pH-Dependent Permeation Through Polysulfone Ultrafiltration Membranes Prepared by Ultraviolet Polymerization Technique

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ABSTRACT: pH-sensitive poly(acrylic acid)-grafted membranes were prepared by an ultraviolet irradiation technique in air at room temperature. Peroxides produced on the membrane surface was quantified by 1,1-diphenyl-2-picrylhydrazyl (DPPH), which indicated that there existed an effective irradiation time for graft polymerization. Through X-ray photoelectron spectroscopy (XPS) measurements, the effective thickness of poly(acrylic acid) grafted onto the surface of a polysulfone membrane was determined to be around 80-100 nm. pH-dependent permeation behavior was noted from the permeation of riboflavin as a model solute. A distinctive flux decline of riboflavin appeared in the range of pH 4–5. Therefore, the flux of the intelligent membrane was controlled by changes in the pH of the external solution, attributed to the changes in the conformation of the grafted chains of poly(acrylic acid), because of the electrostatic force among the dissociated carboxyl groups. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 75–82, 1999

Key words: graft polymerization; UV irradiation technique; peroxide; 1,1-diphenyl-2-picrylhydrazyl; permeability; riboflavin

INTRODUCTION

Many research groups have prepared polymers having specific physicochemical properties for such applications as adhesives,¹ biomaterials,^{2,3} and membranes.^{4–25} They performed a modification of conventional commercial polymers by graft polymerization mainly on the surface of a polymer.

In membrane areas, surface modification of polymers has focused on preventing membrane fouling resulting from the adsorption of retained particles, salts, macromolecules, etc., that cause a

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significant flux decline during the separation operation. By introducing hydrophilic groups^{4,5} and providing some functionalities such as pH sensitivity⁶⁻⁸ and temperature sensitivity^{9,10} on the surface, the regulation of the permeation of solutes was achieved according to the surrounding environments, for example, in the controlled release of drugs. These specific functionalities can be acquired by selecting appropriate functional monomers.

Many methods such as UV irradiation, $^{5,9,11-13}$ ion-beam irradiation, 26,27 electron-beam irradiation, 14,15 γ -irradiation, 3,16,28 plasma treatment, 2,6,9,17 and chemical treatment 18,19 have been used to modify polymers and membranes for specific application. Of these methods, the UV-irradiation method has been widely used in many applications because it is a more convenient and cheaper operation than are other methods.

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Surface graft polymerization by UV irradiation can be classified into three methods according to the reaction procedure: (1) The one-step method 5,20,21 is very efficient. This method is performed by irradiating the polymer in the presence of a solvent containing a monomer. The reaction sites of grafting are controlled mainly by the interaction between the substrate polymer and the solvent. The disadvantage of this method is that it is not able to fully eliminate homopolymerization initiated by free radicals formed during irradiation of the monomer. Grafting can occur both at the surface and in bulk. (2) The preirradiation⁹ method is utilized to minimize the formation of a homopolymer. The polymer is preirradiated in air to produce peroxide groups on the surface. The irradiated polymer is immersed into the monomer solution and grafting is initiated by the thermal decomposition of peroxides. (3) The continuous method^{22,23} is the one in which a polymer is presoaked into a monomer solution containing a photoinitiator or photosensitizer and irradiated to be graft-polymerized on the surface.

In this study, we aimed to prepare a pH-responsive ultrafiltration (UF) membrane grafted with poly(acrylic acid) using a UV-irradiated graft-polymerization technique without using a photoinitiator or photosensitizer. A riboflavin permeation experiment was done to show pH-dependent permeation of the solute through a novel membrane at different pH.

EXPERIMENTAL

Materials

A polysulfone (PSF) UF (Gelman Science, Milwaukee, WI) with a 47-mm diameter, $120-\mu m$ thickness, and 0.2- μ m pore size was used for the modification. It was washed with methanol and dried in a vacuum oven at 40°C for 48 h to remove any wetting agents before use. Acrylic acid (AAc) was used as a grafting monomer and purified by using a glass column filled with an inhibitor remover (Aldrich Co., Milwaukee, WI) and stored in a dark and cold place. 1,1-Dimethyl-2-picrylhydrazyl (DPPH) (Aldrich Co.) was used for the determination of peroxides produced by UV irradiation. It was used as received and stored in a dark place. Toluene (J. T. Baker, Paris, KY) was used after distillation. Riboflavin (Junsei Chemical Co., Tokyo, Japan) was used for the permeation experiment and used as received.

Determination of Peroxide Produced by UV Irradiation

The PSF membrane was irradiated by a mediumpressure mercury lamp (450W, Ace Glass Inc.) at room temperature in air for a predetermined time. Samples were prepared to an area of 8.675 cm^2 and irradiated at a distance of 5 cm below from the lamp for all samples. Peroxides produced on the surface were determined by DPPH. The DPPH $(1 \times 10^{-4} \text{ mol/L})$ solution in toluene was degassed by nitrogen blowing for 60 min. The UV-treated PSF membrane was quickly dipped into the DPPH solution at 60°C for 2 h in a shaking water bath. Using reacted solutions, a consumed amount of DPPH due to peroxides produced on the surface was measured by a UV spectrophotometer (UV-2101PC, Shimadzu) at 520 nm. A calibration curve was obtained by using a DPPH solution of a known concentration.

Preparation of Membranes

The PSF membrane (17.35 cm^2) was weighed precisely and irradiated at the same conditions as in the peroxide-determination experiments. An AAc aqueous solution, 20 wt %, was degassed by nitrogen blowing for 60 min and sampled by 20 mL in a reaction vessel. UV-treated PSF was quickly dipped into the solution at 60°C for 2 h in a shaking water bath. Grafted membranes were washed with deionized water at 70°C for 24 h and dried in a vacuum oven at 40°C for 48 h.

Characterization of AAc-grafted Membranes

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) (Nicolet Model Magna) spectroscopy was used for the analysis of unmodified PSF and PSF-g-AAc membranes at an incident angle of 45°. An X-ray photoelectron spectroscope (PHI5700 ESCA System) equipped with a MgK α X-ray source (1253.6 eV) was used to understand the surface composition of the unmodified PSF and PSF-g-AAc membranes. With a view to observing membrane pore sizes and roughness parameters, a noncontact mode of atomic force microscopy (AFM, Nanoscope III, Digital Instrument Inc.) in air was used to obtain images of the membrane surface topology. Differences in the membrane surface morphology can be expressed in terms of various roughness parameters such as the root mean square (rms) of Z values, the mean roughness, the maximum height, and the 10point roughness. Among these methods, the rms

roughness parameter is used. Here, the rms of Z is the standard deviation of the Z values between the reference markers and is calculated as shown:

$$m rms = \sqrt{rac{(Z_i - Z_{
m ave})^2}{N}}$$

where Z_i is the current Z value; Z_{ave} , the average of the Z values between the reference markers; and N, the number of points between the reference markers.

Riboflavin Permeation Through PSF-g-AAc Membranes

A riboflavin permeation experiment was done using a two-chamber diffusion cell at 37°C. Virgin PSF and PSF-g-AAc membranes with an effective permeation area of 2.82 cm² were used. The concentration of the aqueous riboflavin solution was 40.4 ppm and the solution was prepared by dissolving riboflavin in deionized water at 50°C. One side of the two-chamber cell was filled with the riboflavin solution and the other side with a solution of known pH. The solutions of both chambers were stirred to prevent any concentration polarization. The volume of each solution was 27 mL. The concentration of the permeated riboflavin was calculated with a UV spectrophotometer at 445 nm. A calibration curve was obtained by using a riboflavin solution of a known concentration.

RESULTS AND DISCUSSION

It is known that PSF and poly(ether sulfone) show strong absorption peaks in the wavelength range between 250 and 300 nm.²⁹ During UV irradiation, chain scission, crosslinking, and extensive yellowing occur. UV irradiation in a vacuum or in air yields several degraded products such as gaseous products, oligomeric or polymeric sulfonic acids, and polymeric peroxides.

Kuroda et al.³⁰ reported the tendency of chain scission and crosslinking of poly(ether sulfone) films below and above the glass transition temperature (T_g). Chain scission and crosslinking occur simultaneously in all ranges of experimental temperatures. Crosslinking is dominant at above 170°C, while chain scission is more important at room temperature. Yamashita et al.³¹ reported on the photodegradation of poly(ether sulfone) and PSF in the presence and absence of oxygen over the temperature range from room



Figure 1 Effect of radical density as a function of UV-irradiation time as determined by the DPPH method.

temperature to 225°C and investigated the quantum yields for crosslinking and chain scission by GPC measurements. They showed similar results on the temperature effect of chain scission and crosslinking from the degradation of poly(ether sulfone). However, in the case of PSF, chain scission occurs even at higher temperature. Yamagishi et al.^{5,24} showed that phenoxyphenyl sulfone groups were responsible for the photoreactivity of PSF or poly(ether sulfone), and vinyl monomers were introduced on membranes without a photoinitiator. The modified membranes exhibited the reduction of protein adsorption and lowered membrane fouling.

The grafting of an acrylic monomer on the UVirradiated polymer surface is due to the peroxides, which are thermally degraded at about 60°C and make free radicals. These free radicals initiate the polymerization reaction. Two types of free radicals are produced at the time of thermal degradation: One is a macroradical attached and remaining on the polymer surface, and the other one is a detached one from the surface. These free radicals react with those of DPPH, resulting in a decrease in the UV absorbance of DPPH with an increase of the radical concentration. We can quantify the concentration of radicals by observing the changes in UV absorbance. Radicals are generated from peroxides produced from the PSF membrane.

Figure 1 shows the radical density of the UVirradiated PSF membrane with varying irradiation times. The radical density increased with increasing irradiation time of up to 150 s, and further irradiation slightly decreased the radical

Sample ^a	Irradiation Time (s)	Amount of Grafting $(\mu g/cm^2)$
PSF		
UA1	10	53
UA2	30	57
UA3	90	62
UA4	120	71
UA5	150	104
UA6	180	98

Table IEffect of UV Irradiation Time on theAmount of Grafting of Surface-ModifiedPSF Membranes

UV-Irradiation Technique			
	Atomic (%)		

 O_{1S}

3.92

4.18

4.00

6.28

5.43

5.08

 S_{2P}

5.37

5.01

4.11

5.60

4.37

3.85

 O_{1S}/S_{2P}

0.73

0.83

0.97

1.08

1.24

1.32

Table II XPS Surface Analysis of Surface-

 C_{1S}

90.70

90.81

91.69

87.93

90.20

91.08

Sample

PSF

UA1

UA2

UA3

UA4

UA5

^a A 20 wt % aqueous solution of AAc was used.

density. This indicates that the produced peroxides are partially converted into inactive species, which cannot generate radicals.

Table I summarizes the amount of PAAc grafted onto the surface of the PSF membrane. The graft amount of PAAc increased with irradiation time of up to 150 s, exhibiting the same tendency as did the result from the radical density data. When we further irradiated the PSF samples, the graft amount and radical density of the modified PSF membrane decreased slightly. This means that the long irradiation time does not always provide a merit in the amount of PAAc grafted onto the PSF membranes. Characterization and permeation experiments were done for grafted membranes irradiated up to 150 s.

Figure 2 illustrates the ATR-FTIR spectra of



Figure 2 ATR–FTIR spectra of (a) PSF, (b) UA1, (c) UA3, and (d) UA5 membrane.

PSF and PSF-g-AAc membranes. For graft mem-
branes, a small but new C=O absorption peak
appeared at 1726 cm^{-1} , indicating the grafting of
PAAc onto the PSF UF membrane. This was ob-
viously due to a limited sensitivity of the method.
However, each membrane type could be still iden-
tified whether AAc was grafted onto the PSF
membranes or not.

To investigate the chemical composition of the membrane surface, XPS analysis of the PSF and PSF-g-AAc membranes were performed and is summarized in Table II. The atomic concentration of S_{2P} for unmodified PSF membrane is 5.37% and can be used as a reference assuming that it does not change after UV irradiation. The atomic concentration of grafted membranes, the ratio of O_{1S} to S_{2P} , gradually increases upon prolonging the UV irradiation time up to 150 s (UA5). This clearly indicates that the atomic concentration of O_{1S} in the surface region increases as AAc is grafted further.

An inert gas ion beam was used to ablate the sample surface, and the chemical composition of the new surface was determined by XPS surface analysis. XPS ion-sputter depth profiling is a valuable means for determining the thickness of the graft layer. Typical depth profiles obtained for samples are shown in Figure 3(a,b). One cycle takes about 10 min and the rate of ablation was 10 Å/min. They showed that the intensity of the C_{1S} , O_{1S} , and S_{2P} peaks changed with the depth. The O_{1S} peak intensity gradually decreased as the grafted PAAc surface was ablated with an argon gas ion beam. Note that the ratio of O_{1S} to S_{2P} in UA1 and UA3 was very close to the ratio of O_{1S} to S_{2P} in the unmodified PSF membrane. The effective thickness of the graft layer was calculated and the thickness of the PAAc grafted onto the PSF membrane surface in UA1 and UA3 was



Binding Energy, eV

Figure 3 XPS depth profile of surface-modified PSF: (a) UA1; (b) UA3 membrane. An argon gas ion beam was used to ablate the surface.

determined to be around 80-100 nm. Moreover, we can also determine the thickness of the graft layer from the relation $l = m/\rho A$, where l is the thickness of the graft layer; m, the amount of grafting; ρ , the density of the graft PAAc; and A, the unit area. Here, the PAAc density is approximately 1. The thickness of the UA1 and UA3 samples can be calculated to be approximately 530-620 nm, indicating a large discrepancy between the thickness values determined by the two methods. The thickness determined by the XPS method is much smaller than that by the amount of grafting. This result suggested that the PAAc was grafted not only on the surface of the PSF membrane but also inside the PSF membrane. In this case, an aqueous AAc solution was expected to diffuse into the PSF membrane and the vinyl

monomer was grafted not only at the surface but also within the membrane. Since it was reasonable to assume some interactions between water and the PSF membrane, our postulation on the grafting from the bulk of the membrane could be understandable. Tazuke³² reported that acrylamide was grafted more from the bulk of hydrophobic-oriented polypropylene membranes than on the surface of the membranes when the solvent had strong interactions with the base polymer.

PSF degrades by absorbing UV light in the wavelength ranging from 250–300 nm. The properties of the film change according to the irradiation time and the thickness of the sample. Under UV irradiation, chain scission and crosslinking occur, causing the samples to become brittle with a decrease in tensile strength and elongation at

Sample	Tensile Strength (kgf/cm ²)	Elongation (%)	
PSF	42.8	20.5	
UA1	41.5	30.3	
UA2	39.4	21.0	
UA3	39.8	16.1	
UA4	36.4	17.2	
UA5	35.6	12.0	

Table IIIMechanical Properties of Surface-Modified PSF Membranes

 a These values are the mean of at least five specimens and the deviation from the mean is within $\pm 10\%.$

break (see Table III). However, the change in tensile strength was relatively small and the membranes did not become brittle because the UV irradiation time was short. Therefore, the grafted PSF membranes could still be used as UF membranes. Otherwise, permeation experiments could not proceed.

AFM images of the surface of PSF and PSF-g-AAc membranes are shown in Figure 4. Any topographical changes were not observed between the unmodified membrane and the modified membranes. However, there is a definite variation in the surface roughness of the PSF membranes grafted with AAc by the UV-irradiation technique (see Table IV). The grafted PSF membranes were found to be rougher than was the untreated PSF membrane. However, the roughness of the polymer substrate increased with UV irradiation time of up to 30 s and then decreased thereafter. Reduction in the surface roughness of the membranes with an increasing amount of grafting could be understood on the basis of the filling of the valleys by grafting PAAc chains.

The riboflavin permeability through the original PSF membrane and the PSF-g-AAc mem-



Figure 4 AFM images of surface of (a) as-received PSF, (b) UA2, (c) UA3, and (d) UA5 membranes.

Sample	Area Analyzed (µm)	RMS Roughness ^a (nm)
PSF	5 imes 5	136
UA1	2.5 imes2.5	238
UA2	5 imes 5	222
UA3	5 imes 5	187
UA4	5 imes 5	173
UA5	5 imes 5	173

Table IVSurface Roughness of PSF andPSF-g-AAc Membranes

branes is shown in Figure 5, measured at different pH values. Note that the virgin PSF membrane exhibits no response to the change in pH, whereas the PSF-g-AAc membranes are responsive to the pH change. A remarkable decline in permeability is noted at the pH range of 4–5. From these data, it is clear that the grafted PAAc is responsible for the permeability decline in riboflavin permeation.

It has been reported that the pK_a value of poly(acrylic acid) (PAAc) is 4.8.²⁵ Above pH 4.8, the carboxylic acid groups of the grafted PAAc chains are dissociated into carboxylate ions and have an extended conformation because of the electrostatic repulsion forces between the chains. Extended chains block the pores of the PSF membrane, causing a decrease in the permeability. At below pH 4.8, carboxylic acid groups do not dissociate: The grafted PAAc chains will shrink and be precipitated on the surface. Thus, the pores become open and permeability sharply increases. These conformational changes are obviously due to both intra- and intermolecular interactions between grafted PAAc chains.

As the amount of grafted PAAc increases further, pore blocking overwhelms the conformational changes of the grafted chains due to the interactions of the polymer chains, causing only small changes in the permeability of riboflavin in response to the pH. Therefore, for the UA5 sample, the extension and shrinkage of the grafted chains are hindered, and the extent of the change in the permeability is reduced, meaning that the permeability depends on the amount of grafting and the environmental pH.

CONCLUSIONS

Through this study we modified commercial PSF membranes and investigated the morphology,

mechanical properties, and permeability of the riboflavin of unmodified and modified PSF membranes. pH-responsive membranes were prepared by grafting PAAc onto porous PSF membranes as evidenced by ATR-FTIR and XPS analysis of the modified PSF membranes. The grafting was successfully conducted by a UV-preirradiation method without using a photoinitiator. Upon UV irradiation, the PSF membrane acted as a photoinitiator because of the presence of peroxides at the membrane surface. The modified membranes retain their mechanical properties so that they could still be used as UF membranes. Through the XPS depth profiles analysis, the effective thickness of the grafted PAAc layer in UA1 and UA3 was about 80-100 nm. AFM images of the surface of the PSF membranes illustrated a change in the surface topologies of the membranes, indicating that grafted PSF membranes were found to be rougher than were virgin PSF membrane. However, the roughness of the polymer substrate increased with UV irradiation time of up to 30 s and then decreased thereafter. Reduction in the surface roughness of the membranes with an increasing amount of grafting could be understood on the basis of the filling of the valleys by grafting PAAc chains. The changes in the riboflavin permeation through the PSF-g-AAc membrane are noted particularly at pH 4 and 5 due to the electrostatic repulsion forces



Figure 5 Effect of pH on the riboflavin permeation through (a) (\bigcirc) PSF, (b) (\triangle) UA1, (c) (\square) UA2, (d) (\bigcirc) UA3, (e) (\blacktriangle) UA4, and (f) (\blacksquare) UA5 membranes.

between the carboxylate ions. At above pH 4.8, a pK_a of PAAc, extended chain conformation of the carboxylic acid in the PSF-g-AAc membrane blocks the pore, causing a decrease in the permeability of the riboflavin and vice versa. Also, changes in the permeability of modified membranes depended on the amount of grafting, meaning that further grafting of PAAc on the PSF membrane surface does not guarantee the pH sensitivity of the riboflavin permeation. An optimum grafting amount in terms of pH sensitivity was found to be 53 μ g/cm² in the UA1 membrane that was irradiated for 10 s. This study envisioned the possibility of controlling the permeability of the membrane by varying the pH of the external solution. These pH-responsive membranes will be useful for sensing and modulating external chemical signals and also for drug-delivery application, because they change their chain conformation according to electrostatic interactions between charged groups. Further studies are ongoing to provide temperature sensitivity as well as pH sensitivity to the commercial PSF or polypropylene membranes, and the results will be reported soon.

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