified NYgAM + *bis*-AMa membranes at different graft yields are summarized in Table III. From the tabulated data it is apparent that similarly to the pattern exhibited in the transmission of the bromide solutes, the permeability coefficients of all the metabolite permeants through the annealed NYgAM + *bis*-AMa membranes are significantly higher at all grafting levels than those observed through cellophane. However, since for practical biomedical applications one is mainly concerned with the comparison of the values of the fluxes, we shall limit our discussion to the modification of the latter values as a function of the graft yields.

The relative changes in the fluxes of the solvent and the test solutes through the annealed NYgAM + *bis*-AMa membranes compared with those through the cellophane, as a function of the graft yield, are displayed in Table IV. At the highest level of water uptake of the annealed NYgAM + *bis*-AMa membranes, namely at 100% graft yield (see Introduction), the fluxes of HTO and all the test solutes are higher than through the cellophane membrane. The increase in flux is most noticeable for uric acid and raffinose, the flux of which is higher by 145% and 72%, respectively, than the values determined for cellophane.

Increase in the graft yield results in a decrease in the fluxes of HTO and the test solutes, except for that of inulin. The flux of the latter solute is enhanced by a factor of about 2, upon increase in the graft yield to 500%. Only upon further rise in the graft yield, does the transmission rate of inulin become progressively smaller. At 1190%, the flux of HTO, urea, uric acid, raffinose, and inulin amount to about 52%, 47%, 66%, 46%, and 19%, respectively, of the corresponding flux values through the cellophane membrane. This finding suggests the existence of a sharper "cut-off" point for the transport of inulin through the annealed NYgAM + *bis*-AMa membranes at 1190% graft yield as compared with cellophane.

The difference in the biomedical permselectivity effectiveness, between the annealed NYgAM + *bis*-AMa and the cellophane membranes, can be appreciated by comparison of the flux of HTO, multiplied by the ratio ( $P(\text{urea})/P(\text{inulin})$ ) (PF-1) or by the ratio ( $P(\text{uric acid})/P(\text{inulin})$ ) (PF-2). The PF-1 and PF-2 performance factors (see Table III) indicate that the annealed NYgAM + *bis*-AMa membranes exhibit their highest effectiveness at 1190% graft yield. At that graft level, their PF-1 and PF-2 values are higher than those of cellophane by about 20% and 72%, respectively. Relatively high performance is also observed at 100% graft yield, the PF-1 and PF-2 values amounting to 86% and 193%, respectively, of those exhibited by cellophane.

It should be stressed that the use of PF-1 and PF-2 factors, as criteria of performance, rests on the implicit assumption that in the biomedical separation processes the interest lies in high transport rates of the low molecular weight toxins, accompanied by a relatively small loss of solutes of molecular weight of 5200 and above. On the other hand, if both high transmission rates of the low molecular weight uremic toxins (especially that of uric acid), as well as those of middle molecular weight metabolites (signified by inulin), are

TABLE III  
HTO and Metabolite Permeabilities and Fluxes  
Through the Annealed NYgAM + bisAMa<sup>a</sup> Membranes at 37°C<sup>b</sup>

No.	Permeant	HTO	Permeability (P) × 10 <sup>7</sup> ; (cm <sup>2</sup> s <sup>-1</sup> )				Selectivity		Performance	
			Urea	Uric acid	Raffinose	Inulin	I	II	I	II <sup>c</sup>
			(Flux <sup>b</sup> (F) × 10 <sup>5</sup> ); (cm s <sup>-1</sup> )						× 10 <sup>5</sup> (cm s <sup>-1</sup> )	
	MW	20	60	116	505	5200				
	Stokes radius (Å) <sup>d</sup>	1.13	1.75	3.87	5.48	14.7				
	D × 10 <sup>7</sup> (cm <sup>2</sup> s <sup>-1</sup> )	226	181	116	57.8	21.5				
	Graft yield (%)	Wet Thickness (μ)								
10	100	75 ± 5	44 ± 5	20 ± 2	10 ± 1	0.71 ± 0.07	62	28	5700	2580
			59	27	13.4	0.95)				
11	302	135 ± 5	57 ± 5	28 ± 2	13 ± 1	3.0 ± 0.3	19	9.3	1690	830
			42	21	96	2.2)				
7	506	135 ± 5	58 ± 4	26 ± 2	14 ± 1	2.9 ± 0.5	20	9.0	1380	620
			43	19	10.4	2.0)				
8	804	145 ± 5	48 ± 5	16 ± 2	6.7 ± 0.5	0.59 ± 0.06	81	27	5020	1670
			33	11	4.6	0.41)				
9	1194	165 ± 5	41 ± 3	12.1 ± 0.7	5.9 ± 0.4	0.24 ± 0.07	171	50	7870	2300
			(46)	7.3	3.6	0.14)				
Cell.		18 ± 1	16 ± 1	2.0 ± 0.3	1.4 ± 0.2	0.13 ± 0.02	74	15	6590	1340
			(89)	11	7.8	0.72)				

<sup>a</sup>5 min annealing in 65% aqueous solution of formic acid.

<sup>b</sup>The data in parentheses refer to the flux values (F), calculated as (P)/Wet-Thickness.

<sup>c</sup>Selectivity I = P(urea)/P(inulin); Selectivity II = P(uric acid)/P(inulin); Performance I = F(HTO) × Selectivity I; Performance II = F(HTO) × Selectivity II.

<sup>d</sup>The data for diffusion coefficients in 0.15 M NaCl solution and the radii of the metabolites were taken from Ref. 12.

TABLE IV  
The Ratio of the Flux Values of HTO and Metabolites  
Through NYgAM + *bis*AMa<sup>a</sup> Membranes to Those Through Cellophane

Permeant: Graft yield (%)	Relative flux values				
	HTO	Urea	Uric acid	Raffinose	Inulin
100	1.03	1.11	2.45	1.72	1.32
302	1.00	0.79	1.91	1.23	3.08
506	0.78	0.81	1.73	1.33	2.78
804	0.70	0.62	1.00	0.59	0.57
1194	0.52	0.47	0.66	0.46	0.19

<sup>a</sup>5 min annealing in 65% aqueous solution of formic acid.

required, the membranes in the range of 100–300% graft yield are preferable. At that graft yield range, the flux values of HTO and urea through the NYgAM + *bis*-AMa membranes are comparable to those through cellophane, while those of the uric acid, raffinose, and inulin are significantly higher (see Table IV).

Finally, it is necessary to comment on the relatively high flux of the uric acid through the annealed NYgAM + *bis*-AMa membranes. From the data in Table IV we observe that the ratios of the fluxes of uric acid through the NYgAM + *bis*-AMa to that through cellophane, at all grafting levels, is higher than the corresponding ratios for other solutes. The relatively high permeation of uric acid through the NYgAM + *bis*-AMa membranes could arise from an interaction between the accessible amide groups of the NYgAM membranes and the carboxylic groups of the uric acid. The occurrence of such a chemisorption mechanism could be expected to lead to enhanced solubility, hence to a higher permeability of uric acid through NYgAM membranes. This assumption is supported by a previous finding,<sup>6</sup> that immersion of NYgAM membranes in dilute aqueous solutions of ethylenediaminetetraacetic acid (EDTA) results in tenfold concentration of the latter solute in the aqueous domains of the water-swollen membrane, compared to that in the bulk of the solution.

## CONCLUSIONS

Crosslinking and annealing procedures applied to NYgAM membranes lead to an enhanced water uptake which manifests itself in an increase in the average pore size. The morphological changes in the modified NYgAM membranes cause a rise in the fluxes of water and small ionic solutes, as well as an extension in the spectrum of permeants which can diffuse through the membranes. Regarding transport of bromide solutes in the series HBr–Bu<sub>4</sub>NBr through the treated NYgAM membranes, the increase in the fluxes of the solvent and the ionic permeants is achieved with a sacrifice of the selectivity, resulting in membranes having permselectivity features comparable to those of cellophane.

The main advantage of the modifications of the grafted membranes, NYgAM + *bis*-AMa, appears to lie in the potential application to separation of organic solutes of biomedical interest. At 100% graft yield the flux of uric acid through the modified membranes is higher by a factor of about 2.5 than that through cellophane. In addition, the transport of the individual biological permeants, especially that of inulin, displays a marked dependence on the graft yield of the modified membranes. These characteristic features of the annealed modified membranes, NYgAM + *bis*-AMa, can be of value in clinical dialysis research and bioengineering applications.

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