

Nylon 6 Water-Permeable Membranes Prepared by Electron Beam Radiation-Induced Graft Copolymerization

YAIR HARUVY and ARYEH L. RAJBENBACH, *Pure and Applied
Radiation Chemistry Department, Soreq Nuclear Research Centre, Yavne,
Israel*

Synopsis

Nylon 6 films, 25 μm thick, were grafted with polar monomers in aqueous solution following preirradiation with a 550-kV electron beam accelerator. The graft yield rose linearly with grafting period up to 100% graft and leveled off at a graft yield above 150%. At 100 to 200% graft of several acrylic acid derivatives onto the nylon 6 films, water permeation rates comparable to those of PVA and cellophane films were observed. These high water permeation rates of the grafted nylon films were considered as an indication that some of the acrylate copolymers penetrated throughout the matrix of the host polymer. The highest rates of water permeability were observed in nylon acrylamide grafts.

INTRODUCTION

Graft copolymerization of vinyl monomers on polyamides has been extensively studied and the subject has been reviewed in detail.¹⁻³ Ionizing radiation, which is a convenient method for the generation of free radicals, has been the preferred method of graft initiation. Most of the investigations were instigated to modify surface properties of polyamide fibers and fabrics. Recently, Hayakawa and co-workers⁴ measured the modification of water-vapor permeation rates in nylon films upon grafting with methyl methacrylate (MMA), vinyl acetate (VAC), and vinylpyrrolidone (VPY). The authors did not observe a significant modification of water permeation of Ny-g-MMA and Ny-g-VAC films. Only Ny-g-VPY films displayed a very pronounced increase in H₂O vapor transmission rates. At the highest extent of grafting (about 250%), the permeation rate was about 10 to 11 times higher than through the untreated nylon films. The grafting method employed by Hayakawa and co-workers involved several hours of gamma-irradiation of degassed samples containing nylon films immersed in aqueous monomer solutions. In a few cases, nylon films were irradiated in air at -78°C and subsequently exposed to monomer solutions at 40°C for periods of 24 to 140 h.

In the present study, an effort was made to establish whether intense irradiation of nylon films in air with an electron beam accelerator (EBA) followed by short exposure to aqueous solutions of acrylic acid and its hydrophilic derivatives, such as acrylamide (AM), methacrylamide (MAM), hydroxyethyl acrylate (HEA), hydroxyethyl methacrylate (HEMA), methacrylic acid (MA), and acrylic acid (AA), would lead to a significant increase in water permeation rates. A short exposure of 0.025-mm-thick nylon films to EBA irradiation results in

relatively dense radical population throughout the substrate matrix. Subsequent immersion of the irradiated film in deaerated aqueous solutions of acrylates at 50°C for a period of several minutes should lead to high graft yields of relatively short chains. The penetration of acrylic grafts throughout the nylon film should provide good anchoring for water molecules, thereby establishing favorable conditions for high rates of H₂O vapor transmission throughout the treated films.

It should be noted that the preirradiation method employed in this study is not encumbered by a significant extent of homopolymerization of the acrylic monomers as opposed to systems in which the substrate and monomer are simultaneously irradiated.

EXPERIMENTAL

Grafting Procedure

Samples of nylon film were irradiated in air at room temperature with an insulating core transformer electron beam accelerator (550 kV, 20 mA, high-voltage model) to a total dose of about 10 Mrad and then transferred to a two-arm glass reactor. The film was introduced into the main arm, equipped with a break seal, and connected to a vacuum system through the open end, which was sealed off after evacuation. The monomer solutions were placed in the side arm and after degassing were poured into the main arm through the crushed break-seal. Subsequently, the closed reaction vessel containing the irradiated nylon film immersed in monomer solution was placed in a thermostat.

Water Vapor Permeability Measurements

The water vapor permeability was tested gravimetrically in a controlled environment box held at $37 \pm 1^\circ\text{C}$ and a relative humidity of $30 \pm 5\%$. The measurements were carried out using the conventional cup method following the procedure described in ASTM 96-66B for the determination of evaporation and pervaporation rates, the latter determination referring to a condition whereby the cup is inverted so that the water is in contact with the specimen surface at all times during the test. In several cases when significant dimensional variations were observed within the period of measurement, cotton poplin supports were applied on both sides of the grafted films.

Spectrophotometric Evaluation of Radical Decay

The radical decay rate in irradiated nylon films was evaluated by following the changes in optical absorption at 355 nm.⁵ The measurements were carried out in air at room temperature using a Carl Zeiss PMQ II model spectrometer.

Thermoanalytical Measurements

The heat of fusion of nylon 6 films was measured by the differential scanning calorimetry technique employing a du Pont 990 thermal analyzer. The temperature at the maximum of the thermogram was taken as the melting point, and the heat of fusion was calculated from the area under the endotherm.

RESULTS AND DISCUSSION

Radical Decay

When polyamides are subjected to high-energy radiation, the predominant free radical species is formed by the removal of a hydrogen atom from the α -carbon adjacent to the amide group.⁶ The radical formation gives rise to the appearance of transient color. Thus, the decay of the free radical population in irradiated nylon 6 films can be followed by optical measurements at 355 nm.⁶ The quenching of radicals in nylon 6 films irradiated at room temperature at a dose of 20 Mrad is shown in Figure 1. Experimental difficulties precluded the evaluation of quenching processes at a dose of 12 Mrad which was employed in the grafting experiments. However, the finding of Zimmerman⁶ indicate that the radical termination rates at both doses are quite close.

From the data in Figure 1, we can conclude that within the 15-min interval between the radiation and grafting, only 10% of the radicals decay. The observation that after 24 and 144 h, respectively 32 and 31% of the radical population persists is indicative of the relatively high crystallinity of the nylon 6 films used. These findings are consistent with the conclusions derived from differential scanning calorimetry measurements. Using the procedure of Brennan⁷ and others,^{8,9} we estimate that the crystalline fraction of the films employed is $37 \pm 2\%$. The fast grafting process, which occurs within the period of up to 10 min, during which time the irradiated samples are immersed in the monomer solution, is most likely confined to the amorphous region. Thus, we can conclude that, under our experimental conditions, about 85% of the radicals initially generated in the amorphous region of the 25- μm -thick nylon films used in the experiments are still present at the onset of the grafting process.

Grafting of Acrylic Monomers onto Nylon 6 Films

Figures 2 through 4 show the increase in the extent of grafting with time of the nylon films, preirradiated at a dose of 12 Mrad, upon exposure to aqueous solutions at 50°C. In the case of AM and MAM, the grafting data refer to 10% solutions, since at higher solute concentrations a significant extent of gelation in the solution was encountered. The weight ratio of monomer to nylon was

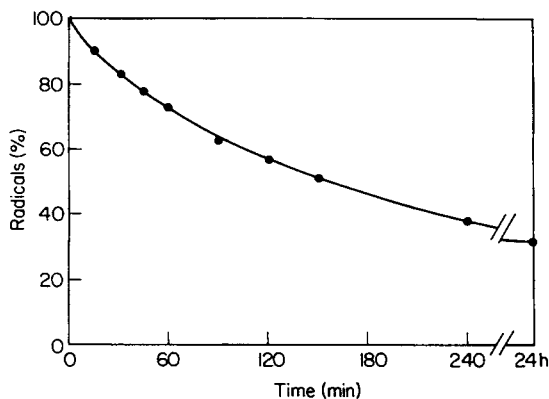


Fig. 1. Decay of radicals in nylon 6 films, 25 μm thick, irradiated at a dose of 20 Mrad. Data obtained from optical density measurements at 355 nm vs. time at 25°C.

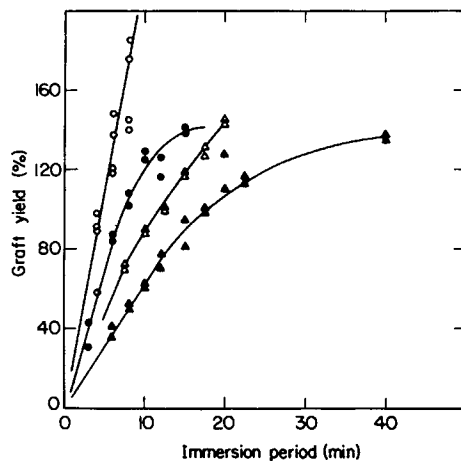


Fig. 2. Percent grafting of AM and MAM on preirradiated nylon 6 films vs. time of immersion at 50°C in 10% aqueous solutions at different monomer-to-nylon weight ratios R : (O) AM, $R = 5$; (●) AM, $R = 2.5$; (Δ) MAM, $R = 5$; (▲) MAM, $R = 2.5$.

changed from 2.5 to 5.0 in order to avoid the effect of depletion of the monomer solution.

For the other monomers, grafting data for 10 and 25% solutions (and weight ratios of 2.5 and 6.25) were recorded. The plots indicate that in all cases grafting proceeded very rapidly. The "induction period" of about 1 min reflects the nonzero heating time; thereafter, grafting yields of 100 to 200% are obtained within a period of 10 to 30 min. The fastest rate of grafting was observed in 25% HEA solution. In the 10% monomer solutions, AM was the most efficient grafting agent; its grafting rate was comparable to that observed in 25% HEA solution. The rate of grafting decreases with time and, in the majority of cases, after a gain of approximately 100% of graft. In the 10% solutions, the decrease

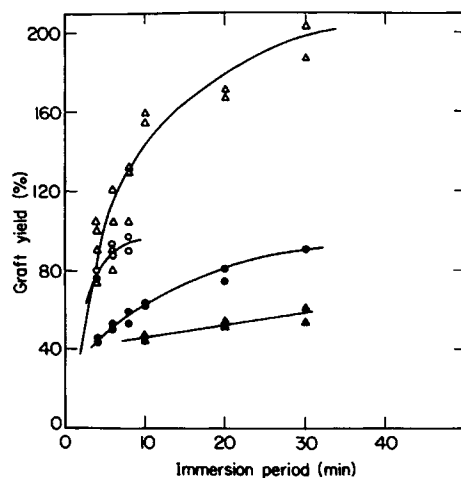


Fig. 3. Percent grafting of MAA and AA on preirradiated nylon 6 films vs. time of immersion at 50°C in aqueous monomer solutions at different monomer-to-nylon weight ratios, R : (Δ) 25% MAA aqueous solution, $R = 6.25$; (▲) 10% MAA solution, $R = 2.5$; (O) 25% AA solution, $R = 6.25$; (●) 10% AA solution, $R = 2.5$.

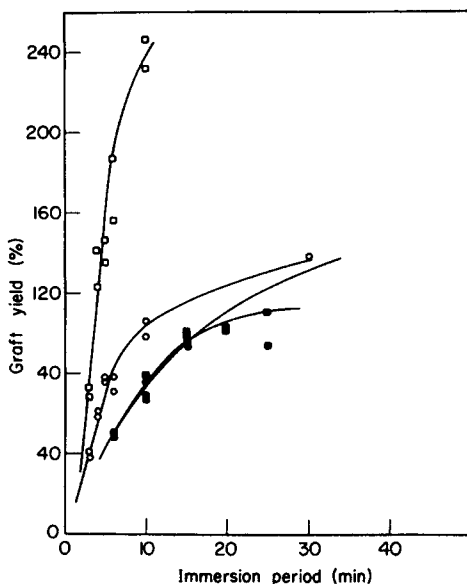


Fig. 4. Percent grafting of HEA and HEMA on preirradiated nylon 6 films vs. time of immersion at 50°C in aqueous monomer solutions at different monomer-to-nylon weight ratios, R : (□) 25% HEA solution, $R = 6.25$; (■) 10% HEA solution, $R = 2.5$; (○) 25% HEMA solutions, $R = 6.25$; (●) 10% HEMA solution, $R = 2.5$.

in the rate of grafting with time reflects, to a large extent, the depletion in monomer concentration, since the initial monomer/nylon weight ratio is only about 2.5. Figure 2 shows that when this ratio is increased, no significant decrease in grafting rate with time is observed.

A more intrinsic reason for the decrease in grafting rate with time could lie in the interplay of diffusional parameters on rates of graft chain propagation and radical termination. It can be easily visualized that the diffusion of aqueous monomers into the nylon backbone is facilitated by the successive formation of grafted acrylate layers. However, upon an increase in the extent of graft, the mobility of the growing acrylic chain in the swollen structure is progressively enhanced, facilitating the radical termination process. It should be mentioned that the grafting process caused significant surface extension (up to 30% in length and width at 100% graft), but very little thickening of the film was observed.

Effect of Temperature on Grafting

The effect of temperature on the rate of grafting was investigated in the case of preirradiated nylon samples immersed in 10% AM solutions. The data plotted in Figure 5 refer to graft yields obtained after a 10-min grafting reaction in the temperature range 25–50°C. The maximum graft yield was observed at 45°C. This temperature is close to the T_g of nylon 6.¹⁰ Thus, it appears reasonable to assume that the decrease in graft yield above 45°C reflects the increase in rate of chain termination reactions due to enhanced nylon backbone mobilities at $T \geq T_g$.

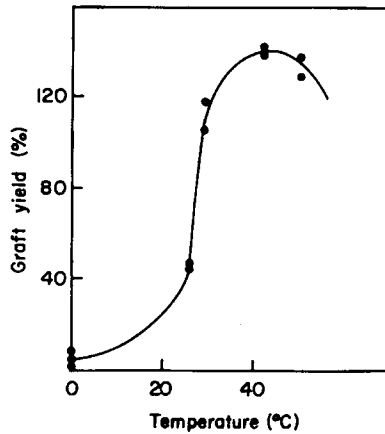


Fig. 5. AM graft yields obtained after a 10-min grafting period at different temperatures (10% AM solution, $R = 2.5$).

Water Permeability of Grafted Films

The rates of liquid and vapor water permeability through grafted nylon films are shown in Figure 6. Except for Ny-g-MAA, the pervaporation rates of the grafted films show a pronounced increase in permeability with extent of grafting up to about 100% graft.

The difference in the effectiveness of the various acrylic monomers in imparting water transport properties to the nylon 6 films can be appreciated from the data in Table I. This table lists data on evaporation and pervaporation rates through 100% grafted films as well as commercial PVA and cellophane films of

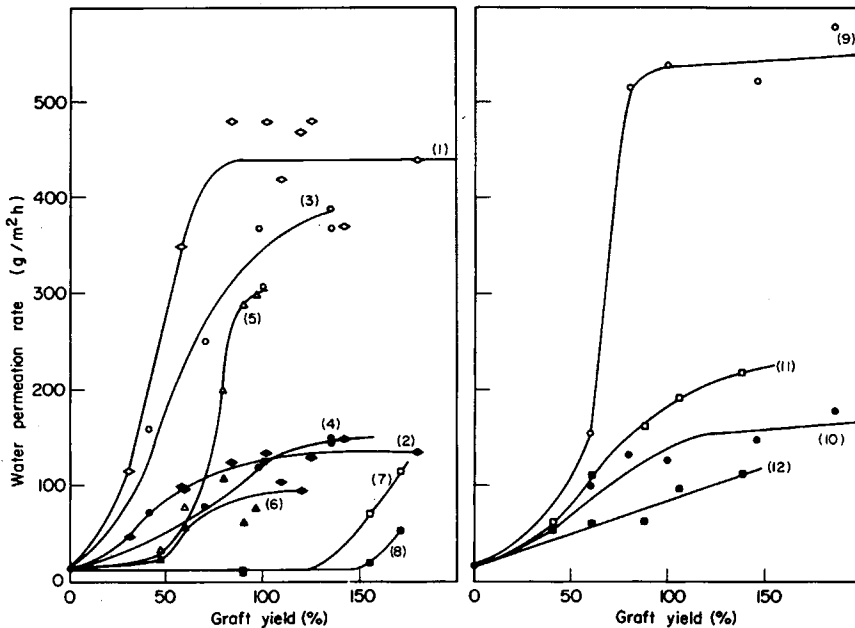


Fig. 6. Pervaporation and evaporation data of Ny-g-AM (1), (2); Ny-g-MAM (3), (4); Ny-g-AA (5), (6); Ny-g-MAA (7), (8); Ny-g-HEA (9), (10); Ny-g-HEMA (11), (12).

TABLE I
Water Permeability of 100% Grafted Nylon 6 Films

System	Thickness, μm	Pervaporation, $\text{g}/\text{m}^2\cdot\text{h}$	Evaporation, $\text{g}/\text{m}^2\cdot\text{h}$
Ny-g-AM	28	420 ± 40	120 ± 20
Ny-g-MAM	28	370 ± 70	120 ± 12
Ny-g-AA	28	380 ± 80	80 ± 20
Ny-g-MAA	28	16 ± 1	14 ± 1
Ny-g-HEA	28	290 ± 60	90 ± 25
Ny-g-HEMA	28	110 ± 10	46 ± 4
PVA	50	300 ± 50	45 ± 5
PVA	30	350 ± 60	60 ± 10
Cellophane (dialysis grade)	10	420 ± 50	170 ± 20

comparable thickness. The difference in H_2O permeability rates through the different films most likely reflects the difference in water affinity of the various monomers employed.

CONCLUSIONS

The results of this investigation indicate that water transport properties of nylon 6 films can be drastically improved by electron beam radiation-induced grafting of acrylic acid derivatives. The radiation technology process employed is very rapid, and graft yields of 100% and more are obtained within a period of less than 30 min.

Some of the grafted films are being evaluated for use as dialysis membranes, and work is in progress to establish transport properties of inorganic salts and metabolites.

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