

Functionalizing of Polyurethane Surfaces by Photografting with Hydrophilic Monomers

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ABSTRACT: Poly(ester urethane) (PU) with functional groups (amide, hydroxyl, carboxyl) on surfaces were prepared by grafting monomers such as acrylamide (AAM), hydroxyethyl acrylate (HEA), and methacrylic acid (MAA) onto the PU membranes. Grafting copolymerization was carried out by the combined use of photooxidation and UV irradiation grafting. The PU membrane was photooxidized in hydrogen peroxide solution under UV light to yield hydroperoxide groups on the surface and then irradiation grafting with monomer in water. The ATR-FTIR spectrum, X-ray photoelectron spectroscopy characterized the grafted copolymers and verified the occurrence of grafting copolymerization. The results showed that the content of hydroperoxide groups yielded was dependent on the photooxidation time and reached maximum at about 8 h. Grafting copolymerization was enhanced when irradiating by UV light. The degree of grafting was increased with the increase of content of hydroperoxide groups, irradiation time, and monomer concentration. The grafting copolymerization was enhanced when an appropriate amount of ferrous ions was added. After grafting, the wettability of PU and the water absorption percentage increased with the degree of grafting. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2505–2512, 2000

Key words: poly(ester urethane); grafting copolymerization; UV irradiation; hydrophilicity

INTRODUCTION

PU is a widely used elastomer due to its good mechanical property. However, the hydrophobic surface restricted its uses to blood-contacting material and hydrophilic plastics. Therefore, it is necessary to improve its surface hydrophilicity. Surface grafting is one of the methods.^{1–5} In the past few years, a number of different methods such as plasma polymerization,¹ γ -ray irradiation,² ozone-induced polymerization,³ cerium (IV) ions, or transition metal activation^{4,5} were used to realize the grafting of PU with vinyl monomers.

Among them, γ -ray irradiation was widely used. However, this method was proceeded by a pre-swelling technology which inevitably produced extensive homopolymer and also allowed the grafting to proceed throughout the bulk of the substrate rather than confining it to the surface layers. Meanwhile, the chemical structure of the surface was prone to change by plasma polymerization and the degree of grafting was low by cerium (IV) ions or transition metal activation. Compared with these methods, UV irradiation polymerization could overcome the shortcomings. Moreover, it conducted conveniently and the cost was low. To realize the UV irradiation polymerization, the photosensitive groups on the PU surface was critical. As hydroperoxide group was UV sensitive,⁶ in this article we attempted to introduce the hydroperoxide groups onto the PU sur-

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face by photooxidizing the PU membrane in hydrogen peroxide solution under UV irradiation. When irradiated under UV light, the hydroperoxide groups on the surface decomposed into macromolecular oxygen radicals and hydroxyl radicals.⁶ The former could initiate the grafting copolymerization and the latter could initiate the homopolymerization. To minimize the homopolymerization, we used ammonium iron (II) sulfate hexahydrate as a reductant. Our experiments showed that combined use of photooxidation and irradiation graft could enhance the grafting polymerization and the high degree of grafting was obtained in short time. To our knowledge, no work has been reported on graft polymerization of monomers onto PU surface by combined use of photooxidation and irradiation grafting under UV light. The present work will describe the results of grafting copolymerization of acrylamide (AAm), 2-hydroxyethyl acrylate (HEA), and methacrylic acid (MAA) onto PU surface.

EXPERIMENTAL

Membrane Preparation

PU membrane was prepared in our laboratory by spreading a THF solution containing a 20 wt % base PU (Estane, BFGoodrich Co., Cleveland, OH, USA) onto a glass plate. The plate was placed in the air at room temperature to evaporate the solvent, then it was dried under vacuum to constant weight. The membrane thus obtained was 0.3-mm thick and was cut into pieces to the size of 1.5×3 cm for photooxidation and graft copolymerization.

Photooxidation

PU membrane was immersed in dimethylformamide (DMF)/H₂O solution for 12 h, then washed with a copious amount of water. The membrane was subsequently placed in 40 mL hydrogen peroxide solution (30%) and UV was irradiated from a high-pressure mercury lamp (250 W) for a given time under stirring at 35°C. The photooxidized membrane was rinsed with water to free excess hydrogen peroxide and dried at room temperature in vacuum.

Grafting Copolymerization

The required amount of monomer, 15 mL aqueous solution of ammonium iron (II) sulfate hexahy-

drate and photooxidized membrane, were charged into a Pyrex glass tube closed with a rubber stopper and then replaced with nitrogen. Graft copolymerization was carried out under UV irradiation at a distance of 12.5 cm for a given time at 35°C. The grafted membrane was rinsed with hot water (70°C) for at least 48 h to remove the homopolymer, and subsequently dried in vacuum at 50°C for 24 h.

Characterization

The grafted membrane was measured by ATR-FTIR, electron spectroscopy for chemical analysis (ESCA). The ATR-FTIR spectra were obtained on a Nicolet Magna-IR560 machine. ESCA spectra were conducted on a ESCA LAB Mark II spectrometer employing AlK_α excitation radiation. The charging shift was referred to the C1s line emitted from the saturated hydrocarbon.

The content of hydroperoxide on the membrane surface was determined by the iodometry method.⁷ Degree of grafting = $(w_2 - w_1)/w_1$, where w_1 and w_2 represented the weight of photooxidized membrane and grafted membrane, respectively. The wettability of the membrane was determined by using the water-absorption method.⁸ The membrane was soaked in deionized water in a beaker at room temperature for at least 24 h. It was then removed, blotted dry, and weighed immediately. The water absorption percent was defined as the difference of the wet mass (w_3) and dry mass of the membrane (w_1): water absorption percent (%) = $(w_3 - w_2)/w_2 \times 100\%$. To reduce the deviation, data were obtained from five parallel results.

RESULTS AND DISCUSSION

Characterization of Graft Copolymers

ATR-FTIR

The change of chemical structure of the surface of membranes before and after grafting was investigated by ATR-FTIR spectroscopy. Figure 1 showed the spectra of control membrane and membranes grafted with AAm, HEA, and MAA. To the control membrane, the amide and ester groups in urethane groups showed the absorption at 3335, 1528, and 1725 cm⁻¹, respectively; the absorption at 1699 cm⁻¹ designated to the hydrogen-bond association of ester and amide groups [Fig. 1(a)]. In the spectrum of AAm-grafted PU membrane [Fig. 1(b)], the

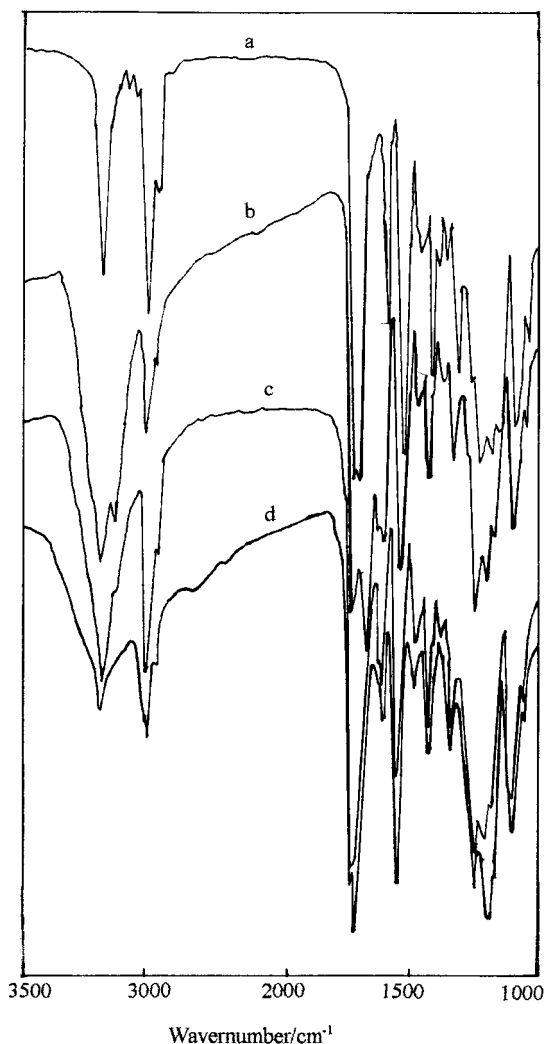


Figure 1 ATR-FTIR spectra of (a) PU, (b) PU-g-PAAm, (c) PU-g-PHEA, (d) PU-g-PMAA.

absorption at 1655 cm^{-1} , which was assigned to the associated amide groups of AAm, appeared obviously,⁸ and a broad absorption at 3338 cm^{-1} resulted from the superposition of the absorption of amide groups of urethane and AAm. The absorption of the hard segment at 1724 , 1597 , 1528 , and 1309 cm^{-1} was depressed. When the PU membrane was grafted with HEA, a broad peak at 3351 cm^{-1} due to the contribution of hydroxyl group was observed,⁹ and the absorption of the hard segment at 3335 , 1597 , and 1528 cm^{-1} depressed obviously as compare with that of the ester groups [Fig. 1(c)]. In the spectrum of polyurethane-graft-poly(methyl methacrylate) (PU-g-PMAA) [Fig. 1(d)], there appeared peaks of carboxyl group at 1705 and 2914 cm^{-1} , and the absorption of the hard segment of PU matrix was depressed. It could be concluded from

above results that the AAm, HEA, and MAA were grafted onto the PU membranes.

ESCA

C1s. The C1s ESCA spectra were shown in Figure 2. The C1s spectrum of control membrane gave four component peaks with the binding energy at 285.0 , 286.6 , 288.8 , and 289.1 eV , respectively [Fig. 2(a)]. The peak at 285.0 eV could be attributed to the saturated carbons. The C1s peak corresponding to the carbonyl of the urethane groups was observed at 288.8 eV . The peaks at 286.6 and 289.1 eV could be attributed to the carbonyl carbon of ester group, respectively.^{10,11} In the C1s spectrum of the AAm-grafted membrane, there appeared an extra peak at 288.5 eV which designated to the carbon in the amide group ($\text{NH}_2\text{-C=O}$) of the AAm unit.⁸ As com-

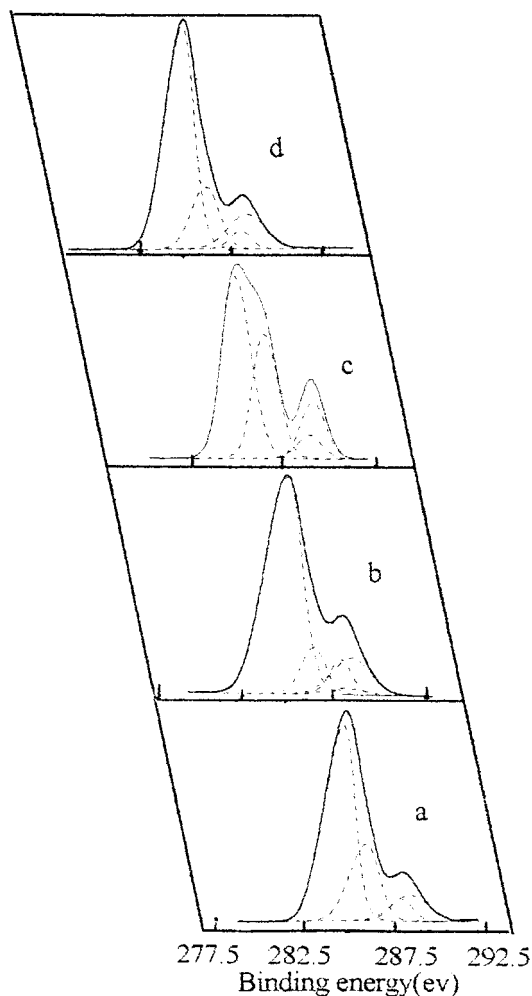


Figure 2 ESCA spectra for C1s of (a) PU, (b) PU-g-PAAm, (c) PU-g-PHEA, (d) PU-g-PMAA.

pared with control membrane, the strength of the binding energy at 286.6 and 289.1 eV in AAm-grafted membrane became smaller, which indicated that the amount of PU on the grafted surface became lower. Contrary to the AAm-grafted membrane, if the strength of the binding energy at 286.6 and 289.1 eV in HEA-grafted membrane was higher than that of control membrane, it indicated that the amount of ester groups on the surface increased, which came from HEA [Fig. 2(b)]. In the C1s spectrum of MAA-grafted membrane, the strength of peaks at 286.6 and 289.1 eV also increased because the carboxyl and ester groups showed almost the same bonding energy¹⁰ [Fig. 2(c)]. After grafting with monomers, the amount of urethane groups on the surfaces decreased as the peak at 288.8 eV became smaller. It could be concluded from the C1s spectra difference between control membrane and grafted membrane that graft copolymerization occurred.

O1s. The O1s ESCA spectra were shown in Figure 3. The O1s spectrum of control membrane [Fig. 3(a)] could be considered as the contribution of oxygen in ester and urethane groups. There were two peaks with the binding energy at 532.9 and 534.3 eV, respectively, which designated to oxygen of C—O bond and C=O bond in ester and urethane groups, respectively.¹⁰ Figure 3(b) showed the O1s spectrum of AAm-grafted PU membrane. It gave an extra peak with the binding energy at 532.2 eV, which assigned to the oxygen in NH₂—C=O coming from the AAm unit.⁸ The curve at 532.0 and 534.3 eV rose obviously in the O1s spectrum of polyurethane-graft-poly(2-hydroxyethyl acrylate) (PU-g-PHEA) and PU-g-PMAA [Fig. 3(c,d)]. It was the result of HEA and MAA unit grafted onto the PU membrane.

N1s. Figure 4 showed the N1s ESCA spectra of PU membranes. The control membrane, PU-g-PHEA, polyurethane-graft-polyacrylamide (PU-g-PAAm), and polyurethane-graft-poly(methyl methacrylate) (PU-g-PMAA) membranes showed only one N1s peak with the binding energy at 400.3 eV, respectively. Comparing the N1s spectrum of control membrane [Fig. 4(a)] and PU-g-PHEA membrane and PU-g-PMAA [Fig. 4(b,d)], the strength of binding energy at 400.3 eV became smaller, which implied that the amount of nitrogen on the grafted surface decreased. It also could be seen from Fig. 4(b) that the strength of N1s of PU-g-PAAm membrane was higher than that of the control mem-

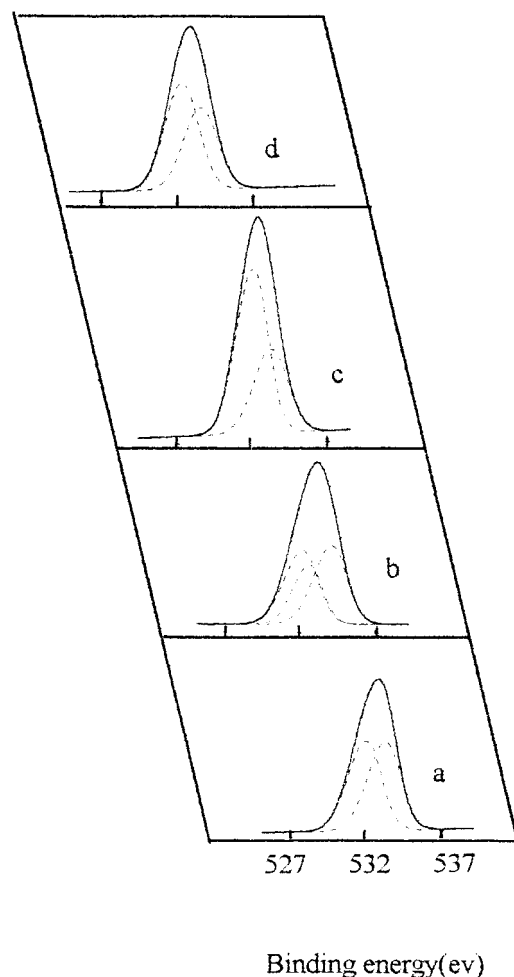


Figure 3 ESCA spectra for O1s of (a) PU, (b) PU-g-PAAm, (c) PU-g-PHEA, (d) PU-g-PMAA.

brane. This could be attributed to the AAm unit grafted onto the PU membrane.

Photooxidation of PU Membrane

The effect of photooxidation on the chemical composition was investigated with ESCA. After irradiation under UV light, the O1s/C1s ratio of the PU surface increased [Fig. 5(a)], which showed that the PU membrane surface could be photooxidized to yield peroxide groups. To determine the content of hydroperoxide groups on the photooxidized PU membrane, we used the iodometry method.⁷ As can be seen from Figure 5(b), the content of hydroperoxide groups increased with irradiation time and reached maximum at about 8 h, and thereafter decreased. It indicated that PU membrane could be effectively oxidized to form hydroperoxide groups under UV irradiation.

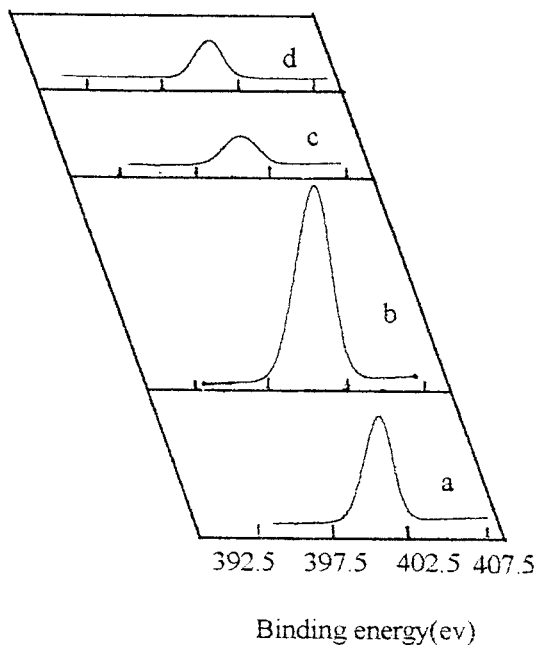


Figure 4 ESCA spectra for N1s of (a) PU, (b) PU-g-PAAm, (c) PU-g-PHEA, (d) PU-g-PMAA.

Grafting Copolymerization

Effect of Photooxidation Time

The variation of degree of grafting as a function of photooxidation time was shown in Figure 6. It was seen from Figure 6 that the degree of grafting

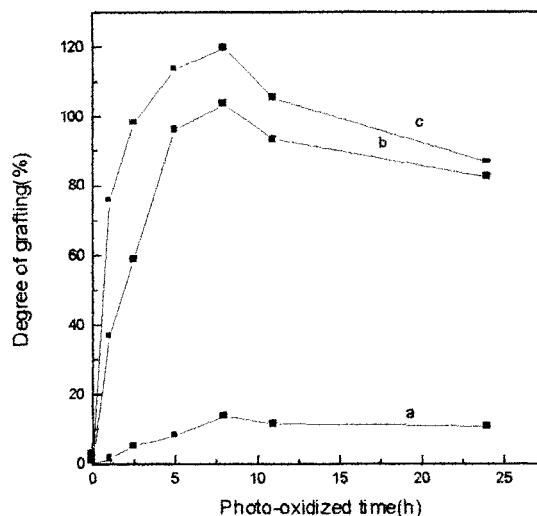


Figure 6 Effect of photooxidation time on the degree of grafting. (a) PU-g-PAAm; (b) PU-g-PHEA; (c) PU-g-PMAA. $[Fe^{2+}] = 2.2 \times 10^{-3} \text{ mol L}^{-1}$; $[AAm] = 1.59 \text{ mol L}^{-1}$; $[HEA] = 1.63 \text{ mol L}^{-1}$; $[MAA] = 1.10 \text{ mol L}^{-1}$; irradiation time of (a) 60 min, (b) 60 min, (c) 80 min.

of each system was increased with photooxidization time within 8 h, and then decreased, which showed the same trend as Figure 5. As other graft conditions remained the same, the degree of grafting of three grafting copolymerization systems was determined by the content of hydroperoxide groups on the surface because they acted as

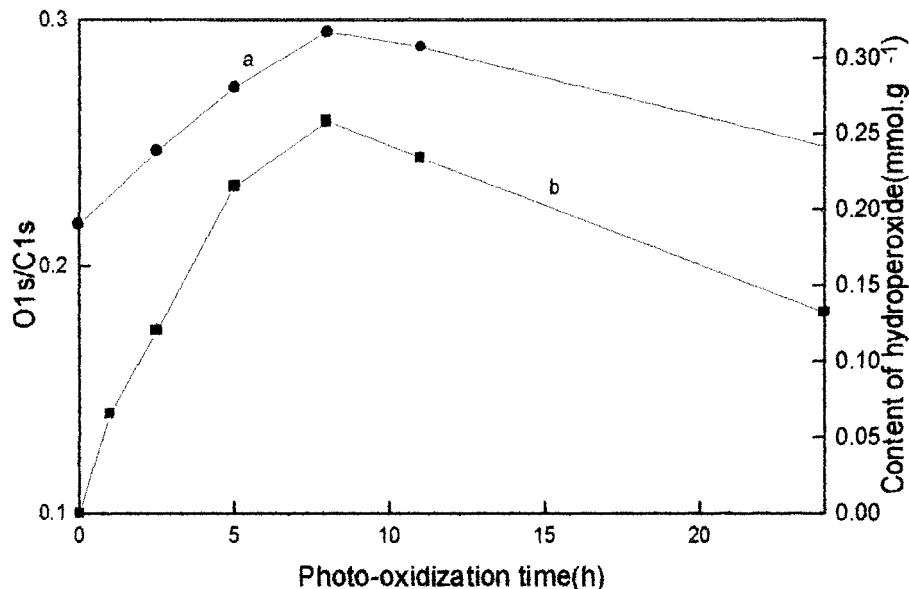


Figure 5 Effect of photooxidation time on the O1s/C1s ratio and content of hydroperoxide on the PU surface.

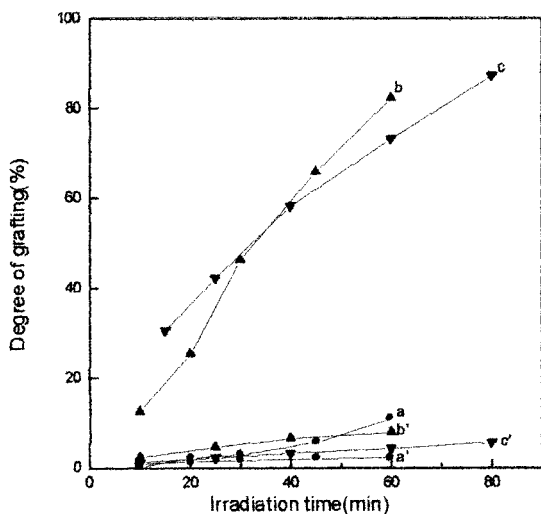


Figure 7 Effect of irradiation time on the degree of grafting. (a) PU-g-PAAm; (b) PU-g-PHEA; (c) PU-g-PMAA. $[\text{Fe}^{2+}] = 2.2 \times 10^{-3} \text{ mol L}^{-1}$; $[\text{AAm}] = 1.59 \text{ mol L}^{-1}$; $[\text{HEA}] = 1.63 \text{ mol L}^{-1}$; $[\text{MAA}] = 1.10 \text{ mol L}^{-1}$; photooxidation time 8 h.

the initiator after being decomposed to form macromolecular oxygen radicals. As shown in Figure 5, the content of hydroperoxide groups was relative to the photooxidation time; therefore the degree of grafting was dependent on the photooxidation time. By increasing the content of hydroperoxide groups, the number of macromolecular oxygen radicals yielded increased and the number of active sites for polymerization increased, as the degree of grafting increased correspondingly.

Effect of Irradiation Time

Figure 7 showed the effect of irradiation time on the degree of grafting. Figure 7(a',b',c') indicated that the degree of grafting of each system was low and increased slightly with irradiation time when placed in darkness without stirring, which implied that the grafting copolymerization could not be conducted effectively only in the presence of ferrous ions. However, after irradiation by UV light, each system had a much higher degree of grafting and increased rapidly with time, especially for HEA and MAA systems [Fig. 7(a–c)]. In the three graft systems, hydroperoxide groups acted as the initiator as the macromolecular oxygen radicals were formed. For each system, when the content of hydroperoxide groups, concentration of ferrous ions, and monomer remained the same, the macromolecular oxygen radicals

formed determined the degree of grafting. The difference of change in degree of grafting between the same two systems irradiated and unirradiated by UV light revealed that the UV irradiation accelerated the reaction. That is, the UV irradiation enhanced the grafting copolymerization.

Effect of Fe^{2+} Concentration

Figure 8 showed that the degree of grafting increased with the Fe^{2+} concentration and then decreased, which indicated that the amount of Fe^{2+} in a suitable range could accelerate the grafting copolymerization and beyond this range the polymerization was retarded. Under UV irradiation, the hydroperoxide groups decomposed into macromolecular oxygen radicals (PO^\bullet) and hydroxyl radicals (HO^\bullet), where the macromolecular oxygen radicals initiate the grafting copolymerization and the hydroxyl radicals initiate the homopolymerization. When the ferrous ions were added, the homopolymerization was retarded because the hydroxyl radicals converted into hydroxyl ions. Meanwhile, the hydroperoxide groups on the PU surface could react directly with Fe^{2+} to form PO^\bullet radicals and to initiate the grafting copolymerization. Although the reaction between PO^\bullet radical and Fe^{2+} ion occurred in the system and formed PO^- , which could not initiate the polymerization, eq (2) was dominated because

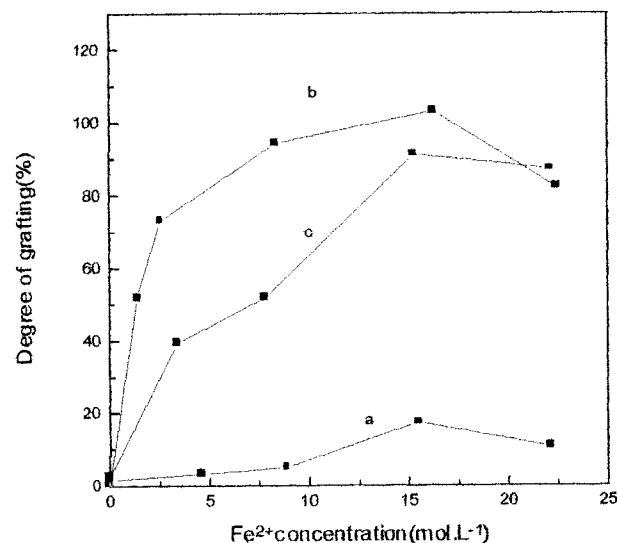
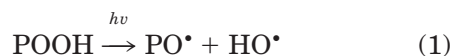


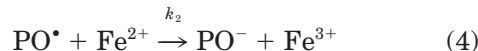
Figure 8 Effect of Fe^{2+} concentration on the degree of grafting. (a) PU-g-PAAm; (b) PU-g-PHEA; (c) PU-g-PMAA. $[\text{AAm}] = 1.59 \text{ mol L}^{-1}$; $[\text{HEA}] = 1.63 \text{ mol L}^{-1}$; $[\text{MAA}] = 1.10 \text{ mol L}^{-1}$; photooxidation time 8 h; irradiation time of (a) 60 min, (b) 60 min, (c) 80 min.

the rate constant $k_1 > k_2$.¹² Comparing the degree of grafting of UV irradiated and non-UV irradiated grafting copolymerization systems (Fig. 6), it could be concluded that the decomposition of hydroperoxide groups was dominated by UV irradiation. When the Fe^{2+} concentration was in a suitable range, as compared with step 4, step 3 was majored and accelerated the grafting copolymerization,¹² and the probability for step 4 increased when the Fe^{2+} concentration was beyond the range that caused the decrease in the degree of grafting.

Hydroperoxide decomposition:



Radical scavenging:



Chain initiation:



where POOH and M represent polymeric species and monomer, respectively.

Effect of Monomer Concentration

The variation of degree of grafting of three polymerization systems as a function of monomer concentration was investigated. The results are presented in Figure 9. It was seen that when the monomer concentration increased, the amount of monomer diffused onto the membrane surface increased and the grafting polymerization sped up, which resulted in the increase of degree of grafting.

As discussed above, three systems have different polymerization characters and reactivity because of the nature of three monomers. It could be seen from Figures 6–9 that the degree of grafting of HEA and MAA systems was higher than that of

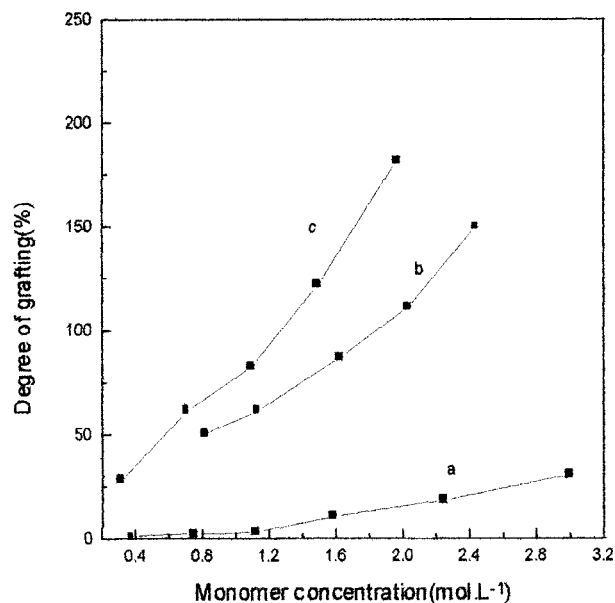


Figure 9 Effect of monomer concentration on the degree of grafting. (a) PU-g-PAAm; (b) PU-g-PHEA; (c) PU-g-PMAA. $[\text{Fe}^{2+}] = 2.2 \times 10^{-3} \text{ mol L}^{-1}$; photooxidation time 8 h; irradiation time of (a) 60 min, (b) 60 min, (c) 80 min.

the AAm system. In the present experiments, the three grafting polymerization systems were all heterogeneous. As other conditions remained the same, the degree of grafting was determined by the diffusion ability of the monomers into the PU membrane surface. Because of the poorest diffusion ability of AAm, the degree of grafting of this system was lower than that of the HEA and MAA systems.¹³ To HEA and MAA systems, when the monomer concentration remained the same, the degree of grafting of HEA system was higher than that of MAA system, which indicated that the diffusion ability of MAA was higher than that of HEA.

Hydrophilicity of PU Membranes

In our experiment, the hydrophilicity of grafted PU membranes was examined by the water absorption percent. Figure 10 indicated that the water absorption percent of the PU membrane increased after its grafting of AAm, HEA, and MAA and increased with the degree of grafting; that is, the hydrophilicity of the PU membranes after grafting was higher than that with no grafting. By adjusting the degree of grafting, the PU with moderate and high hydrophilicity could be obtained. The different slopes were found for

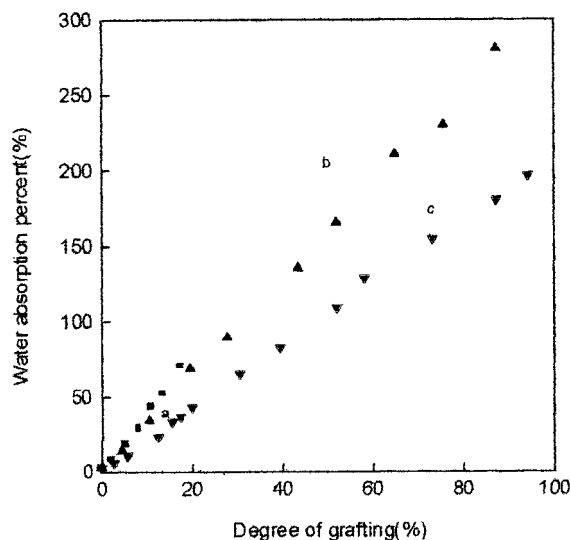


Figure 10 Effect of degree of grafting on the water absorption percent. (a) PU-g-PAAm; (b) PU-g-PHEA; (c) PU-g-PMAA.

grafted membranes, probably due to the different porous characters of the grafted PU membranes.¹³

CONCLUSION

PU membrane was photooxidized and grafted with AAm, HEA, and MAA under UV irradiation. The UV irradiation enhanced the grafting copolymerization of monomers onto PU membrane. Surface analysis verified the occurrence of grafting copolymerization. The hydrophilicity of the grafted membrane was increased with the degree

of grafting. By adjusting the degree of grafting, the PU with moderate and high hydrophilicity could be obtained. It was supposed that the PU membrane with a low degree of grafting could be used as a cytocompatible material and the high degree of grafting could be used as an antithrombogenic material.

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