Grafting onto Tedlar films
by the electron beam preirradiation technique

II. Grafting with acrylamide in a watertetrahydrofurane solution

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Summary
        Polyvinylfluoride (Tedlar) films, 12.5μm and 25μm thick, were grafted with acrylamide monomer (AM) in a mixed solvent of water and tetrahydrofurane (THF), following preirradiation with a 550 kV electron beam accelerator. The highest graft yields were attained with AM/THF/H_2O solutions in which the concentration of THF was in the range of 40–50% (w/w). At this range, the graft yield rise with grafting period was almost linear, and graft yields of 600% and higher were attained at AM concentration of 30% within 12–15 min without significant gelation of the solution. Water permeation rates through the Tedlar films were increased, upon grafting with AM, by a factor of up to 500. Water permeation rates through the Tedlar grafted with acrylamide (TEDgAM) films, grafted in solutions containing at least 30% THF, were high and comparable with those of cellophane films or nylon grafted acrylamide films (NYgAM) of comparable thickness, implicating that the Tedlar film cross-section has been completely penetrated through by the grafted copolymer. The highest rates of water permeability were observed in TEDgAM films grafted in monomer solutions which contained 60% THF.

Introduction
        The Tedlar film is an attractive candidate substrate for radiolytic grafting with hydrophilic monomers, due to its excellent mechanical properties, inherent good barrier properties and its high resistance to radiation induced damage (1-2). In a previous communication (3), experiments of radiolytic grafting onto Tedlar films with AM in aqueous solutions, aiming at the preparation of TEDgAM permselective membranes, were reported. The grafting method used in this investigation was based upon previous experience of fast radiation induced graft polymerization of hydrophilic monomers onto nylon films, in aqueous solution of the monomers, especially grafting of AM (4-7). The NYgAM membranes thus prepared exhibited high permeability to water and solutes and permselectivity features which could be modified by the

preperative parameters of the grafting process. However, upon
applying this gafting metod to grafting onto Tedlar (3), it was
found that its inherent resistivity to penetration of water has
generated a severe obstacle for grafting it with aqueous
solution of AM. This resistivity was manifested in low grafting
rates and hence, a poor penetration of the graft copolymer into
and throughout the Tedlar film. Consequently, despite the
threefold increase in the water permeation rates (GTR) through
the TEDgAM films, as compared with those through the ungrafted
substrate Tedlar film, the GTR values were too low to enable
application of these TEDgAM films as membranes.
    In the present investigation we modify the grafting
method, by utilizing the Tedlar swelling agent THF as a
cosolvent for the monomer, and evaluate the effect of this
grafting method on the rate of grafting and the permeability
characteristics of the thus prepared TEDgAM membranes.

Experimental
    Tedlar films, 12.5μm and 25μm thick (DuPont), acrylamide
(Cyanamide, C.P.) and THF (Merc, C.P.) were used without
further purification. Samples of the Tedlar film were
irradiated to a total dose of 18 Mrads by the electron beam
accelerator as described previously (3). The irradiation was
immediately followed by the grafting step, which was performed
in a solution of AM in a mixed solvent composed of deionized
water and THF. The experimental set-up of the grafting, the
grafting procedure and the determination of the water vapor
permeation rates through the grafted films (both evaporation
and pervaporation rates) were described in detail in a previous
communication (3).

Results and Discussion

The Grafting Process
    THF is a water-miscible solvent which is capable of
swelling and partially dissolving the Tedlar substrate film.
The rationale for the use of the H_2O/THF mixed-solvent is to
swell the substrate film with the monomer solution and thus to
enhance the monomer penetration into it. Similar attitude was
demonstrated by Gombotz and coworkers, who utilized a mixed
solvent of water and ethanol to enhance the radiation induced
grafting of methacrylic acid onto polypropylene (8), thus
maintaining enhanced penetration of the graft into the
substrate polymer and attaining an increase of the graft yield
by a factor of 20. Another rationale for the employment of this
solvent is that it may act as a radical scavanger, terminate
the progress of radical homopolymerization of the AM monomer
(initiated by chain-transfer reactions from the preirradiated
film to the monomer solution) and allow the grafting process to
be performed in more concentrated monomer solutions and to be
carried on for a longer period of time than in the aqueous
solutions, without intrusion by the gelation of the monomer
solution.
    Typical graft yields of AM onto preirradiated Tedlar films
grafted under various experimental conditions, namely cosolvent
(THF) concentration, monomer concentration and grafting period

are displayed in Table I. The grafting step was performed immediately after the preirradiation step to eliminate decay of the radicals in the Tedlar films (3).

Table I: Typical Data of Graft Yields onto Tedlar Films of AM in a Mixed Solvent under Various Experimental Conditions [a]

No.	tedlar type [b]	tedlar thickness (μm)	THF conc. (%)	AM conc. (%)	grafting period (min)	graft yield (%)
1	1	25	0	20	20	117
2	1	25	30	20	20	285
3	1	12.5	0	20	20	475
4	1	12.5	20	20	10	238
5	1	12.5	30	20	10	257
6	1	12.5	40	20	10	375
7	1	12.5	60	20	10	284
8	1	12.5	30	30	12	610
9	2	12.5	20	30	12	290
10	2	12.5	30	30	12	375
11	2	12.5	30	30	15	770
11*						(102)

[a] – Radiation dose = 18 Mrads; Grafting temperature = 50°C.
[b] – Type-1 = 50AM (Medium gloss: contains 2% SiO_2 powder);
Type-2 = 50AG (High gloss: no SiO_2 additive).
* – Sample 11 after homopolymer peeling off.

The first observation during the grafting period was that as expected, the THF cosolvent inhibited the homopolymerization of the monomer in the grafting solution and grafting with monomer solutions at concentrations of 30% and higher were performed for periods of 30 min and longer without significant gelation. Another observation during the grafting processes was the change in the opaqueness of the Tedlar films, which turned into transparent, upon grafting with monomer solutions with THF content of 30% and higher. This feature was related later on with the water permeability characteristics of the grafted TEDgAM membranes.
From the data in Table I it is obvious that the presence of THF in the solvent is crucial for attaining an effective grafting onto the Tedlar substrate. However, comparison of the graft yields in experiments no. 4-7 implies that the influence of the concentration of THF on the rate of grafting is somewhat complex, as presented in Fig. 1.
Fig. 1 presents the graft yield of AM (20% solutions) onto Tedlar films at various concentrations of THF in the monomer solution. Please note that in the solution which contains 20% AM and 80% THF the water content is practically zero.
The influence of the THF content in the monomer solution on the graft yield reflects an interplay of two major effects: the radical scavanging by the THF, and the enhancement of the swelling of the Tedlar film.
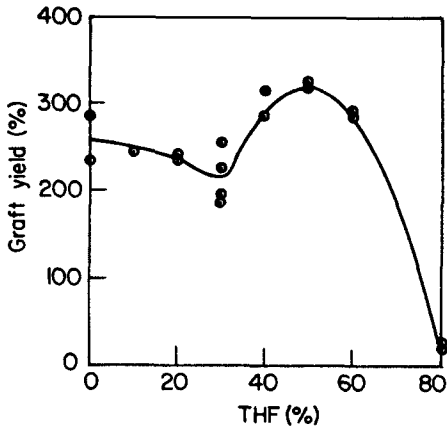
Fig. 1. Grafting of AM onto preirradiated Tedlar films at various concentrations of THF. Dose = 18 Mrad; AM concentration = 20%; Grafting period = 10 min.
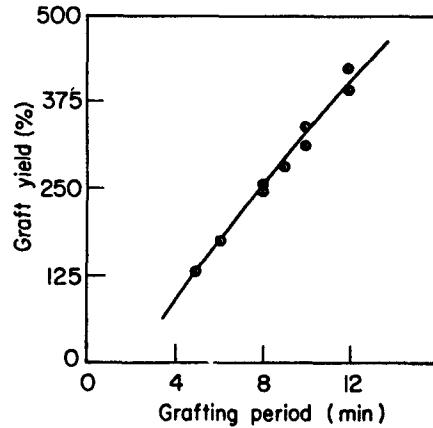
Fig. 2. Grafting of AM onto preirradiated Tedlar films vs. the grafting period. Dose = 18 Mrad; AM and THF concentrations were 20% and 40%, respectively.

In the range of THF concentrations of 0-30%, the slight decrease in the graft yield, upon increase of the THF content in the monomer solution, implies that radical scavanging causes the predominant effect while the enhanced swelling of the Tedlar by the organic solvent is of minor influence at these concentrations.

Conversely, a steep rise in the graft yield is observed at THF concentrations of 30-60%, which most probably reflects the fact that the swelling of the Tedlar substrate by the THF-rich solution and the penetration of AM therein becomes the predominant effect. It is noteworthy that the water-soaked TEDgAM membranes of graft yields exceeding ca. 100%, prepared at these THF concentrations are transparent, in contrast to the opaqueness of similar TEDgAM membranes prepared at THF concentrations of less than 25%. This observation may reflect a uniformity of the water swelling capacity throughout the cross section of the former membranes which may affect the water permeation rates thruogh those membranes.

The steep decrease of the grafting rate upon increase of the THF content to 80% is most probably an outcome of the absence of water in the monomer solution. It can be rationalized as follows: the product of the copolymerization of the grafted monomer, namely the polyacrylamide (PAM), is immiscible in THF. Hence, the PAM chains which are initially grafted onto the outermost regions of the Tedlar film will form a barrier for further penetration of the monomer into the preirradiated substrate film and eventually stop the grafting process.

Fig. 2 displays the rate of grafting of AM onto the preirradiated Tedlar films with a 20% monomer solution in a 1:1 (w/w) H₂O/THF mixture. The relatively high initial grafting

rate: ca. 40%/min is almost constant for at least 12 min
without significant levelling off. This observation is
consistent with the non-gelating nature of the monomer
solution.

For a preirradiation initiated grafting, radical
termination in the grafted regions should lead to a fast
levelling off of the graft yield vs. time, due to the increased
mobility of the radicals in the growing PAM chains, surrounded
by absorbed water. However, the salient feature of the results
displayed in Fig. 2 is an almost constant rate of the graft
yield growth during the first 12 min of the reaction, even
though the graft yields exceed 500% within this period.

In a previous communication (4), it was suggested that
such behavior is due to the existance of a continuous supply of
radicals to the grafted regions of the system by gradual
migration of radicals, originally buried in the crystalline
regions of the substrate and not easily accessible to monomer.
This radicals supply can offset the loss of radicals due to
termination processes of the growing chains. Thus, an
apparently constant rate of grafting onto the Tedlar film can
be maintained for at least 12 min.

The effect of the nature of the substrate Tedlar film on
the efficiency of the grafting process is also demonstrated in
Table I (cf. column 2). Although both substrate films are named
Tedlar, they exhibit different characteristics of the grafting
process. First, the type-1 substrate is grafted in much higher
rate than the type-2 one. This observation can be attributed to
the fact that the SiO_2 additive (2%) in the type-1 substrate
(experiments #1-8 in Table I) has a major contribution to the
enhancement of the grafting rate, most probably by favoring the
penetration of the monomer solution into the Tedlar substrate.
Conversely, the pure Tedlar film (experiments #9-11) exhibits a
much lower rate of grafting than the former one. Furthermore,
when it is grafted to a very high graft yield (cf. #11 and #11*
in Table I) and immersed in boiling water for several hours,
most of the grafted PAM can be peeled off from both sides of
the grafted film leaving a much thinner film of only 102% graft
yield. This phenomenon is not observed in the type-1, silica
added Tedlar substrate. This behavior is consistant with the
observation of the low grafting rate onto the type-2 Tedlar due
to hindered penetration of the monomer solution into this
substrate, the consequent of which is a build-up of a pseudo-
grafted, peelable outer layer, which can form after the peeling
a self-supporting film constituted of PAM homopolymer (which is
identical with cast PAM film, as analized by IR spectroscopy).

Water Permeability Through the TEDgAM Membranes

In Table II, typical data of water permeation rates of the
TEDgAM films prepared from the 12.5μm thick Tedlar films are
presented. It is noteworthy that at THF concentration of 20%
and lower, even graft yields of several hundreds percents are
not sufficient to impart the TEDgAM films significantly higher
water permeation rates. TEDgAM membranes of few hundreds
percents of graft yield, prepared with monomer solutions of THF
content of 30% and higher exhibit the high water permeation
rates which are typical to hydrophilic membranes such as

Table II: Typical Data of Water Permeation Rates
Through the TEDgAM Films, at 37°C

No.	Graft Yield (%)	Water GTR[*] Evaporation g/m²·h	Water GTR[*] Pervaporation g/m²·h	THF in the monomer solution (%)
Tedlar	0	1.2	1.2	—
3	475	7	7	0
4	238	15	15	20
6	375	120	370	30
7	284	100	520	60
NYgAM	100	120	420	—
Cellophane		170	420	—

[*] – GTR denotes Gas Transmission Rate (ASTM E-96-66).
All values are within error limits of $\pm$ 10%.

Cellophane or PVA (commercially available) or NYgAM (4-7).
These findings are not surprising since at graft yields higher
than 100% the grafted PAM in the membrane, the content of which
exceeds 50%, becomes the major constituent in the polymeric
matrix of the membrane. The high THF content in the monomer
solution (>30%) is crucial to maintain complete penetration of
the grafted PAM throughout the cross-section of the substrate
Tedlar film and eliminate a residual ungrafted core. As
demonstrated in the previous communication (3), such ungrafted
core is practically impermeable to water and reduces the
overall permeability coefficient of the membrane, as formulated
in the following equation (9):

$$\frac{L}{Q} = r_1 + r_2 + \sum_i \frac{L_i}{Q_i}$$

L, L_i – the thickness of the membrane and its ith sublayer,
respectively.
Q, Q_i – the permeability coefficient of the membrane and its
i^{th} sublayer, respectively. $Q_i = D_i S_i$.
r_1, r_2 – the surface resistivity to permeation.

(A sublayer with a low Q_i contributes a high L_i/Q_i value to
the total L/Q and hence, lowers the overall permeability
coefficient of the membrane).

Finally, it is also noteworthy that in contrast to the low
permeability TEDgAM films which are all opaque when swollen
with water, in all the highly water permeable TEDgAM films the
absence of an ungrafted core is characterized also by the
typical transparency of these water swollen membranes.

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