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Ultrafiltration Membranes Prepared by Styrene-Grafted Polyvinylpyrrolidone

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ABSTRACT

The suitability of a new grafted copolymer for preparing ultrafiltration membranes was studied. The copolymer was obtained by radiochemical grafting of styrene onto polyvinylpyrrolidone. The membranes were prepared by the phase-inversion technique from *N*-methyl-2-pyrrolidone solutions. Influence of grafting degree and solutions concentration on the ultrafiltration performances were studied. It was demonstrated that for polystyrene grafting values close to 85% w/w and a copolymer solution concentration of 15% w/v, the membranes have a high permeate flux (more than 100 $L \cdot m^{-2} \cdot h^{-1}$) and a good separation factor (more than 95%) for aqueous dextran solutions. The mechanical resistance of the membranes was evaluated and their microscopic structure was examined by SEM.

INTRODUCTION

As it is well known, ultrafiltration (UF) is a membrane-based separation process. UF membranes suitable for industrial applications can be prepared with several polymers or polymeric blends (1–4).

Such materials must have mechanical strength together with high permeability toward solvents (usually water), and appreciable rejection (separation power) toward high molecular weight molecules. Such a compromise can be reached in a few cases from the enormous quantity of polymeric materials available today. For instance, polyvinyl chloride and polyvinylidene fluoride (5, 6) have excellent mechanical characteristics

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and can be easily handled to obtain asymmetric films, but the membranes so prepared have poor permeability toward water due to the hydrophobic character of the polymers. Nevertheless, they can be modified in order to add the required characteristics and to improve membrane performance (5–7).

Many polymers can be considered as candidates for the preparation of good membranes, provided that they have undergone some modifications. The modifications can be obtained by physical (8), chemical (7), or radiochemical methods (5, 6, 9–11) by the formation of grafted copolymers having better features. The radiochemical method allows better control of grafting and avoids the presence of other molecules such as initiators. It also allows for properties in the range between those of the base polymer and those of the grafted polymer.

It is thus possible to give hydrophilic properties (that is, water permeability) to mechanically strong (but hydrophobic) polymers, and vice versa. The first possibility (transforming hydrophobic polymers into hydrophilic ones) has been widely studied by us (5, 9, 12, 13). Lowering the hydrophilicity of a water-soluble polymer has not yet been fully explored. In a preceding work (14) we found that such a technique can successfully control the solubility of polyvinylpyrrolidone (PVP) by radiochemical grafting of styrene (St). The copolymers so obtained proved to be suitable for the preparation of asymmetric membranes by the phase-inversion technique (4).

The purpose of this work is to characterize such membranes and to check their performance in the UF process.

EXPERIMENTAL

Materials and Methods

The following materials were used in our experiments:

N-Methyl-2-pyrrolidone (NMP), reagent grade by Merck, used for dissolving the grafted copolymer.

Dextran T 110, MW 110,000, from Pharmacia Fine Chemicals, was dissolved in water and used to check the membrane rejection power. 0.5 g/L solutions were used.

The membranes were prepared by dissolving the grafted copolymers in NMP at concentrations ranging from 80 to 200 g/L. The solutions (very viscous) were spread over a glass plate to form homogeneous 200 μm thick layers which were then coagulated by plunging the plate into water at 278 K. In a few minutes the asymmetrically porous films separated from the plate surface.

This procedure was carried out at a controlled room temperature (293 K). The membranes so prepared were characterized and their features tested as a function of the degree of grafting.

The water permeability was tested by means of an UF laboratory apparatus equipped with temperature, pressure, and recirculation rate controls (Fig. 1). The permeate flux was evaluated by accurate volume measurements after a 1-hour run and reported as $L \cdot m^{-2} \cdot h^{-1}$. All tests were carried out at 313 K temperature, 200 kPa pressure, and 5 m/s recirculation speed over the membrane surface.

Dextran rejection was evaluated by total organic carbon (TOC) measurements performed on both permeate and feed solutions. An ASTRO 2001 TOC analyzer was used, and the rejection of dextran was reported as TOC decreasing percent. For measuring the bursting strength, a laboratory built apparatus was employed (Fig. 2), suitable for measuring the pressure at which the moist membrane burst. The tests were performed by applying pressure on the dense side of the membrane at a pressure increase rate of 1 kPa/s.

The membrane morphology was studied both by optical and electron microscopy. The optical microscope was a Zetopan-Reichert apparatus; the electron microscope used was a SEM mod Cambridge Stereoscan 250 MK2.

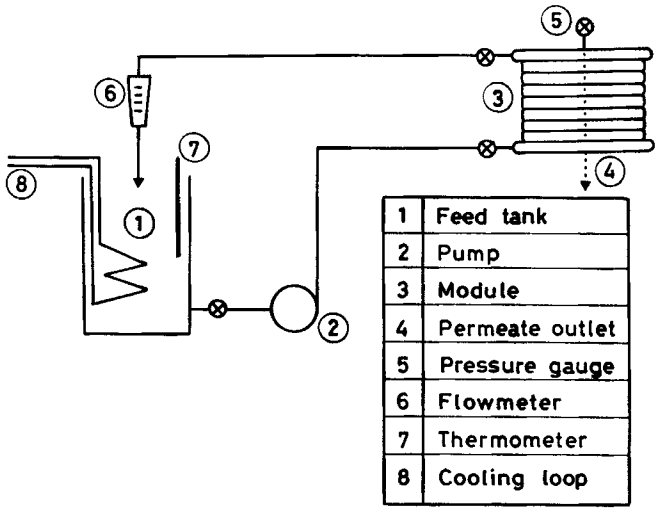


FIG. 1 Ultrafiltration laboratory apparatus schematic.

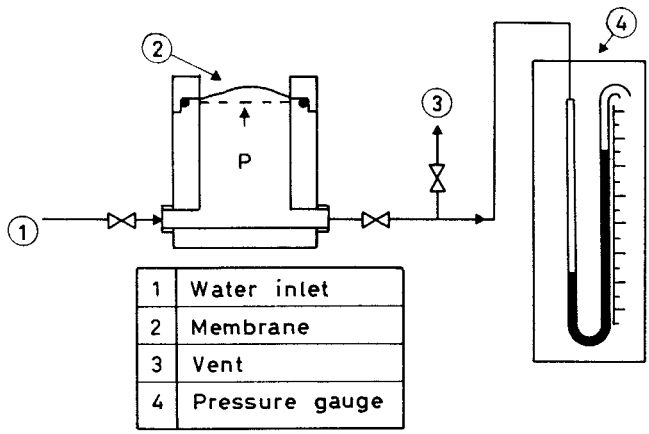


FIG. 2 Bursting strength measurement apparatus.

The membranes to be observed were liquid nitrogen frozen and broken up in order to observe their cross section without mechanical deformation due to the cut. The samples were gold coated before SEM microscopy.

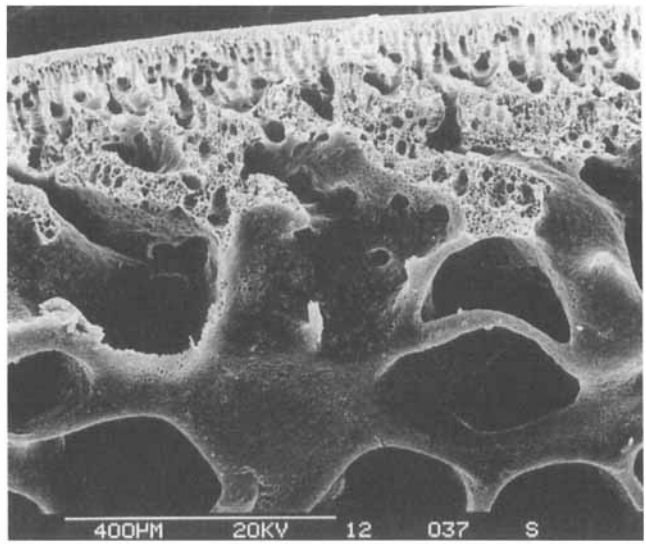
RESULTS AND DISCUSSION

Both optical and electron microscopy confirmed the asymmetrical structure of the membranes. We report here only the micrographs obtained from the SEM because they are more detailed and impressive.

In Figs. 5–8 we present micrographs of several membranes containing different amounts of grafting. For comparison, membranes prepared with pure PSt and PSt/PVP mechanical mixtures were also examined.

The first set of photographs demonstrates that there is a sharp difference between membranes prepared from mechanical mixtures and those made of grafted copolymer. Comparison of Figs. 3 and 4 with Fig. 5 shows that the Pst alone and its mixtures with PVP can provide films having some asymmetry, but both thick and porous layers are highly disordered. In particular, the large pores are quite different from those of the "fingerlike type" typical (4) of asymmetrical membranes. Moreover, the membranes obtained from mixtures were very brittle and could not be tested in the UF apparatus.

Figures 5, 6, 7, and 8 are of membranes prepared with the grafted copolymers, and they show that with increasing amounts of PSt grafting, both the asymmetry of the "dense" layer and the porous support morphol-



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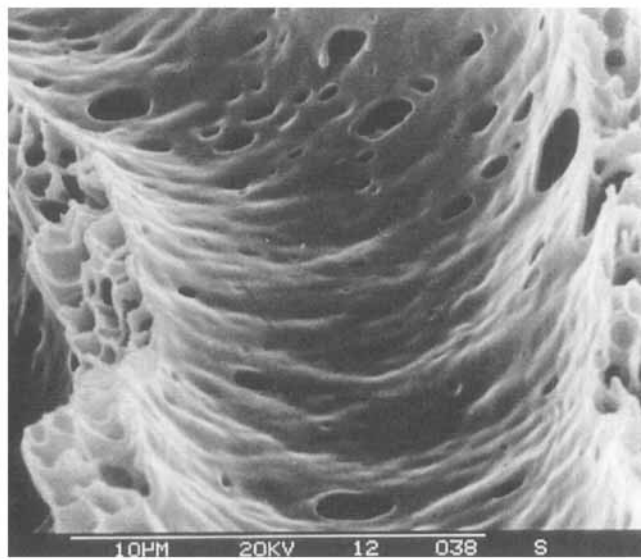

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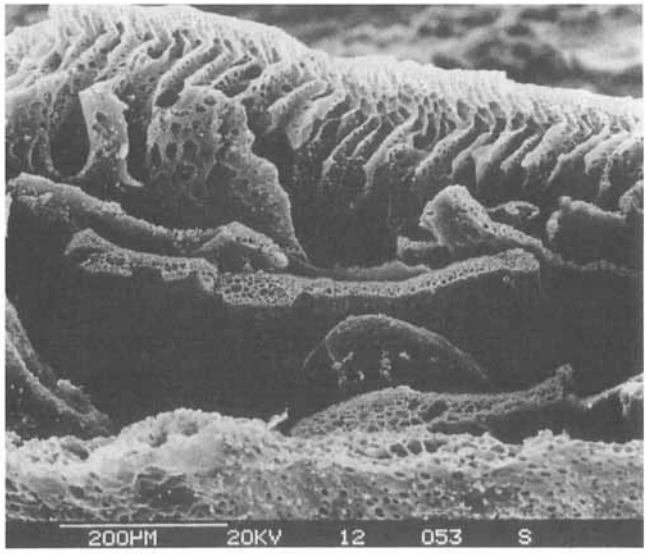
FIG. 3 (a) SEM micrograph of a section of a membrane cast from a mechanical mixture (PSt 90–PVP 10). Casting solution concentration: 150 g/L. Magnification 100×. (b) Porous layer of the same membrane at a magnification of 6000×.



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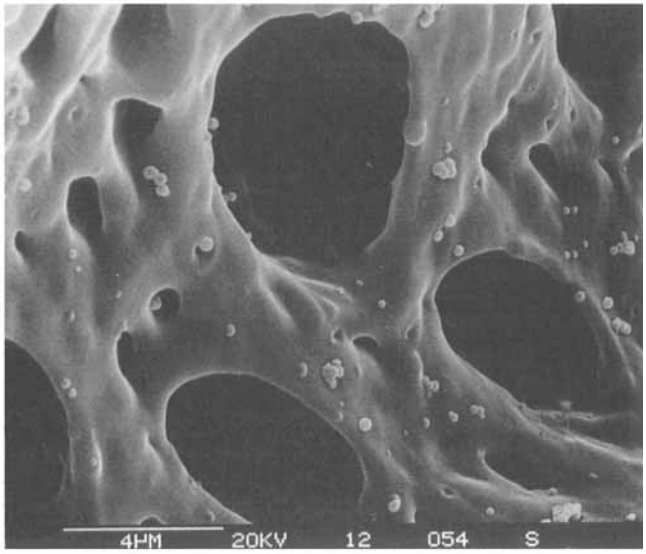

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FIG. 4 (a) SEM observed section of a membrane prepared from pure PSt (MW 250,000). Magnification 130×. (b) Porous layer of the same membrane at a magnification of 6000×.

ogy improve (in the range scanned). At 85% PSt, a fingerlike region is observed.

The toughness of the membrane improves with increased casting solution concentration. This behavior is common for most membranes prepared by the phase-inversion technique, and is strictly related to the viscosity of the solution (17).

ULTRAFILTRATION TESTS

Ultrafiltration tests were performed to confirm the results of the SEM study and to evaluate the true performances of our membranes.

Grafting Percent

The influence of the grafted PSt content on permeate flux (F) and dextran rejection (R, %) was first examined, and the results are reported in Figs. 9 and 10.

The trends of the rejection curves demonstrate that there is an optimal grafting ratio. This value is around 84% PSt content, and also fits the permeate flux curves. It was impossible to scan a wider range of grafting due to the incoherence and brittleness of membranes prepared outside the range mentioned above. The curves shown suggest that the grafting reaction performed by us affects both the physical and chemical characteristics of the membrane, independent of the casting procedure that followed.

The best membranes were obtained in a narrow range of grafting. The following observations can be made concerning UF testable membranes prepared from copolymers of different compositions.

At the left side of the range (lower PSt content), the flux decrease can be explained by taking into account that a higher PVP content increases both the hydrophilicity and the "compliance" of the membrane, so that it would collapse and be compacted under the pressure at which UF runs are made. Moreover, as can be seen in Fig. 5, asymmetry is lost and the final result is a decline in flux.

At higher PSt contents, the decrease in flux is connected with the low hydrophilicity of PSt, while its lower interaction with water-soluble compounds like dextran can contribute to a decrease in rejection.

Membrane performance changes with casting solution concentration in a predictable way: the higher the concentration, the higher the toughness and the rejection power of the membrane. The opposite occurs with permeate flux, as can be seen in Fig. 11.

The data in Fig. 11 are related to a membrane obtained from 84.5% PSt grafted copolymer casting solution. Concentration is of utmost importance in preparing membranes by the phase-inversion technique. Membranes obtained from dilute solutions generally have a large permeability but a poor selectivity and mechanical strength; concentrated solutions have the opposite characteristics. It is therefore necessary to reach the right compromise by studying such parameters.

The solvent used also affects the final performance of membranes (15, 16). For this reason we used only NMP for preparing the membranes. From the experimental data reported in Fig. 11 it can be determined that the best membranes can be obtained from solution concentrations ranging from 10 to 15%. In this range the best compromise between permeate flux and rejection can be reached. A higher concentration (say 20%) causes rejection closer to 100% but much lower permeability. In the case of a concentration lower than 10%, the performances decrease is connected with dense layer defects (due to dust, air bubbles, etc.). This can be confirmed by the shifting of R and F peaks toward higher PSt content (Figs. 9 and 10) for membranes prepared from 8% solutions. The higher PSt

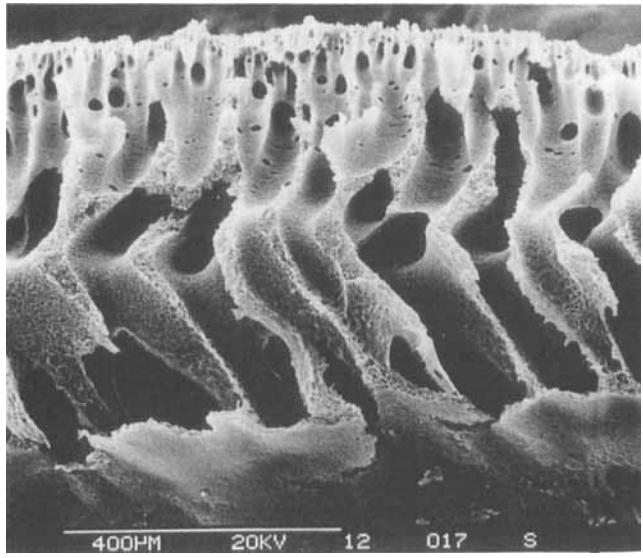
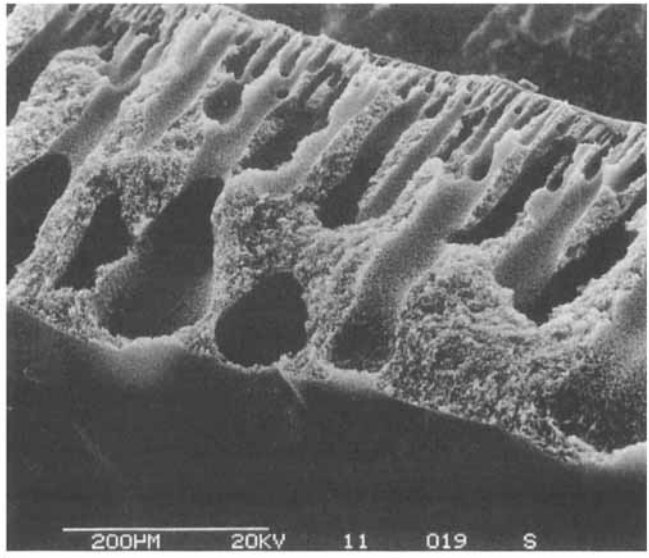


FIG. 5 Influence of grafting on membrane morphology. Sections of membranes prepared from grafted copolymers having: (a) 85% PSt, (b) 82.5% PSt, and (c) 73.5% PSt. Casting solution concentration: 100 g/L. Magnification 150×.



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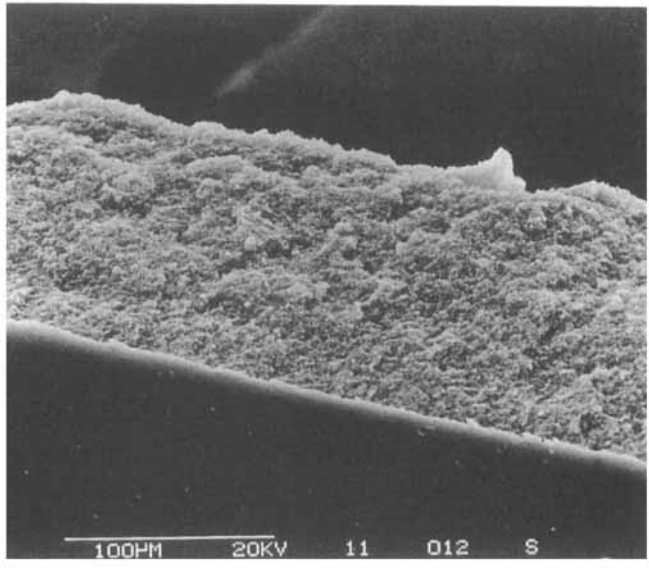

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FIG. 5 *Continued*

content is responsible for a higher solution viscosity and thus better membrane pore control (17).

BURSTING STRENGTH

The usability of membranes is conditioned by their mechanical strength; in particular, they must be able to withstand the pressure applied during the UF process. Accurate bursting strength measurements have been performed on membranes having different PSt contents. The results are reported in Figs. 12 and 13. Each value is the average of three measurements. The curve in Fig. 12 shows the same trend as found in Figs. 9 and 10. These grafted copolymers can be considered to be polymeric "alloys" which, just as with metallic alloys, have particular characteristics at well-defined component ratios. In our case the ratio at which the best mechanical resistance is measured is 84 PSt/16 PVP. This value is almost the same as that at which the best UF performances occur. Membranes so prepared look compact and can be easily handled.

Microscope observation confirms the toughness of their structure. The behavior of bursting strength with solution concentration is not surprising:

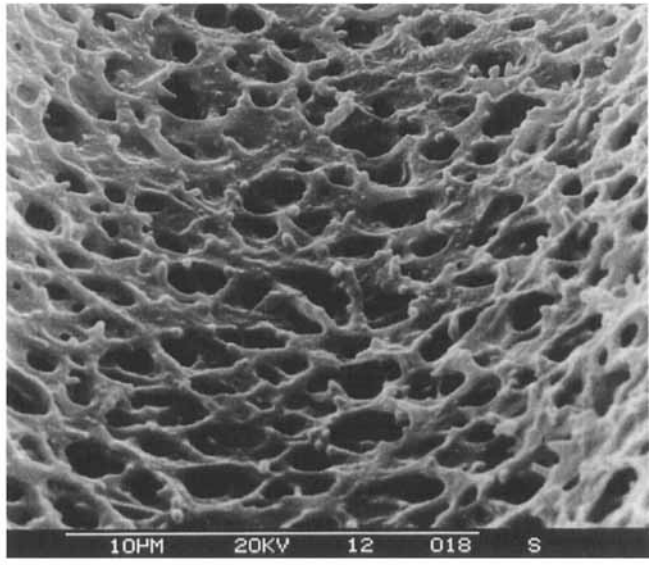

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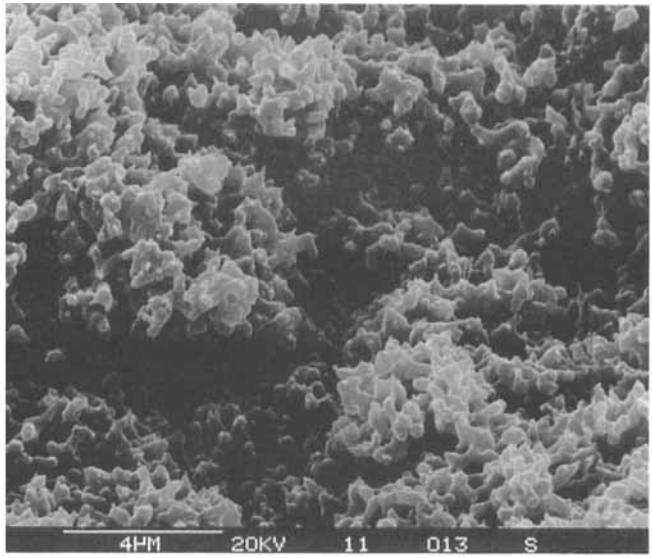
FIG. 6 The same membranes as in Fig. 5 observed in the region of the porous layer (finger-like region). Magnification 6000×.



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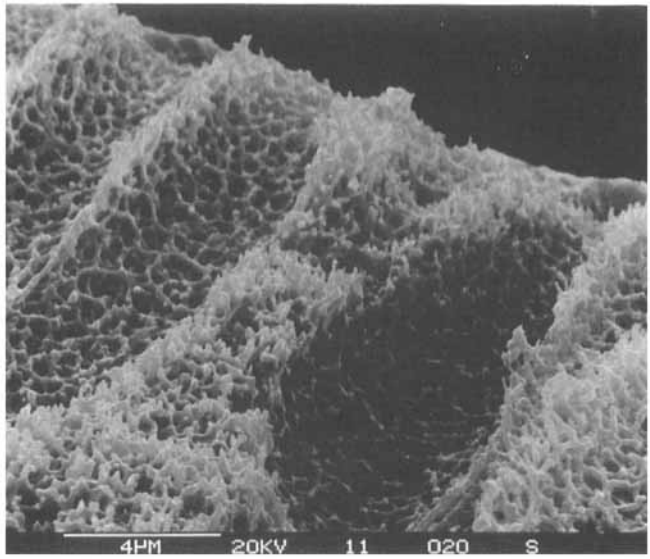

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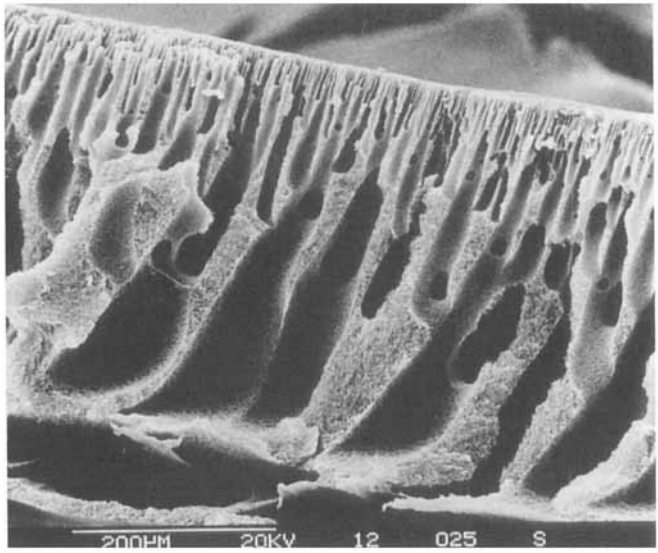
FIG. 6 *Continued*



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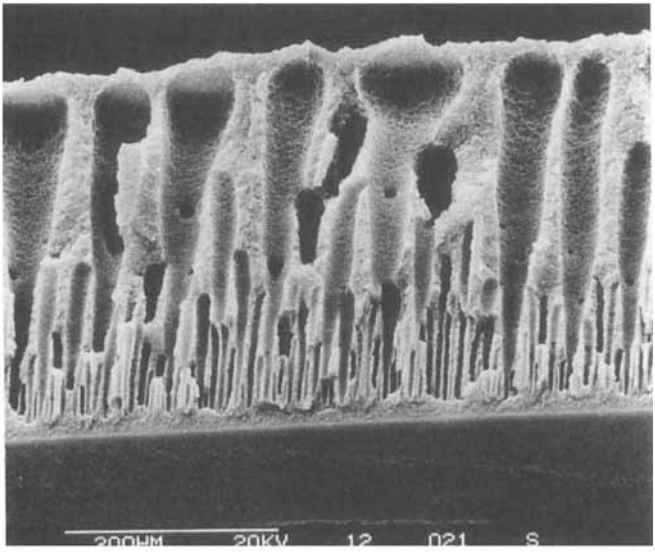

b

FIG. 7 Influence of the casting solutions concentration on the membrane morphology. Sections of membranes prepared from solutions containing (a) 60 g/L and (b) 80 g/L of grafted copolymer. Grafted PSt: 85%. Magnification: 150×.

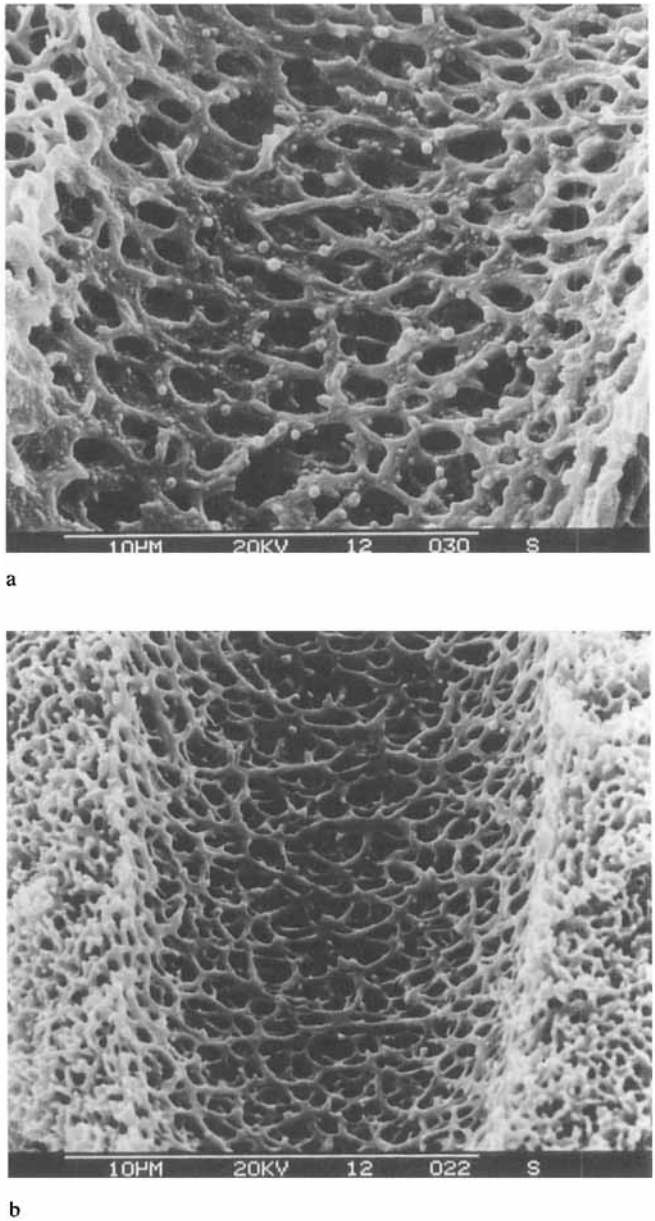

FIG. 8 Membranes observed in the porous region at 6000× magnification: (a) casting solution, 60 g/L; (b) casting solution, 200 g/L.

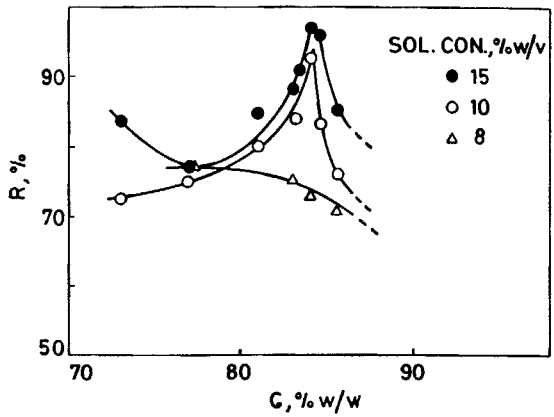

FIG. 9 Influence of PSt grafting G on the rejection power R, measured for three casting solution concentrations.

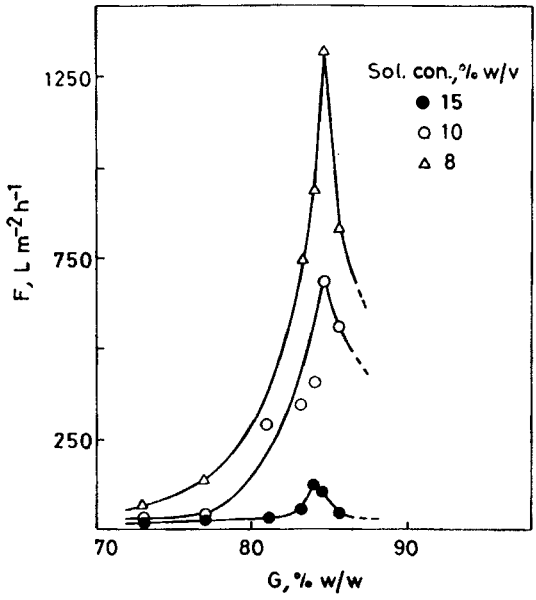

FIG. 10 Influence of PSt grafting G on the permeate flux F, measured for three casting solution concentrations.

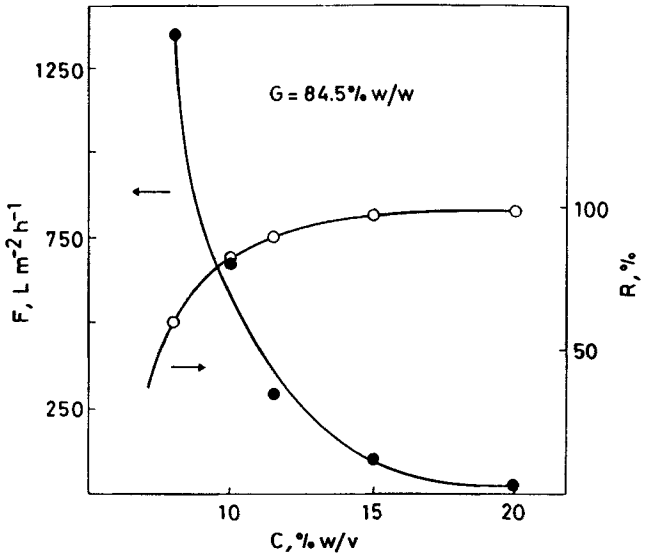

FIG. 11 Influence of casting solutions concentration C on rejection R and permeate flux F.

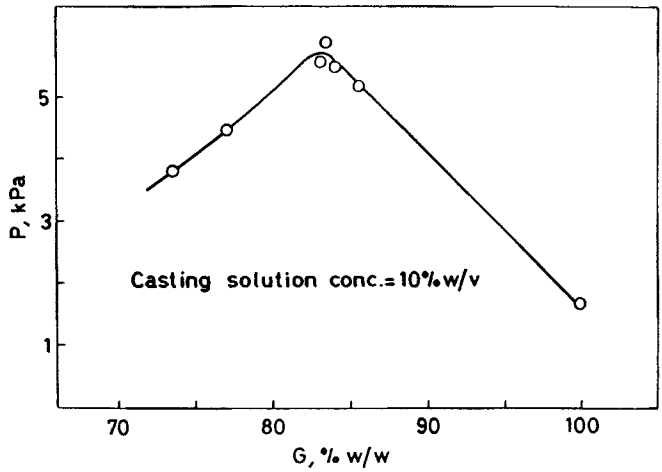

FIG. 12 Influence of PSt grafting G on the bursting pressure P.

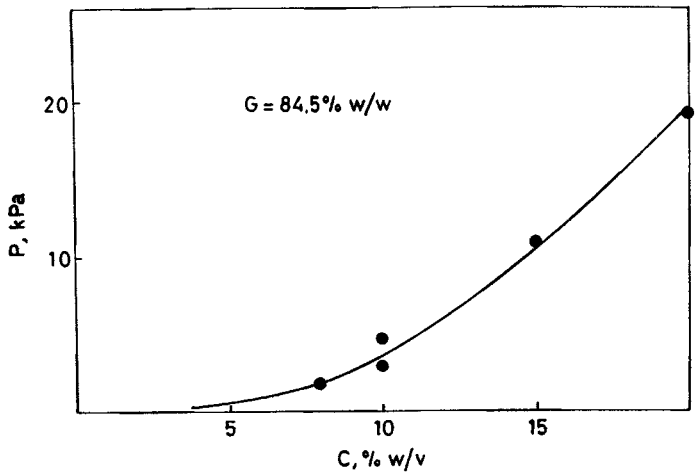

FIG. 13 Influence of the casting solution concentration C on the bursting pressure P.

the only information to be drawn from Fig. 13 is that membranes cannot be prepared from solutions with less than 6% polymer.

CONCLUSIONS

Our experimental results demonstrated that the water solubility of polymers such as PVP can be controlled by radiochemical grafting to a degree sufficient to obtain insoluble products. The new copolymers so synthesized proved useful for preparing UF membranes. The membranes have optimal characteristics in a well-defined range of grafting: UF performances, mechanical strength, and microporous structure can be varied in this range in order to create different kinds of membranes. It is expected that other water-soluble polymers can be grafted in order to obtain membranes suitable for UF processes application. Future research will focus on further exploration of radiochemical grafting for changing the properties of membranes used in separation processes.

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