Surface Modification of Acrylonitrile Copolymer Membranes by Grafting Acrylamide. II. Initiation by Fe^{2+}/H_2O_2

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ABSTRACT: Surface modification of membranes of an acrylonitrile copolymer (PAN) containing 5.5% methyl methacrylate and 4.0% sodium methylpropylenesulfonate by grafting acrylamide (AAm) with ferrous ammonium sulfate/H_2O_2 as an initiator in aqueous medium was studied. The grafted copolymer was verified by infrared spectra, X-ray photoelectron spectroscopy, and a scanning electron microscope (SEM). From the SEM photos, we know that the AAm homopolymer branches were grafted onto the surface of the membrane and the morphology of the PAN membrane did not change. The results showed that the extent of grafting was varied with some parameters, such as the pH value of the medium, reaction time and temperature, and concentration of AAm and H_2O_2. The results of the water-absorption percent of the membrane showed that the wettability of the modified PAN membrane was improved. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1907–1915, 1998

Key words: acrylonitrile copolymer membranes; grafting copolymerization; acrylamide; Fe^{2+}/H_2O_2.

INTRODUCTION

Because of its low cost and high activity, hydrogen peroxide, in the form of Fenton's reagent ($FeSO_4$-H_2O_2) as a redox initiator, has been extensively used for grafting vinyl monomers onto starch,[1–3] cellulose,[4–6] wool,[7,8] gelation,[9] sodium alginate,[10,11] natural rubber,[12] jute fiber,[13] and synthetic polymers such as poly(ethylene terephthalate).[14–16] Godjevargova and coworkers achieved the grafting of diethylaminoethyl methacrylate, dimethylaminoethyl methacrylate, and 2-acrylamido-2-methylpropanesulfonic acid onto acrylonitrile copolymer (PAN) membranes using this initiator.[17,18]

In our previous article, we reported the surface modification of PAN membranes by grafting acrylamide (AAm) with ceric ions as the initiator. The experimental results showed that the structure of the PAN membrane did not change and the wettability of it was improved after modification.[19] In this work, we report on the investigation of grafting AAm onto PAN membranes using the Fe^{2+}/H_2O_2 initiating system.

EXPERIMENTAL

Materials

An acrylonitrile (AN) copolymer containing 5.5 ± 0.3% methyl methacrylate (MMA) and 4.0 ± 0.3% sodium methylpropylenesulfonate (SPS), which will be referred to for brevity simply as

PAN, with a molecular weight 60,000 (Jinshan Petrochemical Co., Shanghai, China) was used. Acrylamide (AAm), ferrous ammonium sulfate (FAS), H_2O_2, poly(ethylene glycol)(PEG, molecular weight 4000), dimethylacetamide (DMAc), and other chemicals were used as received.

PAN membranes were made in our laboratory by spreading a DMAc solution containing a 16 wt % base copolymer and 8 wt % PEG onto 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 10-cm^2 squares for graft copolymerization.

Synthesis

The membranes were first hydrolyzed with an aqueous solution containing 1.5 mol/L NaOH at 50°C for 1 h and were subsequently treated with a diluted solution of HCl and a sufficient amount of deionized water. Then, several pieces of the PAN membranes, which weigh about 0.8–2.0 g separately, were impregnated in a 100-mL aqueous solution (pH 3) containing 5 wt % FAS for 1–1.5 h. After washing with deionized water and blotting, the membranes were added into a 200-mL aqueous solution (pH 5.0) containing 0.4225 mol/L AAm and 0.2545 mol/L H_2O_2 in a typical experiment. The graft reaction was carried out in a three-neck 250-mL cylindrical flask under nitrogen at 60°C for 1–4 h.

Characterization

Grafted membranes were washed thoroughly with warm water (about 70°C) for at least 48 h to remove the soluble homopolymer and then measured. The infrared (IR) spectra of the film specimens made by spreading a DMAc solution of PAN onto a salt plate and drying thoroughly or pressing the mixture of the PAN solution and KBr after drying thoroughly were measured on a Nicolet 205 FTIR spectrometer. After washing with alcohol, the XPS spectra of the membrane samples were measured on a Perkin–Elmer PHI 1600 ESCA system. The conditions were the same as in the previous study.[19] Thus, the existence of PAN-g-AAm and the chemical structure changes of the PAN membranes were examined by IR and XPS. The morphology of the PAN membranes was viewed under a Hitachi-650 scanning electron microscope. The wettability of the membrane was studied using the water-absorption method.

Determination of the Grafting Degree

The grafting degree, defined as the mass ratio of the graft branch to the main chain, was determined by the difference of membrane mass before (W_0) and after (W) grafting according to the following equation:

$$\text{Grafting degree \%} = \frac{W - W_0}{W_0} \times 100\% \quad (1)$$

Determination of the Water-absorption Percent

Samples of PAN membranes were allowed to soak in deionized water in beakers for at least 48 h. They were then removed, blotted dry, and weighed immediately. This was recorded as the wet mass (W') of the membrane. The water-absorption percent, defined as the difference of the wet mass and dry mass of the membranes, were determined by the following equation:

Water absorption percent %

$$= \frac{W' - W}{W} \times 100\% \quad (2)$$

where W is the dry mass of the membranes after grafting. To reduce the deviation, the data were obtained from at least three parallel results.

RESULTS AND DISCUSSION

IR Spectra

Figure 1 shows the IR spectra of PAN, hydrolyzed PAN, and PAN-g-AAm. The IR spectrum of PAN [Fig. 1(a)] reveals the —C≡N stretching vibration at 2243 cm^{-1} [20] and the —C=O stretching vibration at 1732 cm^{-1}.[21] Figure 1(b) shows a higher absorption between 1605 and 1728 cm^{-1} which can be assigned to the C=O asymmetrical stretching in —COOH[22] and a little lower absorption at 2243 cm^{-1}. The results show that the —COOR and —CN groups on the surface of the PAN membranes may be hydrolyzed into —COOH. The IR spectrum of PAN-g-AAm [Fig. 1(c)] exhibits a strong absorption at 1647 cm^{-1}, which can be assigned to the combined motion of NH_2 and CO stretching in the —$CONH_2$ group.
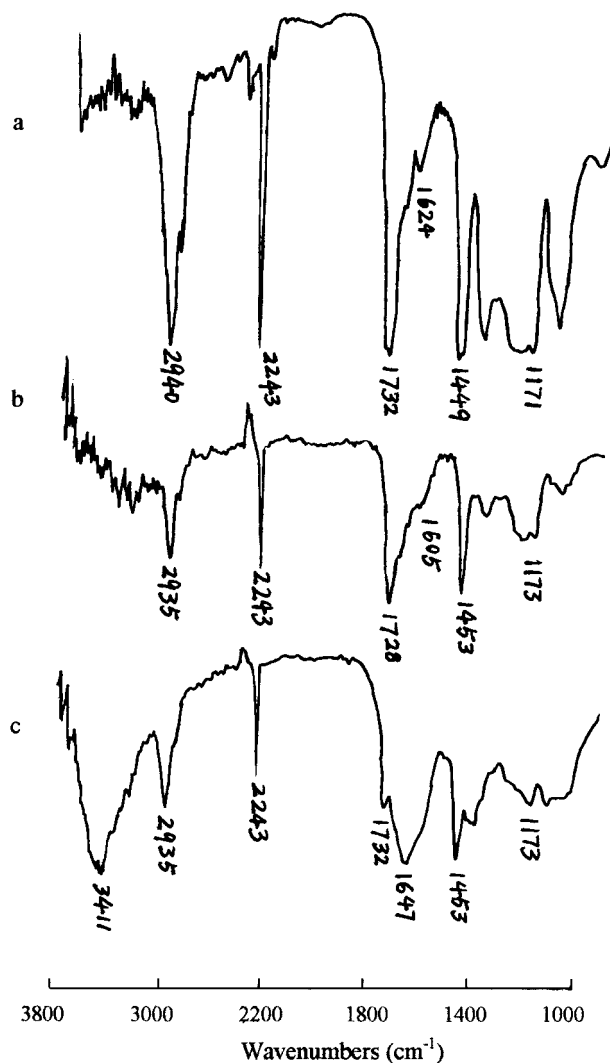
Figure 1 IR spectra of (a) PAN before graft copolymerization, (b) hydrolyzed PAN, and (c) PAN-*g*-AAm prepared in the typical condition.

An absorption at 3411 cm^{-1} is also shown in Figure 1(c), which can be designated to the N—H stretching vibration in NH$_2$.[23] The difference between Figure 1(a) and (c) verifies the existance of PAN-*g*-AAm.

XPS Analysis

C1s

The C1s XPS spectra are shown in Figure 2. Our earlier study[19] showed that the PAN C1s corelevel spectrum gave four component peaks with the binding energy (BE) at 286.54, 289.03, 285.0, and 285.30 eV, respectively. The peak at 286.54 eV can be attributed to the combina-

tion of the two carbon atoms in the AN unit $\{-[CH_2-CH(CN)]_n-\}$.[24] The peak at 289.03 eV can be attributed to the carbon in the ester group of the MMA unit (—COOR).[25] The others can be attributed to the saturated carbons in the backbone. Comparing the C1s spectrum of PAN [Fig. 2(a)] and hydrolyzed PAN [Fig. 2(b)], the strength of the BE at 286 eV in Figure 2(b) is much lower than that in Figure 2(a). It shows that the amount of the nitrile group of the hydrolyzed PAN has become smaller than that of PAN. The small peak at 289 eV in Figure 2(b) also became smaller and combined into the main peak. Thus, we can assume that some —CN groups and ester groups of MMA in hydrolyzed PAN have been hydrolyzed. In fact, the curve at 289 eV in Figure 2(b) is above the baseline where the small peak can be attributed to the carbon in —COOH, the hydrolyzing product.[26] Figure 2(c) shows the C1s XPS spectrum of PAN-*g*-AAm. It gave an extra peak with the BE at 288.5 eV, which can be attributed to the carbon in the NH$_2$—C=O functional group.[27] The C1s spectra's difference between PAN (hydrolyzed PAN) and PAN-*g*-AAm verified the grafting copolymer.

O1s

The O1s XPS spectra are shown in Figure 3. The O1s spectrum of PAN [Fig. 3(a)] can be considered as the contribution of oxygen in the MMA and SPS units. There are three peaks in Figure 3(a), that is, 532.21, 533.77 eV (—CO—OR), and 531.72 (—SO$_3^-$).[19] Figure 3(b) shows the O1s spectrum of hydrolyzed PAN. The curve at 532.2 eV in Figure 3(b) is higher than that of Figure 3(a), which can be attributed to the carbon
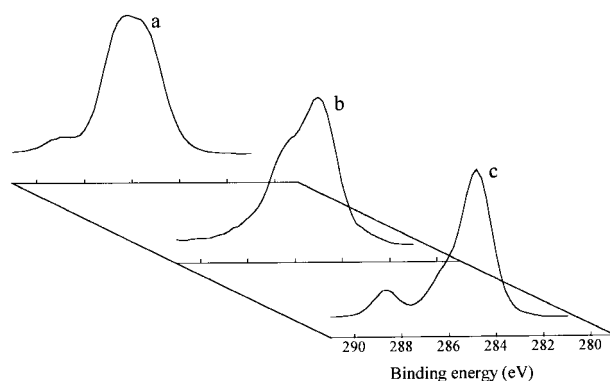

Figure 2 Spectra of C1s XPS: (a) PAN, (b) hydrolyzed PAN, and (c) PAN-*g*-AAm prepared in the typical condition.
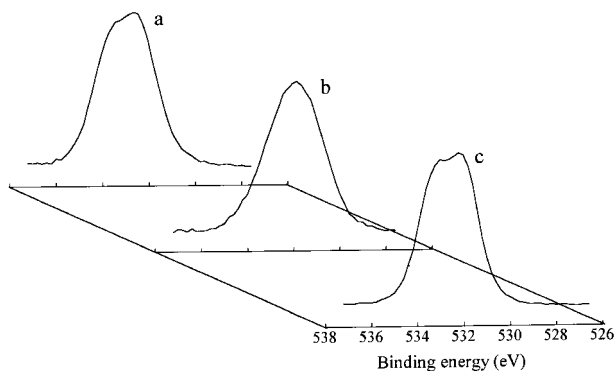
Figure 3 Spectra of O1s XPS: (a) PAN, (b) hydrolyzed PAN and (c) PAN-g-AAm prepared in the typical condition.

in —**C**OOH (ref. 26) coming from the hydrolyzing of —**C**OOR and —CN. The curve at 321.7 eV rose obviously in the O1s spectrum of PAN-g-Aam [Fig. 3(c)]. This can be attributed to the AAm unit grafted onto the membrane according to Beamson and Briggs.[27]

Valence

Figure 4 shows the valence XPS spectra of PAN. The valence spectrum of PAN [Fig. 4(a)] gives a peak at a BE of about 7 eV that coincided with that of Beamson and Briggs.[24] This peak disappeared in the valence spectrum of hydrolyzed PAN [Fig. 4(b)] and PAN-g-AAm [Fig. 4(c)].
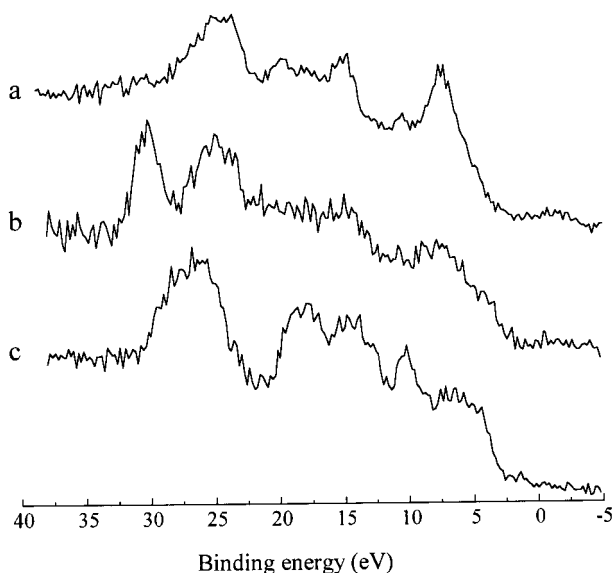

Figure 4 Spectra of valence XPS: (a) PAN, (b) hydrolyzed PAN, and (c) PAN-g-AAm prepared in the typical condition.
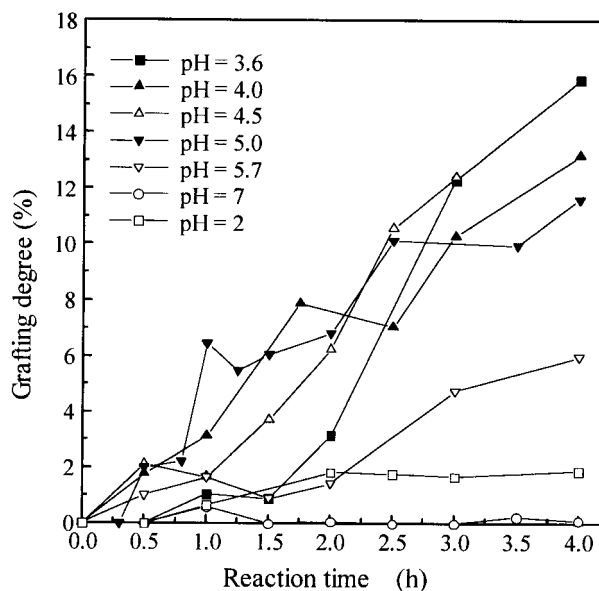

Figure 5 Effect of reaction time on grafting degree: $T = 60°C$; $[M] = 0.4225$ mol/L; $[I] = 0.2545$ mol/L.

There are two peaks in the valence spectrum of hydrolyzed PAN [Fig. 4(b)], which can be attributed to O2s (30 eV, in the carboxyl group)[26] and N2s (24 eV, in the nitrile group),[24] respectively. The valence spectrum of PAN-g-AAm [Fig. 4(c)] was similar to that of PAAm. The peak at 27 eV in Figure 4(c) can be attributed to the O2s in the amide group.[27] The O1s spectra and valence spectra also verified the existing of PAN-g-AAm on the surface of the membrane.

Influence of Reaction Parameters

Reaction Time

The grafting degree increased with increasing reaction time in the different pH media (Fig. 5). With increasing reaction time, the amounts of the hydroxyl radical and macroradical as well as the conversion of the monomer increased. Then, branches increased, that is, the extent of grafting increased.

Effect of pH Value in the Medium

We adjusted the pH of the medium with the common acetic acid buffer and studied the effect of the pH on the grafting degree (Figs. 5 and 6). The results show that the grafting degree was very low when the pH was 2 and was approximately zero when the pH was 7. Only when the pH was 3.6–5.7 did the grafting copolymerization come
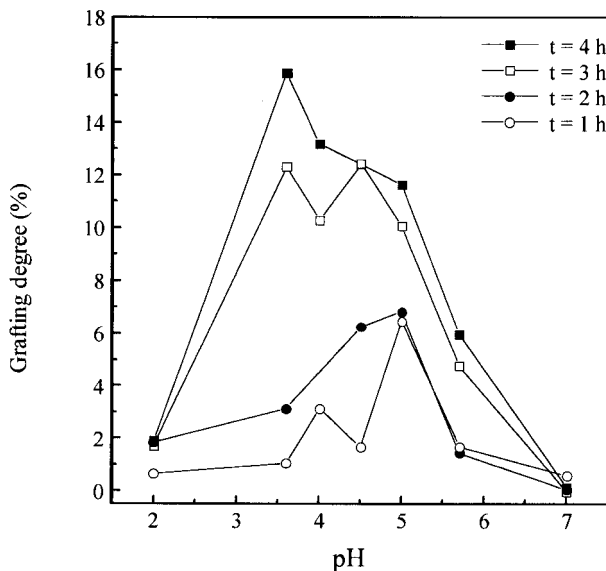
Figure 6 Effect of pH on grafting degree: $T = 60°C$; $[M] = 0.4225$ mol/L; $[I] = 0.2545$ mol/L.

Figure 8 Effect of concentration of AAm on grafting degree: pH 5.0; $T = 50°C$; $[I] = 0.2545$ mol/L.

into play. The extent of the grafting increased with the pH decrease in this range.

In the basic medium, Fe^{2+} was readily attacked by the oxygen in the air and converted into Fe^{3+} which had no initiation action. When the pH was decreased, the activity of Fe^{2+} increased and it interacted with H_2O_2 to give more hydroxyl radicals. The initiation efficiency and the opportunities of grafting copolymerization were increased.
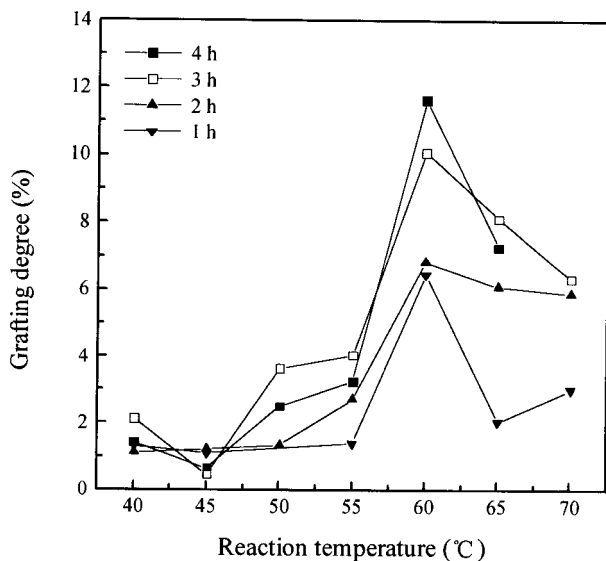
Then, the extent of grafting increased when the pH was changed from 5.7 to 3.6.

When the pH was too low, that is, below 3.6, the Fe^{2+} ions adsorbed on the surface of the membrane can be deabsorbed into the medium. This led to homopolymerization in the medium and the extent of grafting was decreased sharply. This result was different from that of Godjevargova et al.[17,18]

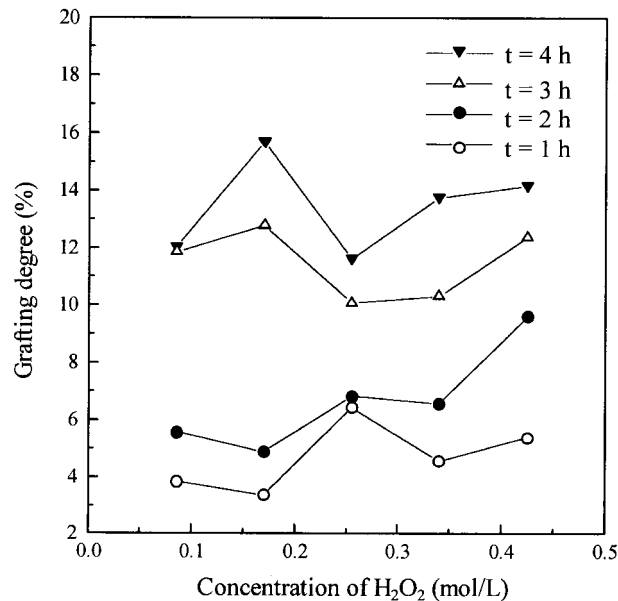

Figure 7 Effect of reaction temperature on grafting degree: pH 5.0; $[M] = 0.4225$ mol/L; $[I] = 0.2545$ mol/ L.

Figure 9 Effect of concentration of H_2O_2 on grafting degree: pH 5.0; $T = 50°C$; $[M] = 0.4225$ mol/L.

Table I   Effect of Parameters on Grafting Efficiency

t^a (h)	Ge^b (%)	pH	Ge^c (%)	T^d (°C)	Ge^e (%)	[M]^f (mol/L)	Ge^g (%)	[I]^h (mol/L)	Ge^i (%)
0.5	23.88	2	14.71	40	12.27	0.1408	0	0.0849	20.84
0.75	14.86	3.6	45.46	45	42.91	0.2817	14.82	0.1696	47.96
1	24.71	4	59.64	50	14.3	0.4225	58.1	0.2545	58.1
1.25	21.23	4.5	62.76	55	31.98	0.5634	46.15	0.3394	48.64
1.5	26.54	5	58.1	60	47.32	0.7042	23.25	0.4241	34.57
2	30	5.7	7.788	65	21.32				
2.5	41.36	7	1.504	70	18.24				
3	47.32								
3.5	62.23								
4	58.1								

^{a} Reaction time.
^{b} Grafting efficiency, $T = 60°C$, pH 5.0, [M] = 0.4225 mol/L, [I] = 0.2545 mol/L.
^{c} $T = 60°C$, $t = 4$ h, [M] = 0.4225 mol/L, [I] = 0.2545 mol/L.
^{d} Reaction temperature.
^{e} $t = 3$ h, pH 5.0, [M] = 0.4225 mol/L, [I] = 0.2545 mol/L.
^{f} Concentration of AAm.
^{g} $T = 60°C$, $t = 4$ h, pH 5.0, [I] = 0.2545 mol/L.
^{h} Concentration of H_2O_2.
^{i} $T = 60°C$, $t = 3$ h, pH 5.0, [M] = 0.4225 mol/L.

Reaction Temperature

The grafting degree increased with elevating the reaction temperature below 60°C, but decreased above 60°C (Fig. 7). When the reaction temperature is elevated, the reactive activity of AAm increased and the reaction rate of Fe^{2+} and H_2O_2 increased to give more hydroxyl radicals. The macromolecular motion can also be strengthened with high temperature. Therefore, the grafting degree increased with increasing temperature. Some of the Fe^{2+} ions can be oxided into Fe^{3+}

Figure 10   Wettability of the grafted PAN membrane.

when the temperature is too high. This may be why the grafting degree decreased when the temperature was elevated above 60°C in our experiments.

Concentration of AAm

Figure 8 indicates that the extent of grafting increased with an increasing concentration of AAm. When the amount of the monomer was increased, the grafting reaction was speeded up and the grafting degree increased.

Concentration of H_2O_2

Figure 9 indicates that the extent of grafting increased with increasing the concentration of H_2O_2 to a small extent. The grafting copolymerization took place in the heterogeneous medium. When the amount of H_2O_2 is increased, the amount of the hydroxyl radical formed in the medium increased and homopolymerization can easily occur. Therefore, increasing the concentration of H_2O_2 resulted in the grafting degree increasing slightly.

In the experiment, we also examined how the above parameters affect the grafting efficiency, that is, the percentage of the grafting copolymer in the whole polymer products on the membrane. The grafting efficiency was calculated according to the following equation:

$$\text{Grafting efficiency } \% = \frac{W - W_0}{W_1 - W_0} \times 100\% \quad (3)$$
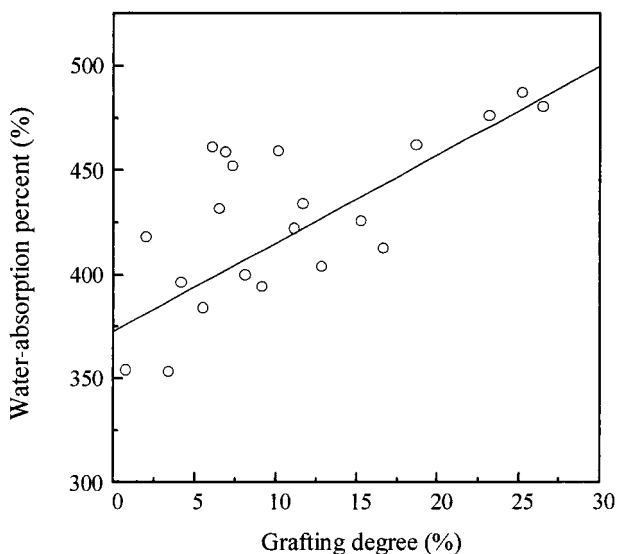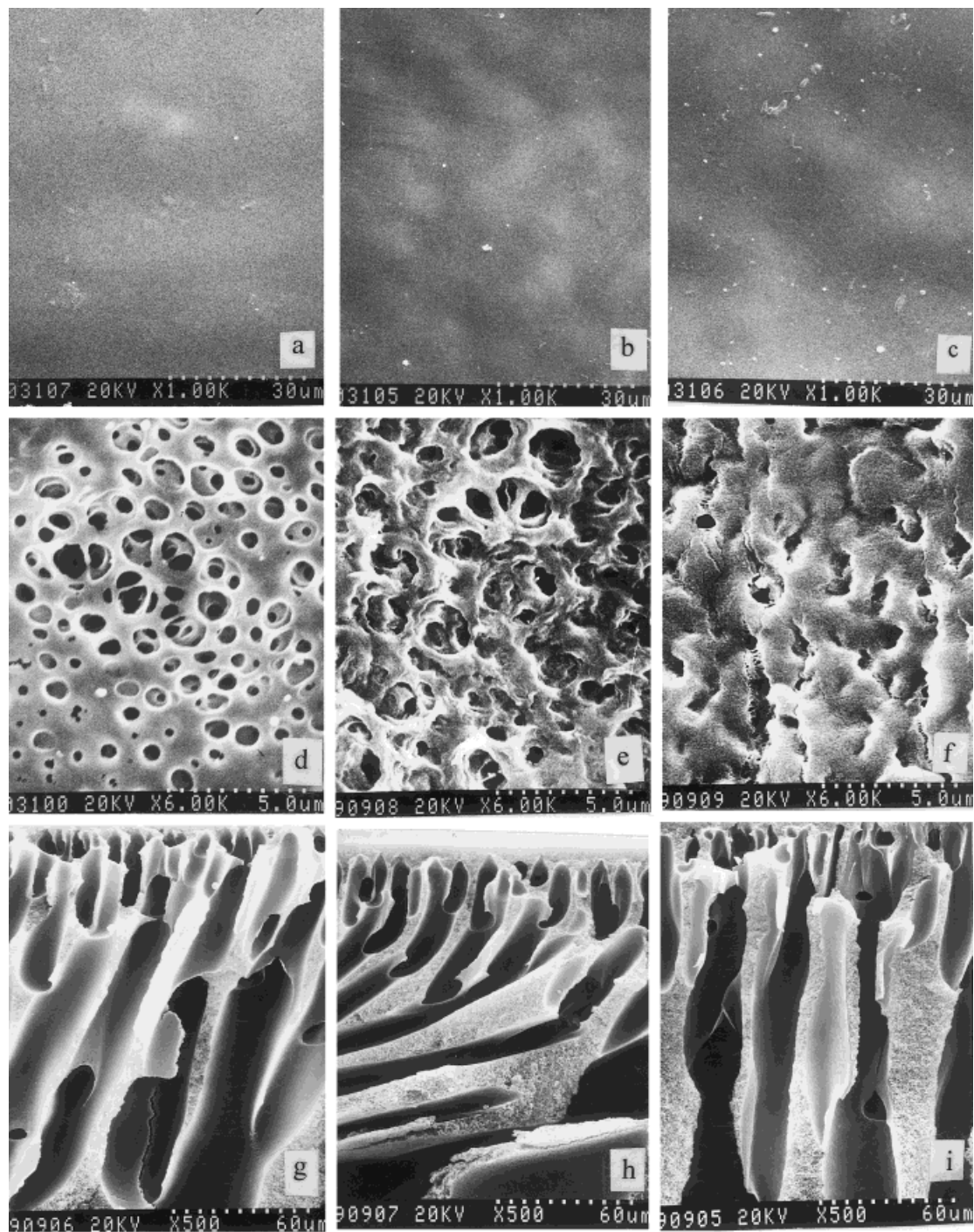
Figure 11 SEM photos of (a–c) top-layer surface; (d–f) sublayer surface; (g–i) cross section; (a, d, g) before grafting; (b, e, h) after hydrolyzing; (c, f, i) after grafting in the typical condition.

where W_1 is the mass of the membrane after grafting and before washing. The results (Table I) show that the grafting efficiency had an increased tendency with the increased reaction time and tended to have a hump when the other parameters varied. Because we just focused on the polymers on the membrane, the soluble homopolymer can be dissolved into the medium during the reaction and a higher deviation came to light.

Effect of Grafting on Wettability of PAN Membranes

We can easily examine the wettability of the PAN membrane by the water-absorption percent. The water-absorption percent of the PAN membrane was calculated by eq. (2). Figure 10 indicates that the water-absorption percent of the PAN membrane tended to increase after its grafting of AAm and increase with its grafting degree, that is, the wettability of the PAN membrane after grafting was higher than that with no grafting.

Morphology of PAN Membranes Under SEM

The structure photos of the PAN membrane before and after grafting are shown in Figure 11. Figure 11(a–c) shows the top-layer surface (facing toward the water side when casting). Figure 11(d–f) shows the sublayer surface (facing toward the glass plate). The fracture cross sections [Fig. 11(g–i)] were obtained by breaking the membranes after cooling in liquid nitrogen. The results showed that the hydrolyzing and grafting did not influence the interior morphology of the membranes. But hydrolyzing made the pore edges smoother [Fig. 11(e)]. After grafting, the graft copolymers were attached on the surface of the membrane and the pores seemed to be blocked slightly [Fig. 11(c) and (f)]. We can assume that the graft reaction occurred on the membrane surface at the beginning and made the reaction in the membrane difficult after that.

Comparison of the Fe^{2+}/H_2O_2 and Ceric Initiating Systems

In the previous article, we discussed the modification of PAN membranes by grafting AAm with ceric ions as the initiator.[19] Now, we can compare the Fe^{2+}/H_2O_2 and ceric initiating systems qualitatively. Although the grafting reactions were all carried out in the best conditions, the results revealed that the grafting degree with Ce^{4+} was much lower than that with Fe^{2+}/H_2O_2. With the ceric initiator, the reactive groups on the membrane may be used up in the earlier beginning and the grafting reaction reached a saturation state after 0.5 h. With the Fe^{2+}/H_2O_2 initiation system, the hydroxyl radicals can be generated in the medium and transferred to the PAN macromolecules on the membrane surface during the reaction so that the grafting reaction can last for a longer time. Whatever initiator was used, the wettability of the modified PAN membranes was improved and the grafting polymers were attached on the surface of the membranes.

From an economical point of view, the price of ceric ammonium nitrate is higher than that of ferrous ammonium sulfate and H_2O_2. Therefore, it is more amenable to use the Fe^{2+}/H_2O_2 initiation system.

CONCLUSION

AAm can be grafted onto the surface of PAN membranes with Fe^{2+}/H_2O_2 as the initiator. IR and XPS proved the existence of PAN-*g*-AAm and also presented the chemical structure changes after hydrolyzing. The extent of grafting was influenced by several parameters such as the pH of the medium, reaction time and temperature, and concentration of AAm and H_2O_2. The wettability of the membrane after grafting AAm was improved. SEM photos showed that the grafting copolymer was attached to the surface of membrane and the grafting reaction did not influence the morphological structure of the membrane.

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