Structure and Morphology of Poly(Tetrafluoroethylene)-Poly(N-Vinylpyrrolidone) Copolymer Membranes

G. MOREL and J. JOZEFONVICZ, *Laboratoire de Recherches sur les Macromolécules, Centre National de la Recherche Scientifique–E.R.A. 607, Université Paris-Nord, Avenue J. B. Clément, 93430 Villetaneuse, France*

Synopsis

The structure and morphology of poly(tetrafluoroethylene)-poly(N-vinylpyrrolidone) (PTFE-PVP) copolymer membranes prepared by direct radiation grafting were studied by using differential scanning calorimetry, x-ray diffraction, and scanning electron microscopy. The granulometry of the base emulsion used in PTFE film forming did not have any influence on the mechanism of radiochemical grafting. Moreover, it is proposed that the size of base grains induces morphologies of grafted membranes which differ markedly from each other. The results are analyzed on the assumption that grafted chains of PVP are formed between the base grains of PTFE and gradually move inward toward the crystalline zones. For a given grafting ratio, the space of distribution of grafted chains inside the PTFE matrix depends on the size of PTFE base grains. A correlation between morphologies of membranes and water permeability of copolymer membranes is indicated.

INTRODUCTION

Fractionation of liquid mixtures by selective transport may be achieved by using hydrophilic membranes such as poly(tetrafluoroethylene) (PTFE)-poly(N-vinylpyrrolidone) (PVP) copolymers.[1] The flux and the selectivity of the transfer depend on the preferential solvation of the proton acceptor, PVP, by one compound of the binary liquid mixture.[2] The performance of the PVP grafted membrane is influenced by the crystallinity of the inert support and is also governed by the diffusional paths.[3] In the particular case of PTFE, performance is related to the size distribution of the PTFE emulsion particles used to cast the base film.[4] This study deals with the contribution of the base film morphology to the distribution of the PVP grafted chains inside the inert film.

EXPERIMENTAL

Membranes

Grafting of N-vinylpyrrolidone (VP) onto poly(tetrafluoroethylene) films (PTFE films) was carried out by direct γ-irradiation.[5] Two kinds of PTFE films were used.

Type-A PTFE films supplied by Société Ugine Kuhlmann were made from a massive cylinder obtained by sintering grains of about 35 μm diameter at 400°C. The massive cylinder was unrolled in a flat sheet, 55 μm thick (Soréflon déroulé).

Type-B PTFE films, 17 μm thick, were DuPont's Teflon films obtained by the multicoating technique from emulsions of grains about 0.3 μm in diameter ("multicoating PTFE"). 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. Stress relieving during casting allows their use at high temperatures without detriment to their dimensional stability.

The PTFE films were irradiated in a 50% solution of VP in pyridine at 50°C and at a dose rate of 100 rad/min. The grafting ratio of the membranes 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 virgin PTFE film.

Differential Scanning Calorimetry

The melting point and the heat of fusion were determined for each grafted membrane using a differential scanning calorimeter: DuPont DSC Cell. The temperature was raised at a rate of 10°C/min and the melting point was taken as the maximum of the thermogram. Sample weights of 10 mg were used for each measurement and scanned in a nitrogen atmosphere. The heat of fusion was calculated from the area under the thermogram by substitution in

$$\Delta H_F \text{mcal/mg} = EA(\Delta T_s)T_s/Ma$$

where E is the calibration coefficient, mcal/°C min; A is the peak area, in.[2]; $\Delta T_s = Y$ is the axis sensivity, °C/in.; $T_s = X$ is the axis sensivity, °C/in.; M is the sample mass, mg; and a is the heating rate, °C/min.

X-Ray Diffraction

Copper $K\alpha$ radiation ($\lambda = 1.54$ Å) was used and the diffraction studies were carried out by using a goniometer and a counter for diffractometry, C.G.R. The transmission technique with flat film consisted of measuring the diffracted intensity of a monochromatic x-ray beam versus the diffraction angle θ.[6] The procedure, developed by Challa et al.,[7] is based on a proportional relationship between the experimental crystalline intensity and the crystalline fraction, and between the amorphous intensity and the amorphous fraction of the polymer. The PTFE crystallinity ratio was expressed by the crystalline area centered at $\theta = 9.2°$ divided by the whole area characteristic of the entire diffracted beam of PTFE.

Scanning Electron Microscopy

The membranes were observed after the PVP was degraded by heating to 340°C (with a heating rate of 50°C/min) in the presence of oxygen and then by quenching at room temperature. Using this procedure, the complete degradation of PVP revealed the PTFE texture in the grafted membrane. The surface and the cross section obtained by fracturing the membranes in liquid nitrogen were

observed with a scanning electron microscope (Siemens-Autoscan). Samples were mounted on a stub, affixed with silver glue, and then coated with a film of gold by vacuum deposition.

Liquid Vapor Transfer of Water

The permeability of water through type-A or type-B PTFE-PVP membranes was studied by using a pervaporation apparatus.[8] Briefly, it 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. A heating jacket surrounding the cell allows temperature changes of the liquid charge.

RESULTS AND DISCUSSION

Effect of γ Radiation on Fine Structure of Original PTFE Film

Above 19°C, PTFE crystallizes in hexagonal structure ($a = b = 5.66$ Å, $c = 19.50$ Å).[9] Because of its very low entropy of fusion, PTFE has a melting point of about 330°C and the helical structure of the fluorocarbon chains permits a very high degree of crystallinity (94%). The structure of PTFE, like the structure of polyethylene consists of alternate sheets of crystalline and noncrystalline materials stacked side by side to form a lamellar structure.[10] Moreover, a particular characteristic of PTFE, in contrast to highly crystalline polyolefins, is that PTFE cannot be molded using the conventional methods for thermoplastics.

When such polymers are γ irradiated, free radicals appear in crystalline and amorphous regions and permit the molecules to undergo either radical reactions or chain recombination in the absence of radical scavengers. A γ-irradiation dose up to 2 Mrad does not produce degradation, but slightly enhances the crystallinity of PTFE.[10]

Effect of γ Radiation and Grafting Ratio on Texture of PTFE-PVP Membranes

Figure 1 shows DSC thermograms for the PTFE (type-B film)–PVP membranes. It can be seen that PTFE has a melting peak over the narrow temperature range from 325 to 334°C, while PVP has a melting peak over the large temperature range from 40 to 100°C. The heat of fusion, which is directly proportional to the degree of crystallinity of PTFE, can be calculated from the thermogram area carried out from several samples with a constant weight of PTFE and with an increasing weight of PVP. The degree of crystallinity of PTFE versus grafting ratio (Fig. 2) slightly decreases as the grafting ratio increases. The endothermic transition of amorphous PVP increases as the weight of grafted PVP increases. Degradation of PVP is observed from 150 to 340°C.

The x-ray scattering curves of several membranes over the angular range, $\theta = 6°$ to 12°, show a partially crystalline PTFE part and fully amorphous grafted PVP chains (Fig. 3). In addition to the PTFE amorphous halo centered at $\theta =$
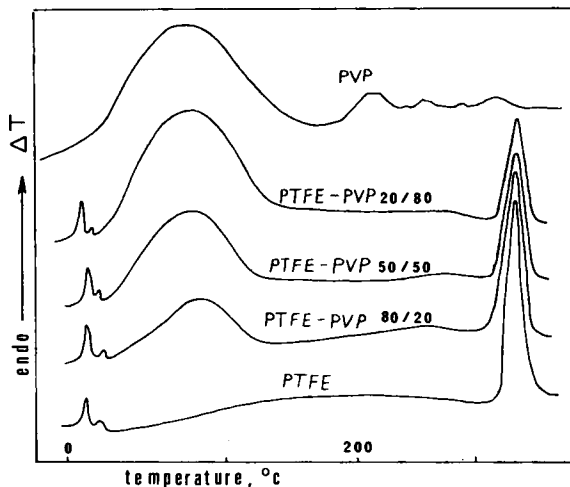
Fig. 1. DSC thermograms of PTFE, PVP, and PTFE-PVP copolymer films; scanning speed, 10°C/min. The samples were weighed in order to analyze a constant weight of PTFE.
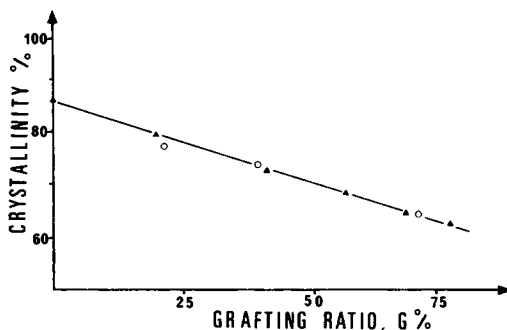

Fig. 2. Effect of the grafting ratio on the percentage of crystallinity of several PTFE-PVP co-polymers: (O) x-ray diffraction measurement; (▲) DSC measurement.

8.2°, this angular range encompasses one crystalline reflection of PTFE at θ = 9.2° and a slight amorphous halo of PVP centered at θ = 10.2°.

The amorphous fraction of PTFE increases with reduction of crystalline PTFE part as grafting proceeds (Fig. 3). The variation of the percentage of crystallinity versus grafting ratio is also plotted (Fig. 2). X-ray diffraction and DSC measurements give analogous data: the percentage of crystallinity of the virgin PTFE was about 86% and linearly decreased to 55% as the grafting ratio was raised to 100%. The grafted PVP chains affect the crystallinity of PTFE in a manner analogous to the variation of the crystallinity of the poly(ethylene)-PVP copolymers.[11] Radiochemical grafting of PVP destroys a part of the crystalline network of the PTFE matrix similarly to grafting of PVP onto polyethylene.[12] Other grafted amorphous polymers such as polystyrene have the same effect on the crystalline PTFE matrix.[6]

Influence of the Initial Nature of the Virgin PFTE Film on the Morphology of Grafted Membranes

Figure 4 shows the DSC thermograms of two kinds of PTFE-PVP copolymers: in the case of type-B PTFE, the grafting ratio lowered the area of the melting
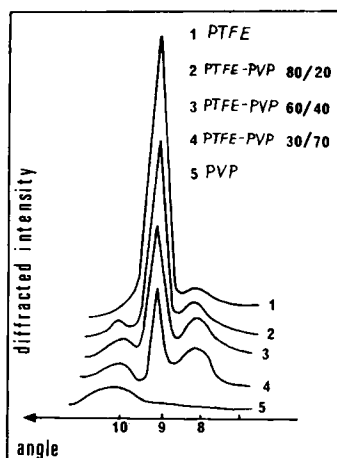
Fig. 3. X-ray scattering curves of PTFE, PVP, and PTFE-PVP copolymer films over the x-ray diffraction angular range, $\theta = 6°$ to $12°$. The samples were weighed in order to analyze a constant weight of diffracting PTFE.
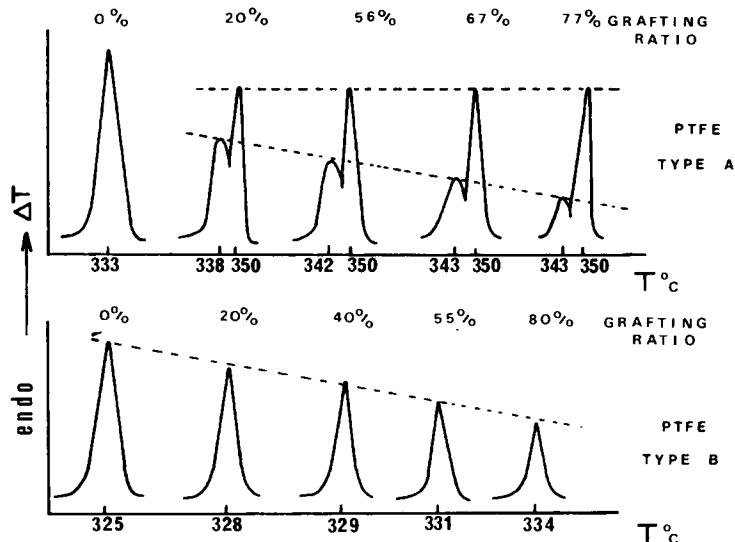

Fig. 4. DSC thermograms of PTFE and PTFE-PVP copolymer films; scanning speed $10°C/min$. The samples were weighed in order to analyze a constant weight of PTFE. The base films are type-A (large grains) or type-B (small grains) PTFE.

peak while the melting temperature increased slightly, and in the case of type-A PTFE, two melting peaks of PTFE appear, respectively, centered at 338–343°C and 350°C as grafting proceeds. These two melting peaks characterize two different morphologies of PTFE.[13] The heat of fusion ΔH_F, proportional to the area of the former peak, decreases while one of the later peaks stays almost unchanged with an increase in grafting (Fig. 5). The crystallites on which PVP was grafted are first thermally destabilized (PVP is degraded at relatively low temperature). Then the first melting peak can be attributed to the domains of PTFE through grafting, since the crystallinity of these domains is progressively destroyed. The second peak is due to the ungrafted PTFE, into the depth of the base grain, whose crystallinity was not affected by the grafting reaction.
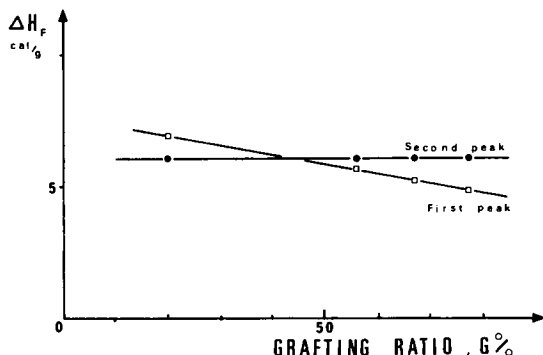
Fig. 5. Heat of fusion ΔH_F vs. grafting ratio. The base film of copolymers is type-A PTFE. The heat of fusion was calculated from the area of the "first peak" and the "second peak," respectively, centered at 338–342 and 350°C.
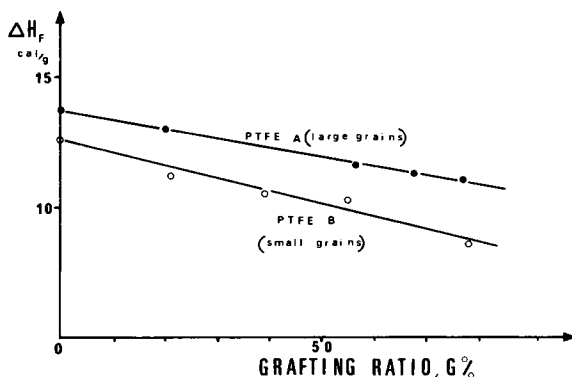

Fig. 6. Heat of fusion ΔH_F of the two types A and B PTFE vs. grafting ratio. The heat of fusion of the type-A PTFE was calculated from the sum of the areas of the two peaks.

Figure 6 shows the heat of fusion of the two types, A and B PTFE, plotted against the grafting ratio. The heat of fusion ΔH_F linearly decreases with increasing grafting. No marked difference between the slopes of the lines is observed. Thus, the grafting process is similar regardless of the PTFE morphology.

Figure 7 shows the DSC melting and crystallization thermograms of type-A PTFE-PVP (grafting ratio, 70%). After the first crystallization, the shoulder of the peak does not appear when it is reheated. The melting point is reduced from 338°C for the first peak and from 350 to 328°C for the second one. Therefore, the grafted chains influence the crystallinity of the polymer matrix, but the effect disappears when crystallites are melted and recrystallized.

These results corroborate the relationship between the morphology of the two types of grafted membrane and the mechanism of the grafting process. Initially, grafting is necessarily limited to a thin layer around the original grains and gradually moves into the depth of the grains as the reaction proceeds.[14] The variation of the melting peaks of type-A PTFE shows that, because of the original PTFE grain size, an important part of the matrix is not involved in the grafting reaction up to 100% grafting ratio. During the grafting process, there is a high probability that diffusing monomer molecules will be trapped and polymerized
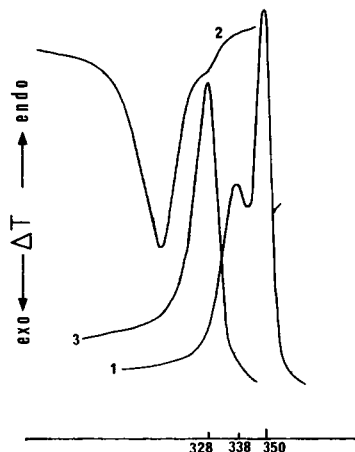
Fig. 7. DSC melting and crystallization thermograms of type-A PTFE-PVP copolymers; scanning speed, 10°C/min: (1) first melting point; (2) crystallization peak; (3) second melting peak.

across the grafted layer instead of reaching ungrafted polymer zones. In contrast, the small grains, which characterize the type-B PTFE, permit destruction of the entire base morphology. Such schematic morphologies of membranes grafted up to about 80% grafting ratio are shown (Fig. 8).

A PVP-PTFE membrane prepared from type-A PTFE presents a heteroge-

PTFE TYPE B
small grains

PTFE TYPE A
large grains
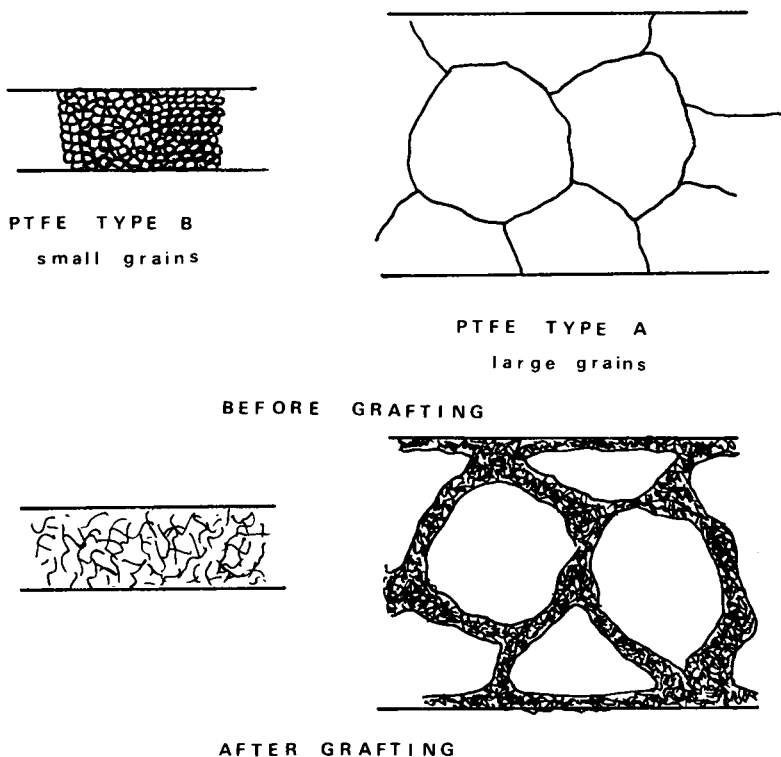
BEFORE GRAFTING

AFTER GRAFTING

Fig. 8. Schematic morphologies of the two types A and B PTFE-PVP membranes (grafting ratio, 80%).

nous morphology where homogenous large grafted zones surround virgin PTFE grains. The morphology of grafted membranes prepared from type B presents a more homogeneous morphology such as those surrounding the virgin grains in the previous case. Consequently, for a given grafting ratio, the grafted zones have more VP sites in type A PTFE-PVP membrane than in type B.

Figure 9 shows the surface and the cross section of a type-B PTFE-PVP membrane (grafting ratio, 80%), [Fig. 9(a)] and [Fig. 9(b)], respectively, before and after cycle to 340°C and cooling at room temperature. Each sample reveals a compact morphology without microholes. Entanglements of fibrils of about 1 μm diameter can be seen, and it was not possible to distinguish the base grains of PTFE in any case (grains of about 0.3 μm in diameter).

In contrast, spherulitic forms from 10 to 20 μm diameter, connected by fibrils can be observed on the surface of the other membranes (grafting ratio, 80%) prepared from type-A PTFE, heated and cooled under similar conditions (Fig. 10). Photomicrographs of similar 55 μm virgin PTFE films before and after PVP grafting presented by Boffa et al.[15] show irregular surfaces without spherulitic forms. In the case of PTFE films after cycle to 400°C and cooling, no tendency to form spherulitic substructure has been observed by Gall.[16] In this paper, similar observations can be made about type-A virgin PTFE heated to 340°C and cooled at room temperature.

The above results indicate that the grafting reaction reveals the original granular texture of type-A PTFE. The electron microscopy confirms that the grafting reaction initially take place in the joints of the base grains, slowly moves inward, and only affects the outside layer of the grains. When type-B PTFE is used, the grafting reaction probably affects the amount of the very small grains and the base morphology of the PTFE does not appear by degrading PVP.
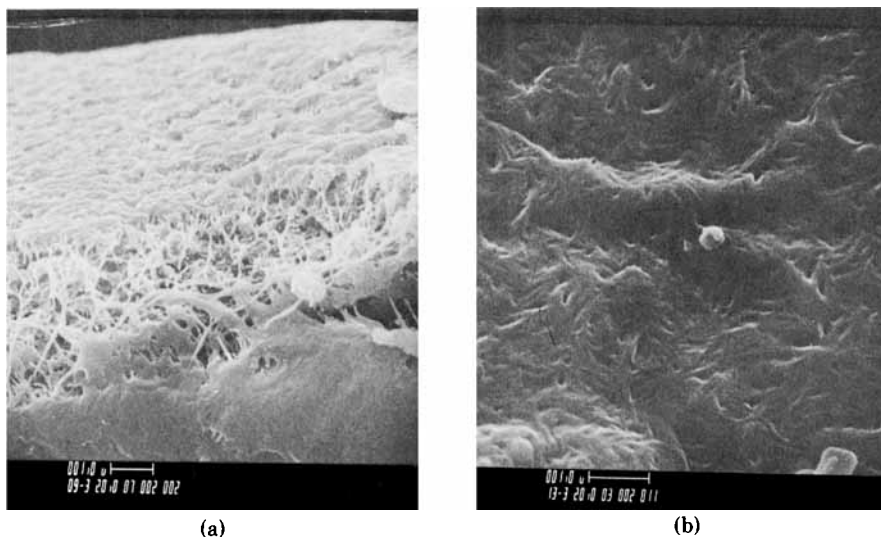

Fig. 9. Scanning electron microscopy of type-B PTFE-PVP membrane (grafting ratio, 80%), surface and cross section, before heating (a) and after heating (b) at 340°C.
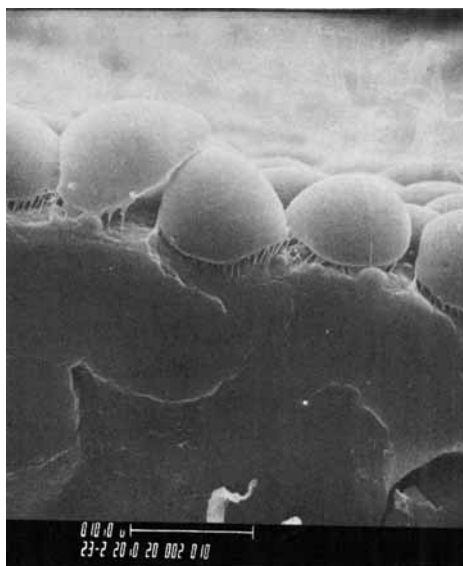
Fig. 10. Scanning electron microscopy of type-A PTFE-PVP membrane, surface and cross section (grafting ratio, 80%) after heating at 340°C.

Liquid-Vapor Transfer of Water Through PTFE-PVP Membranes

Research on hyperfiltration has pointed out that flux and rejection are dependent on the size of base particles in PTFE.[4] Pervaporation tests of pure water were carried out at different temperatures through type-A or type-B PTFE-PVP membrane (grafting ratio, 80%). The results could be expressed by an Arrhenius relation in which the activation energy for pervaporation was 2.4 kcal/mole for the type-A membrane and 3.4 kcal/mole for the type-B membrane.

These data are in good agreement with the two different textures of membrane. In the first case, type-A membranes have wide diffusional paths with high density of hydrophilic sites which easily allows movement of swollen PVP chains. In the second case, type-B membranes are homogenous and the lower density of its hydrophilic sites reduces the free volume of PVP.

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