

Grafting of Acrylamide to Nylon-6 by the Electron-Beam Preirradiation Technique. II. Kinetic Aspects and Film Permeability

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Synopsis

Single- and multilayered laminated nylon-6 films were grafted with acrylamide (AM) using the electron-beam preirradiation technique. Very high grafting yields were obtained within short time periods. Grafting onto single films was shown to proceed via "diffusion free" pseudo zero-order kinetics. Grafting onto multilayered films was diffusion controlled. SEM and EDAX measurements indicate uniform grafting of single-film membranes and asymmetric grafting of membranes prepared by grafting onto multilayered films. The permeability of grafted membranes to a number of permeants was found to increase with extent of grafting. The specific permeability to both water and solutes exceeded that of the dialysis grade cellophane at 500% graft. The selectivity of grafted films towards various solutes had also been found to be higher than that of cellophane.

INTRODUCTION

The electron beam induced graft copolymerization has recently been investigated.¹ It has been shown that grafting of the hydrophilic monomers onto nylon-6 imparts to the grafted films water permeabilities comparable to those of cellophane and polyvinylalcohol. Acrylamide (AM) has been found¹ to enhance effectively the water permeation properties of the grafted films.

In the present study the grafting range of AM was extended up to 1300% and the reaction parameters were investigated in detail. An attempt was also made to prepare asymmetrically grafted membranes and to establish transport properties of solutes through water-swollen AM-grafted nylon films (NYgAM). The electron beam preirradiation, inert gas grafting technique, was employed to produce such membranes at reaction times of 1–2 h. Other methods of grafting onto nylon-6 are considerably slower.^{2–6} The high extent of grafting of AM facilitates accumulation of free water in the membrane, thus increasing its permeability to solutes. The formation of NYgAM asymmetrically grafted membranes was explored in order to examine the possibility that such polymeric structures may combine high selectivity with high permeability to certain solutes.

EXPERIMENTAL

Grafting onto Single Nylon Layer

Biaxially oriented nylon-6 films, 13 μm thick (SNIA Viscoza, Italy) and acrylamide (AM, Cyanamide, C.P.) were used without further treatment. The electron beam preirradiation was carried out with a High Voltage Insulating Core Transformer Electron Beam Accelerator, 550 KV 20 mA Model, at room temperature. No special precautions were undertaken to remove air from the system. The irradiation was immediately followed by the grafting step. The experimental set up for grafting is shown in Figure 1. The preirradiated film was placed in the glass container B and an aqueous solution of the monomer in container A. The reaction vessels were immersed in thermostat at $50 \pm 1^\circ\text{C}$ and purged vigorously with CO_2 . Subsequently, the monomer solution was transported by syphoning from A to B. A slow bubbling of the CO_2 through the system has been maintained during the entire reaction period. The grafted films were rinsed thoroughly with running water and were dried to a constant weight in a vacuum oven at $50^\circ\text{C}/50$ bar.

Preparation and Grafting of Multilayered Laminates

Eight 13 μm thick nylon films were soaked with water, pressed together (at ca. 1 atm), and heated to 110°C . Edges of the laminates were welded. The welded areas were shielded during irradiation by 1 mm thick aluminum bars. Grafting onto the composites was performed following a similar technique to that used for thin films. After completing the grafting reaction, the edges of the laminates were cut, and soaked with water. The individual films were separated, washed, marked, and dried to constant weight in a vacuum oven.

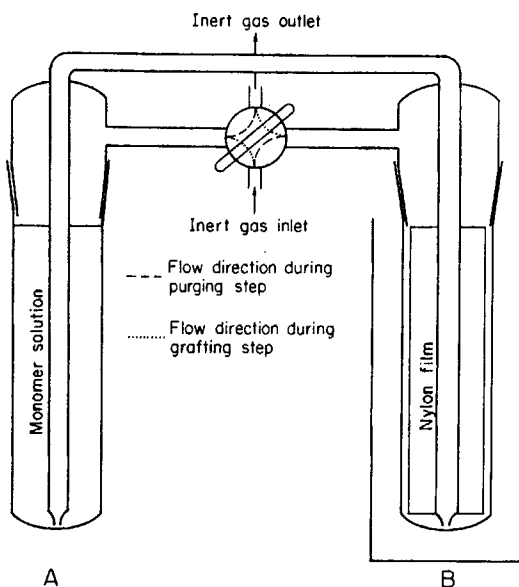


Fig. 1. Schematic representation of the experimental setup for grafting experiments: flow directions during purging step (---) and grafting step (.....).

Permeability Measurements

The transmission of water vapor through the membranes was determined as described elsewhere.¹ The dialytic cell shown schematically in Figure 2 was used for the water and salt permeability determinations. Tritium labelling was used for the water transport measurements. The radioactivity of the aliquot samples was determined with the Packed Tri Carb Liquid Scintillation Spectrometer Model 3320 employing Packard Insta-Gel Liquid Scintillator No. 6013009. Concentrations of halides were determined with the Aminco-Coltove Chloride Titrator Model No. 4-4419.B.

Scanning Electron Microscopy (SEM) Measurements

Grafted membranes were embedded in polyethylene, cut across the membrane, and immersed for 24 h in saturated solution of PdCl_2 . Samples were rinsed with distilled water, dried in vacuum, sputtered with gold, and photographed using the Super III-A-Model, ISI SEM. Concentrations of Pd and Cl were measured using the 711-EDAX attachment of the SEM.

RESULTS AND DISCUSSION

Grafting onto Single Nylon Film

The progress of grafting of AM onto 13 μm thick nylon-6 films, at different radiation doses and monomer concentrations, is shown in Figure 3. The monomer to nylon weight ratio was 100:1, 50:1, and 25:1 for 10%, 5%, and 2.5% solutions of AM, respectively. The high monomer/polymer ratio minimizes the effect of monomer depletion on grafting rates.¹ The salient feature of the results is the constant rate of graft yield growth during the first 15–20 min of the reaction, even though graft yields reach 500% within this period. This is a puzzling observation since one might expect fast radical termination in the grafted regions due to the increasing mobility of the radicals in the growing PAM chains, surrounded by absorbed water (cf. Fig. 4). For a preirradiation initiated grafting, the termination process should lead to a fast levelling off of the graft yield vs. time, unless there is a continuous supply of radicals to the system. We suggest that the observed behavior is due to gradual migration of radicals, originally

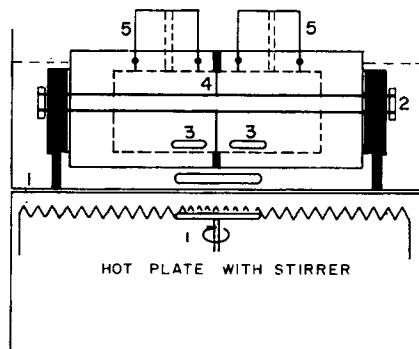


Fig. 2. Dialytic cell used in permeability measurements: (1) thermostated bath; (2) cell holders; (3) magnetic stirring bar; (4) membrane; (5) stopcocks.

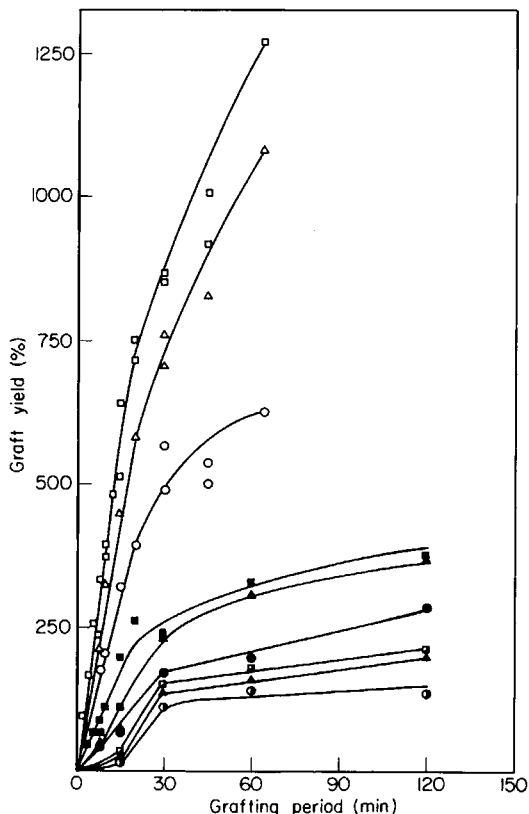


Fig. 3. Graft yield vs. time for single $13 \mu\text{m}$ thick nylon films. Temp = 50°C . The concentrations of AM in the grafting solutions of the experiments were 10% (\square , Δ , \circ), 5% (\blacksquare , \blacktriangle , \bullet), and 2.5% (\blacksquare , \blacktriangle , \bullet). Radiation doses (Mrads): 12 (\square , \blacksquare , \blacksquare), 8.4 (Δ , \blacktriangle , \blacktriangle), and 4.8 (\circ , \bullet , \bullet).

buried in the crystalline regions and not easily accessible to monomer. Supply of these radicals offsets the loss of radicals due to termination processes of the growing chains. Thus, an apparently constant rate of grafting can be maintained for 15–20 min.

In order to prove this hypothesis, films irradiated to 12 MR were immersed, prior to the grafting step, in deaerated hot water (50°C) for periods of 30 and 90 min, respectively. Figure 5 shows the progress of grafting vs. time, for such samples. Their initial grafting rate was very slow. Subsequently, the grafting rates increased to 18.5%/min and 12.5%/min, for samples kept in deaerated hot water for 30 and 90 min, respectively. The slow initial grafting rate of the samples treated in hot water are apparently due to decay of the free radical

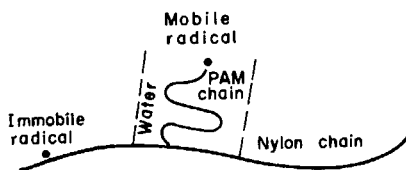


Fig. 4. Schematic illustration of the mobility of radicals in the water-swollen grafted membranes.

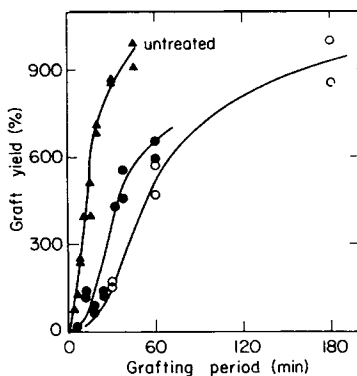


Fig. 5. Graft yield vs. time at 50°C for single 13 μm thick membranes submitted to thermal treatment after irradiation (but prior to grafting). Radiation dose 12 Mrad; grafting condition, 10% AM in water. (Δ) before thermal treatment; (\bullet) after 30 min in deaerated water at 50°C; (\circ) after 90 min in deaerated water at 50°C.

population in the water-swollen amorphous regions of the nylon. The subsequent increase of the grafting rates indicates that the supply of radicals from the crystalline to the amorphous regions plays, indeed, an important role during the grafting process. The fact that the rates of grafting, onto the water-treated samples, are lower and decline earlier than the rates of grafting onto the untreated samples is indicative of the decrease in the population of free radicals during storage in hot water. The existence of a "reservoir" of free radicals in the crystalline regions of irradiated nylon is also confirmed by the observation that the yellow color, characteristic of the nylon radicals,¹ persists when the grafting is terminated during the linear stage of the reaction.

The effect of the radiation dose on the initial grafting rate is shown in Figure 6. It is evident that the dependence of the grafting rate on the radiation dose displays a slightly negative deviation from linearity, which can be attributed to the fact that radical termination is proportional to $[\text{R}]^2$ while the propagation of the graft is proportional to $[\text{R}]^1$ only. This explanation does not apply, however, to the steep increase of the grafting rate in the region of low-radiation doses. We attribute such behavior to the formation of peroxy radicals during

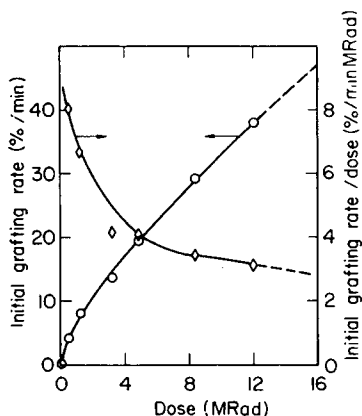


Fig. 6. The effect of the radiation dose on the initial grafting rate. (\circ) Grafting rates; (\diamond) grafting rates normalized for unit radiation dose. $[\text{AM}] = 10\%$.

irradiation of films which contain small amount of residual oxygen. Each of such peroxy radicals can yield three radicals:



The decomposition of the hydroperoxides [cf. eq.(2)] must lead to enhancement of the rate of grafting. The amount of occluded oxygen is small. Hence, the rate enhancement due to the formation of peroxy radicals will be significant at low radiation doses only.

Grafting onto Multilayered Nylon Assemblies

The distribution of graft yields across the multilayered laminated films is summarized in Table I for various radiation doses, monomer concentrations, and grafting periods. After separating the laminate into discrete layers, the graft yield of the outer layers was determined by comparing their weight with that of the innermost layers, which did not undergo any grafting at all (as established by water absorption and IR measurements). It is evident from Table I that only the outermost layers are grafted while the inner ones are totally unmodified at the grafting conditions employed (12–24 Mrads preirradiation, 10–30% AM concentration, 16–60' grafting period).

For the bilaterally grafted 13 μm thick nylon films the diffusion of monomer into the film seems to be faster than its consumption by grafting. The reaction

TABLE I
Average Graft Yields (wt %) in Various Layers of Multilayered Nylon Laminate

No.	Radiation dose (Mrads)	Concn of acrylamide (%)	Time (min)	Layer no.							
				1	2	3	4	5	6	7	8
1	12	10	60	419	255	85	0	0	0	6	60 ^a
2 ^b	12	10	60	332	176	29	0	0	0	0	16 ^a
3	12	10	20	213	3	0	0	0	0	0	1 ^a
4	24	10	16	60	0	0	0	0	0	0	58
5	24	10	20	199	0	0	0	0	0	0	163
6	24	10	23	307	0	0	0	0	0	0	219
7	24	10	60	1000	407	29	0	0	0	72	758
8	24	20	16	230	0	0	0	0	0	14	363
9	24	20	19	300	10	0	0	0	0	0	318
10	24	20	20	432	7	0	0	0	0	4	481
11	24	30	16	128	0	0	0	0	0	0	120
12	24	30	20	405	1	0	0	0	0	1	470
13	24	30	30	888	28	0	0	0	0	15	642
14	48	10	16	53	0	0	0	0	0	0–1	481
15	48	10	20	78	1	0	0	0	0	1	79
16	48	20	16	264	1	0	0	0	0	2	287
17	48	20	20	328	20	0	0	0	0	1	321
18	48	30	16	450	62	0	0	0	0	0	200
19	48	30	20	322	47	0	0	0	0	3	360
20	48	30	20	327	14	0	0	0	0	0	367

^a 10-layer laminate.

^b 0.05% bisacrylamide added to the monomer solution.

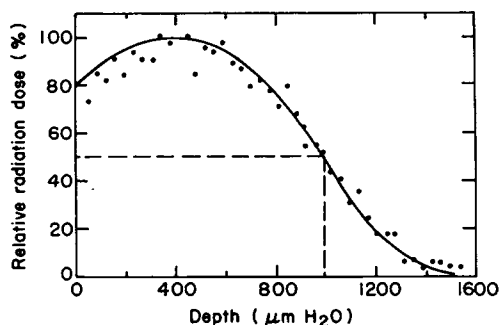


Fig. 7. The distribution of the radiation dose across a multilayered laminate.

kinetics is "diffusion free," and a virtually homogeneous distribution of grafting yields is obtained. The grafting rates become, however, diffusion controlled when the thickness of the nylon substrate is increased, e.g. by lamination of several layers. One must bear in mind that the two different grafting mechanisms are observed in spite of the uniform radical concentration generated by radiation in both single and multilayered films. Typical distribution of the radiation dose across a multilayered system is shown in Figure 7, for the 550-kV electron beam accelerator used in these experiments. From data in Figure 7 it can be concluded that the absorbed radiation dose remains nearly constant up to the thickness of ca. 700 μm (47 layers of 13 μm thick nylon-6).

The asymmetric character of thus prepared membranes is evident from the inspection of SEM picture shown in Figure 8. Two distinct regions are observed in such a membrane, removed from the multilayered laminate, after it is stained

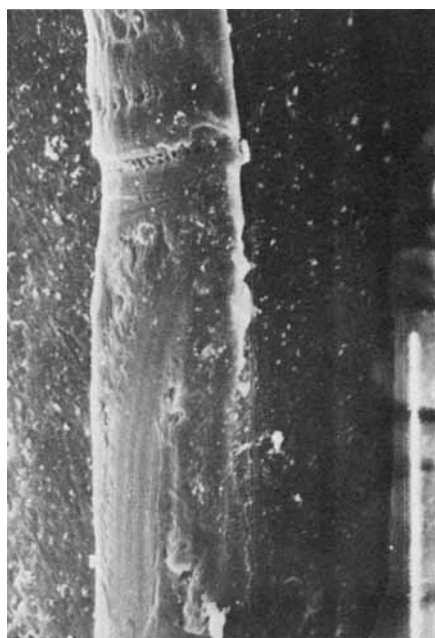


Fig. 8. SEM picture of palladium stained unilaterally grafted outer layer of a multilayered laminate; radiation dose 24 Mrad. Grafting yield 318%. Tilt of the membrane crosssection = 40°. Magnification $\times 333$.

by immersion in aqueous solution of PdCl_2 . The same treatment of a bilaterally grafted single membrane yields a completely uniform material, although the average grafting yield of the former and of the latter membrane is identical (318%). The sharp boundary between the stained and the unstained regions of the unilaterally grafted membrane indicates that the diffusion proceeds by a "progressive shell" mechanism.⁷⁻⁹ Apparently, the rate of diffusion of the water-soluble monomer increases drastically when AM is grafted into nylon, and at a critical grafting yield the reaction becomes "diffusion free." Obviously, the local critical graft concentration corresponding to such transition is attained at a much lower average grafting yield for a bilaterally grafted membrane than for the unilaterally grafted laminate.

The concentration of PdCl_2 in the membrane may be expected to be proportional to the concentration of PAM in the grafted nylon, since only the former amide is capable to form complexes with the palladium ions. Accordingly it is reasonable to assume that the concentration profile of Pd^{2+} and Cl^- in the membrane reflects on the concentration profile of PAM. Concentrations of palladium and of chlorine across the membranes, determined with EDAX attachment to SEM, are depicted graphically in Figure 9. Such quantitative measurements confirm the qualitative conclusions based on visual inspection of picture shown in Figure 8. The asymmetric character of the unilaterally grafted membranes indicated by scanning electron microscopy has also been confirmed by preliminary ESCA measurements. Both SEM and ESCA results are indicative of the concentration gradients of PAM across the membrane. They are insensitive to changes in grafting yields when the grafting yields are

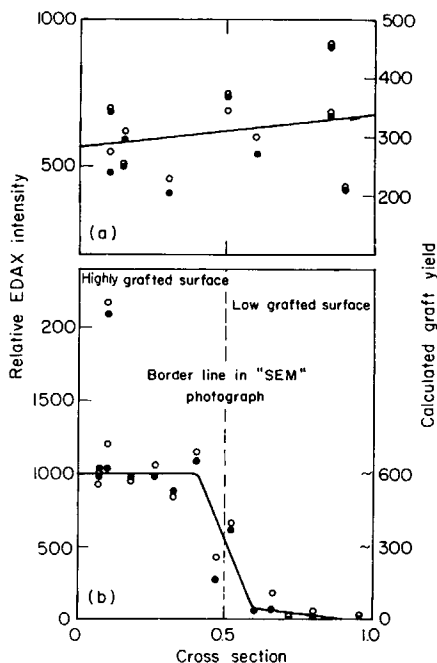


Fig. 9. Concentration profiles of Palladium (●) and chlorine (○) in a grafted membrane stained with PdCl_2 . Graft yield 318% AM. (a) Bilaterally grafted single film, radiation dose 12 MRad; (b) unilaterally grafted outer layer of a multilayered laminate, radiation dose 24 Mrad.

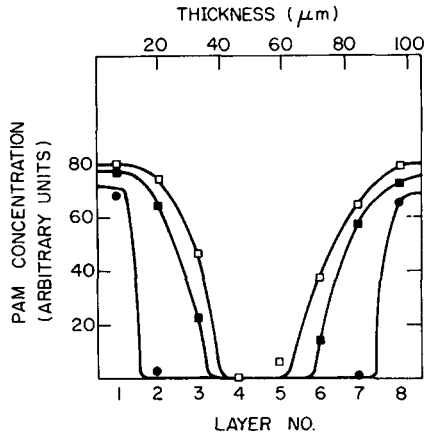


Fig. 10. Schematic representation of the concentration profiles of AM in the unilaterally grafted multilayered laminate. Radiation dose 12 MRad; concentration of AM in grafting solution 10%. Grafting times (min): (●) 20; (□, ■) 60. (■) 0.05% bisacrylamide added.

high, e.g., an increase from 400% to 700% in the grafting yields corresponds to an increase in the concentrations of PAM in the membrane from 80% to 87% only. The average grafting yields of the individual layers of the multilayered laminate, determined gravimetrically from their respective weight increase (cf. Table I), were used together with SEM results for the evaluation of the concentration profile of PAM in the unilaterally grafted multilayered systems. Results are shown schematically in Figure 10.

Water and Salt Permeation through Grafted Membranes

Figure 11 shows the water vapor transmission rates GTR of the NYgAM

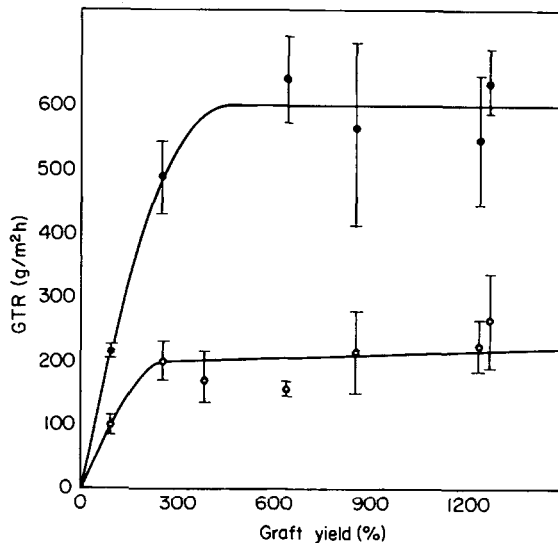


Fig. 11. Water vapor transmission as function of grafting yield of the bilaterally grafted nylon-6 film, the pervaporation (●) and the evaporation (○) experiments.

membranes measured by the evaporation and prevaporation procedures (cf. Ref. 1). Water transmission rates increased up to 300% graft yield because of the corresponding large changes in the chemical composition which affect both the solubility and the diffusion coefficient of water in the membranes (cf. Fig. 12). However, they level off at higher graft yields. In the "plateau" region the rates of water transmission through the grafted membranes are by ca. 50% higher than the rates of water transmission through an 18 μ thick cellophane.

The thickness of the unoriented nylon films increases by 12% only¹ at a grafting yield of 100%. However, for the presently investigated, highly oriented films, a considerable increase in thickness, due to grafting, is noted. Such films cannot undergo area expansion when grafted, because of the highly stretched state of the polymeric chains. Hence, the volume increase manifests itself by an increase in thickness. A further increase in the thickness of the grafted membranes occurs when they are swollen by water. Levelling off of the water transmission rates at higher graft yields may be due to the compensating effects of increase of the values of permeability coefficients and of membrane thickness.

The permeabilities of grafted membranes to water and permeants of varying size are summarized in Table II. They are compared with those obtained for a cellophane film. It is evident that the permeabilities of all investigated molecules and ions increase with the increased grafting yields. Permeability of the NYgAM films to water, NH_4Br , and KBr exceeds the permeability of cellophane, when their grafting yield exceeds 500%. At such graft yield the NYgAM membranes are highly swollen by water. Hence, it may be assumed that the permeating salts are dissociated into free ions. Note that the ionic radius of the NH_4^+ and of the K^+ cations are nearly identical (ca. 2.8 Å). The permeability of the NYgAM membranes towards HBr is the highest among the investigated bromides. For membranes at low grafting yields, this may perhaps be attributed to the solubility of HBr in the organic phase, since such membranes contain "bound" water only. However, the highly water-swollen, highly grafted membranes contain "free" water. Permeation of HBr , dissociated into free ions, must be related to the fast diffusion of protons which "drag" with them the Br^- as counterions. Differences in the relative permeabilities to water and HBr of cellophane and of NYgAM at different grafting yields may be explained in a

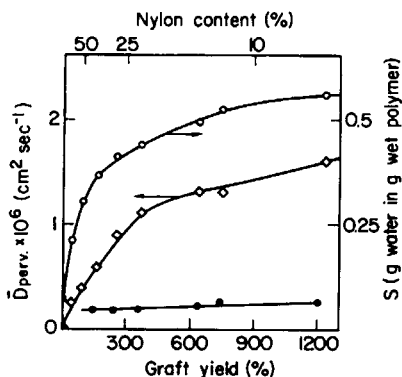


Fig. 12. Solubility of water and average values of the diffusion coefficients as function of graft yield of the bilaterally grafted nylon-6 film: values of \bar{D}_{perv} (\square) and S (\circ , \bullet), samples equilibrated in water (\circ) and in air with 30% humidity (\bullet).

TABLE II
Water and Salt Permeability through NYgAM Membranes at 37°C

Membrane	Permeant Stokes radius of cation ^a (Å)	Graft yield (%)	Thickness (μm)	Permeability coefficient (P) (10 ⁷ cm ² ·s ⁻¹)						HTO	Flux × 10 ⁵ (cm·s ⁻¹)		Performance (cm·s ⁻¹) Flux × 10 ⁵ ×	
				Pr ₄ NBr	Et ₄ NBr	Me ₄ NBr	NaBr	1.25 ^b	1.25 ^b		1.25 ^b	0.26 ^b		$\frac{P_{\text{HBr}}}{\delta}$
1	204	48 ± 1	10	0.066 ± 0.006	0.073 ± 0.008	0.16 ± 0.01	0.26 ± 0.02	0.83 ± 0.05	0.90 ± 0.08	1.0 ± 0.06	3.9 ± 0.2	8 ± 1	59 ± 9	472
2	249	57 ± 1	—	0.11 ± 0.1	0.19 ± 0.02	0.42 ± 0.03	0.65 ± 0.06	2.2 ± 0.1	2.8 ± 0.2	2.8 ± 0.2	10.2 ± 0.6	18 ± 1	93 ± 15	1674
3	582	92 ± 1	16	0.71 ± 0.05	1.08 ± 0.07	2.3 ± 0.2	3.6 ± 0.3	9.0 ± 0.6	11.3 ± 0.7	11.8 ± 0.5	24 ± 2	26 ± 3	34 ± 5	884
4	856	125 ± 5	50	1.2 ± 0.2	—	4.2 ± 0.5	5.9 ± 0.6	15 ± 2	18 ± 2	18 ± 2	39 ± 3	31 ± 9	33 ± 9	1023
5	1270	140 ± 5	116	1.8 ± 0.2	3.0 ± 0.3	6.2 ± 0.5	9.6 ± 0.9	18 ± 1	24 ± 2	23 ± 2	51 ± 5	36 ± 5	28 ± 7	1008
6/8 ^c	470 ^d	100 ± 10	—	0.24 ± 0.03	—	0.38 ± 0.05	0.6 ± 0.1	—	2.0 ± 0.3	2.0 ± 0.3	16 ± 3	16 ± 5	67 ± 33 ^e	1072
6/8 ^c	470 ^d	100 ± 10	—	0.21 ± 0.04	—	—	—	—	—	—	11 ± 2	11 ± 3	52 ± 30 ^f	572
Cellophane	18 ± 1	—	16	2.6 ± 0.4	3.1 ± 0.4	5.2 ± 0.5	6.4 ± 0.9	9.1 ± 0.9	12 ± 1	11 ± 1	13 ± 1	73 ± 12	5 ± 1	365

^a Ref. 10, p. 120.

^b Calculated from values of limiting equivalent conductivities (Λ⁰), Ref. 10, p. 454.

^c Unilaterally grafted asymmetric membrane.

^d Average graft yield of the second layer. Average graft yield of the adjacent layer is 1%.

^e High graft surface faces the salt compartment of the dialytic cell.

^f Low graft surface faces the salt compartment of the dialytic cell.

similar fashion. The relationship between $P_{\text{H}_2\text{O}}$ and P_{HBr} may, therefore, reflect on the relative amounts of free and associated water in the grafted membranes. The relative selectivities of the NYgAM membranes towards various bromides are summarized in Table II (cf. column 14). We defined the selectivity parameter S as the ratio between the flux of HBr and the flux of tetrabutylammonium bromide through the membrane. Inspection of the tabulated values of S shows that NYgAM membranes are definitely more selective than cellophane. The selectivity of the grafted membranes decreases as graft yield is increased. However, the increase in flux is moderate. Comparison of the values of the performance factors, defined as flux multiplied by selectivity, makes this even more evident. The highest performance factor is obtained for 250% of graft. At higher graft yields the performance factor decreases and it levels off at ca. 600% graft. While both the permeability and the selectivity of the AM-grafted membranes is higher than that of cellophane, the actual flux of HBr through the highly grafted membranes is lower than through an 18 μm thick cellophane film. This is due to the fact that the grafted membrane is five times as thick as cellophane used for comparison. It must be stressed that the increase in thickness, due to grafting, is a general phenomenon accompanying grafting onto oriented films.¹¹

The polyacrylamide (PAM) content of the grafted films approaches 90% at high graft yields. Such membranes may actually be regarded as PAM cross-linked by nylon. The insolubility in water of these PAM membranes must be attributed to crosslinking. Their water uptake is, however, very high and it may exceed 50% (cf. Fig. 12). Large fraction of water absorbed by such membranes is obviously in the form of "free water." Indeed, the permeability coefficient of HTO through membrane No. 5 (cf. Table II) divided by the solubility of water in such a highly grafted membrane (cf. Fig. 12) yields $D_w^{37^\circ} = 2.1 \times 10^{-5} \text{ cm}^2/\text{s}$, a value only slightly lower than that of the self-diffusion coefficient of water.

CONCLUSIONS

The electron beam induced grafting of acrylamide on nylon films provides a fast and convenient method of preparation of hydrophilic membranes in a wide range of compositions. A variety of possible applications, such as RO, dialysis, and supports for anchored drugs or enzymes, may be envisaged for such membranes. It seems that their performance may be enhanced by grafting them in an asymmetric fashion.

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