

## **Grafting onto TEDLAR films by the electron beam preirradiation technique**

### **I. Grafting with acrylamide in aqueous solution**

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#### Summary

Polyvinylfluoride (tedlar) films, 12.5-25  $\mu\text{m}$  thick, were grafted with acrylamide monomer (AM) in an aqueous solution, following preirradiation with a 550 kV electron beam accelerator. The graft yield rose with grafting period up to 285% and 475%, for the 25  $\mu\text{m}$  and the 12.5  $\mu\text{m}$  tedlar films, respectively, and then levelled off due to gelation of the solution.

Water permeation rates through the tedlar films were increased, upon grafting with AM, by a factor of up to 3. Water permeation rates through the tedlar grafted with acrylamide (TEDgAM) films were relatively low, as compared with those of cellophane films or nylon grafted acrylamide films (NYgAM) of comparable thickness, implicating that only part of the tedlar film cross-section has been penetrated through by the grafted copolymer. The highest rates of water permeability were observed in 12.5  $\mu\text{m}$  films grafted with 475% acrylamide.

#### Introduction

Radiation induced graft copolymerization onto fluoropolymers has been widely investigated, especially onto polytetrafluoroethylene (PTFE) (1-4). Minor effort has been directed to the investigation of radiation induced grafting onto other fluoropolymers (5-8). Poly-vinylfluoride (Tedlar) films have excellent mechanical properties, good inherent barrier properties (9) and, conversely to PTFE, is highly resistant to radiation induced damage (10). These characteristics make it an attractive substrate candidate for radiolytic grafting with hydrophilic monomers, aimed at the preparation of permselective membranes. The resistivity of tedlar to the penetration of water may generate an obstacle for grafting with aqueous solutions of hydrophilic monomers. This may lead to low grafting rates and difficulty in grafting throughout the tedlar film, a requirement which is necessary for the preparation of water permeable membranes.

In previous communications (11-14) we have reported about methods for fast radiation induced graft polymerization of hydrophilic monomers onto nylon films, especially grafting of AM. The NYgAM membranes thus prepared exhibited high permeability to water and solutes and permselectivity features which could be modified by the preparative parameters of the grafting process. In the present investigation we try to adapt

these methods to the fast grafting of hydrophilic monomers onto tedlar, aiming at graft penetration throughout the substrate film, thus forming a water permeable membrane. Acrylamide was chosen as the preferred monomer due to its ease of handling and the promising characteristics of membranes prepared by grafting it onto nylon (13) and polyethylene films (15).

### Experimental

#### Grafting Procedure

Tedlar films, 12.5 and 25  $\mu\text{m}$  thick (DuPont) and acrylamide (Cyanamide, C.P.) were used without further treatment. Weighted samples of the tedlar film were irradiated at room temperature, with a High Voltage Insulating Core Transformer Electron Beam Accelerator, 550 kV 20 mA model, to a total dose of 6-31 Mrads. No special precautions were undertaken to remove air from the system. The irradiation was immediately followed by the grafting step. The experimental set-up is shown in Fig. 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 a bath thermostatted at  $50 \pm 1^\circ\text{C}$  and purged vigorously with  $\text{CO}_2$ . Subsequently, the monomer solution was transported by syphoning from A to B. A slow bubbling of  $\text{CO}_2$  through the system has been maintained during the entire reaction period. The grafted films were rinsed thoroughly with running water and dried to a constant weight in a vacuum oven at  $50^\circ\text{C}/50$  mbar.

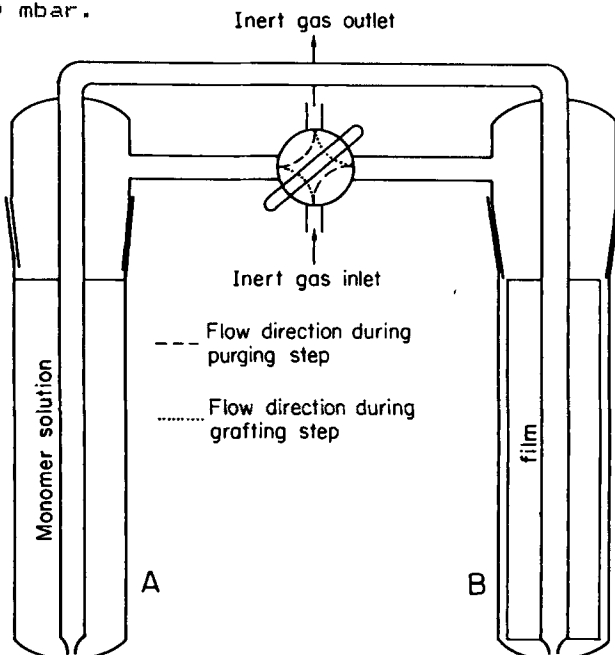


Fig. 1: Experimental setup for grafting experiments in an inert atmosphere. Flow direction: (----) during the purging step and (.....) during the grafting step.

### Measurements of Water Vapor Permeability

The water vapor permeation rates through the grafted films were determined gravimetrically in a controlled environment chamber 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 a modified version of 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 surface of the specimen at all times during the test.

### Results and Discussion

Graft yields of tedlar films grafted with AM under various experimental conditions, namely radiation dose, monomer concentration and grafting period, are displayed in Table I. Performing of the grafting step immediately after the preirradiation was found to be crucial, due to the fast decay of the radicals in the tedlar films, manifested by the gradual disappearance of the reddish color of the radical species in tedlar. Early experiments have shown that at radiation doses of 12 Mrads and lower, which were found useful in the grafting of AM onto nylon (11), graft yields of a few percent (#1 in Table I) were attained after a grafting period of an hour and longer. Increasing the dose to 18 Mrads led to measurable but poor graft yields onto 25  $\mu\text{m}$  tedlar films, at a monomer concentration of 10% (#2-4 in Table I), thus monomer concentrations of 20% and higher were utilized (#5-14), with the penalty of earlier gelation of the AM solution (initiated by chain transfer of radicals from the grafted film to the monomer). Under these experimental conditions, a graft yield as high as 285% was attained after 30 min, just before the occurrence of severe gelation of the monomer solution.

Table I: Experimental Grafting Conditions and Graft Yields

No.	Radiation dose (Mrad)	Tedlar thickness ( $\mu\text{m}$ )	Monomer conc. (%)	Grafting temperature $^\circ\text{C}$	Grafting period (min)	Graft yield (%)
1	6	25	10	50	10	3
2	18	25	10	50	10	9
3	18	25	10	50	15	13
4	18	25	10	50	20	27
5	18	25	20	50	10	53
6	18	25	20	50	15	95
7	18	25	20	50	20	117
8	18	25	20	50	30	285
9	21	25	20	50	20	106
10	31	25	20	50	10	8
11	18	12.5	20	50	10	284
12	18	12.5	20	50	10	234
13	18	12.5	20	50	20	475

A further increase of the monomer concentration caused very fast gelation of the solution and confronted us with a severe problem of the attachment of homopolymer onto the grafted film. On the other hand, increasing the dose beyond 18

Mrads resulted in a decrease in the graft yields (compare #9 and #7, or #10 and #5 in Table I). This observation implies that the grafting rate, which is determined by (among other factors) an interplay between the concentration of free radicals and the density of crosslinks in the host tedlar matrix, will maintain its maximal values at a dose near 18 Mrads.

Grafting onto the 12  $\mu\text{m}$  tedlar films resulted in graft yields which were more than four times higher than those of the 25  $\mu\text{m}$  films, implicating that the grafting rate under these experimental conditions is diffusion limited.

Water permeation rates of the TEDgAM films thus prepared from the 12  $\mu\text{m}$  and 25  $\mu\text{m}$  thick tedlar films are presented in Table II. These permeation rates are very low and resemble more closely those of the tedlar than those of nylon-grafted-acrylamide (NYgAM) or cellophane films. This observation, and the similarity between the evaporation and pervaporation rates implicate that the graft copolymer is most probably limited to the near surface layers and does not penetrate throughout the film. This conclusion was confirmed by inspection of dyed crosssections of the grafted films.

Table II: Water Permeation Rates Through TEDgAM Films at 37°C

No.	Graft yield (%)	Water GTR* evaporation g/m <sup>2</sup> -h	Water GTR* pervaporation g/m <sup>2</sup> -h
Tedlar	0	1.2	1.2
7	117	1.6	1.6
8	285	3	3
11	475	7	7
NYgAM	100	120	420
Cellophane		170	420

\* - GTR denotes gas transmission rate. All values are within error limits of  $\pm 10\%$ .

However, the increase of the water permeation rates suggests that a significant part of the cross-section of the substrate tedlar film, in both the thick and thin films, was highly grafted with polyacrylamide and became permeable to water. The further penetration of the grafting into the substrate tedlar films, which is needed for their complete permeabilization to water, may be achieved by the addition of a co-solvent to the AM solution. Such solvent should cause some swelling of the tedlar substrate thus enhancing the penetration of the monomer solution into the film and accelerating the grafting process. The preferable solvent should also be a mild radical scavenger and hinder the homopolymerization and gelation of the monomer solution, thus enable us the extension

of the grafting period and the achievement of higher graft yields.

Nevertheless, in the present graft distribution the core of the tedlar film is ungrafted and interposes as a barrier layer in the middle of the TEDgAM copolymer film, resembling a "double asymmetric membrane". It may be of interest to adjust the enhanced grafting process so as to keep this ungrafted core thin enough to allow the water-swollen TEDgAM membrane to be permeable to water and yet serve as a permselective "skin" and effect the retention of solutes by the grafted copolymer membranes.

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