

New Membranes Bearing Pyridinic Ligands by Plasma Graft Polymerization

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ABSTRACT: 2'-(2-Pyridyl)ethyl methacrylate (2-PEMA) synthesized in our laboratory was grafted onto the surface of polyacrylonitrile (PAN) ultrafiltration membranes by plasma-induced graft copolymerization. The plasma was used to activate the surface of PAN membranes before the grafting reaction. The amounts of peroxides created by plasma treatment were determined using 2,2-diphenyl-1-picrylhydrazine (DDPH). Influences of plasma treatment power, time, monomer concentration, presence of inhibitor, and solvents on polymerization were investigated. Surface functionalization was characterized by FTIR-ATR, ESCA, SEM, and water-contact angles. Grafting yield was shown to increase with the monomer concentration and if a mixture of H₂O/CH₃OH was used. Hence, it was possible to show that plasma treatment was a good technique to introduce ligands with coordinating properties by modifying the surface of the PAN membranes. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 359–366, 1998

Key words: plasma-induced graft polymerization; surface modification; pyridinic ligands; polyacrylonitrile

INTRODUCTION

Nowadays, the great interest in membrane technologies is generating the development of new polymeric materials with specific properties. These polymers may be obtained either from new monomers or by chemical modification of available ones.^{1–3} As their surface properties are usually more important than their bulk ones, a great deal of research is being devoted to surface modification of polymer membranes.

Graft polymerization appears to be an efficient way to realize these surface modifications. Such a process may be initiated by formation of

free radicals at the polymer surface generated by UV⁴ or plasma^{5,6} irradiation techniques. These two methods differ only in the way the free radicals appear at the polymer surface: directly, from the electrons in the plasma procedure and, indirectly, through an energy transfer to a photosensitizer necessary to achieve surface polymer activation by UV irradiation.⁷ We chose the plasma technique that modifies the polyacrylonitrile (PAN) membranes by grafting functional groups onto their surfaces, leading to chemical structural modifications. Such plasma treatments of PAN membranes have already been studied as well as has the grafting of substrates such as acrylic acid (AA), methacrylic acid (MAA), and 2-hydroxyethyl methacrylate (HEMA), leading to physical modifications of the membranes obtained.^{8,9}

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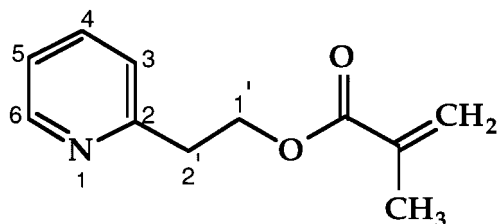
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In this work, we developed the preparation of PAN ultrafiltration membranes modified by the surface grafting of 2'-(2-pyridyl)ethyl methacrylate (2-PEMA) using a plasma treatment. The choice of a pyridine-containing substrate relies on the coordinating ability of the pyridine ligands.^{10,11} Such a material containing recognition sites may lead to supramolecular devices performing selective binding with the properties of organized materials.¹² For instance, it has been shown that polymeric membranes bearing pyridine groups may have applications such as the facilitated transport of CO₂ or halogen ions.^{13,14} The aim of this work was to determine the best grafting conditions for the 2-PEMA substrate as well as to study the characteristics of the grafted membranes.

EXPERIMENTAL

Materials

The PAN membranes used in this study were donated by the Tech Sep Society. They are microporous (pore diameter \approx 25 nm) with an asymmetric structure. They are composed of polyamide fibers on one side and PAN polymer on the other and have been made hydrophilic by surface treatment (presence of bands corresponding to carbonyl groups on the FTIR-ATR spectra). 2,2-Diphenyl-1-picrylhydrazine hydrate (DDPH, 95%), methacryloyl chloride, HEMA, and 2-(2'-hydroxyethyl)pyridine were purchased from Aldrich (Steinheim, Germany). The structure of the 2'-(2-pyridyl)ethyl methacrylate (2-PEMA) synthesized is as follows:



A solution of methacryloyl chloride (1 equiv) in dichloromethane (50 mL) was added dropwise to a solution of a 2-(2'-hydroxyethyl)pyridine (1 equiv) and pyridine (1.5 equiv) in dichloromethane (250 mL). The mixture was then stirred at room temperature for 12 h. The solution was extracted three times with a mixture H₂O/CH₂Cl₂ (50/50). The organic layers were collected and dried on anhydrous sodium sulfate and the solvent evapo-

rated to dryness. The liquid obtained identified by mass spectroscopy and NMR spectroscopy was pure enough to be used as such in the grafting step.

Yield 79%. ES-MS m/z = 191. ¹H-NMR δ (CDCl₃): 1.85 (s, 3H, CH₃); 3.15 (t, 2H, CH₂-2'); 4.5 (t, 2H, CH₂-1'); 5.5 (s, 1H, =CH); 6.05 (s, 1H, =CH); 7.2 (m, 2H, CH-3,5); 7.6 (t, 1H, CH-4); 8.6 (d, 1H, CH-6). ¹³C-NMR δ (CDCl₃): 18.6 (CH₃); 37.8 (CH₂-2'); 64.2 (CH₂-1'); 122.0 (C-5); 123.8 (C-3); 125.8 (=CH₂); 136.6 (C=CH₂); 136.7 (C-4); 149.8 (C-6); 158.5 (C-2); 167.6 (C=O).

Plasma-induced Graft Polymerization

Plasma graft reactions were carried out in a reactor with a capacitive coupling. The system consisted of the following components: two circular (50 cm²) parallel electrodes separated by 6 cm, placed inside a vessel made of Pyrex (diameter: 250 mm, length: 200 mm), an rf power supply (Celes, 440 kHz), a vacuum pump (Alcatel 2012 A), and a pressure gauge (Leybold AG 288 1082).

Plasma treatment was initiated using a frequency of 440 kHz and a power of 30 or 50 W. The He pressure inside the reactor was 40 or 80 Pa maintained for 10–300 s. The preweighed membrane was placed on the reactor inox electrode linked to earth. The reactor system was evacuated for 30 min until a final pressure of 2×10^{-2} Pa was reached. Then, the helium flow was introduced at the desired pressure for 10 min. Only then was the plasma generated by an electric discharge. After plasma treatment, the helium flow was stopped, the vacuum broken with air, and the membrane soaked in a water/methanol (50/50) solution of 1–5 wt % monomer. Argon was bubbled through the solution at 70°C for 24 h. After this grafting time, the membrane was purified by Soxhlet extraction with water for 6–8 h and dried in a desiccator at room temperature under reduced pressure.

The grafting yield was calculated according to

$$\text{Weight yield} = \frac{M_1 - M_0}{M_0} \times 100$$

with M_0 the membrane weight after plasma treatment and M_1 the membrane weight after grafting and extraction. We settled on the technique by studying the plasma graft polymerization of PAN membranes with HEMA as already described.⁹

Peroxide Determination

We chose to measure the peroxide amounts with DDPH, according to Suzuki et al.¹⁵ The thermic decomposition of the membrane surface peroxides by the DDPH free radicals was followed spectroscopically by observing the consumption of DDPH absorbance. The preweighed membrane was put in a $7.5 \times 10^{-5} M$ degassed toluene solution of DDPH and kept at 70°C for 1 h. For each assay, two blank solutions were used: an original one and a solution containing the untreated membrane. The consumed amount of DDPH was calculated from its absorption coefficient of $1.18 \times 10^{-4} \text{ L mol}^{-1} \text{ cm}^{-1}$ at 520 nm and 0 for its products. The result was normalized to the outer membrane surface area exposed to the plasma treatment.

Swelling Study

Preweighed samples of the PAN membranes, after Soxhlet washing and drying, were soaked in the desired solvent or solvent mixture for 14 h. The percent swelling was calculated from the following equation:

$$\text{Percent swelling} = \frac{W_s - W_0}{W_0} \times 100$$

W_0 and W_s represent, respectively, the dry and the swollen weight of the polymer membrane.

Monomer Analytical Methods

¹H- and ¹³C-NMR spectra were recorded on a Bruker AC250 spectrometer. Chemical shifts are given in ppm. ¹H-NMR multiplicity abbreviations are s, singlet; d, doublet; and t, triplet.

Mass spectra were obtained on a Platform II Micromass spectrometer using positive electrospray ionization in a mixture acetonitrile/water/formic acid (49.9/49.9/0.2). The source temperature was 50°C; the eluent flow rate, $10 \mu\text{L min}^{-1}$; and the cone voltage, 50 V.

Surface Analytical Methods

Contact angles of PAN membranes were measured under water using a manual goniometer. Three water drops were applied to the membrane surface and angles were measured on both sides of the drops.

FTIR-ATR spectra were recorded using a Nicolet 710 spectrometer equipped with an ATR unit

(ZnSe crystal, 45°, Nicolet Instrument Corp.). Samples of equal size (7 cm^2) were pressed against both sides of the crystal. Usually, spectra were obtained after 128 scans at a nominal resolution of 4 cm^{-1} . UV-visible spectra were obtained with a Philips PU 8710 spectrophotometer (Philips Analytical Cambridge).

The scanning electron microscopic (SEM) studies of the graft membrane were done with a Hitachi S 4500 microscope operating at 5 kV. A magnification of 3×10^5 times and resolution of 1.5 nm could be reached.

A system SIA-200 Riber UHV situated at the Institut des Sciences des Matériaux et des Procédés in Odeillo (France) was used to carry out the X-ray photoelectron spectroscopy (XPS) using an AlK α source at a pass energy of 1486.6 eV. The X-ray radiations were filtered by an Al sheet of 100- μm thickness. The angle of the electron beam to the sample surface was fixed at 60°.

RESULTS AND DISCUSSION

Peroxide Determination

The free radicals created at the membrane surface by plasma treatment are converted into peroxides during exposure to air prior to graft polymerization.^{8,16} As these peroxides are the species which initiate the copolymerization,¹⁷ we attempted first to determine what were the best conditions leading to the highest peroxide level on the membrane without damaging its surface. Among all the methods proposed to detect peroxides,^{8,18} we chose the one described by Suzuki et al.¹⁵ using the conversion of DDPH free radicals by peroxides. Two kinds of plasma treatments in different conditions were used. One (1) was done under a He pressure set to 40 Pa at a power of 30 W, and the other (2), under 80 Pa at 50 W. In each case, we observed the change of peroxide amounts as a function of the plasma exposure time. The results reported in Figure 1 show that both curves have the same behavior: the peroxide concentration per centimeter squared of the membrane increases quasilinearly initially and then decreases. This result is in accordance with those described in the literature.^{15,19}

Thus, it appears that larger exposure to He plasma does not lead to the formation of more peroxides. The best amount is obtained with the following plasma treatment conditions: time, 120 s; power, 50 W; and He pressure, 80 Pa. As

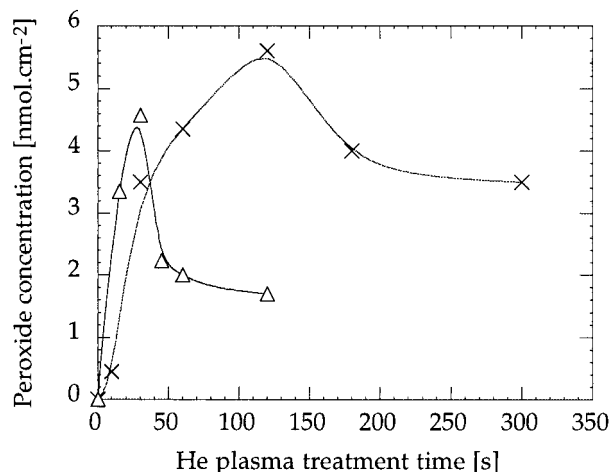


Figure 1 Amount of peroxides after 1 h at 70°C (toluene), induced by He plasma excitation of PAN membranes as a function of plasma treatment time: (Δ) He, 40 Pa, 30 W, immediately exposed to air, assay after 10 min (1); (\times) He, 80 Pa, 50 W, immediately exposed to air, assay after 10 min (2).

the SEM photographs show [see Fig. 2(a–c)], surface modifications appear for both treatments (1)

and (2): the pore number diminishes and their average diameter decreases (≈ 15 nm). However, whereas with treatment (1) the PAN membrane globular structure is retained, with treatment (2), the PAN reticulation increases too much.⁸ Thus, the first conditions (30 s, 30 W, 40 Pa) were chosen to initiate the monomer grafting. It may be noticed that the peroxide amounts determined here are comparable with those obtained by Ulbricht and Belfort.⁸

Graft Polymerization

After plasma activation of the PAN membranes, they were soaked in a deaerated monomer solution and kept as such at 70°C for 24 h. It was shown by Osada et al.²⁰ that vinyl monomers polymerize more slowly in organic solvents than in water. In our case, because of the insolubility of 2-PEMA in water, we used mixtures of water and organic solvents with longer grafting times. After the end of the grafting reaction, the membranes were washed out by water extraction in a Soxhlet in order to eliminate the homopolymers which may form an ungrafted deposit on the membrane surface.

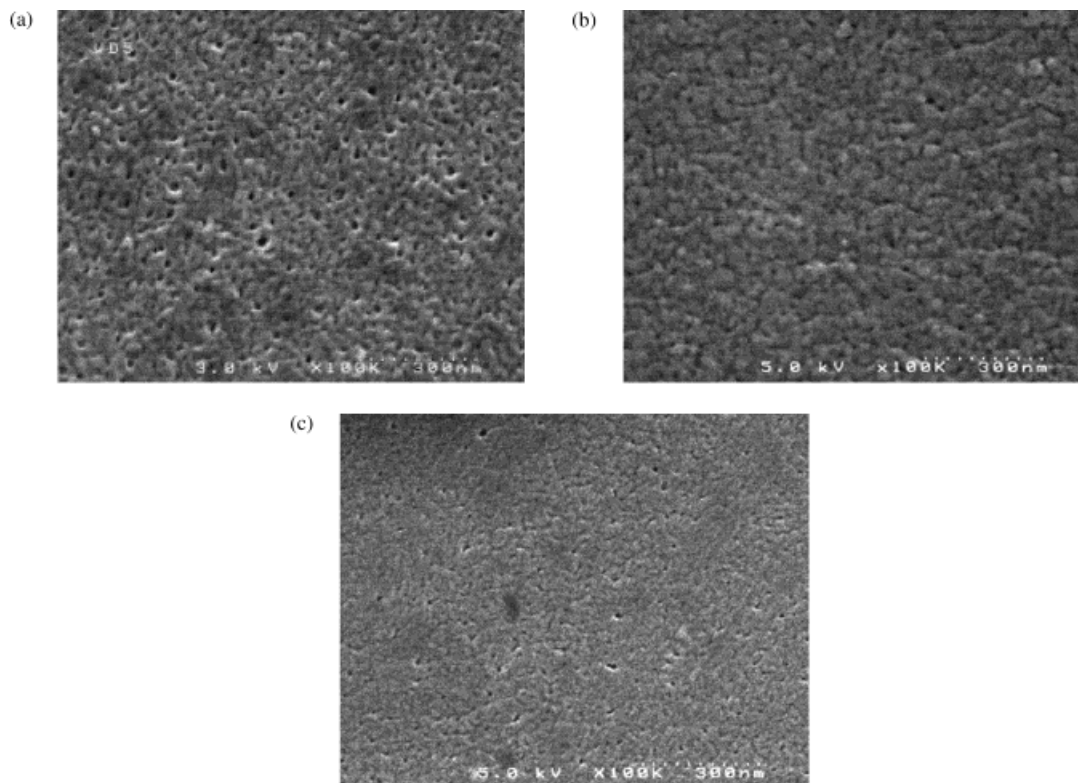


Figure 2 SEM micrographs of PAN membrane surfaces: (a) untreated; (b) He plasma-treated (50 W, 120 s, 80 Pa); (c) He plasma-treated (30 W, 30 s, 40 Pa).

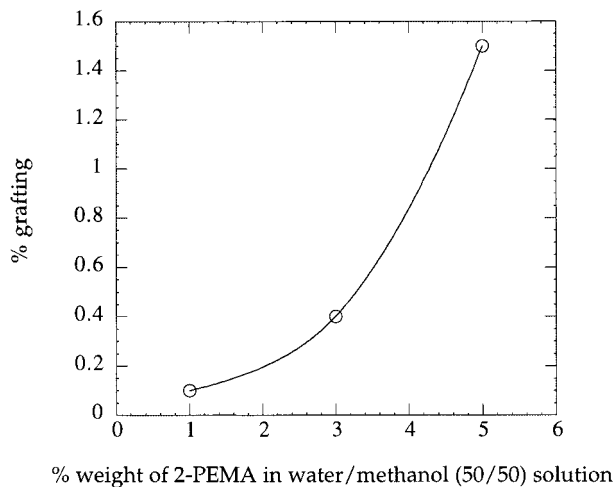


Figure 3 Grafting yield as a function of the 2-PEMA concentration.

A blank experiment was performed on a membrane without previous plasma excitation. As displayed by its weight and its SEM study, such a membrane does not undergo any grafting, showing that the activation surface is a necessary step for grafting to occur.

Effect of Monomer Concentration

We studied the effect of 2-PEMA concentration on the percentage grafting yield in a water/methanol (50/50) solution (see Fig. 3): the greater the 2-PEMA concentration, the higher the weight increase. This result is also reflected on the SEM photographs which show increased membrane thickness with higher monomer concentration.

This increase of grafting degree (precision of weight measurement ≈ 0.2 mg) with the 2-PEMA concentration is in agreement with the literature results.²⁰ The maximal concentration used for the grafting solution (5 wt %) is far from a possible gel effect which would lead to a decrease of graft amount because of the insolubility of *p*-2-PEMA in its own monomer.²⁰

Effect of Solvent

Most researchers have realized grafting reactions in aqueous solutions—first, because water solubilizes the monomers to be grafted and, second, because such a medium increases the polymerization rate.²⁰ We investigated the grafting reaction of 2-PEMA on plasma-activated PAN membranes in three different solutions: water/methanol (50/50), methanol, and cyclohexane. In Table I are

Table I Percent Weight Increase and Percent Swelling of PAN Membranes as a Function of Solvents

Percent	Solvent		
	H ₂ O/CH ₃ OH	CH ₃ OH	C ₆ H ₁₂
Weight increase ^a	1.5	0.5	0.4
Swelling	300	220	212

^a Percent grafting conditions: 5 wt % solutions of 2-PEMA at 70°C for 24 h.

gathered the weight increase and swelling observed in these three media.

The results show that the use of a solvent mixture leads to a higher weight increase, which is in accordance with the literature.^{20,21} One of the factors which could explain this behavior is the swelling changes in the different media. As shown in Table I, the maximum swelling is obtained in the water/methanol solution, the other two giving very close results. Such a correlation between swelling ability and graft yield has already been shown²⁰ in the case of polypropylene films.

Effect of Inhibitor Concentration

Inhibitors such as Mohr's salt have been used²¹ to minimize the formation of homopolymers. In our case, whatever is the 2-PEMA concentration in water/methanol (50/50) solutions, the presence of Mohr's salt increases the grafting yield by inhibiting the formation of hydroxyl radicals which are the species undergoing the homopolymerization.²¹ However, we have not used it because of the presence of Fe³⁺ in the grafted layers (ESCA measurements) and because of the uneven morphology of their surface.

Evidence of Grafting

Contact-angle Measurement

The change of water-contact angles is an easy and fast method to observe the possible modifications undergone by the grafted surface. Applying extra-pure water drops on the parent and 2-PEMA-grafted membrane surfaces gives respective contact angles of 57° and 63° (manual goniometer precision $\approx 2^\circ$). These close values may be explained by the 2-PEMA structure which contains both hydrophilic and hydrophobic moieties. It may be noticed that the water-contact angle of treated PAN membrane (30 s, 30 W) is 80°.

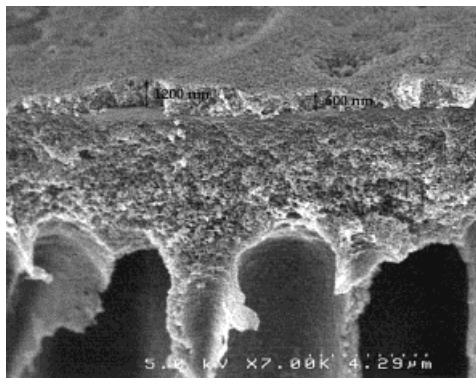


Figure 4 SEM microscopic cross section of 2-PHEMA-grafted PAN membrane.

Scanning Electron Microscopy

The observation by SEM of the grafted PAN membranes corroborates the formation of dense layers with a thickness of 600 nm to 1.2 μm (see Fig. 4). Furthermore, this technique allows one to verify that grafting on the plasma-treated PAN membranes occurs mainly at their surface. Another interesting result is the reactivity difference of HEMA and 2-PHEMA. In the same grafting conditions (5 wt % of monomer in a water/methanol, 50/50, solution in the presence of Mohr's salt for 24 h at 70°C), the two monomers do not lead to the same weight increase: 3% for 2-PHEMA and 141% for HEMA. Such a difference may be explained by the steric hindrance of the pyridine ring in 2-PHEMA which prevents the free radicals from approaching. This very different behavior of 2-PHEMA and HEMA is obvious in the way that they polymerize (see Fig. 5). HEMA gives nice crystals and 2-PHEMA leads to globular structures.

FTIR Spectroscopy

The occurrence of grafting has been confirmed with IR spectroscopy by observing blank and

modified membranes. Figure 6 shows representative examples of IR spectra for the parent PAN membrane compared to the plasma-treated and 2-PHEMA-grafted ones. The broad band between 3000 and 3600 cm^{-1} results from NH and OH absorptions,⁸ confirming the PAN modification during the plasma treatment. The carbonyl band at 1730 cm^{-1} observed for the parent membrane originates from a previous surface treatment undergone by the membrane to make it hydrophilic (see Materials). However, its intensity, if compared to the band produced by the nitrile group at 2243 cm^{-1} , increases much after grafting with regard to the parent membrane as well as to the plasma-treated one. This observation confirms the presence of 2-PHEMA whose ester function gives a band at 1730 cm^{-1} . The spectrum of the grafted membrane shows also the presence of two new bands at 800 and 1260 cm^{-1} , characteristic, respectively, of substituted pyridines and dialkyl-ethylenes.

It may be noticed that the spectrum given by the grafted membrane is disturbed by absorptions belonging to the underlying PAN membrane, the grafted layer not being thick enough to avoid IR penetration. The sampling depths with the ZnSe crystal (45°) were calculated to be 514 nm at 4000 cm^{-1} and 3161 nm at 650 cm^{-1} . However, it must be pointed out that these values are overestimated by the calculation method giving this depth.²²

ESCA Study

The elemental composition of the layer grafted onto the PAN membrane surface may be determined by ESCA. Results obtained for unmodified, plasma-treated, and grafted PAN membranes with and without Mohr's salt are summarized in Table II. The difference between the theoretic

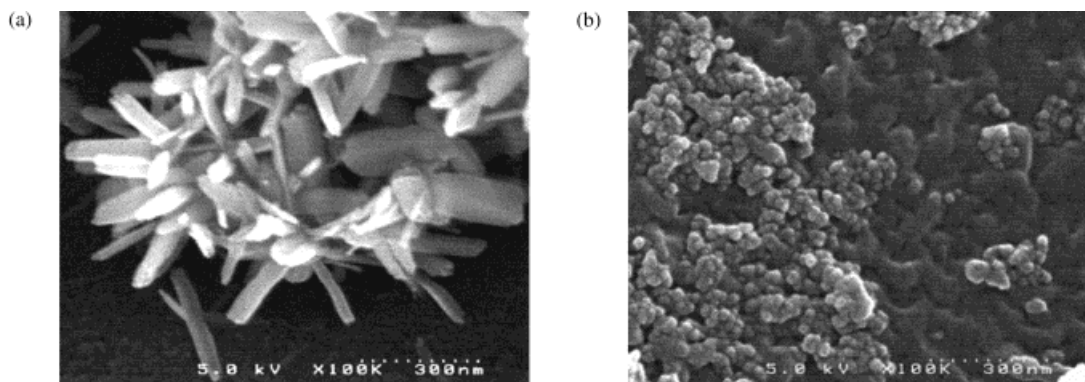


Figure 5 SEM photographs of (a) HEMA crystals and (b) 2-PHEMA globular structure.

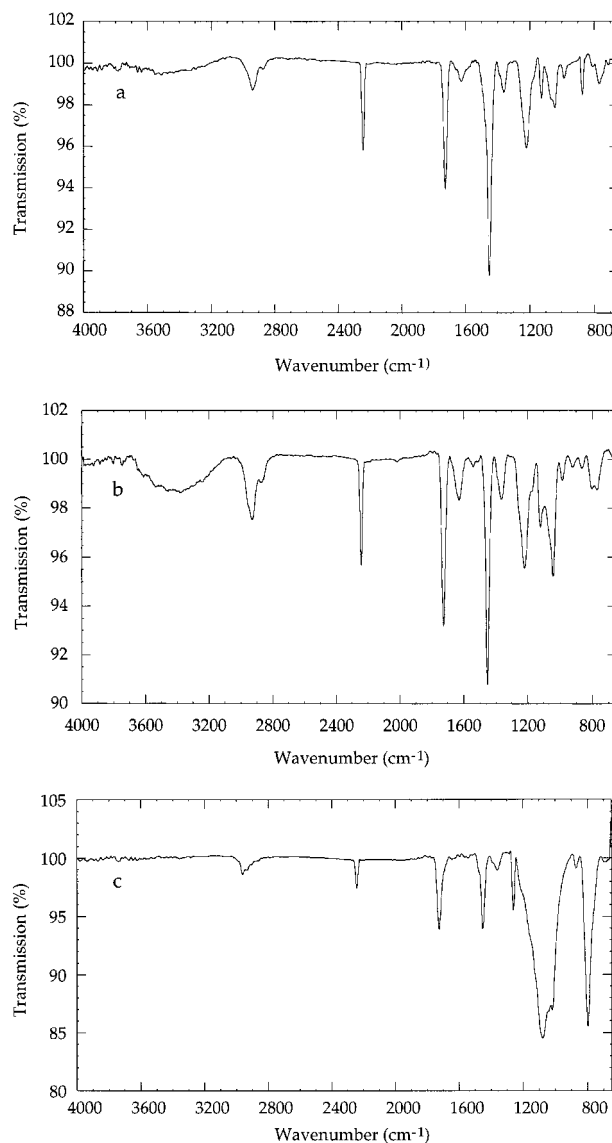


Figure 6 FTIR-ATR spectra with a ZnSe crystal (45°) of the surface of PAN membranes: (a) unmodified; (b) plasma-treated; (c) 2-PHEMA-grafted PAN membrane, after He plasma (40 Pa, 30 W, 30 s), 10 min oxidation in air and 24 h at 70°C in 5 wt % solution (water/methanol 50/50) of 2-PHEMA.

composition of PAN (75% C and 25% N) and that found for the parent PAN membranes used here (77% C, 19% N, 5% O) is due to the surface treatment they have undergone to make them hydrophilic. Significant modifications are observed after He plasma treatment: after 30 s exposure time at 30 W, the oxygen content increases from 5 to 13% while a large decrease (19 to 9%) in nitrogen content is observed. These changes are certainly due to the formation of peroxides on the PAN membrane surface. In the case of 2-PHEMA-grafted membranes, ESCA data show that their

elemental composition is close to that calculated for 2-PHEMA itself (78% C, 15% O, 7% N). The lower N content observed may be due to the occurrence of a transesterification reaction between 2-PHEMA and the methanol used as a solvent. The presence of N in the PAN membrane grafted with HEMA may be explained by the nature of the layer with this monomer, which is not dense. The ESCA study of 2-PHEMA-grafted membranes obtained in the presence of Mohr's salt shows the presence of Fe^{3+} species which are formed by oxidation of Fe^{2+} complexes in the grafting con-

Table II ESCA Data for Untreated, Plasma-treated, and Grafted PAN Membranes

	% C	% N	% O	% Fe
PAN untreated	77	19	5	
PAN- <i>t</i> (30 s 30 W)	78	9	13	
PAN- <i>g</i> -2-PEMA	76 (78) ^a	3 (7) ^a	20 (15) ^a	
PAN- <i>g</i> -2-PEMA + Mohr's salt	54	3	34	8
PAN- <i>g</i> -HEMA + Mohr's salt	73 (70) ^a	2	24 (30) ^a	1

^a Theoretical values.

ditions (70°C) and which must be retained because of an easy coordination with pyridine nitrogen atoms, which cannot occur with HEMA. These ferric cations present in the grafted layer may still be coordinated to some oxygen-containing ligands belonging to the Mohr's salt, which may explain the higher oxygen content in these conditions.

CONCLUSIONS

PAN ultrafiltration membranes could be grafted with water-insoluble 2-PEMA when pretreated with He plasma and exposed to air. The graft polymerization was initiated by peroxide groups formed upon plasma treatment after they were decomposed by heating. The various amounts of grafted 2-PEMA onto PAN membranes were obtained using different reaction conditions. The reaction conditions that we chose to use were 5 wt % 2-PEMA in a water/methanol (50/50) solution maintained at 70°C during 24 h. This result demonstrates that it is possible to graft pyridine-bearing ligands onto PAN membranes using plasma-graft polymerization and opens the way toward the introduction of various polydentate receptor molecules having specific coordinating abilities.

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