Ultrafiltration Membranes Obtained by Grafting Hydrophilic Monomers onto Poly(vinyl Chloride)

FERNANDO VIGO and CLAUDIO ULIANA, *Institute of Industrial Chemistry, Genoa University, Corso Europa 30, I-16132 Genoa, Italy*

Synopsis

The grafting of vinylacetate (VAc) or hydroxyethylmethacrylate (HEMA) onto poly(vinyl chloride) (PVC) has been performed by means of γ-rays or chemical initiators. The grafted polymer so obtained has been separated by selective extraction and submitted to IR spectroscopy in order to check the amount of grafting. The grafting percentage was measured as a function of the grafting conditions. Using the above-mentioned polymer, dissolved again in DMF, asymmetric ultrafiltration membranes have been prepared by the phase inversion technique. The membranes have been tested with Dextran solutions. Their performances have been studied as functions of the grafting amount. The values of rejection and permeating flux demonstrated the effectiveness of the treatment in enhancing the performances of PVC ultrafiltration membranes.

INTRODUCTION

Ultrafiltration membranes can be obtained from poly(vinyl chloride) (PVC) dissolved in the adequate solvent, using the phase inversion technique.[1-3] Membranes so prepared show water permeability and rejection to macromolecular solutes, though the performances are not outstanding[3]; moreover, they possess good mechanical strength[2] and can be stored in dry form. It has been demonstrated[4] that the addition of very small amounts of hydrophilic groups to the polymeric PVC chains is successful in increasing both water permeability and rejection.

The required groups can be introduced by means of several techniques, among which the grafting reaction stands out. Graft copolymerization can be accomplished with the aid of chemical initiators or by ionizing radiations (for example, X-, γ-, β-rays). This technique has been used for quite a long time to induce chemical properties changes in polymers[5] and then to prepare selective membranes.[6-8]

It has been recently demonstrated that the grafting performed in solution (i.e., with the polymer and the monomer to be grafted, both dissolved in the same solvent) is useful for obtaining homogeneously grafted copolymers[9] which can give ultrafiltration membranes with the phase inversion technique.

The purpose of the present study is to apply this method starting from PVC grafted with hydrophilic monomers; we chose vinylacetate (VAc) and hydroxyethylmethacrylate (HEMA) as monomers to be grafted by means of chemical and radiochemical initiations. The influence of some grafting parameters (such as reaction time, temperature, and monomer concentration) were studied, as well as the ultrafiltration performances and structure morphology of the membranes prepared.

Journal of Applied Polymer Science, Vol. 38, 1197–1209 (1989)
 CCC 0021-8995/89/071197-13$04.00

EXPERIMENTAL

Materials Used

Poly(vinyl chloride) (PVC), powder, 99.99% pure, 120,000 MW, was supplied by ANIC S.p.A. (Milan). Vinylacetate (VAc), by Fluka, was vacuum-distilled to free it from the stabilizer, and then stored at −20°C. Hydroxyethylmethacrylate (HEMA), by BDH, was vacuum-distilled in the presence of cuprous chloride and then stored at −20°C. Dimethylformamide (DMF), by Merck, was dried with molecular sieves before using. Tetrahydrofuran (THF), by Merck, reagent grade. Methanol, by Merck, reagent grade. Dextran, by BDH, 110,000 MW, was dissolved in water at 0.1% by weight concentration. Benzoyl peroxide (BPO), by Merck, was vacuum-dried at 40°C before using.

Grafted Copolymer Preparation

Glass vials were filled with a solution of 0.1 kg PVC/L in DMF and the monomer that had to be grafted; in the case of grafting performed by chemical initiator, BPO was also added. The mixture was then bubbled with pure nitrogen for 1 h. The sealed vials were placed in a thermostatic bath or (in the case of radiochemical grafting) submitted to γ-rays from a Co^{60} source. After the time required to accomplish the grafting reaction, the vials were opened, and their content poured into distilled water in order to precipitate the copolymer. The solid residue, washed with water and dried, was extracted with boiling methanol to remove the homopolymers as much as possible (PVAc and PHEMA). After a 16-h extraction, the residue was vacuum-dried overnight at 60°C.

Grafting Yield Evaluation

In order to measure the composition of the graft copolymer, it was dissolved in THF; the solution so obtained was then evaporated on the KBr window, and the resulting thin film was examined by means of a 983 Perkin-Elmer IR spectrometer. The grafting content was evaluated by measuring the absorbance peak height at 1742 cm^{-1} (corresponding to $=CO$ groups vibrations) and comparing it to that due to the absorbance of $=CH_2$ groups (at 1435 cm^{-1}). Calibration curves, obtained in the same manner from mixtures of PVC/PVAc or PVC/PHEMA, allowed us to evaluate the grafting percent, which was then expressed as a weight percentage of graft PVAc or PHEMA over the whole copolymer after extraction with methanol.

Membranes Preparation

The methanol-insoluble fraction of the graft copolymers was used to prepare the ultrafiltration membranes according to the following procedure: Graft PVC was dissolved in DMF in order to obtain a clear solution having 0.1 kg polymer/L; the solution was cast on a glass plate and, immediately after, coagulated in iced water. The membranes had a thickness of about 130 μm, depending on the type and amount of grafting. The membranes were dried at room temperature and stored in order to be tested in an ultrafiltration plant.

Membrane Performances Measurement

The ultrafiltration tests were performed using a stainless steel loop equipped with a centrifuge pump, with pressure, temperature, and recycling rate controls and fed with a 0.1% by weight solution of Dextran. Flat membranes 0.1 × 0.05 m were used, and all the tests were run at 40°C, 200 kPa, and 5 m/s recycle rate. The values of permeating flux and rejection were taken after 1 h test run. The rejection to Dextran was measured by colorimetric reaction with sulfuric acid and phenol.[10]

Electron Microscopy

Dry membrane samples were frozen by liquid nitrogen and then broken down; the fractured side was gold-shadowed and submitted to SEM by a Cambridge Stereoscan 250-K electron microscope.

RESULTS AND DISCUSSION

Graft Copolymers Preparation

Chemical Grafting

Influence of Reaction Time. According to the technique previously described, mixtures of PVC solution and monomer (VAc or HEMA) were kept at 70°C for different periods of time. The concentration of initiators (BPO) was 5 g/L. The ratio (of weight) between monomer and PVC was 2.5 in the case of grafting with VAc and 0.5 in the case of HEMA. The low ratio HEMA/PVC was chosen to avoid the formation of crosslinked gels which is favored by high monomer concentration and long reaction time.[11]

The experimental data are reported in Figure 1; they show that, in both cases, the grafting gives steady values after a 24-h reaction. This behavior can

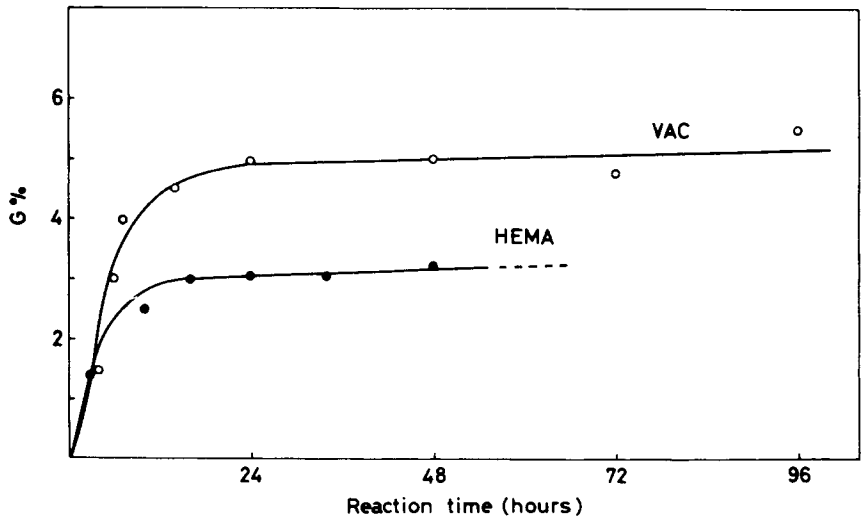


Fig. 1. Grafting percent (G%) vs. reaction time in the presence of 0.5% of BPO. Reaction temperature 70°C; VAc/PVC ratio 2.5; HEMA/PVC ratio 0.5.

be explained considering that the amount of radicals created in the reaction mixture is proportional to the BPO concentration, keeping the other conditions constant.

These radicals are responsible for the grafting reactions, and, as soon as they are consumed by termination reactions, the growth of grafted chains stops.

In the case of VAc grafting, the reaction seems to be more effective, and DMF soluble copolymer can still be collected after a 96-h reaction. In the case of HEMA the tests duration was limited to 48 h, due to the formation of crosslinked gels which could not be separated from the grafted PVC.

Influence of Monomer Concentration. Vials containing increasing ratios of monomer/PVC concentration were kept 24 h at 70°C in presence of 5 g BPO/L. The grafting data obtained are reported in Figure 2. Two facts can be remarked. First, the VAc/PVC ratios range is nine times wider than in the case of HEMA/PVC, due to the above-cited necessity of avoiding HEMA crosslinking; this fact could let us imagine the impossibility to achieve grafting yields much higher than 8% (see the HEMA plot). Fortunately, this assumption is not verified in the case of radiochemical grafting, as will be shown further on. The second remark concerns the kinetic features of the reaction: Plotting the data in a logarithmic graph, it can be drawn out that the grafting percent expressed as Grafted polymer/PVC matrix (R) depends on the monomer/PVC (r) ratio according to the following relation:

$$R = Kr^a$$

where a is close to 1 at low grafting values. As soon as the grafting becomes higher than 6%, the a value starts increasing, due to the so-called "gel effect,"[12] which reduces the termination rate of the radicals.

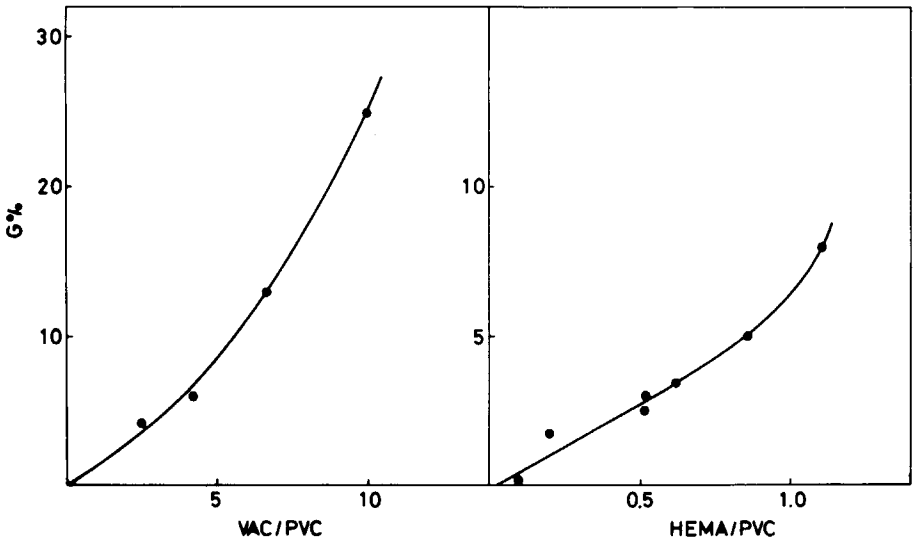


Fig. 2. Grafting percent (G%) vs. the ratio monomer/PVC. Reaction in the presence of 0.5% of BPO. Reaction time 24 h; reaction temperature 70°C.

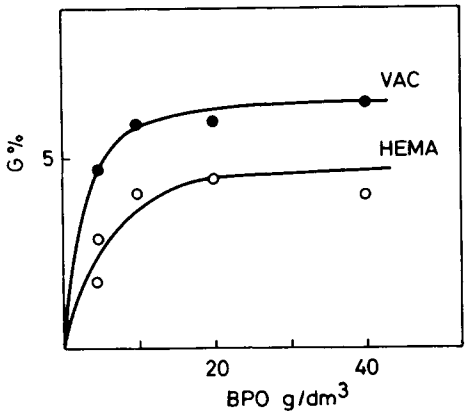


Fig. 3. Grafting percent (G%) vs. the BPO concentration. Reaction time 15 h; reaction temperature 70°C; VAc/PVC ratio 2.5; HEMA/PVC ratio 0.5.

Influence of the Initiator Concentration. Mixtures at constant monomer/PVC ratio were reacted for 15 h at 70°C in presence of increasing percentages of BPO. The results are reported in the plot of Figure 3. As is well known,[11] in the BPO-initiated radical polymerization the reaction rate is proportional to the square root of BPO concentration. Referring to the plot in Figure 1, it can be supposed that 15 h is a reaction time short enough to try an evaluation of the grafting rate. The rough values so obtained confirm the above-cited trend; there is nothing surprising about it, if we consider that our kind of grafting is similar to a normal solution polymerization.

Effect of Temperature. The grafting reaction was performed at temperatures ranging between 30 and 90°C, with mixtures having VAc/PVC ratio = 2.5 and HEMA/PVC = 0.5. The reaction duration was 24 h. The degrees of grafting obtained at various temperatures do not show significant differences. This seems to be in contrast to common experience according to which a dependence of the degree of polymerization on temperature should exist. The apparent temperature independence of the degree of polymerization might be due to the fact that its variation with temperature is affected by several parameters (chain length, number of initiating sites, and transfer reactions), which act in an opposite direction.

Radioinduced Grafting

The grafting was accomplished by simultaneous irradiation technique, carried out at room temperature with PVC, monomer, and DMF mixtures prepared and treated in the same way described for chemical grafting. The irradiation dose rate was 1.92 Gy/min, and the influence of the dose on the grafting yield was recorded.

The radiochemical technique enables us to control in a better way the "supply" of the radicals to the reacting mixture, i.e., the initiation stage of the grafting. It can be reasonably imagined that better results can be therefore obtained, avoiding complications connected with decomposition kinetics of chemical initiators and consequent contamination of the copolymer with residual molecules of the initiator.

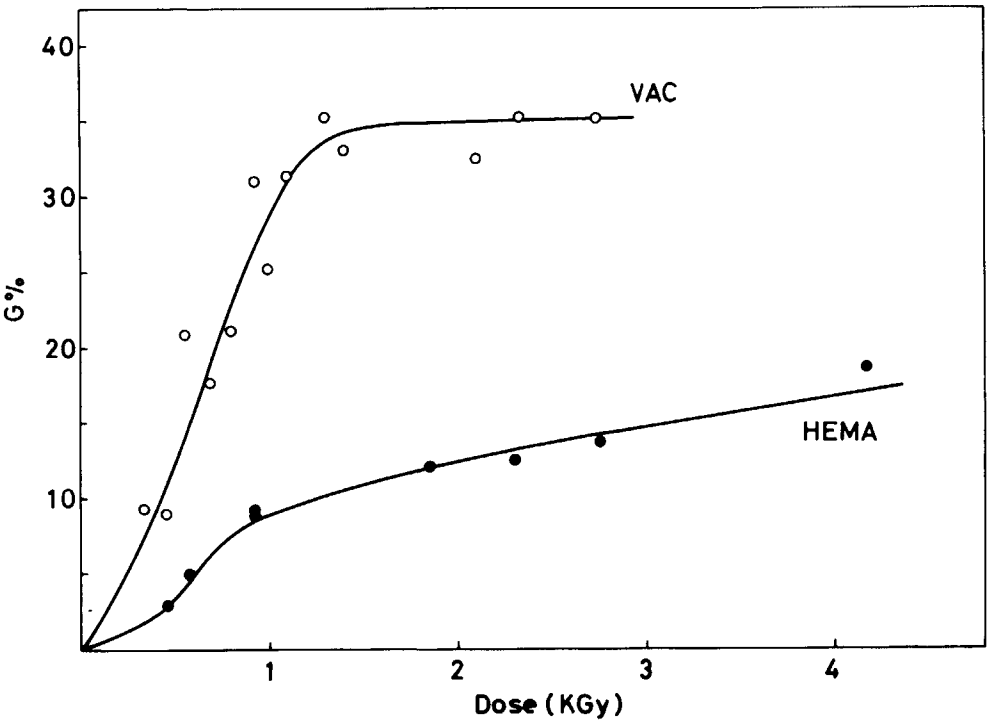


Fig. 4. Radioinduced grafting percent (G%) vs. absorbed dose. Dose rate 1.92 Gy/min; VAc/PVC ratio 2.5; HEMA/PVC ratio 0.5.

The data reported in Figure 4 seem to confirm our statement, as far as the grafting yield is concerned. Comparing the grafting values of VAc with those obtained with HEMA, it must be kept in mind that the ratio monomer/PVC is five times higher in the case of VAc. As in the case of chemical grafting, this discrepancy is due to the need of avoiding formation of crosslinked HEMA gels.

As shown in Figure 4, in both cases the grafting goes through an "induction period," which is typical of these kinds of reactions[12] (due to impurities or residual oxygen), and reaches a maximum value corresponding to 35% in the case of VAc. On the contrary, the grafting of HEMA seems to keep growing with the dose.

According to experimental exams obtained by IR spectroscopy and electron microscopy, this behavior can be therefore explained: The VAc grafting "plateau" trend is due to a compromise between high grafting degrees (which are typical of the previously mentioned "gel effect") and the consequently increased solubility of the copolymer in methanol; the technique we used allows us only to evaluate the percentage of PVAc in the *insoluble* fraction of the grafted PVC.

A fraction grafted to a higher degree can be collected from the methanol solution, as demonstrated by our experimental tests.[9] The same comments could be made as a first approach, in the case of HEMA. The different trend above 1.5 kGy is probably due to crosslinked homopolymer which can be hardly separated from the graft. Electron microscopy confirms this hypothesis.

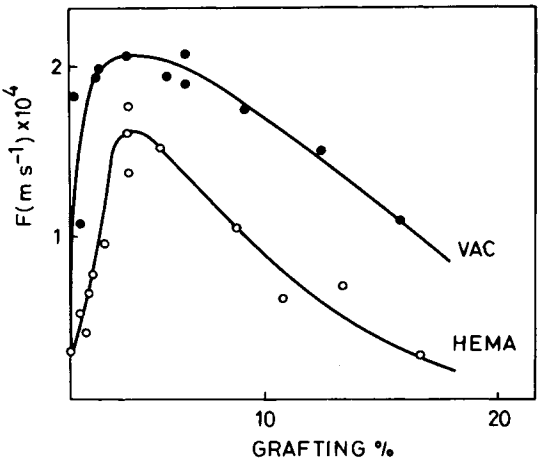


Fig. 5. Permeate flux (F) vs. grafting %.

Membranes Characterization

The asymmetric membranes prepared by the technique previously described were tested in an ultrafiltration cell in order to evaluate their permeability and rejection to Dextran. Moreover, they were examined by SEM with the purpose of connecting ultrafiltration performances with structure morphology.

Ultrafiltration Performances

The permeate flux of the membranes is reported in Figure 5 as a function of the grafting percentage. The grafting values are related to both chemical and radiochemical initiations, as no significant differences were noticed concerning the behavior of the membranes. Rejections are reported, in the same manner, in Figure 6. All data were collected after 1-h ultrafiltration tests. The trend of the plots in Figures 5 and 6 suggests that a small percentage of grafting is sufficient to greatly enhance the flux and rejection properties. The permeability enhancement can be put in relation to the hydrophilicity increase of the

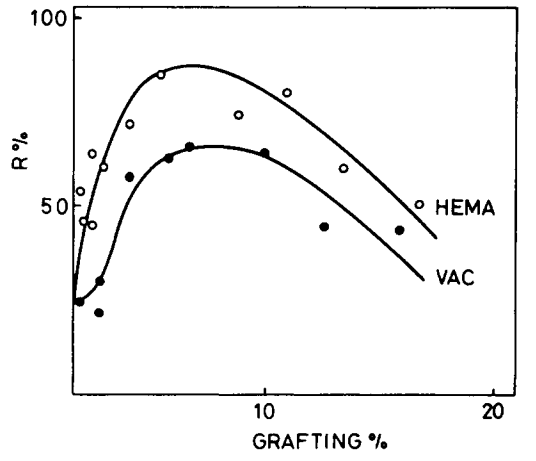


Fig. 6. Rejection to Dextran 110,000 vs. grafting %.

TABLE I
Water Absorption and Elongation Characteristics of PVC, PVAc, and PHEMA

Polymer	Water absorption (%)	Elongation at break (%)
PVC	0.4	2
PVAc	3	20
PHEMA	40.4	400

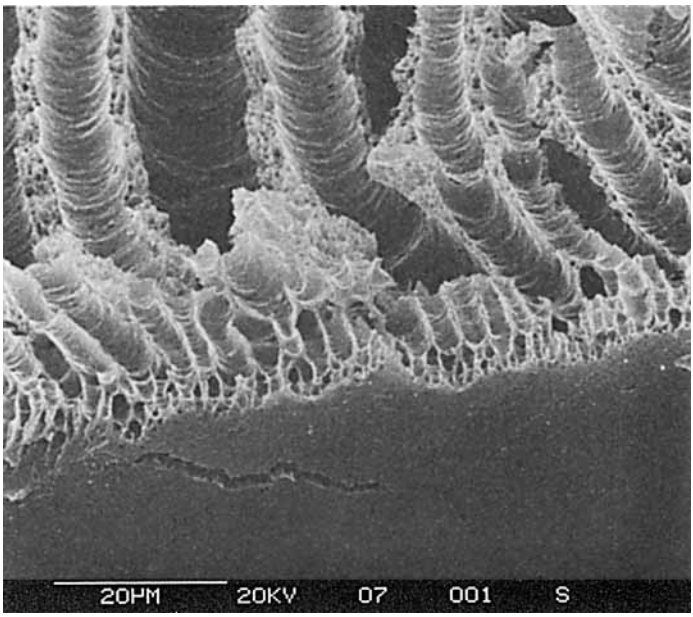
PVC after grafting with VAc or HEMA. In Table I some water absorption values are reported for PVC-, PVAc-, and PHEMA-dense films (water uptake measurements performed on the membranes are scarcely meaningful, due to the presence of spongy structures). Rejection increase may be connected with the increased polarity of the graft copolymer and/or with a change in the "dense" skin structure. The latter parameter is very difficult to study, and we were not able to check it either by electron microscopy or by some porosity temptative tests. Both graphs go through a maximum value at 4% grafting in the case of flux, and approximately 6% in the case of rejection. The further decrease in flux performance can be explained taking into account some mechanical characteristics of PVAc and PHEMA. In Table I one can see that the elongation at break of PVAc and PHEMA is fairly greater than PVC. Membranes prepared from them by the technique previously described[13] would not withstand the pressure required for ultrafiltration without deep structure alterations. Pore elastic deformation and the squeezing of a spongy structure can be responsible for rejection and flux decrease. Our experimental checks have demonstrated that through our technique neither PVAc nor PHEMA are suitable for asymmetric membranes.

Moreover, beyond a certain PVAc or PHEMA graft percentage the membrane starts losing the PVC characteristics, which have proven suitable for good asymmetric structures.[1] As a consequence, the degree of asymmetry of the membrane undergoes a change, leading to structures that do not allow the achievement of high performances; this seems to be confirmed, to a certain extent, by electron microscopy observations.

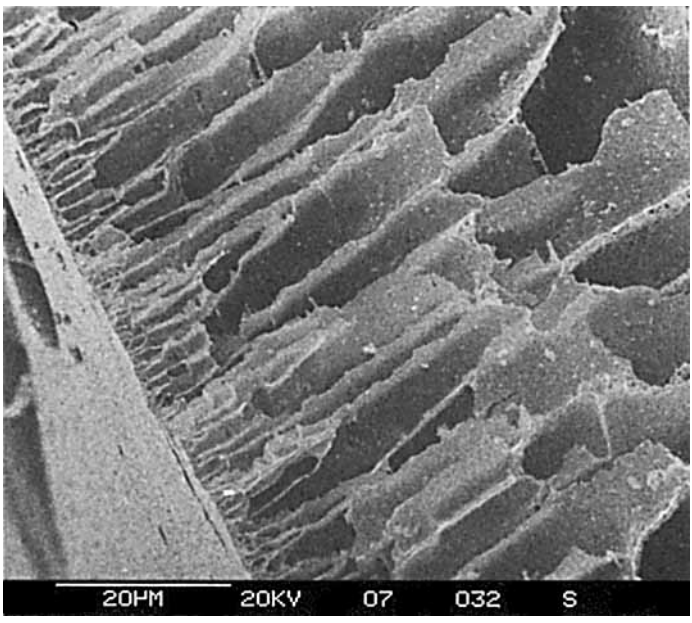
Electron Microscopy

Membranes prepared from graft copolymers having different amounts of PVAc or PHEMA were submitted to electron microscopy according to the previously described technique. Putting clearly in evidence the dense skin of asymmetric membranes seems to be a very difficult task, even with highly sophisticated electron microscopy techniques. The dense active skin gradually fades into the porous support and inevitably affects the characteristics of the skin. Much attention was thus paid in examining the structure close to the "dense" surface of the membrane. Several microphotographs were taken; some of them seem most significant and are reported in Figure 7, together with one that is typical of ungrafted PVC.

Comparing each one of these photographs, it can be noticed that the fingerlike structure underlying the membrane "skin" is originally characterized by many and narrow tubular macropores while, increasing the PVAc or

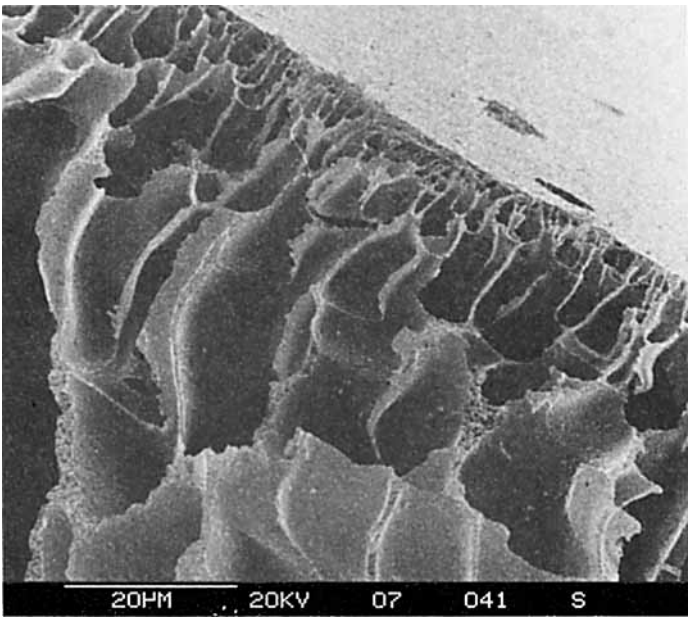


(a)



(b)

Fig. 7. Cross section of membranes having different grafting content: (a) ungrafted PVC; (b) 3% PVAc-grafted PVC; (c) 17% PVAc-grafted PVC; (d) 3.5% PHEMA-grafted PVC; (e) 18% PHEMA-grafted PVC; (f) 18% PHEMA-grafted PVC (detail).



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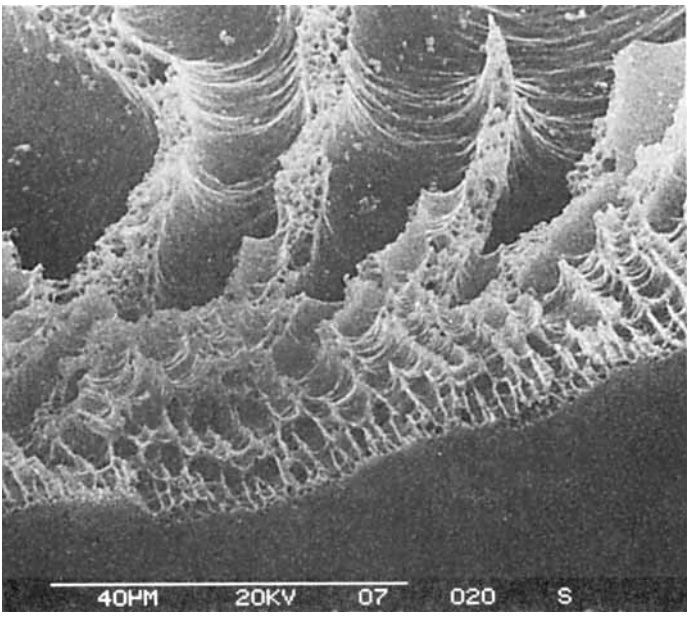
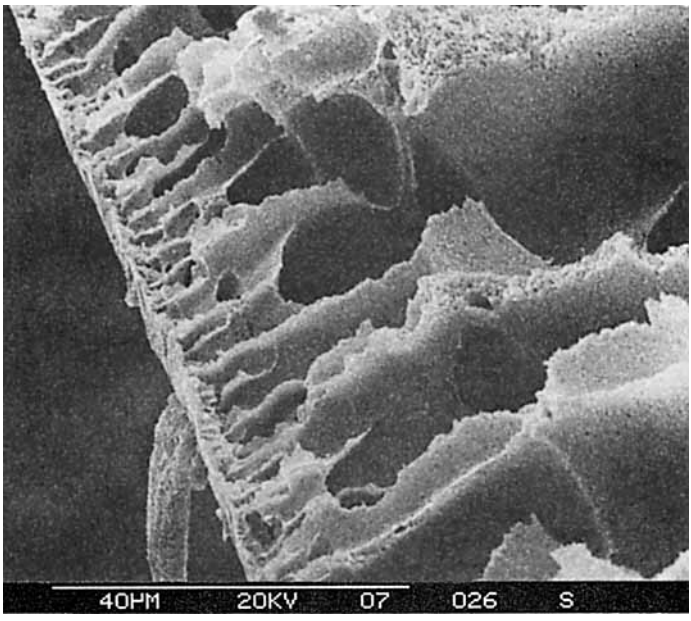
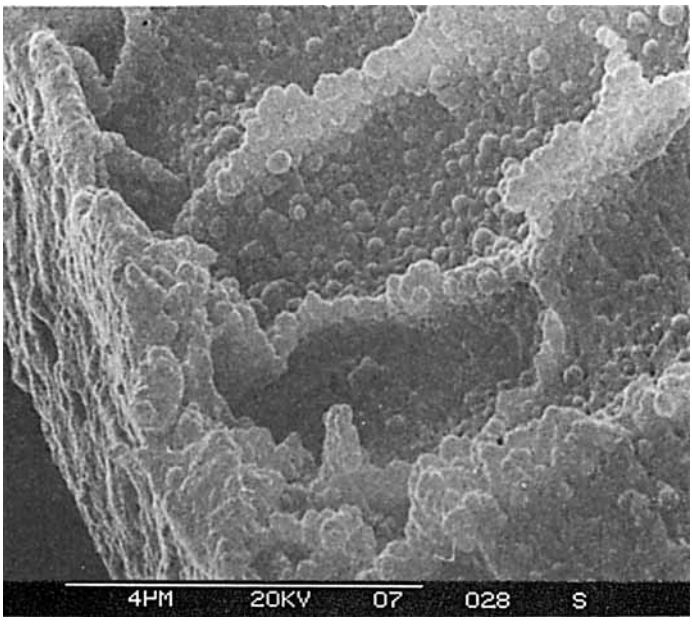


(d)

Fig. 7. (*Continued from the previous page.*)



(e)



(f)

Fig. 7. (*Continued from the previous page.*)

PHEMA content, they gradually become wider and more irregular; moreover, they seem to interfere with the dense layer which also becomes more indistinct when the membrane is obtained from highly grafted copolymers. This stands out clearer with PHEMA-grafted membranes. Moreover, we have noticed the presence of globular structures [see Fig. 7(f)] that can be attributed to crosslinked PHEMA homopolymer unextracted by the hot methanol washing.

CONCLUSIONS

The results achieved in our study show that grafting of VAc and HEMA onto PVC dissolved in DMF is easy to perform, by means of chemical or radiochemical imitations. The radiochemical technique seems more promising, suitable to obtain higher yields and to reduce crosslinking reactions among PHEMA chains.

The graft copolymers we obtained consist roughly of two main fractions: one soluble in methanol (highly grafted) and other insoluble. The latter has proven to be suitable for preparing ultrafiltration membranes: Optimal results are obtained with moderate grafting degrees. This fact together with the microscopic observations demonstrates that, in order to get good ultrafiltration membranes, it is of the utmost importance to introduce hydrophilic groups in the PVC matrix, avoiding too many drastic changes in its solubility characteristics. Therefore, a good membrane should have the same structure of those prepared from PVC alone, with a better water affinity. This is also in agreement with the data found in preceding studies.[4,14]

Our purpose is to go on studying this technique, exploiting the properties of other monomers like acrylonitrile or acrylamide, with the aim of better characterizing, by fractioning, the grafting products. If we are successful, it will be possible to choose the proper graft copolymer in order to better "tailor" the membranes.

Further chemical modification of the graft are not to be excluded, in order to enhance the hydrophilicity without increasing the number of grafted chains. The work is in progress, and we hope that we will be able to report about it in the near future.

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Received December 17, 1987
Accepted December 22, 1987