Grafting of Poly(ethylene glycol) Monoacrylate onto Polycarbonateurethane Surfaces by Ultraviolet Radiation Grafting Polymerization to Control Hydrophilicity

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ABSTRACT: In this study, we used a UV radiation grafting method to modify the surface of the biomaterial polycarbonateurethane (PCU). Hydrophilic poly(ethylene glycol) monoacrylate (PEGMA; number-average molecular weight = 526) as a macromolecular monomer was grafted onto the PCU surface by UV photopolymerization. The Fourier transform infrared and X-ray photoelectron spectroscopy results of the graft-modified PCU confirmed poly[poly(ethylene glycol) monoacrylate] block grafting onto the surface. We investigated the effects of the reaction temperature, macromolecular monomer concentration, UV irradiation time, and photoinitiator concentration on the grafting density (GD) in detail. Furthermore, we investigated the effects of GD under various process conditions on the water uptake and water contact angle. The modified materials had a high water uptake and low water contact angle, which indicated that the hydrophilicity of the PCU surface was improved significantly by the introduction of the hydrophilic poly(ethylene glycol) blocks on the surface. The anticoagulant properties of the material might also have been improved. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3717–3727, 2011

Key words: biomaterials; hydrophilic polymers; photopolymerization; polyurethanes; surface modification

INTRODUCTION

In recent years, many kinds of artificial organs and biomedical devices made of polymeric biomaterials have been developed quickly because of the development of biomedicine engineering and biomaterials. Specially, products concerning the therapy of blood recycling system diseases, such as artificial blood vessels, heart valves, and blood vessel brackets, have been widely used in clinical settings.[1–3] However, the clinical results are not very satisfactory in the long term because of the formation of thrombus; this is one of the main factors that restricts the use of these devices that directly contact streaming blood.[1] Polycarbonateurethane (PCU) has been used as a medical material in recent years; it is considered to offer relatively beneficial hemocompatibility and mechanical properties compared to other synthetic materials.[4–6] Indeed, it has been used to prepare a variety of medical devices, including blood bags, catheters, vascular grafts, and portions of artificial hearts.[7–9] However, PCUs are not completely thromboresistant, as platelet adhesion/activation can still occur when they are in contact with blood for extended periods of time.[10–12]

The hemocompatibility of biomaterials is mainly affected by the physical and chemical characteristics of the surface. A rapid and effective way to improve the hemocompatibility of biomaterials is to optimize their material surfaces but not significantly change their intrinsic mechanical properties. Photoinduced grafting polymerization from a polymeric substrate with hydrophilic monomers has attracted researchers' attention as a novel technique capable of controlling wetting behavior or improving biocompatibility over the native characteristics of polymers.[13]

Poly(ethylene glycol) (PEG) is generally known as a biocompatible material and is most often used as a hydrophilic polymer in surface modification. PEG is an uncharged polyether with the chemical formula $H—(OCH_2CH_2)_n—OH$, which is the simplest structure of a water-soluble polymer. PEG can be grafted to biomaterial surfaces and provide a biocompatibility

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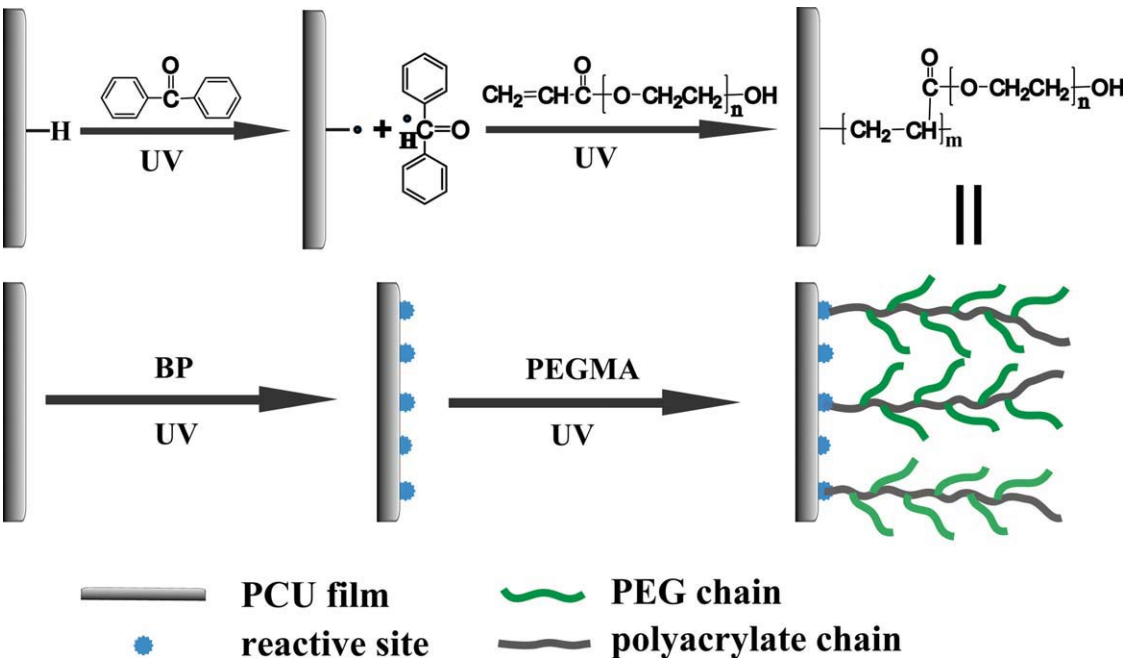

Figure 1 Schematic description of the PEGMA grafting from a PCU film with BP as a photoinitiator. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

layer, which reduces the absorption of plasma albumen and red blood cells[14–17] because of its characteristics of hydrophilicity, large exclusion volume, and unique coordination with surrounding water molecules in an aqueous medium.[18–20] Moreover, PEG has unique properties of nontoxicity and nonimmunogenecity, which are very important for biomaterials.[21–24] To further enhance the compatibility of a material, researchers have introduced new functional groups [e.g., amino group, sulfonic group,[25] heparin,[26] arginine-glycine-aspartic acid (RGD)[27]] to the end of the PEG chain.

However, it is necessary to attach PEG to a polymeric surface or to crosslink it to form a network because it is highly soluble in water, and then, in the same pinning density conditions, the number of effective PEGs is limited. To improve this disadvantage, surface-modified materials can be prepared by grafting copolymerization with poly(ethylene glycol) monoacrylate (PEGMA) macromonomer via grafting polymerization. In the surface grafting copolymerization to modify materials, reactive sites or groups on the materials surface have to be introduced first by gas plasma,[28] ozone,[29] UV radiation treatment,[30–33] or other methods.[34] Therefore, photografting polymerization is a promising method for the surface modification of polymers because photografting is a relatively simple, energy-efficient, and cost-effective process.[35] Iguerb and Bertrand[30] prepared an antifouling surface through the grafting polymerization of PEGMA onto the surface of a poly(methyl methacrylate) film under UV irradiation. The photografted PEG surface exhibited excellent protein repellence when the inhibition of protein adhesion was investigated by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary-ion mass spectrometry with bovine serum albumin as a model protein. Joung et al.[31] prepared a new hyperbranched surface of poly[poly(ethylene glycol) monoacrylate] [poly(PEGMA)] by photopolymerization using a dithiocarbamyl group as an iniferter. This highly dense architecture of PEG chains with hydrophilicity and chain mobility is expected to be used effectively in bioimplantable substrates or micropatterned or nanopatterned surfaces for the immobilization of bioactive molecules in biomedical fields. Sebra et al.[32] reported on the photografting polymerization of PEGMA to create cell-responsive chemically and biologically active surfaces that manipulated cell response. Stachowiak[33] investigated the grafting polymerization of PEGMA and the ability of poly(PEGMA) to prevent protein adsorption. Photografted layers of poly(PEGMA) decreased protein adsorption to less than 2% of that with unmodified surfaces.

In this study, PEGMA, as a hydrophilic macromonomer, was grafted onto a PCU surface to increase its hydrophilicity. Specifically, UV-photoinduced grafting polymerization was used to graft PEGMA onto the polyurethane surface to modify the hydroscopicity and hydrophilicity of the material. Figure 1 shows the process of PEGMA grafting from a PCU film with benzophenone (BP) as a photoinitiator. The effects of the reaction temperature, macromolecular monomer concentration, UV irradiation time, and photoinitiator concentration on the grafting density (GD) were investigated in detail. Furthermore, the relations of the GD and material surface properties were also examined.

EXPERIMENTAL

Materials and methods

PCU (Chronoflex C) with a number-average molecular weight of 1.1×10^5 g/mol was purchased from Cardio International, Inc. (New York, USA) BP (≥99%) as a photoinitiator was purchased from Jiangtian Chemical Technology Co., Ltd. (Tianjin, China). PEGMA (average number-average molecular weight = 526, containing 10 ethylene glycol units) was purchased from Sigma-Aldrich (Beijing, China). PEGMA was passed through a column containing inhibitor-remover beads of a basic anion-exchange resin at 50°C (Guangfu Fine Chemical Research Institute, Tianjin, China). Tetrahydrofuran (THF), ethanol, and acetone (analytical grade) were obtained from Tianjin Jiangtian Chemical Technology Co.

The surface chemistry of the materials was characterized by a Bio-Rad FTS-6000 transmission Fourier transform infrared (FTIR) spectrometer (Hercules, California, USA). Chemical elements and their statuses were determined by a PHI-1600 X-ray photoelectron spectrometer (PerkinElmer, Massachusetts, USA) with an MgKα X-ray source under 2×10^{-8} Torr. Low-resolution survey scans were performed at 187.85 eV with a step of 0.8 eV and high-resolution survey scans at a pass energy of 29.35 eV with a step of 0.25 eV. The core-level signals were obtained at a photoelectron takeoff angle of 45°. The elemental compositions were calculated from peak areas, and spectra bands of C1s and O1s were deconvoluted into subpeaks by XPSPEAK41 spectrometer software (Taiwan, China). The surface morphologies were observed with a Philips XL 30 scanning electron microscopy (SEM) (Eindhoven, Holland). The solvent-cast PCU film thicknesses were measured with a digital thickness gage.

The wettability changes of the grafting PCU surfaces were characterized by static contact angle measurements with the sessile drop technique. The measurements were performed at room temperature on a Kruss EasyDrop goniometer (Kruss, Hamburg, Germany) equipped with a digital photoanalyzer with 3 μL of distilled water. The values of the contact angles shown in this article are the average of at least six measurements.

Preparation of the PCU films

A suitable amount of PCU was dissolved in THF to prepare 8 wt % solutions, and the mixture was evenly spread on a glass Petri dish, which was aligned perfectly horizontal to ensure that film had uniform thickness. The dish was kept in a chemical hood for 48 h to allow the THF to evaporate. The film was removed from the Petri dish and cleaned in ethanol by an ultrasonic cleaner for 10 min. Finally, the film was completely dried at 60°C for 6 h *in vacuo*. The prepared film was cut into 2.5×4.0 cm^2 pieces as specimens for the surface modification experiments.

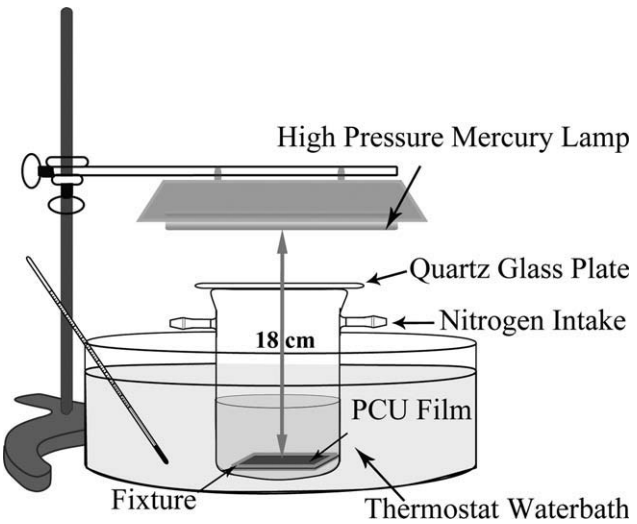

Figure 2 Schematic diagram of the experimental apparatus for the UV grafting of PEGMA onto the PCU films.

UV grafting polymerization of PEGMA onto the PCU surface

The preweighed PCU films were dipped into an acetone solution containing BP as a photosensitizer, extracted, and then dried in air for 30 min under dark conditions to obtain PCU films containing BP on the surface. The concentrations of the BP acetone solution were varied from 40 to 120 mg/mL. The dried films were clamped with self-made fixtures, subsequently immersed into a PEGMA monomer water solution with a defined concentration, and then put into the UV reactor in a water bath that was made in our laboratory (Fig. 2). After a 10-min purge of nitrogen gas, UV irradiation was carried out for a given time under a nitrogen environment. PEGMA was photografted onto the PCU films at a given temperature under a 300-W high-pressure mercury lamp. The distance between the PCU film and the UV lamp was 18 cm. After irradiation, the grafted films were taken out from the reaction processor and washed with ethanol by vibration to remove absorbed oligomer, homopolymer, and unreacted macromonomer for 8 h; then, they were washed finally with pure water for 24 h. Subsequently, they were dried to a constant weight as a dry weight in a vacuum oven at 60°C.

GD of PEGMA on the PCUs was calculated by the following formula:

$$GD(\mathrm{mg/cm^2}) = (w_1 - w_0)/S$$

where w_0 and w_1 are the weights of the blank and dried modified films, respectively, and S is the

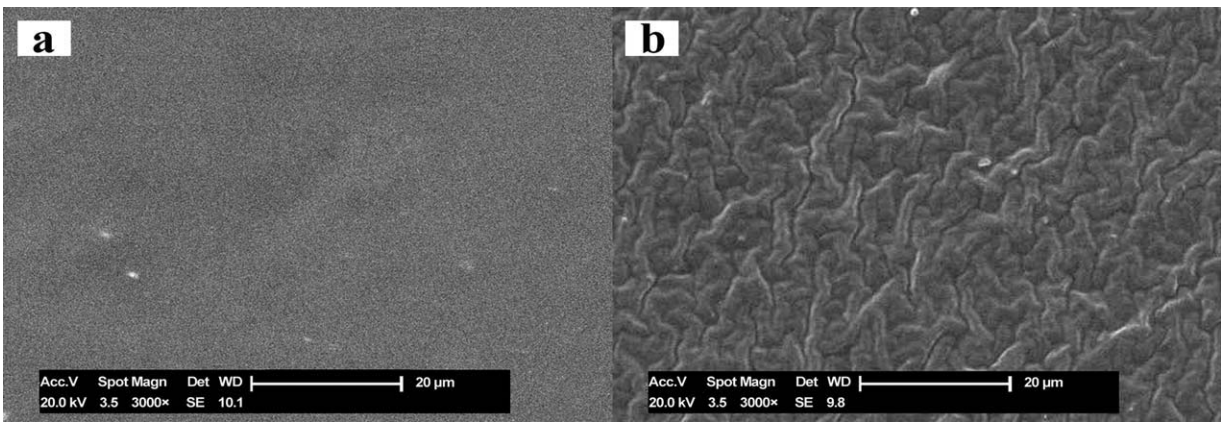

Figure 3 Surface SEM micrographs of the (a) blank PCU film and (b) modified film (reaction condition: BP concentration = 100 mg/mL, PEGMA concentration = 20 wt %, reaction temperature = 60°C, and irradiation time = 60 min).

surface area of the PCU film. All of the results were the average of three parallel experiments.

To measure the hydroscopicity, the modified films were soaked in distilled water for 24 h, taken out and wiped rapidly with filter paper, and then weighed immediately. The water content was calculated as the ratio of the absorbed water weight to the dried film weight. The hydroscopicity of the grafted films was characterized by the per-unit water uptake (WU) according to the following formula:

$$WU(\mathrm{mg/cm^2}) = (w_2 - w_1)/S$$

where w_2 is the weight of the modified film after immersion in water for 24 h. All of the results are the average of three parallel experiments.

RESULTS AND DISCUSSION

Surface morphologies of the PCU film and graft PCU films

The surface morphologies of the blank PCU and modified PCU films were characterized with SEM and are shown in Figure 3. The blank PCU film was uniform and even, whereas the modified PCU film presented a rough surface and earthwormlike texture with an approximate width of 2 μm. The photografting of PEGMA led to a morphology change in the PCU film surfaces, which resulted in changes in the physical and chemical characteristics of the surfaces.

FTIR spectra of the PCU and graft PCU films

The PCU film was characterized by FTIR spectroscopy before and after the photografting polymerization of PEGMA. Figure 4 shows the FTIR spectrum of the blank PCU film. The peaks at 2939 and 2863 cm^{-1} corresponded to the antisymmetric and symmetrical stretching vibration peaks of CH_2 in PCU. The absorption peaks at 1724 and 1530 cm^{-1} were responsible for the carbonyl groups and the C—N bonds, respectively. The peak at 1466 cm^{-1} was the symmetry bending vibration peak of the CH_2. The 1253-cm^{-1} bond was assigned to ester C—O—C stretching in the polycarbonate segments.

The modified PCU films should not have had any adsorbed homopolymer or unreacted PEGMA because they were easily soluble and washed off in water and ethanol during a strong washing process. As shown in the FTIR spectra (Fig. 4), in addition to the aforementioned peaks of the PCU film, characteristic peaks (1454, 1101, 948, and 848 cm^{-1}) of PEG were clearly observed in the modified film. Particularly, characteristic peaks of the ether bond at 848 and 1101 cm^{-1} strongly proved that PEGMA was grafted onto the film surface.

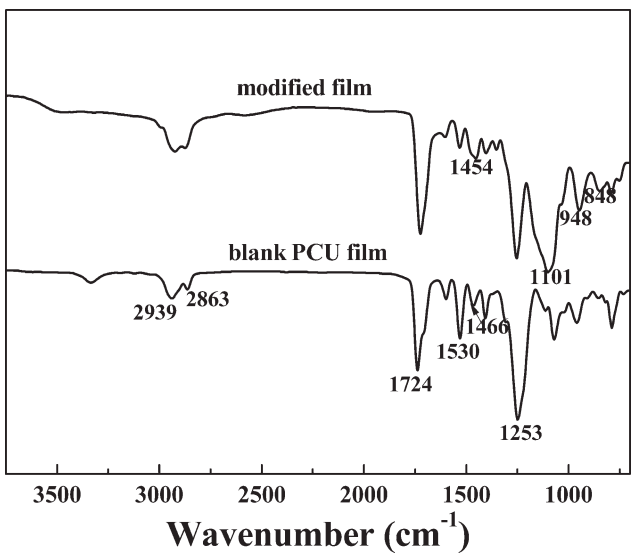

Figure 4 FTIR spectra of the blank PCU film and modified film (reaction conditions: BP concentration = 100 mg/mL, PEGMA concentration = 20 wt %, reaction temperature = 60°C, and irradiation time = 60 min).

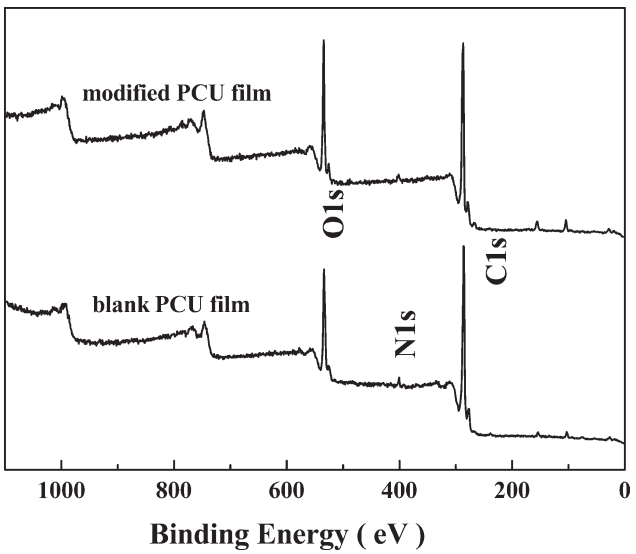

Figure 5 XPS spectra of the blank PCU film and modified film (reaction conditions: BP concentration = 100 mg/mL, PEGMA concentration = 30 wt %, reaction temperature = 80°C, and irradiation time = 60 min).

XPS spectra of the PCU and graft PCU films

The XPS spectra for the blank PCU surface and PEGMA-modified PCU surface illustrated the changes in the carbon, nitrogen, and oxygen compositions in the top surface layer before and after the PEGMA photografting reaction. An increase in the O1s (533-eV) peak intensity and a decrease in the C1s (285-eV) peak intensity for the PEGMA-grafted PCU compared to the blank PCU film were observed (Fig. 5). This change tendency, reflecting the elemental composition, was also found for various PEGMA-grafted PCU films with changing PEGMA concentrations and other reaction conditions. The XPS results indicate that the PEG blocks were attached to the PCU surface through the photografting polymerization.

The elemental compositions of the blank PCU and the surface-modified PCU as determined by XPS were calculated and are listed in Table I. As shown in Table I, the O1s content on the modified PCU surface was found to increase by 2.5% compared with the blank PCU. This increase did contribute appreciably to the grafting of the PEG blocks. The C1s content on the modified PCU surface decreased from 77.9 to 75.7%, whereas the N1s content decreased slightly.

To further confirm the hypothesis of the grafting of PEGMA onto the surface, the chemical environments of C1s and O1s were analyzed by XPSPEAK software; the curve fitting and analysis results are shown in Figure 6 and summarized in Table II. The *C*—O content increased significantly from 15.1 to 38.3% after grafting polymerization in the high-resolution scan; this indicated that PEGMA was grafted onto the PCU surface. The content of ether (C—*O*—C) in the chemical environment of O1s increased significantly from 13.1 to 27.3%, whereas the content of carbonyl (O—C=*O*) and ester (—*O*—C=O) decreased obviously. This phenomenon might have been due to the PCU surface being covered with poly(PEGMA) blocks, which had many PEG blocks as side chains (Fig. 1). Therefore, these results confirm the poly(PEGMA) block grafting onto the surface of the PCU films.

Grafting polymerization of PEGMA onto the PCU films

Yang et al.[36] reported that photoinduced radical polymerization with BP as a photoinitiator favored living polymerization at low free-radical concentrations and low chain mobility. The end groups of semipinacols derived from methacrylic acid and BP on the polyethylene surface could reinitiate the polymerization of methacrylic acid under UV irradiation. So, we used a low concentration of BP to induce the grafting polymerization of PEGMA onto the PCU surfaces in this study. When acetone was used as the solvent of BP, it permeated the PCU films rapidly and carried BP molecules into these films because of the slight swelling of PCU. The higher BP concentration resulted in a higher content of BP in the PCU films. The BP concentration was a key factor influencing the grafting polymerization. The reaction process of grafting polymerization was illustrated as follows: first, the physically adsorbed BP in the PCU surface was excited to the triplet state upon UV irradiation; then, it extracted a hydrogen atom from an α-methyl group of the PCU chains to generate a surface radical that was capable of initiating the grafting polymerization of PEGMA; finally, the sequential grafting polymerization was performed. Because of the relatively low reactivity of macromonomers compared to small acrylate monomers, the effect of the photoinitiator concentration in the acetone solution on GD was investigated and is shown in Figure 7. PEGMA almost did not photopolymerize at 60°C in the solution when the PCU film

TABLE I
Elemental Composition of the Blank PCU and Surface-Modified PCU as Determined by XPS

Sample	Atomic concentration (%)		
	C1s	O1s	N1s
Blank PCU	77.9	20.3	1.9
Modified PCU[a]	75.7	22.8	1.6

[a] Reaction conditions: BP concentration = 100 mg/mL, PEGMA concentration = 30 wt %, reaction temperature = 80°C, and irradiation time = 60 min.

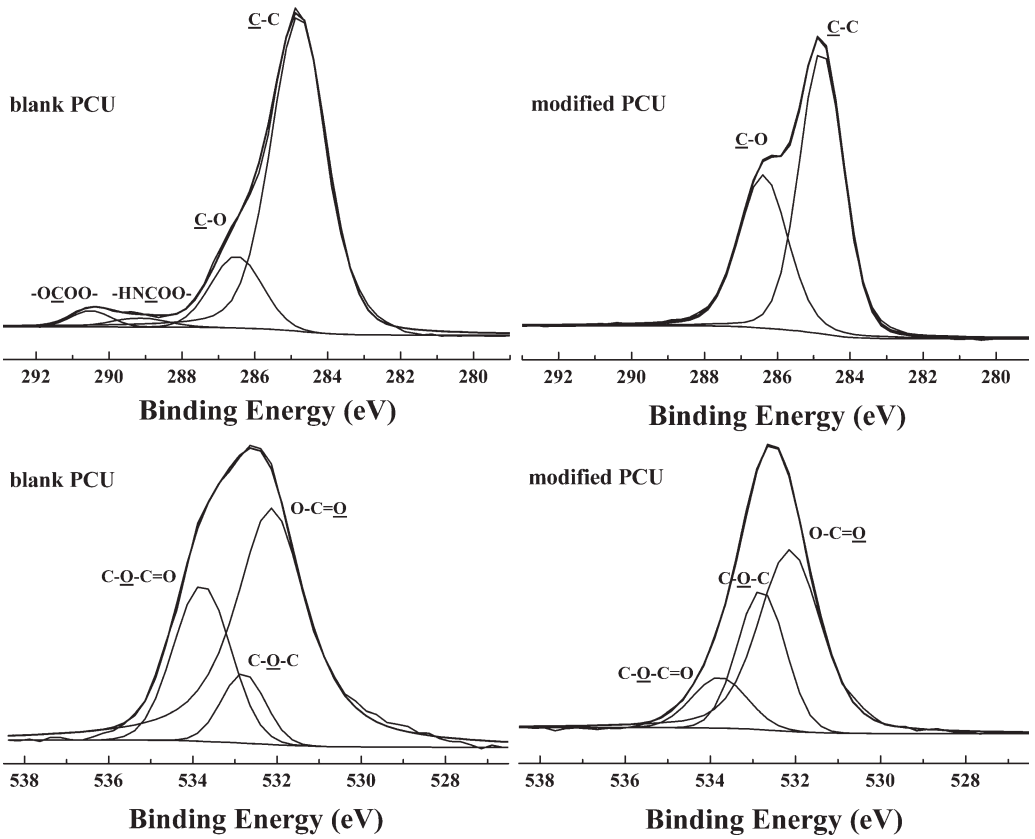

Figure 6 C1s and O1s XPS spectra of the (a) blank PCU and (b) the surface-modified PCU films (reaction conditions: BP concentration = 100 mg/mL, PEGMA concentration = 30 wt %, reaction temperature = 80°C, and irradiation time = 60 min).

was not dipped into the initiator solution. No detectable photografting amount on the PCU surface was observed when the PCU films did not have any initiator. BP was pre-entrapped in the films by dipping in BP solution and was used as a photoinitiator to enhance the photopolymerization. GD increased significantly to 2.36 mg/cm^2 when the initiator concentration in the acetone solution increased from 0 to 60 mg/mL. When the photoinitiator concentration in the solution increased from 60 to 120 mg/mL, GD increased slightly and gradually from 2.36 to 2.57 mg/cm^2.

The free-radical generated from BP under UV irradiation initiated the grafting polymerization of PEGMA onto the PCU surface. The conceivable termination reaction of the graft system was mainly accomplished by the combination of growing chain radicals and semipinacol radicals. Among the terminations, the disproportionation, coupling, and production of benzopinacol prevented further growth of the graft chains. The semipinacol groups on the PCU film surface could not be activated and decomposed into active free radicals to reinitiate the polymerization of PEGMA under UV irradiation. Yang et al.[36] also found similar results, in that the end groups of semipinacols derived from poly(acrylic acid) free radicals and BP on the polyethylene surface could not reinitiate the photopolymerization of acrylic acid (AA). Therefore, grafting polymerization was stopped by the inactive terminations. An attempt to

TABLE II
C (1s) and O (1s) Elemental Composition of the Blank PCU and the Surface-Modified PCU by XPS Method

	C (1s) (%)				O (1s) (%)		
Sample ID	C—C	C—O	—HNCOO—	—OCOO—	C—O—C	O—C=O	—O—C=O
Blank PCU	80.2	15.1	2.1	2.6	13.1	62.6	24.3
Modified PCU*	61.7	38.3	0	0	27.3	52.5	20.2

* Reaction conditions: BP concentration, 100 mg/mL; PEGMA concentration, 30 wt %; reaction temperature, 80°C; irradiation time, 60 min.

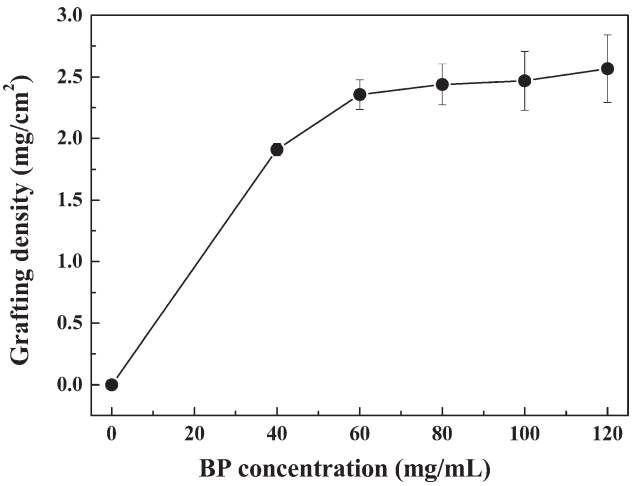

Figure 7 Effect of the BP concentration in the acetone solution on GD (reaction conditions: PEGMA concentration = 10 wt %, reaction temperature = 60°C, and irradiation time = 60 min).

continue the grafting reactions for a high GD by the dipping of the film in a high-BP-concentration solution failed (Fig. 7) because the triplet state of the photoinitiator might have extracted a hydrogen atom from an α-methyl group of the macromonomer PEGMA to generate a radical; this could have initiated the homopolymerization of PEGMA but not grafting polymerization.

Influence of the process conditions on the grafting polymerization

Influence of the monomer concentration on the grafting polymerization

Figure 8 shows the changes in GD of the grafted PEGMA with increasing PEGMA concentration. When monomer concentration was 5 wt %, GD reached 2.43 mg/cm^2. GD increased from 2.43 to 3.16 mg/cm^2 with increasing macromonomer concentration from 5 to 30 wt %.

GD gradually and slightly increased with increasing PEGMA concentration. The results demonstrate that the influence of the macromonomer concentration on GD was much lower than that of the small molecular monomer acrylate. The main reason for this might have been steric effects, which prevented the macromonomer from free movement. The double bonds at the end groups in the macromonomers were hindered to diffuse to the chain free radicals on the surface. Meanwhile, the chain free radicals were embedded by the hydrophilic side chains of poly(PEGMA). Those effects decreased the polymerization rate of PEGMA on the surface.

Influence of the reaction temperature on the grafting polymerization

The effects of the reaction temperature on the grafting polymerization of PEGMA were also investigated when the BP concentration was 100 mg/mL, the PEGMA concentration was 10 wt %, and the irradiation time was 60 min (Fig. 9). The UV irradiation brought heat to the solution and led to an increase in the solution temperature from room temperature to 45°C in 60 min upon exposure to the UV lamp. Reaction temperatures from 50 to 90°C were investigated to avoid the disturbance of the UV lamp.

GD increased slightly from 2.24 to 2.55 mg/cm^2 when the reaction temperature increased from 50 to 90°C. This indicated that the reaction temperature had a slight influence on GD. There were two propagation reactions in the surface photografting polymerization process; these resulted in the growth of

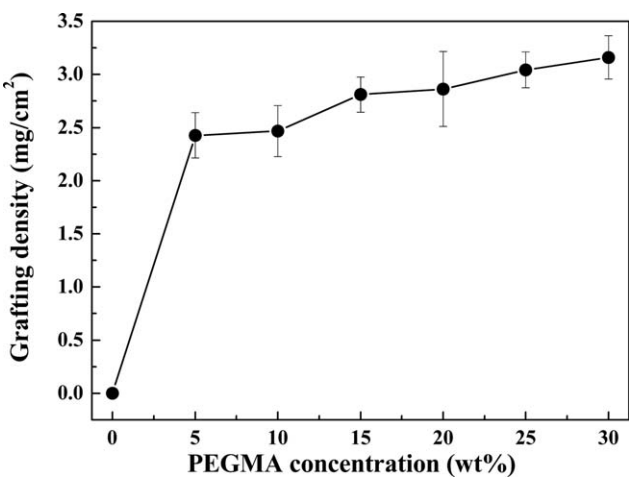

Figure 8 Effect of the PEGMA concentration on GD (reaction conditions: BP concentration = 100 mg/mL, reaction temperature = 80°C, and irradiation time = 60 min).

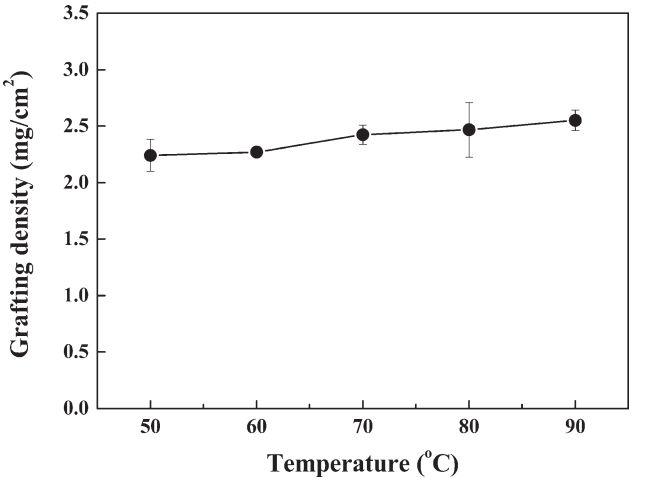

Figure 9 Effects of the reaction temperature on GD (reaction conditions: BP concentration = 100 mg/mL, PEGMA concentration = 10 wt %, and irradiation time = 60 min).

the homopolymers of poly(PEGMA) and graft polymers on the surface of the PCU film. One end of the chain, free radicals were fixed on the PCU film surface; this enhanced their steric hindrance. As expected, the mobility and vibrational frequency of chain free radicals on the surface were much lower than those of semipinacol free radicals and homopolymer free radicals. When the reaction temperature was high, the chain free radicals had a high mobility. As a result, the propagation reactions showed more sensitivity to the reaction temperature than the termination reactions. Yang and Ranby[37] also found that a high reaction temperature had a positive effect on the efficiency of the photografting polymerization of AA onto the polyethylene surface; this resulted from a high propagation reaction at a high reaction temperature. The grafting efficiency of AA increased significantly from 30 to 85% when the reaction temperature was increased from 25 to 70°C. Compared with this result, the increase in GD of PEGMA was relatively low when the temperature increased from 50 to 90°C in this study. This indicated that a high reaction temperature was also favorable for the thermally activated homopolymerization of PEGMA, which resulted in the formation of poly(PEGMA) in the solution. The low diffusion ability of the macromonomers and the aforementioned effects induced GD to increase slightly.

Influence of the irradiation time on the grafting polymerization

Figure 10 shows the changes in GD of PEGMA with the irradiation time. As shown in Figure 10, GD increased to 3.04 mg/cm^2 when the irradiation time was 90 min and leveled off from 90 to 120 min. The surface of the PCU film was covered by considerable amounts of poly(PEGMA) after 90 min of reaction. It was more difficult for the PEGMA macromonomer to diffuse from solution to reach the active center on the PCU surface to continue the chain growth of the free radicals. On the other hand, the PEGMA monomer and the free radicals at the end of homopolymer chains met easily in solution; this resulted in the growth of the homopolymer chains because of low steric hindrance. This effect resulted in no further significant increases of GD but a high solution viscosity because more homopolymers of PEGMA with high molecular weights were formed in solution when the reaction time exceeded 90 min.

GD of the PEGMA reached only about 3.04 mg/cm^2 after 90 min of irradiation; this indicated that the grafting reaction rate was slower than that of the small monomers, such as *N*-vinylpyrrolidone, acrylates, and AA. The grafting percentage of *N*-vinylpyrrolidone was reported to reach a value around 36% (ca. 100 mg/cm^2) after only 10 min of irradiation.[38] For the AA monomer, the graft degree was 6 wt % (ca. 20 mg/cm^2) after about 30 min of irradiation.[39] This could be ascribed to the low reactivity, high steric hindrance, and low movement ability of PEGMA, as mentioned previously. Meanwhile, the hydrophobic chain free radicals on the PCU surface could have been tightly embedded in the high hydrophilic PEG side chains in water solution; this also decreased the grafting polymerization rate. The highly hydrophilic PEG on the surface was hydrated with water; this further hindered the diffusion of the PEGMA macromonomers from solution to the active free radicals. Compared with small molecular monomer such as acrylates, PEGMA showed a low grafting ability onto the material surfaces.

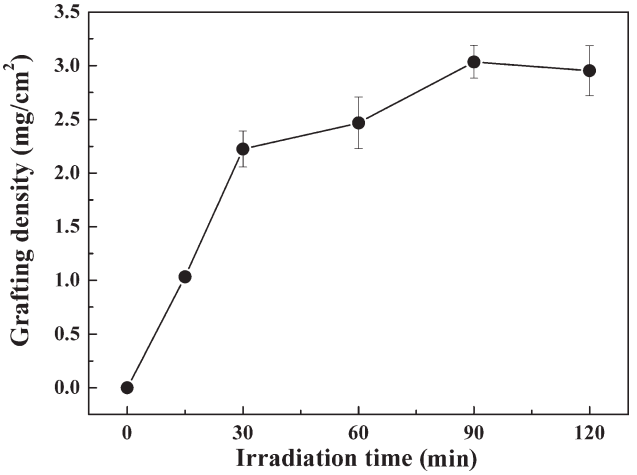

Figure 10 Effect of the irradiation time on GD (reaction conditions: BP concentration = 100 mg/mL, PEGMA concentration = 10 wt %, and reaction temperature = 80°C).

Water contact angles of the graft films

The water contact angle was used to characterize the interfacial hydrophilic properties. The grafting distribution of poly(PEGMA) blocks on the resulting films was supposed to form a uniform polymer hydrogel-like layer.[40] The PEG side blocks and polyacrylate blocks on the PCU-*g*-PEGMA film surfaces were favorable for the improvement of the hydrophilic film surface. PEG blocks were more hydrophilic and showed a lower water contact angle value than the polyacrylate blocks. The blank PCU film exhibited hydrophobic surface properties with a high water contact angle of about 86.0°, whereas the PCU film modified with PEGMA showed hydrophilic properties as indicated by a low water contact angle (ca. 60.0°), which confirmed that an effective modification of the PCU surface was carried out during the irradiation process. As expected, the modified PCU surface became more hydrophilic after the photografting of PEGMA. Moreover, as shown in the SEM

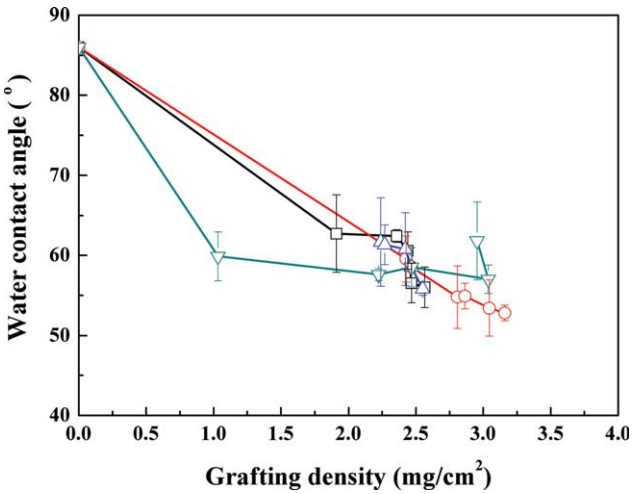

Figure 11 Effect of GD on the water contact angle of the PCU films modified with various reaction conditions: (□) BP concentration = 40–120 mg/mL, PEGMA concentration = 10 wt %, reaction temperature = 60°C, and irradiation time = 60 min; (○) PEGMA concentration = 5–30 wt %, BP concentration = 100 mg/mL, reaction temperature = 80°C, and irradiation time = 60 min; (Δ) reaction temperature = 50–90°C, BP concentration = 100 mg/mL, PEGMA concentration = 10 wt %, and irradiation time = 60 min; and (▽) irradiation time = 15–120 min, BP concentration = 100 mg/mL, PEGMA concentration = 10 wt %, and reaction temperature = 80°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

graph (Fig. 3), the modified film had a much rougher surface than the blank PCU film and, thus, displayed a high wettability and low water contact angle.

Figure 11 shows the relationship between GD of the PCU films modified with PEGMA and the water contact angle under various reaction conditions. As expected, the water contact angle decreased with increasing GD. When GD reached 1.00 mg/cm^2, the hydrophilicity of the PCU films was greatly improved, as indicated by the obvious decrease in the water contact angle of the modified PCU films.

Water uptake of the graft films

PEG is a well-known biomedical polymer with a high biocompatibility and resistance to platelet and protein adsorption due to its mobility in aqueous environments; this causes a decrease in the interfacial tension between its polymeric surfaces and blood plasma.[41] These findings seemed to be caused by the volume restriction effects derived from the highly flexible and hydrophilic PEG chains.[14] The amount of absorbed water was measured to estimate the hydrophilicity of the grafted layers formed on the PCU films. The water uptake per unit area of the modified PCU film could have been influenced by the hydrophilicity of the surface, GD, and structures of the grafted layer. Therefore, the results of water uptake reflect the structure of the grafted layer and indirectly indicate the relationship between the grafting process conditions and structure of the grafted layer.

When PEG chains of poly(PEGMA) were immersed in water, the water molecules diffused into the hydrophilic swollen phase, and water uptake of the films reached saturated adsorption after a long immersion time.[12] In our experiment, the modified PCU films were soaked in distilled water for 24 h to ensure saturation adsorption. Figure 12 shows the water uptake of the modified PCUs measured at 25°C after 24 h of immersion. The water uptake of the hydrophobic blank PCU film was generally very low; experiments proved that its value was only 0.28 mg/cm^2, whereas the water uptake of the PCU films grafted with hydrophilic PEGMA (reaction conditions: BP concentration > 60 mg/mL, PEGMA concentration > 5 wt %, irradiation time > 60 min) usually reached above 3.00 mg/cm^2.

One curve (□) in Figure 12 shows that the water uptake increased proportionally to GD of the modified PCU films prepared by dipping in BP of various concentrations. As mentioned previously, GD of the PCU films depended on the number and length of grafted chains. With increasing BP content in the PCU films, the number of activated initiators on the

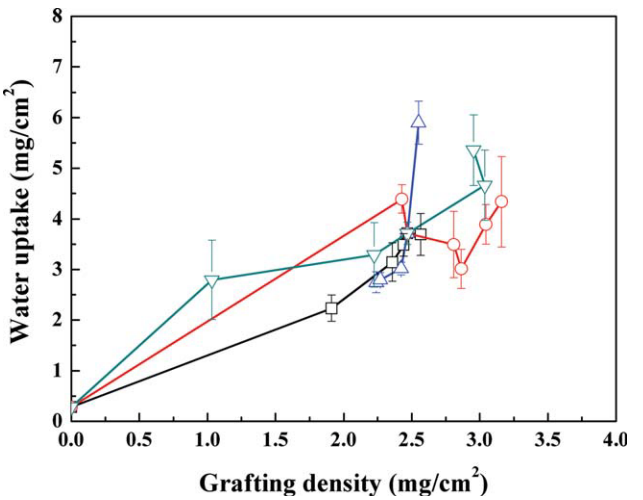

Figure 12 Effect of GD on the water uptake of the PCU films after immersion in water at 25°C for 24 h. The films were prepared by various reaction conditions: (□) BP concentration = 40–120 mg/mL, PEGMA concentration = 10 wt %, reaction temperature = 60°C, and irradiation time = 60 min; (○) PEGMA concentration = 5–30 wt %, BP concentration = 100 mg/mL, reaction temperature = 80°C, and irradiation time = 60 min; (Δ) reaction temperature = 50–90°C, BP concentration = 100 mg/mL, PEGMA concentration = 10 wt %, and irradiation time = 60 min; and (▽) irradiation time = 15–120 min, BP concentration = 100 mg/mL, PEGMA concentration = 10 wt %, and reaction temperature = 80°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

film surface increased upon UV irradiation; this resulted in an increase of the number of grafted chains. This led to increases in GD and water uptake. The BP content had a significant effect on the number of grafted chains but a slight one on their length.

Another curve (○) in Figure 12 shows the relationship of the water uptake and GD of the modified PCU films prepared with different PEGMA concentrations. Unexpectedly, a linearly increasing relationship between the water uptake and GD was not observed. When the PEGMA concentration increased from 5 to 20 wt %, the water uptake decreased from 4.39 to 3.01 mg/cm^2. When the PEGMA concentration increased further to 30 wt %, the water uptake increased again. The probable reason was that the transfer of free-radical species to the macromonomer PEGMA and grafting chains increased, and the grafted chains formed with more branches. The branched grafting chains twisted to decrease the diffusion of water molecules into the grafted layer. GD increased and the water uptake decreased when the PEGMA concentration increased from 5 to 20 wt %. The opportunity for growth of the active species with the macromonomers increased when the PEGMA concentration was above 20 wt %; therefore, the length of the grafted chains and the amount of effective PEG segments increased, and the water uptake also increased.

The relationship of GD and the water uptake of the modified PCU films prepared at different reaction temperatures is plotted with a curve (Δ) in Figure 12. When the reaction temperature was in the range 50–90°C, the water uptake increased approximately linearly with GD. Because the BP content remained constant, the number of active free radicals on the film surface was approximately the same; this resulted in a similar number of grafted chains of poly(PEGMA). The increasing reaction temperature led to an increase in GD because of the growth of the grafted chain length; this eventually led to an increase in the water uptake accordingly.

Another curve (▽) in Figure 12 shows the relationship of the water uptake and GD of the modified PCU films, which were prepared with various irradiation times. GD of the modified PCU films increased with increasing irradiation time, as mentioned previously; this corresponded to the increase in water uptake. When the irradiation was prolonged to 120 min, some of the grafted PEGMA chains might have broken because of photodegradation. The competition of photodegradation and photografting polymerization affected GD; it resulted in a slight decrease in GD when photodegradation was higher than polymerization. The photodegradation of the grafted layer reduced the twist of the grafted chains, which allowed water molecules to diffuse more easily into the interior of the grafted layer; therefore, the water uptake of the modified PCU films increased.

CONCLUSIONS

Hydrophilic PEGMA macromonomer was successfully grafted onto the PCU films under UV irradiation. The grafted poly(PEGMA) chains on the surface had many PEG blocks as side chains, in which the end hydroxyl groups were introduced as functional groups for further modification. FTIR, XPS, water contact angle measurement, and water uptake measurement of the modified PCU films confirmed the PEGMA grafting. When the PCU film was photografted in a 20 wt % PEGMA solution at 60°C for 60 min, the C—O—C fitting peak of the O1s peak showed a high intensity compared with that of the black PCU film. GD increased with increasing PEGMA macromolecular monomer concentration and BP concentration in the acetone solution, whereas the reaction temperature had a slight influence on GD. An increase in the UV irradiation time was favorable for an increase in GD, but when the irradiation time was greater than 90 min, the photolysis of grafted chains competed with photopolymerization and resulted in a lower GD.

The water uptake and water contact angle of the modified PCU films showed that the photografted PCU surfaces exhibited excellent hydrophilicity because of the hydrophilic poly(PEGMA) blocks on the surface. It was possible to introduce anticoagulant groups or substances onto the surfaces to further improve the hemocompatibility of the polyurethanes by means of the coupling of the hydroxyl functional groups with heparin and other bioactive molecules. We found in our study that the appropriate grafting conditions were as follows: BP content = 100 mg/mL, PEGMA concentration = 15 wt %, reaction temperature = 70°C, and irradiation time = 90 min. The hemocompatibility of poly(PEGMA)-grafted PCU films prepared under these optimum conditions will be measured in our laboratory.

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