Surface Modification of Acrylonitrile Copolymer Membranes by Grafting Acrylamide. I. Initiation by Ceric Ions

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ABSTRACT: Surface modification of membranes of an acrylonitrile copolymer (PAN) containing 5.5% methyl methacrylate (MMA) and 4.0% sodium methylpropylenesulfonate by grafting acrylamide (AAm) with cetric ammonium nitrate as initiator in the aqueous medium has been studied. Results showed that the extent of grafting was varied with some parameters, such as dimethyl formamide and Tween-20 amount in the reaction solution, concentration of AAm, and reaction time. The grafted copolymer was verified by infrared spectra and X-ray photoelectron spectroscopy. Both of these methods also showed that the ester group of MMA unit on the surface of PAN membranes may be partially hydrolyzed into carboxyl group in the copolymerization condition. Surface and pore structures of PAN membranes after grafting were viewed under a scanning electron microscope (SEM). From SEM photos we know that AAm homopolymer branches were grafted onto the surface of the membrane and the morphology of membrane did not change. Results of contact angle of isooctane on the membrane under water showed that the wettability of the modified membrane was improved. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1521–1529, 1997

Key words: acrylonitrile copolymer membranes; graft copolymerization; ceric ions; acrylamide

INTRODUCTION

Surface modification of polymer is one method of changing its chemical and physical properties. The modified polymer may be better than its original state in wettability, compatibility, bondability, etc.[1] Surface graft copolymerization is one of the most useful methods and is applied widely.[2–5]

As a type of membrane material, poly(acrylonitrile)(PAN) and AN copolymers have been investigated by many researchers in the fields of dialysis, pervaporation, and ultrafiltration.[6–9] After modification, the PAN membrane becomes more stable and can be used in more difficult condition.[6] Grafting hydrophilic monomers improves the hydrophilicity of PAN membranes and enables the membrane to support glucose oxidase.[3]

Several workers have reported on the modification of cellulose membrane via graft copolymerization using ceric ions as initiator. The graft copolymerization is generally presumed to result from propagation by radical sites generated on

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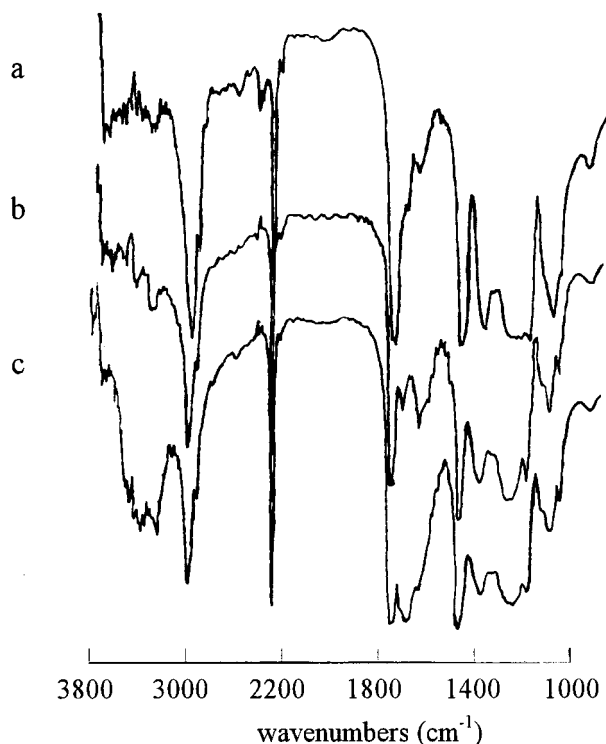
Figure 1 IR spectra of (a) PAN before graft copolymerization, (b) PAN treated in the reaction condition of graft copolymerization but no CAN, and (c) PAN-*g*-AAm prepared in the typical condition.

the backbone of polymers. Thus, initiation of graft copolymerization is considered to result from propagation by radicals formed on the cellulose backbone by the oxidation reaction of Ce^{4+} with functional groups in cellulose macromolecules, such as —OH.[10–12] There are many functional groups in the main chain of AN copolymers, e.g., —CN and —COOR. According to the mechanism of graft copolymerization onto cellulose, modification of AN copolymer membranes via graft copolymerization with ceric ions as initiator would be practicable. In view of the reason mentioned above, we have examined the surface modification of AN copolymer membranes by grafting acrylamide onto it.

X-ray photoelectron spectroscopy (XPS) is a good method for analyzing the surface structure of organic and nonorganic substrates. Detailed information on the surface structure can be gained through XPS spectra.[13,14] In this article, we have studied the chemical structure of PAN membranes by C1s, O1s, N1s, and valence XPS spectra, and calculated the surface grafting degree from the peak synthesis of the C1s core-level spectra.

EXPERIMENTAL

Materials

An AN copolymer containing $5.5 \pm 0.3\%$ methyl methacrylate (MMA) and $4.0 \pm 0.3\%$ sodium methylpropylenesulfonate (SPS), which will be referred to for brevity simply as PAN, with molecular weight 60,000 (Jinshan Petrochemical Company, Shanghai, China) was used. Acrylamide (AAm), ceric ammonium nitrate (CAN), polyethylene glycol (PEG, molecular weight 4,000), and other chemicals [dimethyl formide (DMF), Tween-20, nitric acid, and isooctane] were used as received.

PAN membranes were made in our laboratory by spreading a DMF solution containing 16 wt % base copolymer and 8 wt % PEG on a glass plate, coagulating the mixture in water at 20°C, and then washing it with water to remove the water-soluble additive and solvent. The membranes so obtained were 0.1–0.3 mm thick and were cut into about 1-cm^2 squares for graft copolymerization.

Synthesis

In a typical experiment, 0.1 g of PAN membranes were immersed in a 50-mL aqueous solution containing 0.4225 mol/L AAm, 0.04 mol/L HNO_3,
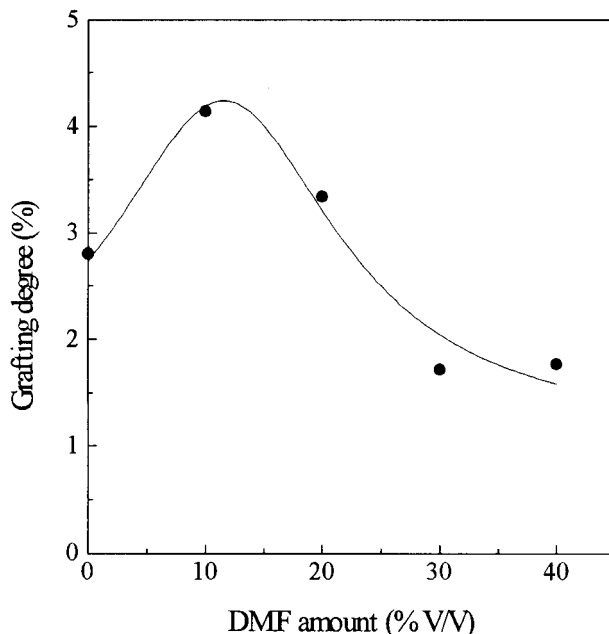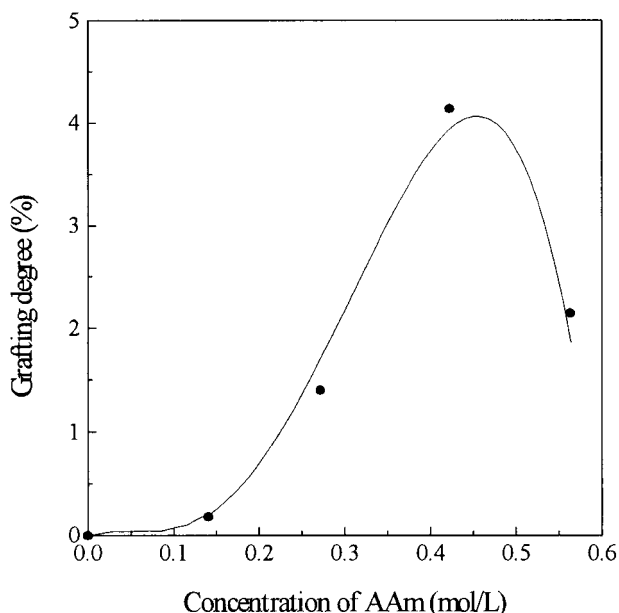

Figure 2 Effect of DMF amount on grafting degree: [AAm] = 0.4225 mol/L, [CAN] = 4.7×10^{-3} mol/L, [HNO_3] = 0.04 mol/L, $T = 60$°C, $t = 1.5$ h.
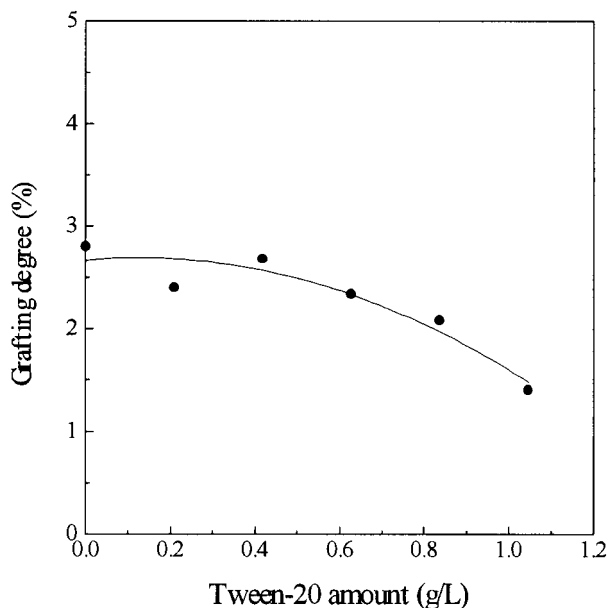
Figure 3 Effect of Tween-20 amount on grafting degree: [AAm] = 0.4225 mol/L, [CAN] = 4.7×10^{-3} mol/L, [HNO$_3$] = 0.04 mol/L, T = 60°C, t = 1.5 h.

and 5 mL DMF for 1 h at 60°C, and then CAN was added into the reaction mixture so that the concentration of CAN was 4.7×10^{-3} mol/L. The graft reaction was allowed to carry out in a one-neck 100-mL round-bottom flask under nitrogen at 60°C for 1.5 h.

Figure 4 Effect of AAm concentration on grafting degree: [CAN] = 4.7×10^{-3} mol/L, [HNO$_3$] = 0.04 mol/L, DMF 10%, T = 60°C, t = 1.5 h.
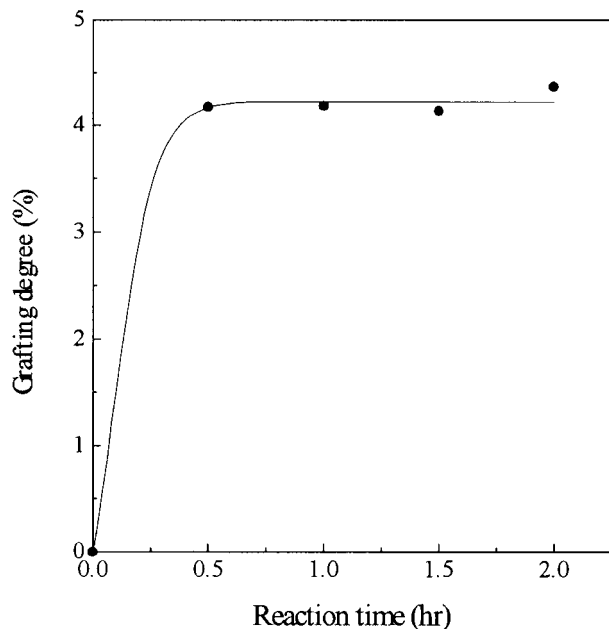

Figure 5 Effect of reaction time on grafting degree: [AAm] = 0.4225 mol/L, [CAN] = 4.7×10^{-3} mol/L, DMF 10%, [HNO$_3$] = 0.04 mol/L, T = 60°C.

Characterization

Grafting membranes were washed thoroughly with hot water for at least 24 h to remove the soluble homopolymer and then measured. The infrared (IR) spectra of the film specimens made with a hot hydraulic press were measured on a Nicolet 205 FTIR spectrometer. After washing with alcohol, the XPS spectra of membrane samples were measured on Perkin-Elmer PHI 1600 ESCA system. The residual pressure in the spectrometer was 1.1×10^{-8} Pa. A Mg anode (1253.6 eV), powered at 250 W, was used as an X-ray source. The constant pass energy was 23 eV. Analyzed area was 0.8 mm^2. The XPS spectra were curve-fitted after calibration. Thus the existence of PAN-g-AAm and the structure changes of PAN were examined by IR and XPS. The morphology of PAN membrane before and after grafting was viewed under a Hitachi-650 scanning electron microscope. The wettability of membrane was studied by means of the contact angle method in a JY-82 contact angle instrument (Chengde Test Instrument Factory, Chengde, China).

Determination of the Grafting Degree

Grafting degree (g_w), defined as the mass ratio of the graft branch to the main chain, was deter-
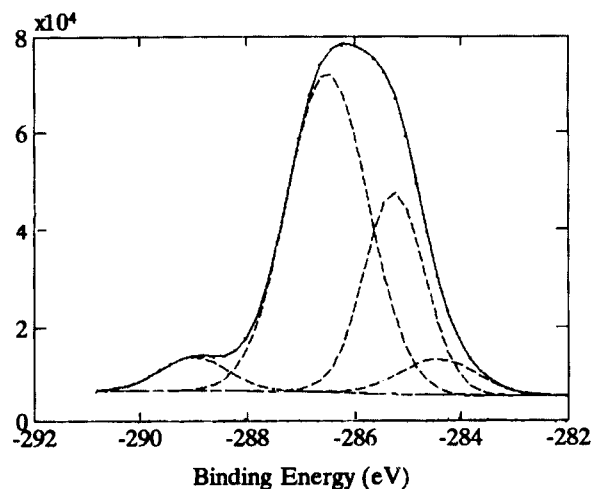
(a)
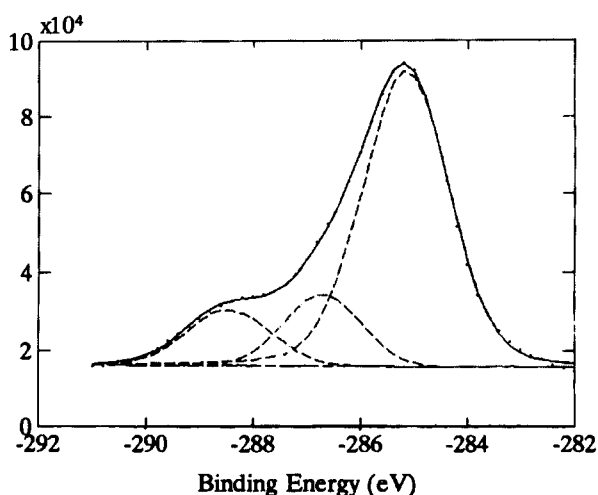
(b)

Figure 6 Spectra of C1s XPS: (a) PAN and (b) PAN-*g*-AAm prepared in the typical condition.

mined by the difference of membrane mass before (W_0) and after (W) grafting according to the following equation:

$$g_w = \frac{W - W_0}{W_0} \times 100\%$$

RESULTS AND DISCUSSION

IR Spectra

Figure 1 shows the IR spectra of PAN, PAN-*g*-AAm, and PAN after treatment in the same reaction condition but with no CAN. The IR spectrum

of PAN [Fig. 1(a)] reveals the —C≡N stretching vibration at 2244 cm^{-1},[15] and the —C=O stretching vibration at 1732 cm^{-1}.[16] The IR spectrum of PAN-*g*-AAm [Fig. 1(c)] exhibits a strong absorption at 1672 cm^{-1}, which can be assigned to the combined motion of NH$_2$ and CO stretching in the —CONH$_2$ group. An absorption at 3205–3337 cm^{-1} is also shown in Figure 1(c), which can be designed to N—H stretching vibration in NH$_2$.[17] The difference between Figures 1(a) and (c) verifies the existing of PAN-*g*-AAm. On the other hand, Figure 1(b) shows a higher absorption at 1620 cm^{-1}, which can be assigned to C=O asymmetrical stretching in —COOH.[18] This shows that the —COOR group on the surface of PAN membrane may be hydrolyzed into —COOH.

Influence of Reaction Parameters

DMF Amount in the Medium

The extent of grafting increased with the amount of DMF added to the medium (Fig. 2), below 10%. When the DMF amount was above 10%, the grafting degree decreased to a lower value than that with no DMF in the medium. Since DMF is a good solvent of PAN, the solution including a little DMF can swell part of PAN macromolecules on the membrane surface. Thus macromolecules on the membrane surface became looser, they contacted with monomers more easily, and the grafting degree was increased. When the DMF amount was much greater, a few PAN macromolecules could be dissolved into the solution and the grafting degree based on the mass of PAN membrane was decreased.

Tween-20 Amount in the Medium

The graft copolymerization was carried out in the heterogeneous condition. The PAN membrane in solid is hydrophobic. The AAm monomer was dissolved in the medium. A little surfactant in the solution may intensify the contact between monomers and PAN molecules, so we examined the effect of Tween-20 amount in the medium on the grafting degree (Fig. 3). The extent of grafting was decreased after adding Tween-20 to the medium. The result was not in conformity with our original idea. Adding Tween-20 probably increased the AAm homopolymerization and then decreased the grafting degree.

Concentration of AAm

Figure 4 shows that the extent of grafting increased with increasing the AAm concentration to

Table I Synthesis Peak Area of C1s XPS Spectra and g_x Value

| Sample | Peak Area | | | | g_x |
	285.10	286.54	288.59	289.03	
PAN	33.7[a]	60.6	—	5.8	—
PAN grafted for 0.5 h	62.8	25.7	6.6	4.9	17.9
PAN grafted for 1 h	54.5	35.0	10.2	0.4	40.0
PAN grafted for 1.5 h	57.4	30.3	12.0	0.3	48.1
PAN grafted for 2 h	59.2	29.4	11.1	0.2	40.3

[a] Total number of peak area at 250.0 and 250.30.

a maximum value, and then decreased. Before the maximum value, the extent of grafting increased with increasing amount of monomer. When the grafting degree was over maximum value, the amount of AAm homopolymer also increased with increasing amount of monomer and then the grafting degree decreased.

Reaction Time

The grafting degree increased with increasing reaction time (Fig. 5), but it did not increase greatly after 0.5 h. This conformed to the free radical polymerization principle and showed that the rate of the graft-AAm copolymerization was very fast. After 0.5 h, the reactive groups on the membrane surface may be used up and ceric ions no longer able to generate free radicals at the interface, so that the graft copolymerization reveals a saturation state.

XPS Analysis

C1s

The C1s XPS spectra are shown in Figure 6. Peak synthesis of the PAN C1s core-level spectrum [Fig. 6(a)] gives component peaks with binding energy (BE) at 286.54, 289.03, 285.0, and 285.30 eV. The peak at 286.54 eV can be attributed to combination of the two carbon atoms in the AN unit $\{-[CH_2-\underline{C}H(\underline{C}N)]_n-\}$.[19] The peak at 289.03 eV can be attributed to the carbon in the ester group $(-\underline{C}OOR)$.[20] The peaks at 285.0 and 285.30 eV can be attributed to the other saturated carbons in the backbone, such as $-[\underline{C}H_2-\underline{C}HX]_n-$, respectively.[20] The BE of the latter saturated carbon is a little higher than that of the first. Since the MMA unit in terpolymer PAN was of low percentage, the peak at 289.03 eV was small.

Figure 6(b) shows the C1s XPS spectrum of

PAN-g-AAm. It gave an extra peak with BE at 288.59 eV, which can be attributed to the carbon in the $NH_2-\underline{C}=O$ functional group.[21] The C1s
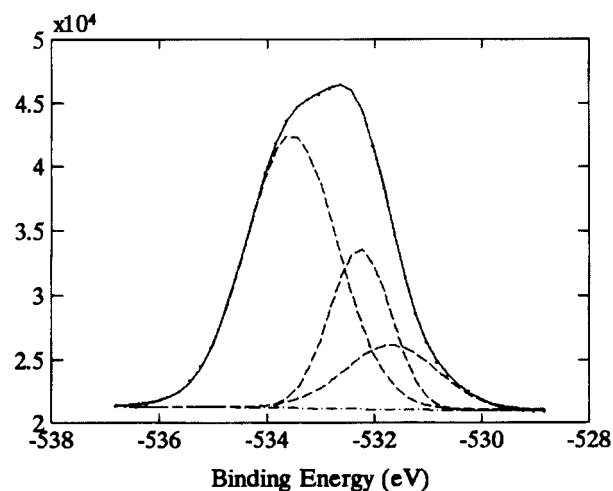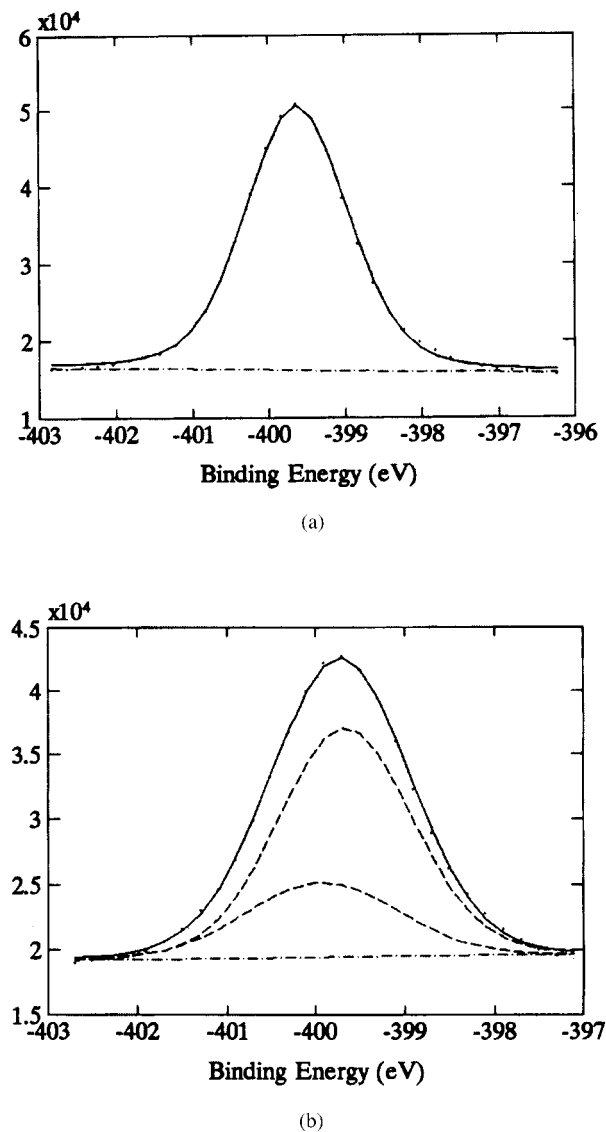

(a)
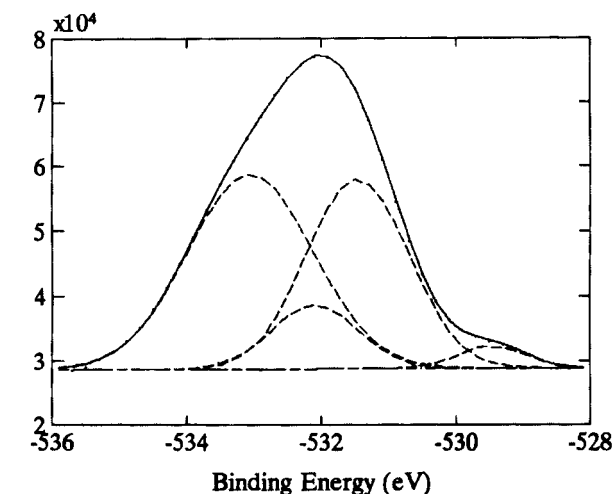
(b)

Figure 7 Spectra of O1s XPS: (a) PAN and (b) PAN-g-AAm prepared in the typical condition.

(a)

(b)

Figure 8   Spectra of N1s XPS: (a) PAN and (b) PAN-
g-AAm prepared in the typical condition.

spectra's difference between PAN and PAN-*g*-
AAm verified the grafting copolymer.

Loh and colleagues[14] have calculated the density of AAm polymer copolymerized onto polyimide films from the C1s XPS core-level spectra. The surface grafting degree (g_x) of PAN-*g*-AAm membrane can also be calculated from the C1s XPS spectra using the following expression in light of Loh and associates:

$$g_x = \frac{A_{288.59}M_{\text{AAm}}}{(A_{285.10} - 2A_{288.59})M_{\text{AN}}} \times 100\%$$

where $A_{288.59}$ and $A_{285.10}$ represent the peak area

of 288.59 eV and 285.10 eV, respectively; M_{AAm} and M_{AN} refer to the molecular weights of AAm and AN, respectively. Here, $A_{288.59}$ gave the number of AAm unit. Simply stated, we "fit" the saturated carbon peak into one at 285.10 eV. If we ignore the small number of MMA and SPS units, the peak area of 285.10 can be considered as the total number of AN unit and double AAm unit. The factor 2 refers to the two backbone carbons in the AAm unit.

The peak area data of C1s XPS spectra and the surface grafting degree of PAN-*g*-AAm are listed in Table I. It shows that the g_x value increased with increasing the reaction time. Surface grafting degree was higher than that of grafting degree, which was based on the bulk PAN membrane, but the regularity of g_x is similar to that of g_w.

The data in Table I also show that the area of peak at 289.03 eV became smaller with increasing reaction time. This may result from the hydrolysis of —COOR group in MMA unit. The result here agreed with that of IR.

O1s

The O1s XPS spectra are shown in Figure 7. There are three peaks in PAN spectrum [Fig. 7(a)], i.e., 531.72, 532.21, and 533.77 eV. They are attributed to oxygen in the SPS unit ($-SO_3^-$),[22] and
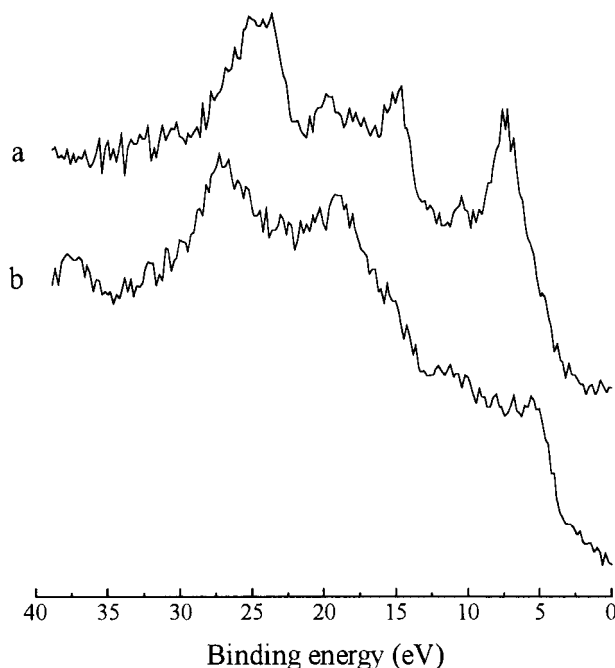
Figure 9   XPS valence spectra: (a) PAN and (b) PAN-
g-AAm prepared in the typical condition.
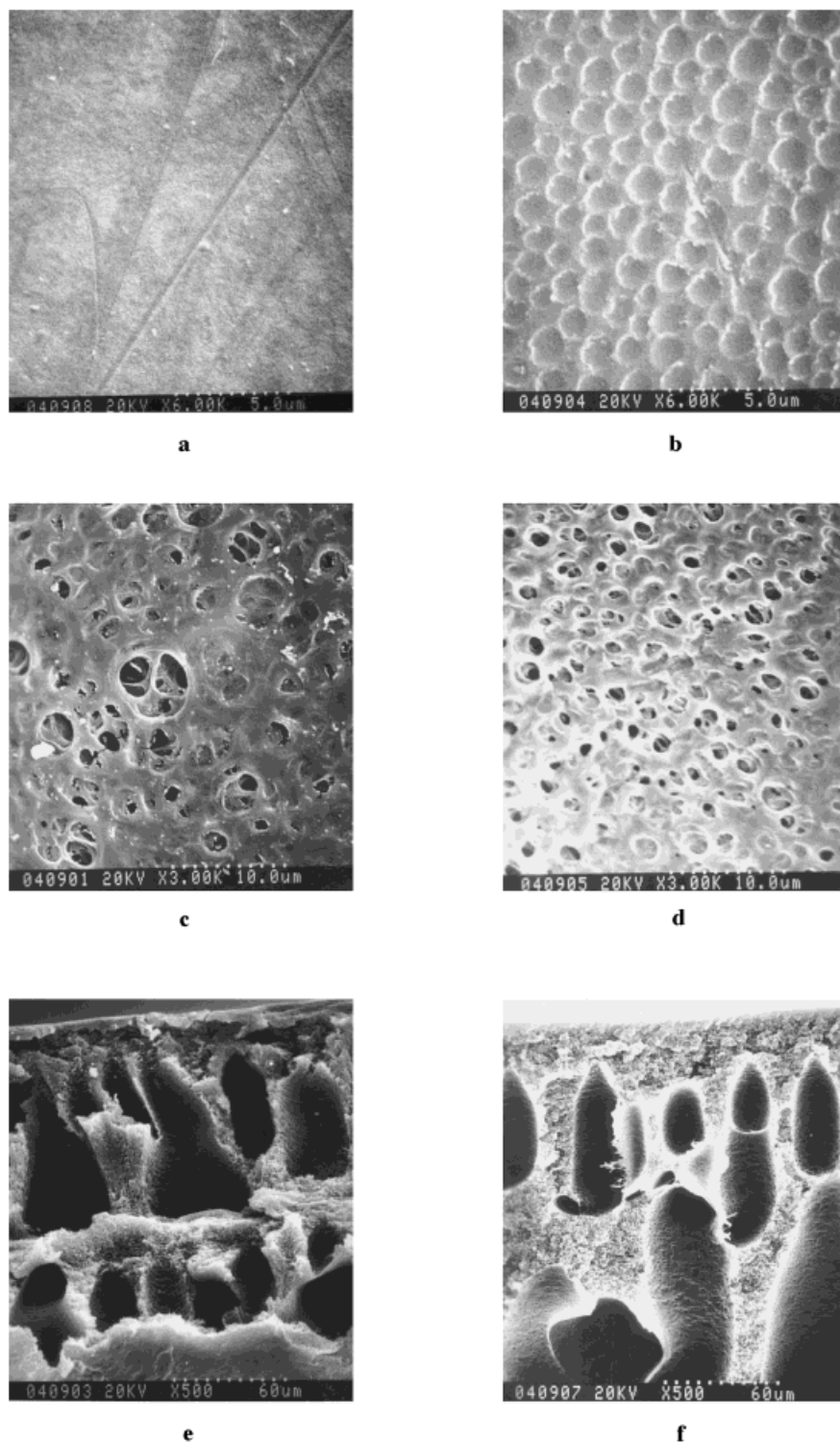
Figure 10   SEM photos: The front surface of PAN membrane (a) before and (b) after grafting in the typical condition, the back surface of PAN membrane (c) before and (d) after grafting in the typical condition, and the section of PAN (e) before and (f) after grafting in the typical condition.

the two oxygen atoms in the —CO—OR group, respectively.[20] The peak at 531.72 eV in the O1s spectrum of PAN-*g*-AAm [Fig. 7(b)] became higher. This can be attributed to AAm unit grafted on the membrane, because the BE of oxygen in CONH$_2$ is 531.54 eV.[21] Figure 7(b) shows an extra peak at 529.40 eV. The extra peak may be attributed to the oxygen in cerium oxide[23] absorbed on the membrane surface, which was generated from initiator after graft reaction.

N1s

The N1s XPS spectra are shown in Figure 8. There is only one peak at 399.57 eV in the N1s spectrum of PAN [Fig. 8(a)], which is attributed to the nitrogen atom in the CN group.[19] There is an another peak at 399.83 eV in the spectrum of PAN-*g*-AAm [Fig. 8(b)]. This can be attributed to nitrogen in the CONH$_2$ group.[21]

Valence

Figure 9 shows the valence XPS spectra of PAN and PAN-*g*-AAm. The spectrum of PAN [Fig. 9(a)] gives a peak at BE of about 7 eV that coincides with Beamson and Briggs.[19] This peak disappears in the spectrum of PAN-*g*-AAm [Fig. 9(b)]. The spectrum of PAN-*g*-AAm is similar to that of PAAm.[21] O1s, N1s, and valence spectra also verified the existing of PAN-*g*-AAm on the surface of the member.

Morphology of PAN membranes under SEM

The structure photos of PAN membrane before and after grafting are shown in Figure 10. The front surface of the membrane was smooth before grafting and rough after grafting [Fig. 10(a,b)]. The hilly grafted AAm polymer on the membrane surface is obviously visible. The back surface photos [Fig. 10(c,d)] and the section photos [Fig. 10(e,f)] show that the pore structure of membrane had little change after grafting.

Effect of Grafting on Wettability of PAN Membrane

We can readily examine the wettability of PAN membrane by contact angle measurement. The contact angle (θ) of isooctane on PAN membrane

Table II   Result of Contact Angle (Membrane/Isooctane/H$_2$O)

Sample	$\theta°$
PAN	70 ± 3
PAN grafted for 0.5 h	60 ± 4
PAN grafted for 1 h	60 ± 5
PAN grafted for 1.5 h	56 ± 5
PAN grafted for 2 h	53 ± 4

was measured in the water (Table II). Every θ was the average of nine pair of values. The contact angle of PAN was increased after its AAm grafting. This is to say that wettability of PAN membrane after grafting is higher than that with no grafting.

CONCLUSION

AAm can be grafted onto the surface of PAN membranes with ceric ions as initiator. The grafting degree was influenced by several parameters. IR and XPS proved the existence of PAN-*g*-AAm, and also presented the chemical structure changes between PAN and PAN-*g*-AAm. The surface grafting degree of PAN-*g*-AAm can be calculated from the synthesis peak area of the C1s XPS spectra. SEM photos showed that the grafting copolymer was attached to the surface of the membrane and grafting reaction did not influence the morphological structure of the membrane. Wettability of the membrane was improved after AAm grafting.

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