Pervaporation Membranes Prepared by Radiochemical Grafting of N-Vinylpyrrolidone onto Films

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Synopsis

The pervaporation performances of membranes obtained by radiation grafting of N-vinylpyrrolidone onto poly(tetrafluoroethylene), polyethylene, polybutene, and poly(dimethylsiloxane) films were studied using a water–dioxane azeotropic mixture. The influence of the following parameters was examined: grafting ratios, radiation dose rates, nature of the base films, poly(tetrafluoroethylene) film-making methods, and structural transition. An attempt has been made to interpret the results in terms of variations in the number, size, and density of the grafted domains which form the diffusion paths for the permeating molecules. Based on this interpretation, a general rule is proposed for selecting adpated methods to prepare efficient pervaporation membranes.

INTRODUCTION

In preceding studies[1,2] the promising properties of membranes used to separate by pervaporation a number of solvent mixtures have been reported. Adequate productivity and high separation were achieved by using a film of poly(tetrafluoroethylene) grafted with N-vinylpyrrolidone (PTFE–PVP membrane). In a recent publication,[3] we have shown that the preferential solvation displayed by PVP dissolved in various mixed solvents could be correlated to the selectivities observed through a PTFE–PVP membrane. It was concluded that a general approach to the selection of a membrane for the separation of a binary organic mixture could be to select a polymer which preferentially absorbs, in solution, a large quantity of one of the two solvents.

Even if this active polymer is not soluble in either solvent, the high affinity toward one of the solvents usually leads to the destruction of the membrane or at least to a significant loss in its integrity. Then, it is necessary to incorporate the chosen polymer in a more stable structure. This is usually achieved by copolymerization or by blending with another polymer selected to be completely insoluble and structurally unaltered in contact with each of the mixture's components.

Beside the intrinsic properties of the specific chosen polymer, we have to take into account the effect of the microstructure of the final membrane on the flux and separation factor. The grafting to an existing film provides a good way to study separately the contribution of the base film nature and of the grafting method to the membrane performance.

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Journal of Applied Polymer Science, Vol. 23, 2397–2407 (1979)

0021-8995/79/0023-2397$01.00

The present paper reports on the properties of membranes prepared by grafting, under irradiation, and in varying conditions, increasing amounts of N-vinylpyrrolidone onto polymer films of different chemical and morphologic nature. The efficiency of the membranes so obtained was tested by measuring pervaporation flux and selectivity of a water–dioxane azeotropic mixture.

EXPERIMENTAL

Membranes

The poly(tetrafluoroethylene) (PTFE) films, 17 μm thick, were Teflon films obtained by the multicoating technique from emulsions of grains about 0.3 μm in diameter ("multicoating Teflon"). The method consists of casting the emulsion on a steel sheet, then heating at about 400°C and repeating the operation several times in order to reach the desired film thickness.

PTFE films, 55 μm thick, were supplied by Société Ugine-Kuhlmann. They were made from a massive cylinder obtained by sintering grains about 35 μm in diameter at 400°C (Soréflon déroulé).

The polyethylene (PE) films and the polybutene (PB) films were supplied by Societé Ethylene Plastique. The high-pressure and low-pressure PE films, 15 and 17 μm thick, contained 50% and 85% crystalline phase, respectively. The isotactic PB films, 20 μm thick, showed about 90% crystalline phase.

The poly(dimethylsiloxane) (PDMS) films from Essilor International were 400 μm thick.

Grafting of N-vinylpyrrolidone (VP) into PTFE and PE films was carried out by direct irradiation according to a previously described technique.[4,5] The method of grafting on radiation-peroxidized polymers[6,7] was chosen in the case of PB and PDMS films. After irradiation, the grafted films were soaked in water. After 24 hr, a sample of the film was vacuum dried and weighed. The extracted homopolymer was precipitated from water. The extraction was repeated until constant weight of the sample was achieved. The grafting ratio was expressed by the weight ratio:

$$\%G = [(W - W_0)/W_0] \times 100$$

where W is the weight of the grafted membrane and W_0 is the weight of the original film.

Swelling Ratio

A piece of membrane, after drying to constant weight (W), is immersed in the liquid at 25°C. After sorption equilibrium is reached, the piece is rapidly taken out of the bath, blotted free of surface liquid, and weighed (W_1). The swelling ratio is defined by

$$\%S = [(W_1 - W)/W] \times 100$$

Membrane Thickness

The membrane thickness was determined with a Mauser micrometer (applied pressure 20 g). The precision was about 5%.

Apparatus

The pervaporation apparatus, previously described,[1] consists of a pervaporation cell which holds the membrane and the liquid, a circulation pump to agitate the mixture, and traps to condense the pervaporate removed from the membrane by means of a vacuum pump (vacuum of 10^{-1} mm Hg). The weight and the composition of the samples collected in the traps were determined at regular intervals of time.

Two factors were selected to describe the characteristic data of a pervaporation test which was carried out with a binary system consisting of two liquids, A and B: (1) the pervaporation flux Φ, expressed in kilograms per hour per square meter of membrane, and (2) the selectivity factor α defined by

$$\alpha = \frac{Y_A/Y_B}{X_A/X_B}$$

where Y_A = weight concentration of A in the pervaporate, Y_B = weight concentration of B in the pervaporate, X_A = weight concentration of A in the pervaporant, X_B = weight concentration of B in the pervaporant, and A = species which is preferentially pervaporated.

The mixture of azeotropic composition at 760 mm Hg investigated was water–dioxane (18.4 wt-% water). Experiments were performed at 25°C.

RESULTS AND DISCUSSION

Influence of Grafting Reaction Parameters on Pervaporation Results of PTFE–PVP Membranes

We have previously reported[8] that the nature and the composition of the grafting medium have a strong influence on the final properties of the grafted membranes tested in pervaporation with a water–dioxane mixture. It has been shown that when the grafting reaction is carried out in the presence of benzene, a nonsolvent for PVP, the membrane could display a relatively high flux (up to 1 kg/hr·m^2) but always a low selectivity ($\alpha = 14$). On the other hand, some films modified by irradiation in a pyridine solution of the monomer are more selective ($\alpha > 30$) than those obtained by using a benzene solution. However, they have lower fluxes (about 0.5 kg/hr·m^2).

In order to better understand the properties of the membranes prepared in pyridine and to attempt to get membranes with both high flux and selectivity, 55 μm thick PTFE films were irradiated in 50% solution of VP in pyridine at 50°C. The dose rates were 380, 100, and 30 rad/min. Figures 1(a) and 1(b) are respectively plots of the thickness and of the swelling ratio of the membranes in the azeotropic water–dioxane mixture versus the grafting ratio.

At the higher dose rates (100 and 380 rad/min) the curves show an initial increase followed by constant values of both thickness and swelling ratio although the grafted VP content increases. The transition of the curves is observed at

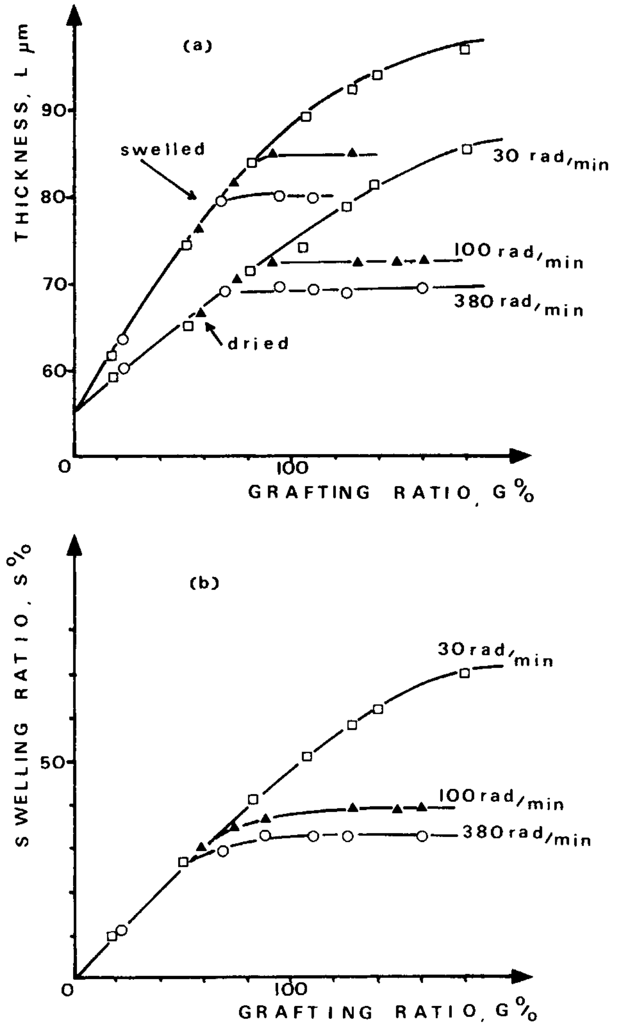

Fig. 1. Plot of membrane thickness (a) and swelling ratio (b) in water–dioxane azeotropic mixture vs. grafting ratio: 55 µm thick PTFE films irradiation in a VP–pyridine solution (50 vol-% VP) at 50°C and different dose rates (shown on curves).

a dose of about 2 Mrads. Below 2 Mrad, we have observed that the PVP homopolymer is easily leached out and only one or two extraction steps are sufficient to obtain a constant weight of the grafted film. Above 2 Mrad, the PVP homopolymer is extracted with difficulty and has a higher molecular weight. For the highest grafting ratio, practically no homopolymer could be leached out and the films displayed a characteristic three-dimensional structure (low flexibility-hardened).

At low dose rate (30 rad/min) both swelling ratio and thickness increase with grafting ratio. No break is observed at the highest grafting ratio (250%), which is reached with a total dose lower than 2 Mrad.

Figure 2 shows several series of pervaporation data for the water–dioxane azeotropic mixture obtained with these membranes. The curves depend on the dose rate: (1) When the grafting is carried out under a low dose rate (30 rad/min)

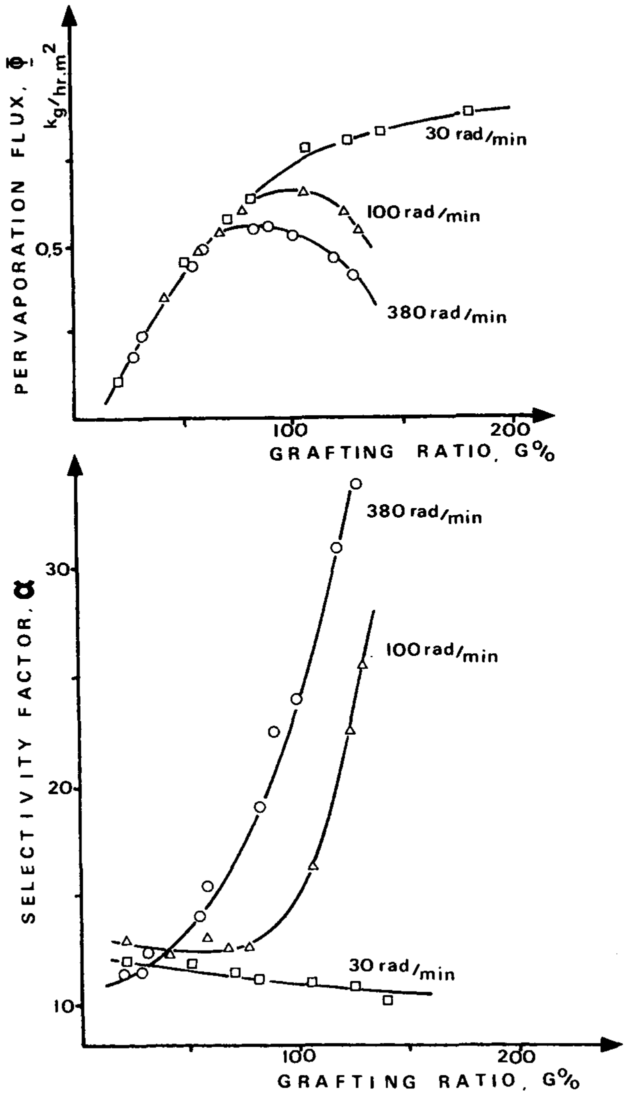

Fig. 2. Effect of grafting ratio and dose rate on flux and selectivity factor: water–dioxane azeotropic mixture, 55 μm thick PTFE films irradiated in a VP–pyridine solution (50 vol-% VP) at 50°C and different dose rates (shown on curves). Water is preferentially pervaporated.

the pervaporation flux increases with the grafting ratio while the selectivity factor remains nearly constant. (2) On the contrary, when the dose rate exceeds 100 rad/min the pervaporation flux goes through a maximum (the position of the maximum is shifted toward a lower grafting ratio when the dose rate is raised) while the selectivity factor increases with the grafting ratio.

These results can be explained as follows: the grafted chain takes place inside the PTFE matrix, probably in the interstitial volume between the grains. At low grafting ratios the swelling is proportional to the amount of PVP as long as the PTFE matrix has not reached its elastic limit. The flux through the membranes is proportional to the grafting ratio and consequently to the swelling ratio as was generally expected.[8,9] The selectivity factor is nearly constant.

When the irradiation dose is increased, the PVP domains between the PTFE crystalline grains become more and more dense because the strong resistance of the PTFE network prevents them from further swelling. For the highest dose, some branching or crosslinking between PVP homopolymer and grafted PVP may occur. In prevaporation, the compactness of the PVP domains hinders the movement of the permeating molecules and the flux consequently decreases. As the grafting ratio increases, there are more and more active polymeric sites for a given volume of swelled membrane, the global preferential solvation increases, and consequently the selectivity factor increases.

Influence of Nature of Base Film

In order to examine the influence of the nature of the base film, four inert preexisting films of about the same thickness were chosen: two polyethylene (PE) films, one polybutene (PB) film, one poly(tetrafluoroethylene) (PTFE) film. The advantage of the polyolefins is to prepare the flat sheet membranes using the conventional methods for thermoplastics.

Grafting of the Base Films. The high-pressure (hp), 50% crystalline phase and 15-μm-thick and the low-pressure (lp), 85% crystalline phase and 17 μm thick PE films were irradiated in a VP–pyridine mixture (50 vol-% VP) at 50°C and at a dose rate of 40 rad/min. The conversion curves plotted in Figure 3 show that the kinetics of the graft copolymerization onto PE films are classical and the results are comparable to those obtained with PTFE films.[5] Therefore, a slight difference appears between the curves, attributable to the different degrees of crystallinity of the two PE films. The data show that 0.5 Mrad is sufficient to obtain a 150% grafting ratio. The PB membranes were prepared from irradiation-peroxidized PB films at 21°C and dose rates of 40 and 100 rad/min (doses 0.46 and 1.00 Mrad). The grafting reaction was carried out in pure VP at 21°C, and the grafting ratios were respectively 32% and 51%. The PTFE films were irradiated in a VP–pyridine mixture (50 vol-% VP) at 50°C and at a dose rate of 30 rad/min.

Pervaporation Experiments. All these membranes were tested in perva-

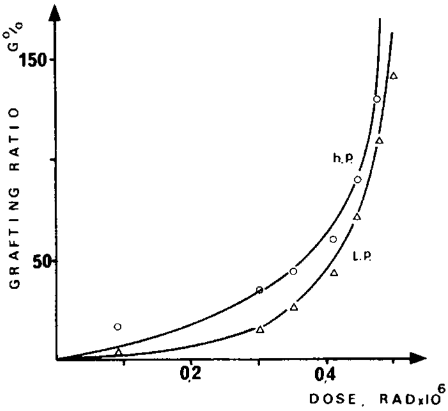

Fig. 3. Grafting ratio as function of irradiation dose for VP grafting to PE and PTFE films: (○) 15 μm thick high-pressure PE; (△) 17-μm-thick low-pressure PE. Films irradiated in a VP–pyridine solution (50 vol-% VP) at 50°C and 40 rads/min.

poration. Their performances are shown in Figure 4 as functions of the grafting ratio. The flux, Figure 4(a), is proportional to the grafting ratio, and it is apparent that all the results can be plotted, in first approximation, on the same straight line. However, the fluxes through the PTFE–PVP membranes are a little higher than those observed through the other membranes.

The values of the selectivity factors, Figure 4(b), depend greatly on the nature of the base film. It appears that the higher the crystallinity of the film, the higher is the selectivity factor. This fact supports the assumption that the grafting process takes place especially in the amorphous parts of the films around the crystalline domains: for films of lower crystallinity, the grafted polymer chains are dispersed into the films and offer a great number of diffusion paths for the permeating molecules. To the contrary, the grafted membranes obtained from films of higher crystallinity have fewer diffusion paths, but in these paths the concentration of the active solvation sites is higher and both the diffusion and the preferential solvation are enhanced. Consequently, for the same grafting ratio we find the same flux but a higher selectivity than through the less crystalline grafted films.

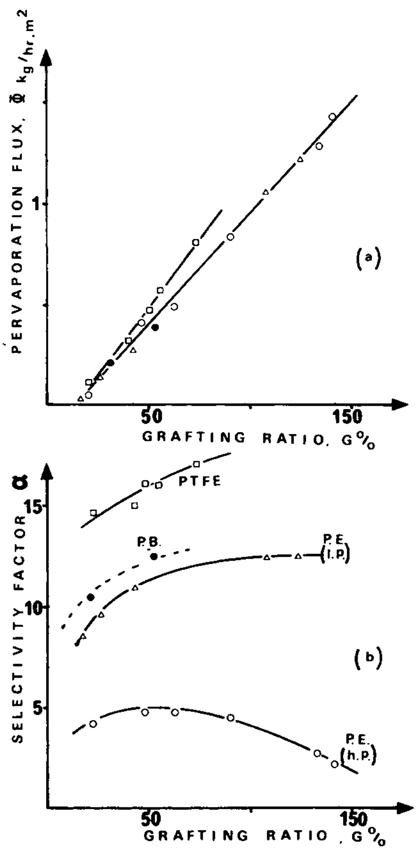

Fig. 4. Effect of grafting ratio on flux (a) and selectivity factor (b). Pervaporation of a water–dioxane azeotropic mixture through PVP-grafted membranes prepared from different base films: (○) 15 μm thick high-pressure PE (50% crystalline phase); (△) 17 μm thick low-pressure PE (85% crystalline phase); (●) 20 μm thick PB (90% crystalline phase); (□) 19-μm-thick PTFE (95% crystalline phase). Water is preferentially pervaporated.

The preceding membranes were obtained by grafting an inert crystalline support, that is to say, a film which, before grafting, is not swelled by water or dioxane. If we graft an amorphous film which swells in dioxane, we can expect a higher flux and a lower selectivity. To verify this, a membrane was prepared from perirradiated poly(dimethylsiloxane) (PDMS) film (dose 1.0 Mrad) in pure VP at 90°C. Under such conditions, a grafting ratio of 10% is achieved. The pervaporation of the water–dioxane azeotropic mixture shows that the flux reaches a value of 0.25 kg/hr·m^2 in spite of the great thickness of the membrane (400 μm). Moreover, as was expected, the pervaporate is enriched with dioxane ($\alpha = 4$).

Influence of PTFE Film Characteristics

It has already been reported that the performances of PTFE-grafted membranes in reverse osmosis[10] or in pervaporation[11] are influenced by the initial nature of the PTFE base films. The properties of the two different PTFE films (19 μm multicoating Teflon and 55 μm Soréflon déroulé) used for this study afford new evidences of the influence of the method employed to prepare PTFE films. The results are shown in Table I and Figures 5 and 6.

The membranes were prepared under the same conditions: the films were irradiated at 30 rad/min and 50°C in a VP–pyridine mixture (50 vol-% VP). The two kinds of membranes show the same relative increase in thickness as the grafting ratio increases (Fig. 5). But the Soréflon déroulé films, which are prepared by sintering large grains of PTFE (35 μm), give membranes less selective and more permeable, relatively to their higher thickness, than the multicoating Teflon prepared from a suspension of much smaller grains (0.3 μm) (Table I and Fig. 6).

Munari and al.[10] have reported that for "multicoating" PTFE films grafted with styrene and then sulfonated, the smaller the particle size of the PTFE, the higher was the salt rejection and the lower the water permeability in reverse osmosis. Then we can consider as a general trend that the capacity of the par-

TABLE I
Effect of Grafting Ratio on Membrane Thickness and Pervaporation Data of Water–Dioxane Azeotropic Mixture[a]

Grafting ratio, G, %	Thickness, μm	Pervaporation flux, kg/hr·m^2	Selectivity factor α
	19-μm-Thick "Multicoating Teflon" Films		
21	20	0.11	14
39	21.5	0.38	15
42	22	0.30	15.2
47	22	0.45	16
55	22.5	0.56	16
73	23.5	0.8	17
	55-μm-Thick "Soréflon Déroulé" Films		
19	59	0.4	13
53	65	0.45	12.5
81	72	0.63	11.5
105	75	0.8	11

[a] PTFE films irradiated at 30 rad/min and 50°C in VP–pyridine solution (50 vol-% VP).

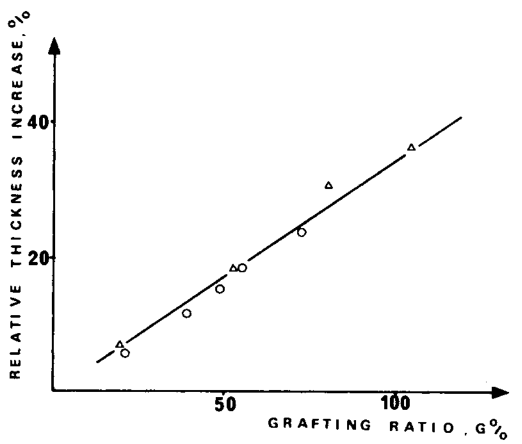

Fig. 5. Relative thickness increase as a function of grafting ratio: (○) 19-μm-thick "multicoating Teflon"; (△) 55 μm thick "Soréflon déroulé." Relative thickness increase = $[(e_m - e_0)/e_0] \times 100$, where e_0 = thickness of the base film and e_m = thickness of the dried grafted membrane.

ticles to arrange themselves in a more ordered and compact structure during the sintering of the grains leads to membranes which are more selective and less permeable.

Influence of Crystal–Crystal Transition of PTFE

At 19°C, PTFE shows a crystal–crystal transition from the monoclinic form in which chain rotation is restricted (below 19°C) to a hexagonal form where the molecules can rotate around their chain axes (above 19°C).[12]

Experiments of pervaporation of water–dioxane azeotropic mixture were carried out at temperatures ranging from 5 to 51°C with two PTFE–PVP membranes prepared from 19 μm thick PTFE films. The films were irradiated at 100 rad/min and 21°C inVP–pyridine mixture (50 vol-% VP). The Arrhenius plots of the prevaporation fluxes show a break at about 19°C (Fig. 7).

The diffusion of permeating molecules is enhanced by the possibility of rotation of the PTFE chains when the temperature is higher than 19°C. It must be pointed out that the effect of this structural transition on the flux is important since the energy of activation is lowered by more than 20% from its value below 19°C.

CONCLUSIONS

In the present paper it was shown that the grafting reaction parameters, the crystallinity of the inert support, and the nature of the poly(tetrafluoroethylene) base film affect the pervaporation performances of the PVP grafted membranes. All these parameters are related to the distribution and the mobility of poly(vinylpyrrolidone) chains. On the other hand, an increase in the compactness of the membrane related to the high density of active groups is presumed to increase the selectivity between the two diffusing species while the high mobility of the active chains tends to increase the pervaporation flux.

In order to prepare a dense membrane that will exhibit in pervaporation both a high selectivity factor and a high flux, it appears that the results obtained in

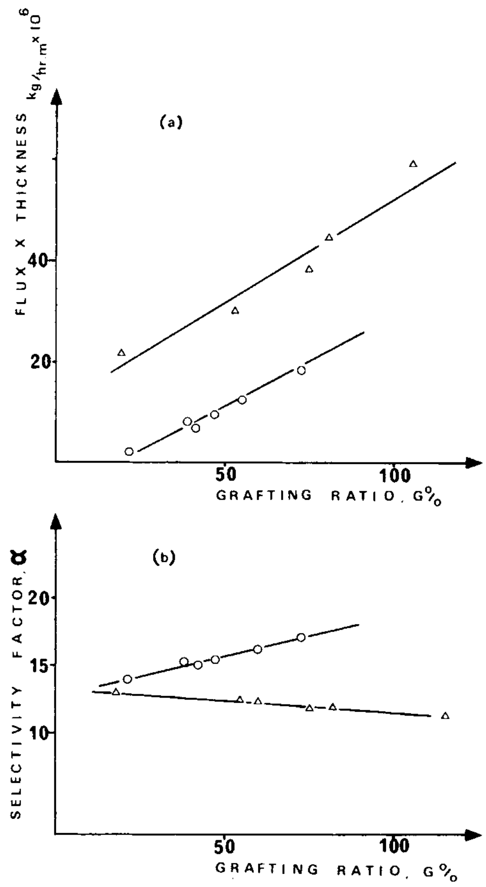

Fig. 6. Effect of grafting ratio on the product flux × thickness (Φ × e) (a) and selectivity (b). Pervaporation of a water–dioxane azeotropic mixture through PVP-grafted membranes prepared from two different PTFE base films: (○) 19 μm thick "multicoating Teflon;" (△) 55 μm thick "Soréflon déroulé." Water is preferentially pervaporated.

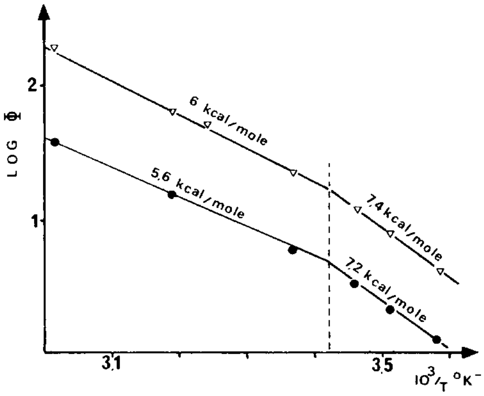

Fig. 7. Arrhenius plots of pervaporation flux of a water–dioxane azeotropic mixture through two PTFE–PVP membranes prepared from 19-μm-thick "multicoating Teflon": (●) grafting ratio 48%; (△) grafting ratio 56%.

this study support the following rule: the method of incorporating a specific given polymer into a chemically and mechanically stable structure must be selected in such a manner that active sites of the polymer will be arranged in a great number of small dense "domains." A greater number will give a higher flux, denser domains will give a higher selectivity. However, if the domains are too dense, the flux will decrease, and if too numerous or too large, poorer chemical and mechanical properties will result.

Under these conditions statistical copolymerization or crosslinking of the active polymer seem not to be appropriate methods. An alternate method such as grafting copolymerization of preexisting films, if the grafting is not too homogeneous but takes place only in specific domains of the initial matrix, appears to be a good method. Blending could also give efficient membranes, and we can moreover expect that if some phase separation occurs during the membrane formation, the performances will be better.

We consider however that the assumption upon which the precedent rule is based needs to be carefully verified. The investigations now undertaken will form the subject of a following paper.

The authors wish to express their sincere thanks to Professor Jean Neel of the Ecole Nationale Supèrieure des Industries Chimiques–Nancy, who encouraged the conduct of the present study.

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Received April 11, 1978