Comparison of Two Approaches to Grafting Hydrophilic Polymer Chains onto Polysulfone Films

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ABSTRACT: To reduce the surface protein adsorption of polysulfone (PSf) film, we improved the hydrophilicity of this film by photochemical grafting of methoxypoly (ethylene glycol) (MPEG) derivatives on its surface. Grafting was achieved with both the simultaneous method and the sequential method. Surface analysis of the grafted film by X-ray photoelectron spectroscopy (XPS) revealed that the PEG chains had successfully grafted onto the surface of the film. The grafting efficiencies by simultaneous and sequential methods were 20.8% and 10.2%, respectively. With an atomic force microscope (AFM), the surface topography of PEG-grafted films by these two methods was compared. Static water contact angle measurement indicated that the surface hydrophilicity of the film had been improved. Protein adsorption measurement showed that the surface protein adsorption of the modified film was significantly reduced compared with that of the unmodified PSf film. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3818–3826, 2007

Key words: hydrophilic polymers; photochemistry; irradiation; modification; films

INTRODUCTION

Polysulfone (PSf), a popular engineering material, is widely used in many fields due to its good mechanical, thermal, and chemical stability. The hydrophobicity of this material, however, causes serious plasma protein adsorption, resulting not only in the activation of different defense systems in blood, e.g., coagulation, complement, and fibrinolysis, but also in the adhesion and activation of blood cells. Therefore, its application as a biomaterial has been restricted to some extent.

There are many reports on the modification of the surface of PSf with other monomers or polymers, including chlorosulfonic acid, propane sulfone, DNA, phospholipid, poly(vinyl pyrrolidone) (PVP), and poly(ethylene glycol) (PEG).[1–6] Among these materials, one of the most effective candidates for providing protein-resistant or blood-compatible surfaces appears to be PEG. PEG is well known for its extraordinary ability to resist protein adsorption, and this property is believed to have resulted from its hydrophilicity, large excluded volume, and unique coordination with surrounding water molecules in an aqueous medium. Thus, modification with PEG was considered one of the most important and effective strategies to improve the surface property of PSf.

Modification of PSf material with PEG could be carried out by many methods, such as coating, blending, and grafting techniques.[6–16] Among these methods, the photochemical surface modification technique is attractive and has several advantages. Mild reaction conditions and moderate temperature may be applied; high selectivity is possible by choosing the reactive groups or monomers and respective excitation wavelength; it can be easily incorporated into the end stages of a manufacturing process. PSf has intrinsic photoreactivity, and the ultraviolet (UV)-induced modification of the surface of PSf with PEG has been reported in the literature.[10,13,14,16] In general, there are mainly two approaches for the immobilization of polymer chains onto the surfaces of materials by UV-irradiation. One is direct grafting of polymer chains containing photoreactive groups with UV-irradiation; the other approach is grafting the photoinitiator on the substrate by means of UV-irradiation first, followed by covalent coupling of the target polymer chains. In the literature, almost all were carried out with the former approach, the latter is not involved.

In this work, to reduce the surface protein adsorption of PSf film, we attempted to graft PEG chains onto the surface of the PSf film by means of two methods: the simultaneous method and the sequential method. By the simultaneous method, PEG chains were directly grafted onto the PSf film surface with UV-irradiation; by the latter, 4-azidobenzoic acid (AzBA) was grafted onto the PSf film surface with UV-irradiation first, and then reacted with

ω-amino-monomethoxypoly(ethylene glycol) (MPEG–NH$_2$). Modified films were characterized by contact angle, protein adsorption, X-ray photoelectron spectroscopy (XPS), or atomic force microscopy (AFM). Some surface properties between the two modified PSf films were compared, including the content of the surface elements, the grafting efficiency and surface topography.

MATERIALS AND METHODS

Materials

Polysulfone (PSf, Ultrason® S 2010, BASF Aktiengesellschaft, Ludwigshafen, Germany) was used to prepare the films. 1,3-(3-dimethylaminopropyl)ethylcarbodiimide (EDC) was supplied by ACROS Organics (Springfield, NJ). Bovine serum albumin (BSA) was purchased from the Beohringer Mannheim (Mannheim, Germany). 4-Azidobenzoic acid (AzBA), 4-azidobenzoylimino-monomethoxypoly(ethylene glycol) (ABIMPEG, Mn ∼4448 g/mol) and ω-amino-monomethoxypoly(ethylene glycol) (MPEG–NH$_2$) were prepared and characterized.[17] The chemical structures of the MPEG–NH$_2$ and the ABIMPEG are shown in Figure 1. In the synthesis of the MPEG–NH$_2$ and the ABIMPEG, a commercial MPEG reagent (polyethylene glycol 5000 monomethyl ether; Fluka, Buchs, Switzerland) was used.

Film preparation

The PSf film was prepared by hot embossing. The polymer was dried in an oven at 130°C for 3 h, to remove absorbed water vapor before use. The molding process was carried out in an XLB-D400402 Plate vulcanizer machine (Qingdao Third Rubber Machinery Factory, Qingdao, China). The prepared film was cut into pieces ∼1.5 cm long and 1.5 cm wide for immobilization of PEG chains. Each film was ∼2 mm thick.

Immobilization of PEG chains on PSf film

Grafting PEG chains on PSf film by simultaneous method

The PSf film was first immersed in aqueous ABIMPEG solutions of different concentrations for several hours, then incubated in a vacuum oven at 40°C with and without nitrogen atmosphere protection, respectively. All the above operations were carried out in the dark. The following irradiation was carried out in two ways. One is direct irradiation, whereas the other is irradiation after wetting the surface of the film with redistilled water. Both methods were carried out at 40°C for 5 min (power = 125 W, λ$_{max}$ = 365 nm). To rinse the irradiated surface of the film thoroughly, the UV-treated film was immersed in
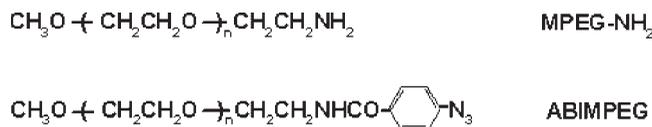

Figure 1 Schematic structures of MPEG–NH$_2$ and ABIMPEG.

redistilled water, shaken for 24 h, and then ultrawashed in deionized water 3 times (5 min each). Finally, the cleaned film was dried at 40°C and was kept in a desiccator before use.

Grafting PEG chains on PSf film by sequential method

There are two steps for grafting PEG chains on PSf film by the sequential method:

1. *Grafting photoinitiator on PSf film with UV-irradiation*: The PSf film was immersed in ethanol solution of AzBA and aqueous sodium hydroxyl solution of AzBA for several hours, respectively, and then incubated in a vacuum oven at 40°C; irradiated at 40°C for 5 min after wetting with ethanol, and distilled water respectively. The film treated in aqueous sodium hydroxyl solution of AzBA was immersed in a 0.4 mol/L aqueous HCl solution, shaken for 24 h, and then washed in redistilled water 3 times (1 h each). Both films were then treated by the above-mentioned cleaning process.
2. *Immobilization of PEG chains*: The prepared film was immersed in a solution of EDC (2.0 mg/mL in water, adjusted to pH = 4.5–4.7) and kept there on a shaker at 0 ∼ 4°C for 2 h. It was added to MPEG–NH$_2$ and reacted at 0–4°C for 4 h, then at room temperature for 24 h, before ultra-rinsing with deionized water for 3 times (5 min each). Finally, the film was dried at 40°C and kept in a desiccator before use.

X-ray photoelectron spectroscopy measurement

XPS measurements were used to determine the chemical composition of MPEG and the surface of unmodified and modified PSf films. The measurements were performed on a Kratos XSAM-800 spectrometer with an Mg Kα X-ray source (1253.6-eV photons). The data were recorded and processed using XPS PEAK 1.0 software; the binding energy of various core-level spectra (Cls) in different chemical environments is shown in Table I.

AFM measurement

AFM measurements were used to investigate the surface topography of the films, performed on a SPI

TABLE I
Binding Energy of Various C1s in Different Chemical Environment

C1s	C=C	C—C	C—S	C—O (C—N)	—COO— (—CONH—)
Binding energy (eV)	284.7	284.8	285.31 ± 0.12	286.53 ± 0.25	288.42 ± 0.15

3800 N/SPA-400 system (Seiko Instruments, Tokyo, Japan) with a silicon nitride tip, operated at room temperature in air. The topographic and phase data were recorded simultaneously. The data collected for the height image were manipulated to generate a three-dimensional (3D) view of the sample. The 3D visualization aids in interpreting the height and phase images. To compare the surface topography of the two modified films, the imaging parameters were kept constant for the samples. These imaging conditions correspond to moderate tapping according to Magonov et al.[18] Under these moderate force tapping conditions, phase data are sensitive to local stiffness differences of domains in the top several nanometers from the uppermost surface.[19]

Contact angle measurements

Measurement of the contact angle between water and a material surface is one of the easiest ways to characterize the hydrophilicity of the material. The surfaces of the unmodified and two modified PSf films were characterized by static water contact angle measurement with an Erma static contact angle instrument (Erma Optical Works, Tokyo, Japan) on 3 μL of distilled water at 25°C. The results reported were the mean values of 15 replicates.

Protein adsorption

The adsorption experiments were carried out with BSA, using Tris-HCl buffered solution (pH = 7.2). The modified films were immersed in Tris-HCl buffer solution for 16 h before 200 μL of buffer solution containing 1 mg/mL BSA were placed on the surface of the films and left for 16 h at 15°C in a dark place, then gently rinsed with buffer solution. The rinsed solution was collected. The protein concentration of the solution was determined by the Coomassie Brilliant Blue method with a Vis-UV/visible spectrophotometer (Beijing Purkinje General Instrument, Beijing, China) at 595 nm.[20] According to the absorption value and standard colorimetric absorption curve of BSA, the amount of protein adsorption can be calculated.

RESULTS AND DISCUSSION

Covalent immobilization of PEG chains onto PSf films

Upon UV-irradiation, aryl azide groups first undergo irreversible photolysis generating nitrogen gas and a highly reactive nitrene intermediate and are then inserted into C—H bonds.[10] In our work, a commercial MPEG reagent was chosen to preparation of ABIMPEG and MPEG–NH$_2$. However, it was reported that the reagent contained considerable amounts of bifunctional PEG.[21] Hence, the synthesized ABIMPEG consisted of a mixture of mono- and bi(aryl azide) PEGs and PEG. Accordingly, the synthesized MPEG–NH$_2$ contained amounts of NH$_2$–PEG–NH$_2$.

In the case of grafting PEG chains onto the PSf film by the simultaneous method, the highly reactive nitrene intermediate may undergo the following five types of reactions: (1) insertion into the PSf chains; (2) insertion into the PEG chains; (3) crosslinking reaction between the PSf chains; (4) crosslinking reaction between the PEG chains; and (5) crosslinking reaction between the PEG and the PSf chains. Among these reactions, (1) and (2) belong to those of monofunctional PEG derivatives, and the others are probably caused by the presence of bi(arylazido)-functionalized PEGs. Reactions (1), (4), and (5) will result in the covalent immobilization or grafting of PEG chains onto the PSf substrate.

Compared with the simultaneous method, the nitrene intermediate produced in the sequential method inserted only into the PSf chains, and no crosslinking reaction occurred. The following covalent immobilizing PEG chains onto the PSf substrate may experience two reactions: (1) the condensation reaction of a chain-terminal amine group of MPEG–NH$_2$ with a carboxyl group of AzBA immobilized on the PSf film surface; and (2) the reaction of both amine groups of the NH$_2$–PEG–NH$_2$ with the carboxyl groups. For illustrative purposes, the surface-grafted and crosslinked PEG chains are depicted in the ''standing up'' conformation on the PSf surface in Figure 2, although this microstructure probably exists only in an aqueous environment.

XPS analysis

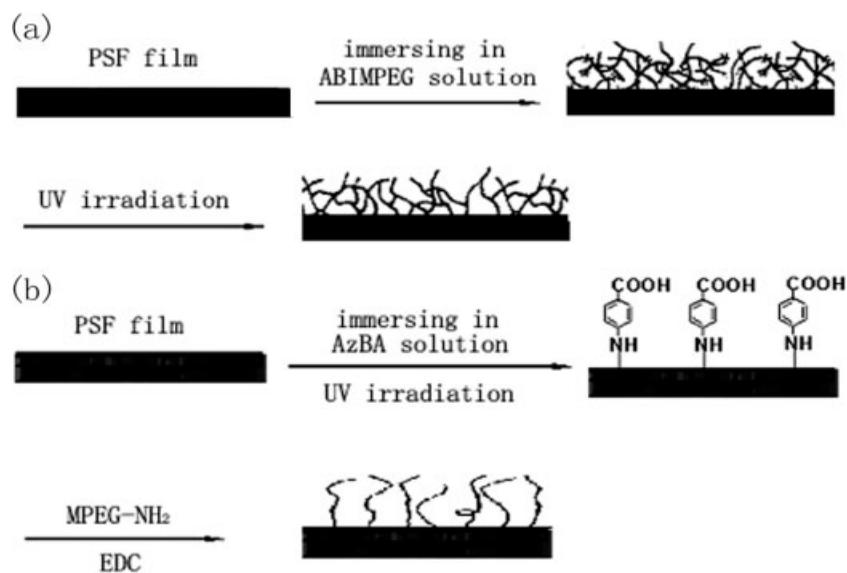Figure 3(a) shows the C1s of the surface of the unmodified PSf film. The three peak components at

Figure 2 Schematic description of graft PEG chains onto PSF film by (a) simultaneous method and (b) sequential method.
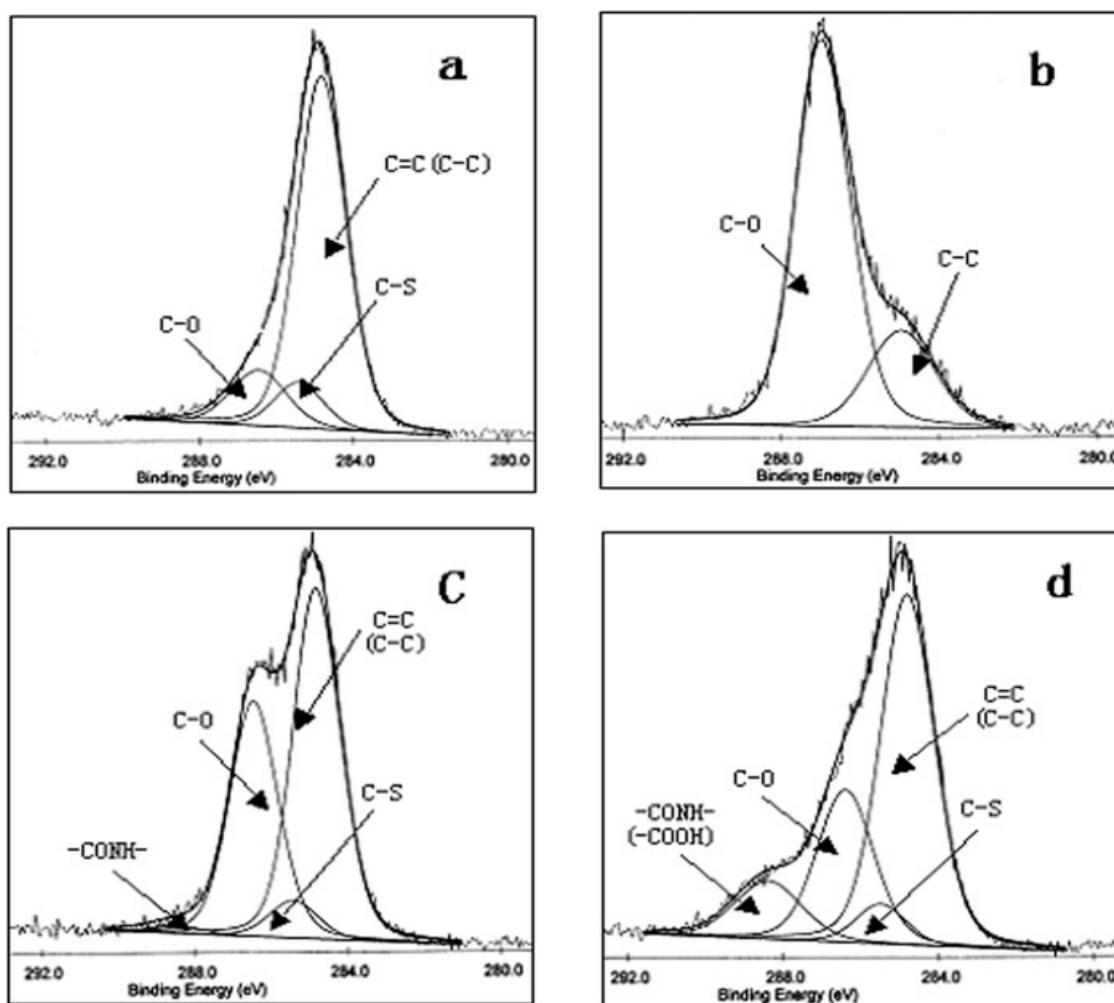

Figure 3 C1s curve fittings of (a) unmodified PSF film; (b) MPEG; (c) modified PSF film by simultaneous method; (d) modified PSF film by sequential method.

TABLE II
XPS Element Contents of MPEG, Unmodified PSf Film, and Modified PSf Films

Sample	Element, mole fraction (%)				O/C
	C_{1S}	O_{1S}	S_{2P}	N_{1S}	
PSf	80.9	17.4	1.7	—	0.22
MPEG	71.0	29.0	0	—	0.41
MPEG- PSf[a]	72.6	25.9	0.6	0.9	0.36
MPEG- PSf[b]	73.4	21.8	0.8	4.0	0.29

[a] Grafting PEG chains on PSf film by simultaneous method.
[b] Grafting PEG chains on PSf film by sequential method.

the binding energies of ~284.7, 285.3, and 286.5 eV are attributed to the C=C, C—S, and C—O species, respectively. The Cls of the MPEG [Fig. 3(b)] consists of two peak components at the binding energies of ~286.5 eV and 284.8 eV, attributable to the C—O and C—C species, respectively. Figure 3(c,d) shows the Cls of the two modified PSf film surfaces. Compared with Figure 3(a), there is a peak of —CONH in the two modified surfaces. It can been seen in Tables II and III, after PEG grafting, in both the simultaneous method and the sequential method, that the C=C (C—C) peak component undergoes a distinct decrease (from 76% to 55.2%, and 57.0%, respectively). Note that the difference between the binding energies of C=C species and C—C species is only 0.1 eV; thus, it is difficult to distinguish them. On the contrary, the C—O peak component has increased clearly (from 13.7% to 37.6%, and 25.7%, respectively), suggesting that a large number of C—O bonds have been introduced. The presence of the nitrogen element indicates the formation of —CONH groups on the film surface.

The above results confirm that the PEG chains had been successfully immobilized on the PSf film surface. The difference between the two methods was that the content of nitrogen element in the sequential method was much higher than in the other simultaneous method. This can be understood as the fact that carboxyl groups that had immobilized on the PSf film surface hadn't reacted with MPEG–NH$_2$ thoroughly.

It is well known that the grafting efficiency is one of the most important factors with which to evaluate the grafting effect. In general, the grafting efficiency is calculated by gravimetric change of material before and after grafted.[6,13,22] However, for grafting hydrophilic polymer, the problem is that hydrophilic polymer will inevitably absorb water vapor, resulting in doubtful results. According to the results of XPS analysis in this study, it can be seen that a great number of elements of carbon and oxygen appeared on the surface of the PSf film. Therefore, in order to reduce error, the data of elements of carbon and oxygen in Table II was used to calculate the grafting efficiency. The repeated structural units of PSf, AzBA, and MPEG–NH$_2$ were $C_{27}H_{22}O_4S_1$, $C_7H_5O_2N_3$, and $C_{203}H_{408}O_{101}$ ($M_n = 4448$), respectively. The number of PSf repeated structural units per unit area on the surface of the PSf film are assumed m. For grafting MPEG on the PSf film by the simultaneous method, the grafting efficiency can be calculated from the following equation:

$$\frac{O}{C} = \frac{101mx + mx + 4m}{203mx + 7mx + 27m} = 0.36,$$

where x is the grafting efficiency of the modified film by simultaneous method (the number of MPEG repeated structural units per PSf repeated structural unit); the result was 0.208. The grafting efficiency by the sequential method can be calculated by the same method; the result was 0.102. The grafting efficiency

TABLE III
XPS C1s Curve Fittings of MPEG, Unmodified PSf Film, and Modified PSf Films

Sample	C_{1s} Peak, mol fraction (%)				
	C=C	C—C	C—S	C—O (C—N)	—CONH— (—COO—)
MPEG	—	23.1	—	76.9	—
PSf	76.6		9.7	13.7	—
PSf-MPEG[a]	55.2		5.9	37.6	1.3
PSf-MPEG[b]	57.0		5.8	25.7	11.5

[a] Grafting PEG chains on PSf film by simultaneous method.
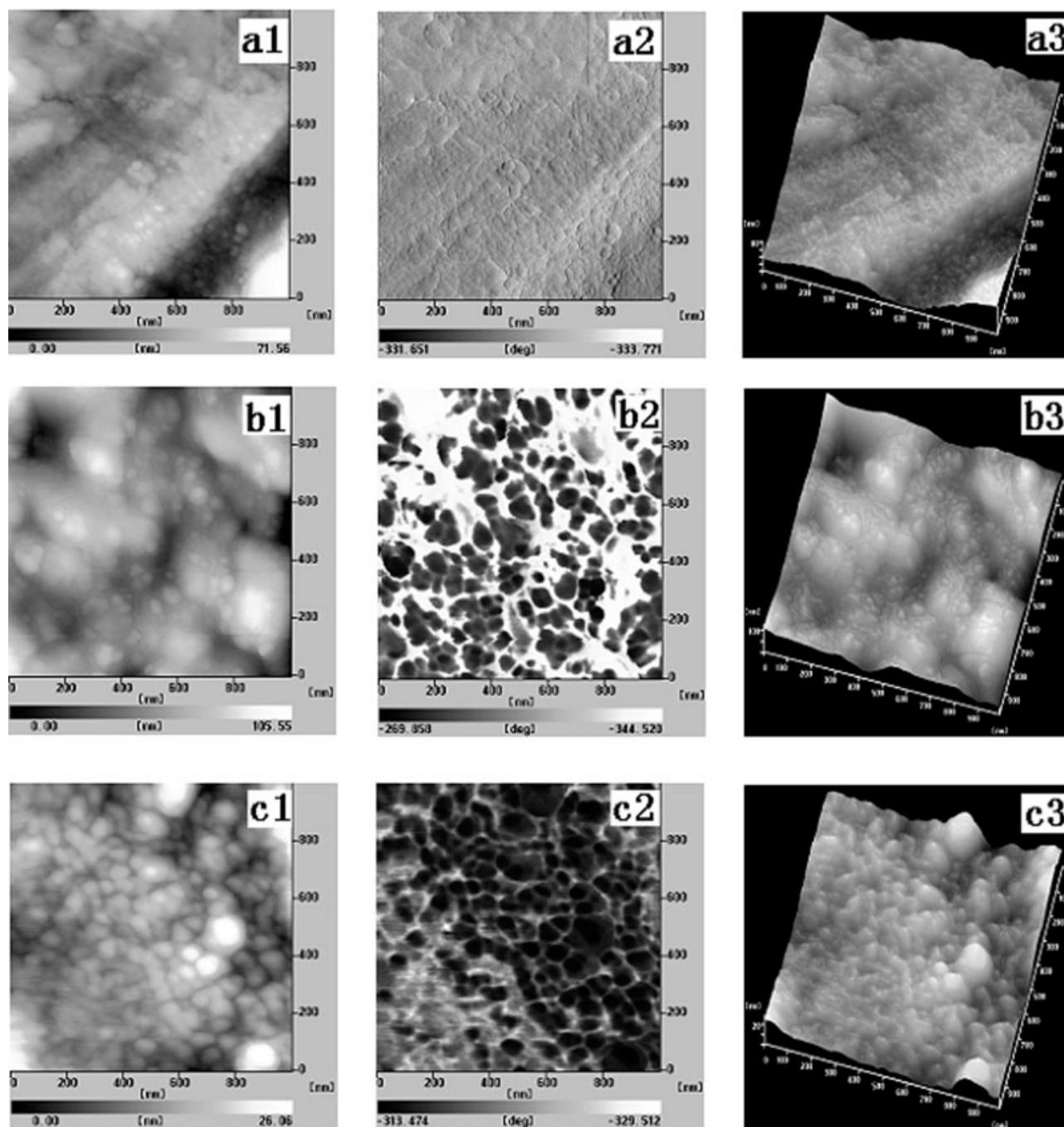[b] Grafting PEG chains on PSf film by sequential method.

Figure 4 AFM images of unmodified and modified PSF films. Unmodified PSF film: (a1) height image; (a2) phase image; (a3) 3D view. Modified PSF film by simultaneous method: (b1) height image; (b2) phase image; (b3) 3D view. Modified PSF film by sequential method: (c1) height image; (c2) phase image; (c3) 3D view.

in the simultaneous method was found to be double that in the sequential method. The explanation for this phenomenon was that the simultaneous method has more grafting sites, as discussed above. In addition, PEG chains grafting onto the surface of PSf film in the sequential method would exhibit two stages.[23,24] The first stage would be one of fast grafting, in which the rate would be controlled by center-of-mass diffusion of the polymer chains through the solvent to the film surface. The second stage would be one of slow grafting, in which the rate would be controlled by diffusion of free chains through the already tethered layer to reach the surface. Grafting in the second stage would proceed at a progressively slower and slower rate because of the progressive increase in the energy barrier with the increased number of tethered chains per unit area of substrate. This slow grafting would be expected to continue to
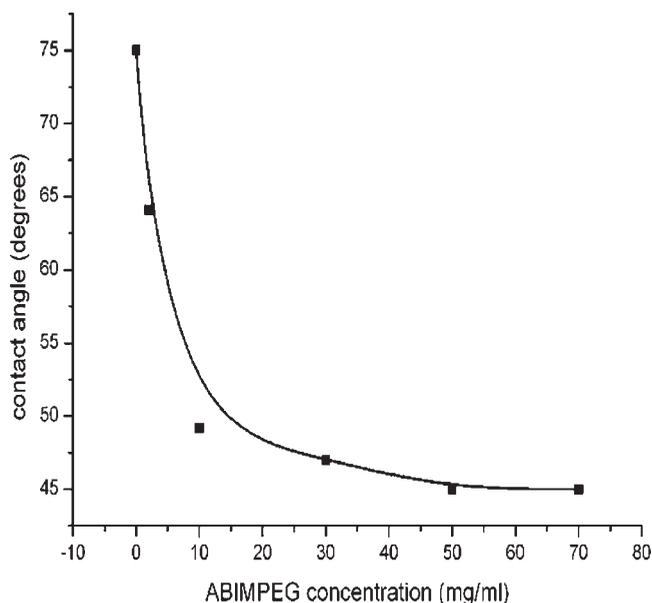
Figure 5 Effect of ABIMPEG concentration on the contact angle. Incubation in nitrogen atmosphere for 15 h. UV-irradiation in wet state for 1 h.

Figure 6 Effect of incubation time on the contact angle; ABIMPEG concentration: 33 mg/mL. (a) incubation in atmosphere; (b) incubation in nitrogen atmosphere.

saturation; i.e., a natural stopping point at which the energy benefit of chemical reaction of chain ends with the surface would be offset by the entropy cost of chain stretching.

AFM analysis

Figure 4 shows the surface topography of the unmodified and the two modified films. Images of every film surface consist of height image, phase image, and 3D view. From the phase images, it can be seen that the surface topography of both modified films displayed an obvious two-phase structures; i.e., the discontinuous dark phase appeared in the bright continuous phase. Whereas the phase image of the unmodified film was essentially featureless, indicating the surface was probably homogeneous without any distinct phase separation. Although the phase images exhibited a higher contrast than height images, it can be seen that the dark region in the phase images corresponded to bright regions in the height images, which was recognized by comparing the contrast of the identical region. That is to say, the dark phase located on the uppermost surface. In contrast, it is clear that the bright phase corresponds to the hard region and the dark phase belongs to soft region, since the region with the higher modulus appeared to be brighter in the AFM operating conditions. Further, PSf is stiffer than PEG at room temperature. Therefore, we tentatively assign the PSf to the bright phase and the PEG to dark phase. These findings are consistent with the XPS measurement, which showed that
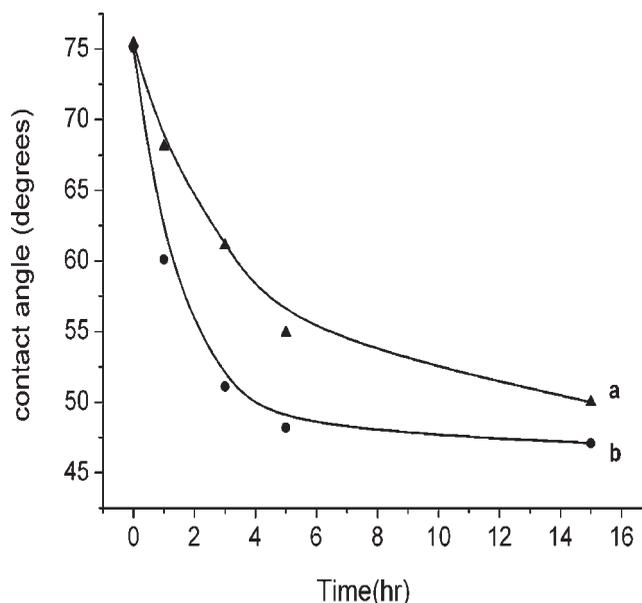
the PEG chains had been successfully immobilized on the surface of the PSf film.

Comparison of the two modified films showed that PEG coverage in the sequential method was apparently bigger than that of in the simultaneous method. This finding was in disagreement with the XPS measurement, which indicated that the simultaneous method had higher grafting efficiency. We
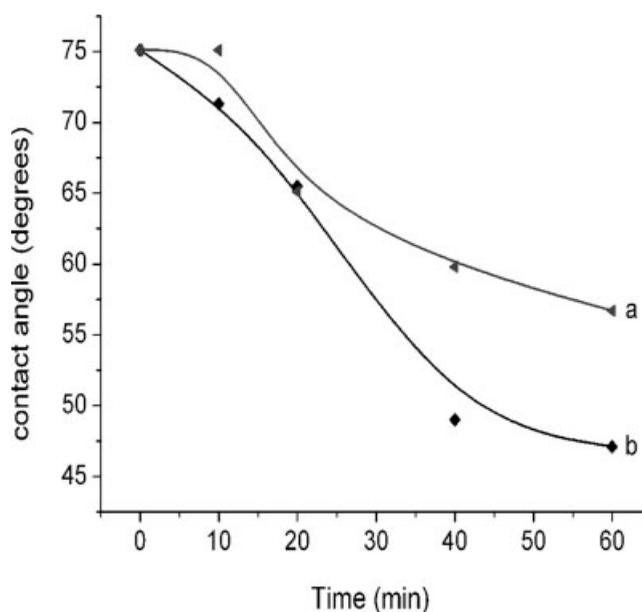

Figure 7 Effect of UV-radiation time on the contact angle. ABIMPEG concentration: 33 mg/mL; incubation time: 15 h; incubation in nitrogen atmosphere. (a) radiation in dry state; (b) radiation in wet state.

Films	PSf	AzBA–PSf (ethanol solution)	AzBA–PSf (distilled water)	MPEG–PSf
Contact angles (Degrees)	75.1 ± 2.9	73.1 ± 2.6	63.2 ± 3.2	52.5 ± 2.8

deduced that this was due to a thicker PEG layer grafted onto the surface of the film in the simultaneous method, which can be demonstrated in part by the relative height contrast in the height images. This phenomenon is intrinsic to the methods of the grafting PEG chains onto the PSf film surface. For the simultaneous method, the nitrene intermediate produced by the UV-irradiation reaction can react not only with the C—H bond in the PSf film surface, but also with the adjacent C—H bond in PEG chains. Thus, it is possible that a branched PEG layer formed on the film surface.[13] Furthermore, the crosslinking reactions could play an important role in making a tight connection of PEG chains. While for the sequential method, a PEG monolayer would be obtained because the chain-terminal amine group of the PEG chain can react only with the carboxyl group of AzBA immobilized on the surface of the PSf film.

Contact angle analysis

In the simultaneous method, the effect of the ABIMPEG concentration on the static water contact angle was examined. With the increased concentration of the ABIMPEG solution used to treat the film, the contact angle for the ABIMPEG-immobilized film decreased, as shown in Figure 5. The degree of the contact angle was found to be significantly affected by the ABIMPEG concentration, and to be decreased with the increase in the ABIMPEG concentration up to 50 mg/mL. When the concentration of the ABIMPEG solution was >50 mg/mL, the decrease showed no significant difference.

The effects of the incubation and radiation time of the PSf film immersed in the ABIMPEG solution (33 mg/mL) on the static water contact angle showed the same tendency as the effect of the ABIMPEG concentration. The contact angle decreased rapidly at the beginning, but there was no obvious change later. Furthermore, incubation under nitrogen atmosphere produced better effects (Fig. 6), which can be understood because the nitrogen atmosphere environment was advantageous for the adsorption of ABIMPEG on the surface of the PSf film. At the same time, the radiation in wet state also showed better effects (Fig. 7). Compared with the radiation in dry state, the radiation in wet state can minimize not only the destructive effects of UV-irradiation onto the film surface, but also enhance the necessary

orientation of the more hydrophobic photoreactive aryl azide groups towards the surface of the film.[10]

In the sequential method, we made two AzBA solutions (water and ethanol). The static water contact angle of the modified film surface treated with the AzBA–water solution had decreased from ~ 75° to ~ 63° (Table IV). But there was no significant change for that with another solution. It is possible that nitrene intermediate produced by the UV-irradiation reacted with ethanol immediately rather than with the film surface, so the modification was not achieved. For the film surface treated with the AzBA water solution, the static water contact angle was ~ 52° after immobilization of MPEG, indicating that the hydrophilicity of the modified film has been improved.

Protein adsorption

It is well known that the amount of protein adsorbed on the surface of a material is one of the dominant factors in evaluating blood compatibility. The amounts of BSA adsorbed on the films were determined before and after the immobilization of ABIMPEG, as shown in Figure 8. With the increase in the concentration of the ABIMPEG solution used to treat
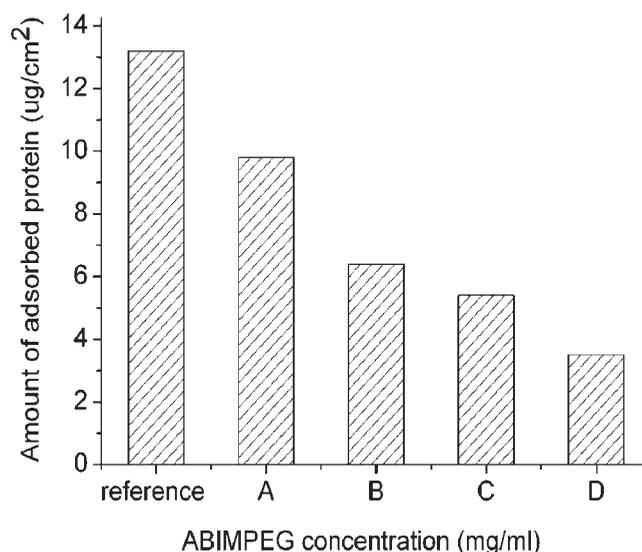
Figure 8 Amount of adsorbed protein on PSF films in dependence on ABIMPEG concentration. Reference: unmodified film. A, 2 mg/m; B, 10 mg/mL; C, 30 mg/mL; D, 50 mg/mL.

the film, the amount of BSA adsorbed on ABIMPEG-immobilized film decreased, presumably because the amount of immobilization of ABIMPEG is different. Compared with the unmodified film, the surface of the modified film adsorbed less protein, indicating an increase in hydrophilicity after immobilization of ABIMPEG. Therefore, the blood compatibility of the polymer was improved. Theoretically, BSA was not adsorbed on PEG. The adsorption phenomenon indicates that the film surface was not thoroughly covered by the grafting PEG chains, which was also observed in other experiments and was not solved completely.

CONCLUSIONS

In the current study, we prepared PEG-grafted PSf films with UV-irradiation by means of two methods. In the simultaneous method, the effect of some important factors, including ABIMPEG solution concentrations, incubation, and UV-radiation time, on the static water contact angle was investigated. The degree of static water contact angle of the PSf film-grafted PEG chains was obviously lower than that of the unmodified PSf film, suggesting that the hydrophilicity of the film surface had been improved. It was found that the PSf film-grafted PEG chains had a lower protein adsorption than that of the PSf film. This is attributed to the increased hydrophilicity of the PSf film-grafted PEG, as the hydrophilic surface is known to reduce the protein adsorption.[20] For the sequential method, the hydrophilicity of the film-grafted PEG chains was also been improved. Surface analysis of the film-grafted PEG chains by XPS and AFM showed that the two methods produced distinct differences in grafting efficiency and surface topography. This is explained by the difference between the two methods in the grafting process. Despite this, the hydrophilicity of the two surfaces of PSf films was improved, indicating that the PEG-grafted films prepared by UV-irradiation have potential for use in the biomedical field.

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