

# Surface Modification of Poly- L-Lactide by Photografting of Hydrophilic Polymers towards Improving Its Hydrophilicity

ZUWEI MA,<sup>1</sup> CHANGYOU GAO,<sup>1</sup> JUN YUAN,<sup>2</sup> JIAN JI,<sup>1</sup> YIHONG GONG,<sup>1</sup> JIACONG SHEN<sup>1</sup>

<sup>1</sup> Department of Polymer Science And Engineering, Zhejiang University, Hangzhou, China 310027

<sup>2</sup> State Key Laboratory of Silicon Material Science, Zhejiang University, Hangzhou, China 310027

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**ABSTRACT:** Poly-L-lactide (PLLA) has been used to prepare scaffolds to guide tissue regeneration in tissue engineering research. However, one of the limitations to the use of PLLA as an ideal biomaterial is its high hydrophobicity. To improve the hydrophilicity of PLLA, hydrophilic polymers were grafted onto PLLA membrane surfaces through the combination of photooxidization in hydrogen peroxide and subsequent ultraviolet (UV)-induced grafting copolymerization in the monomer solution. Three kinds of modified PLLA membranes (i.e., PLLA-g-polyhydroxyethyl methacrylate, PLLA-g-polyacrylamide, and PLLA-g-polymethacrylic acid) were obtained, resulting in the more wettable PLLA membranes. The occurrence of the grafting polymerization was confirmed by attenuated total reflectance infrared spectroscopy (ATR-IR) and X-ray photoelectron spectroscopy (XPS) analysis. Surface morphology of the modified PLLA membranes was studied by scan electronic microscopy (SEM). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2163–2171, 2002

**Key words:** graft copolymers; modification surfaces; biocompatibility

## INTRODUCTION

In recent years, biodegradable polymer scaffolds with large areas per unit volume have become particularly attractive in three-dimensional tissue culture for the creation of tissue-engineered organs, such as articular cartilage<sup>1,2</sup> and artificial skin.<sup>3</sup> Poly-L-lactide (PLLA) is one such polymer that is widely used because of its good biodegradability and biocompatibility. After a desired time *in vivo*, the PLLA scaffold degrades into L-lactic acid, which is a cellular metabolite, leaving tissues devoid of any foreign materials.

However, one of the limitations to the use of PLLA is its high hydrophobicity.<sup>4</sup> Its static water

contact angle, measured by the captive bubble method, is 71°. <sup>5</sup> The adhesion rate of human endothelial cells on PLLA is only 8% after 30 min and 10% after 1 h, compared with a corresponding 43% and 59% on tissue culture polystyrene (TCPS), whose static water contact angle is 35°. <sup>5</sup> Although the relationship between cell behaviors and surface properties of biomaterials is not completely understood, it has been widely accepted that cells prefer to attach to hydrophilic surfaces than hydrophobic surfaces. <sup>5</sup> It has been demonstrated that cells attach and spread more easily and effectively on hydrophilic surfaces modified with positively charged amine groups than on hydrophobic surfaces, both in the presence and absence of serum. <sup>6</sup> Other studies have demonstrated that maximum cell attachment was observed on materials with moderate wettability (water contact angle between 20 and 60°). <sup>5,7</sup>

Correspondence to: C. Gao (cygao@mail.hz.zj.cn).

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Hence, surface modification of PLLA to improve its hydrophilicity is necessary. Moreover, the hydrophilic groups, such as hydroxyl, amide, and carboxyl, have potential reaction properties that can be used to further immobilize biologically active ligands, such as adhesion peptides and glycosaminoglycans, to produce bioactive surfaces.<sup>8</sup> In the past few years, methods to improve the surface hydrophilicity of polymers, such as plasma treatment,<sup>9,10</sup>  $\gamma$ -ray irradiation-induced grafting,<sup>11</sup> photo-induced grafting,<sup>12</sup> and chemical grafting,<sup>13,14</sup> were widely used to graft hydrophilic vinyl monomers onto hydrophobic polymer surfaces. Among these methods, the combination application of photooxidization and UV-induced grafting copolymerization has been successfully used in grafting hydrophilic polymers onto polyurethane (PU) surfaces.<sup>15,16</sup> The attachment and growth rate of human umbilical vein endothelial cells on the modified PU membranes were greatly improved.<sup>17</sup>

Here we report the surface modification of PLLA using the same method. Hydrophilic polymers [i.e., polyhydroxyethyl methacrylate (PHEMA), poly-acrylamide (PAAm), and poly-methacrylic acid (PMAA), containing —OH, —CONH<sub>2</sub>, and —COOH, respectively] were immobilized onto PLLA by UV-initiated grafting copolymerization. After modification, the wettability of PLLA membrane surfaces was considerably improved.

## EXPERIMENTAL

### Materials

The PLLA was synthesized using the method described by Schindler and Harper<sup>18</sup> The 1,4-dioxane (analytical degree) was obtained from Shanghai Chemical Industries Company, Ltd. with out any further purification. PLLA membranes were prepared by spreading the 1,4-dioxane solution containing 6 wt % PLLA ( $M_n = 200,000$ ,  $M_w = 400,000$ ) onto stainless steel plates. The membranes were placed in the air at room temperature to evaporate the 1,4-dioxane, then were dried under vacuum to constant weight. The membranes obtained were  $\sim 0.7$ -mm thick and were cut into  $2 \times 2$ -cm pieces. Before use, the membranes were cleaned by immersion in ethanol for 30 min, followed by distilled water at room temperature for 30 min, and then dried under vacuum to constant weight. The vinyl monomers

were purified either by distillation under vacuum for hydroxyethyl methacrylate (HEMA, Sigma) and methacrylic acid (MAA, Sigma) or by recrystallization from acetone for acrylamide (AAm, Sigma).

### Photooxidization and Grafting Copolymerization

The PLLA membrane was placed in 40 mL of hydrogen peroxide solution (30%) which was stirred for a given time at 50°C under UV light generated from a high-pressure mercury lamp (250 W). Then the photooxidized membrane was rinsed with deionized water to remove the excess hydrogen peroxide and dried at room temperature in a vacuum. The membrane was then immersed into the monomer solution of a given concentration in a Pyrex glass tube purged with nitrogen. Graft polymerization was carried out under UV irradiation at a distance of 12.5 cm for 60 min at 50°C.

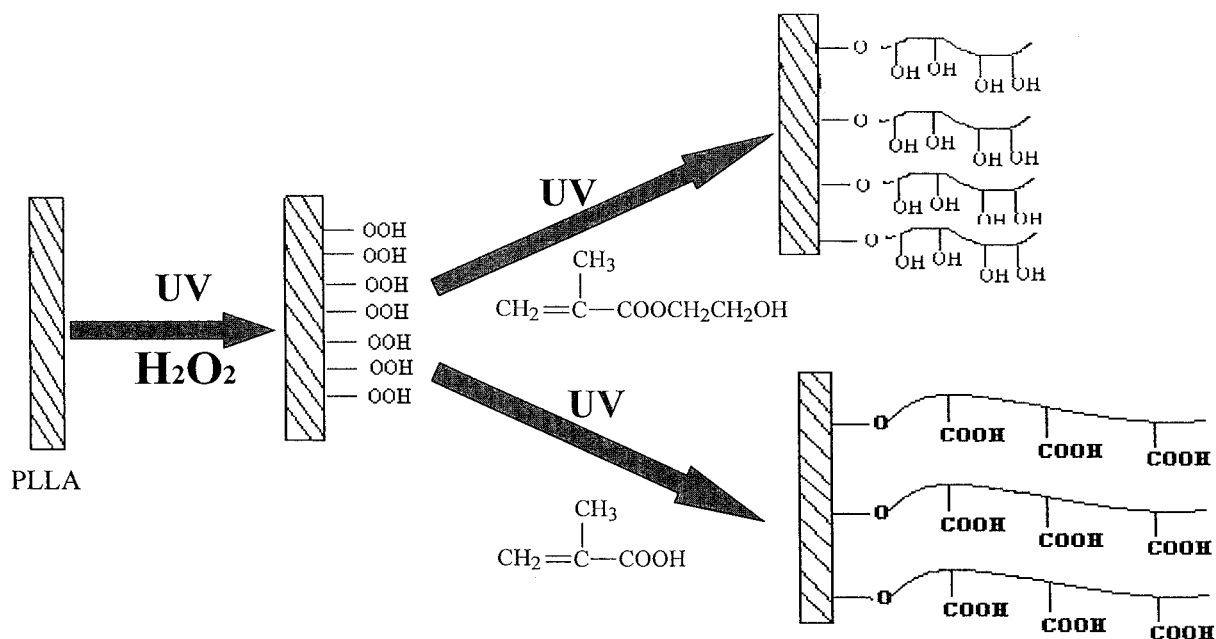
The grafted membrane was rinsed with deionized water at 70°C to remove the homopolymer.<sup>19</sup> The membrane was occasionally brushed with a cotton swab to aid the removal of the final trace of the homopolymer. To verify the effectiveness of this method, a control experiment was done as follows. PLLA membranes were immersed in PHEMA, PAAm, or PMAA solution for 60 min at 50°C, then were rinsed using the method already described. The attenuated total reflectance-infrared (ATR-IR) and X-ray photoelectron spectroscopy (XPS) spectra of these membranes were the same as that of the control PLLA membrane (spectra are not shown).

The grafted membrane was subsequently dried in vacuum at room temperature for at least 24 h before characterization.

### Characterization

The content of hydroperoxide on the membrane surface was determined by the modified iodometry method.<sup>20</sup> The ATR-IR spectra were obtained on a Nicolet Magna-IR560 machine. XPS spectra were obtained on a ESCA LAB Mark II spectrometer employing ALK $\alpha$  excitation radiation. The charging shift was referred to the C(1S) line emitted from the saturated hydrocarbon. The take off angle of the XPS was 30°. The intensity ratio of C(1S) : O(1S) : N(1S) is 1 : 2.85 : 1.77.

The wettability of the membranes was characterized by static water contact angle and water adsorption ratio. The sessile contact angle (SCA)



**Figure 1** Schematic representation of the photooxidation and the subsequent UV-induced grafting copolymerization.

was determined by placing a tiny drop of water ( $0.8 \mu\text{L}$ ) on the surface and recording the angle between the horizontal plane and the tangent to the drop at the point of contact with the substrate. Captive bubble contact angle (CBCA) was measured by observing the air bubble in water at room temperature within 30 s after it contact with the polymer surface.<sup>5</sup> For both methods, each value was averaged from 15 measurements. The water adsorption ratio was determined by first immersing the membrane ( $w_1$ ) in deionized water at room temperature for 24 h. The membrane was then removed, blotted dry, and weighed immediately ( $w_2$ ). The water adsorption ratio was defined as  $(w_2 - w_1)/S$ , where  $S$  is the surface area of the membrane.<sup>21</sup>

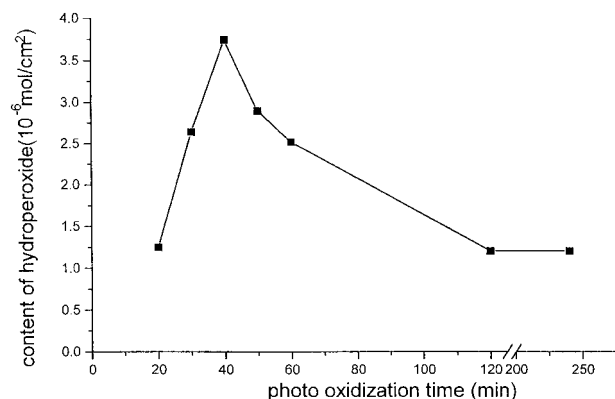
## RESULTS AND DISCUSSION

The UV-induced grafting of the hydrophilic monomers onto PLLA membranes can be achieved by the combination of photooxidation and UV-induced grafting copolymerization. Photooxidation resulted in hydroperoxide groups on the surface of the membrane, which under UV light decomposed into macromolecular radicals  $\text{P-O}\cdot$ , where P represents polymer chain, and free hydroxyl radicals  $\text{OH}\cdot$ . The macromolecular radicals initiated graft-

ing copolymerization whereas the hydroxyl radicals initiated homopolymerization. Hence, photooxidation of the polymer surface to introduce hydroperoxide groups is the key step in UV-induced grafting (see in Figure 1).

### Grafting Copolymerization

The content of hydroperoxide groups on the surfaces of the photooxidized PLLA membranes was determined by the iodometry method.<sup>20</sup> The concentration of the hydroperoxide groups increased with photooxidation time and reached maximum at  $\sim 40$  min and then decreased, as shown in Figure 2. A similar variation trend of hydroperoxide content has also been observed on PU membranes.<sup>16</sup> The explanation is that the UV light can induce both the generation and the decomposition of peroxide. Irradiation for a longer time is more in favor of the decomposition. Therefore, 40 min is thought to be the optimal photooxidation time for further grafting to yield a maximum degree of grafting. Previous work has demonstrated that the degree of grafting under UV light irradiation increases with irradiation time.<sup>16</sup> In this paper, the irradiation time was controlled at 1 h. If the irradiation time was too long, there would be too much homopolymer in the bulk solution, making



**Figure 2** Effect of photooxidation time on the content of hydroperoxide on the surface of PLLA membrane.

the rinsing of the homopolymers from the surfaces of the modified membranes very difficult.

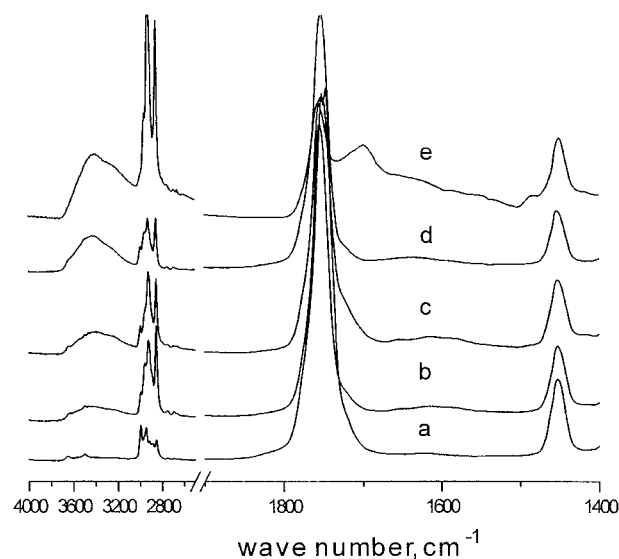
It was difficult to quantitatively determine the grafting degree on the modified PLLA membranes because the amount of the grafted hydrophilic polymers could not be weighed effectively. In contrast, previous work has demonstrated that using the same grafting method, the grafted hydrophilic polymers on the PU membranes could be gravimetrically detected.<sup>16</sup> There is no big difference between the content of hydroperoxide groups yielded on PLLA and PU membranes. The possible reason for the lower grafting degree on PLLA is that the repulsion between the hydrophobic PLLA surface and the hydrophilic monomers is stronger because the wettability of PLLA is poorer than that of PU, which leads to a lower monomer concentration near the PLLA membrane surface. Moreover, PLLA is degradable and it may hydrolyze during the process of the photografting. However, the occurrence of the grafting copolymerization can be confirmed by ATR-IR and XPS spectroscopy.

### Surface Characterization

The ATR-IR spectra showing the alteration of the chemical composition on PLLA membrane surfaces after grafting are presented in Figure 3. According to the molecular structure of PLLA, there is no absorption above  $3000\text{ cm}^{-1}$ , which is attributed to the stretching vibration of O—H or N—H, but a strong absorption exists at  $\sim 1750\text{ cm}^{-1}$  due to the existence of the abundant carbonyl groups in the bulk PLLA. Therefore, the emergence of the broad absorption between 3000

and  $3700\text{ cm}^{-1}$ , which can be assigned to hydroxyl groups in PHEMA, amide groups in PAAM, and carboxyl groups in PMAA, proves that the grafting copolymerization had occurred, producing PLLA copolymers (i.e., PLLA-g-PHEMA, PLLA-g-PAAM, and PLLA-g-PMAA, respectively) on the membrane surfaces. The quantitative analysis data are listed in Table I. The intensity ratios of C—H stretching vibration ( $2800\text{--}3000\text{ cm}^{-1}$ ) absorption to the absorption of the carbonyl groups ( $\sim 1750\text{ cm}^{-1}$ ) were increased after grafting because the contents of  $\text{CH}_2$  and  $\text{CH}_3$  are higher in the grafted polymers. The results in Table I also revealed that for the monomer HEMA, a higher O—H absorption intensity was obtained using a higher monomer concentration, indicating that the grafting degree increased with the monomer concentration.

The alteration of the surface chemical composition was further investigated by XPS. The C(1S) spectra of the control and modified membranes are shown in Figure 4. Detailed chemical information on the outer-most layer of the membrane surfaces was obtained by fitting the XPS spectra with standard peak values corresponding to the known binding energies of carbon functionalities.<sup>22,23</sup> All binding energies were referenced to the saturated hydrocarbon at  $285.0\text{ eV}$ . The C(1S) spectra of all the samples gave three main peaks,



**Figure 3** ATR spectra of (a) control, (b, c) PLLA-g-PHEMA, (d) PLLA-g-PAAM, and (e) PLLA-g-PMAA: monomer concentration, 5% [except for (c), which was 25%]; photooxidation time, 40 min; irradiation time, 1 h.

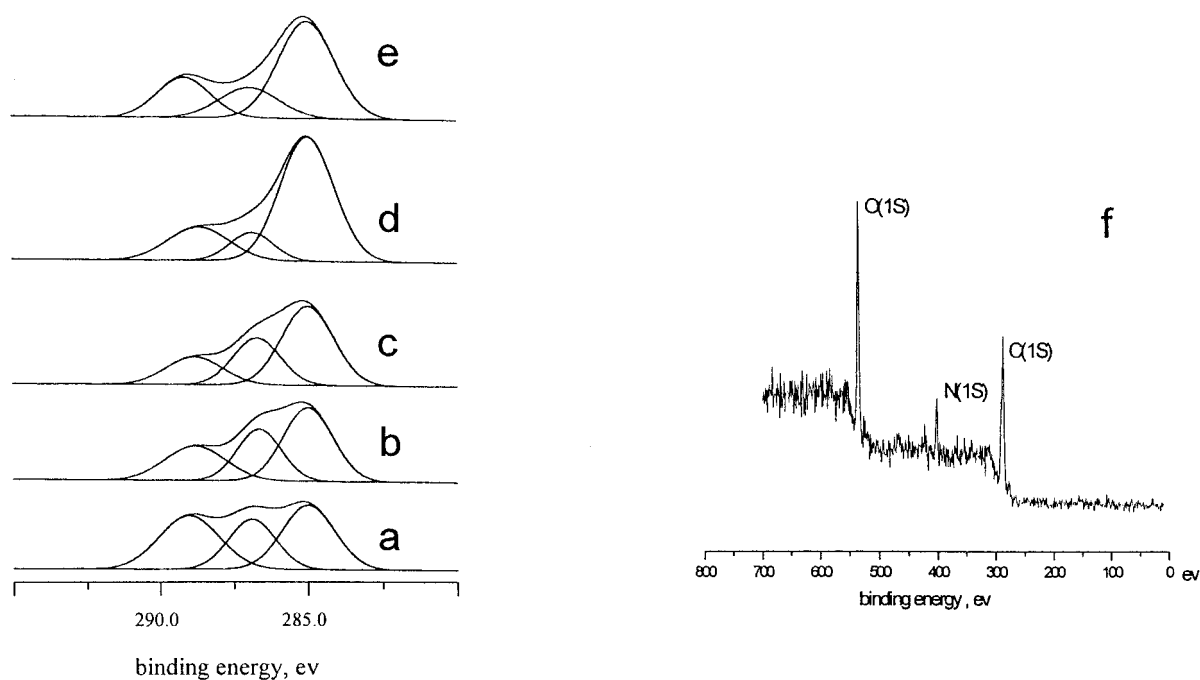
**Table I** ATR Analysis of Control and Modified PLLA Membranes

Sample	Area Ratio of the peak at 2800–3000 $\text{cm}^{-1}$ to the Carbonyl Peak	Area Ratio of the Peak at 3000–3700 $\text{cm}^{-1}$ to the Carbonyl Peak
Control	0.31	
PLLA-g-PHEMA <sup>a</sup>	0.99	0.52
PLLA-g-PHEMA <sup>b</sup>	0.92	0.90
PLLA-g-PAAm <sup>a</sup>	0.74	1.77
PLLA-g-PMAA <sup>a</sup>	3.0	4.2

<sup>a</sup> Monomer concentration, 5%.<sup>b</sup> Monomer concentration, 25%.

with binding energy at  $\sim 285.0$ ,  $\sim 286.6$ , and  $\sim 289.0$  eV, which correspond to the saturated hydrocarbons, carbon atoms with a single bond to oxygen ( $\text{O}-\text{C}-\text{C}=\text{O}$  or  $-\text{C}-\text{O}-\text{C}=\text{O}$ ), and carbon atoms in carbonyl groups ( $-\text{C}=\text{O}$ ), respectively. In the C(1S) spectra of all modified membranes, the area percentage of the peak at 285.0 eV in the total C(1S) peak was larger than that of the control membrane (see Table II) because PHEMA, PAAm, and PMAA all have higher content of saturated hydrocarbons (50, 66, and 75%, respectively) than PLLA (33%). In the spectra of

the membranes grafted with PAAm and PMAA, the peaks at 286.6 eV were much smaller than that of the control membrane (Table II) because these two polymers do not have carbon atoms with a single bond to oxygen. All modified membranes had a higher mole ratio of C to O than the control membrane because the mole ratios of C to O in PHEMA (2 : 1), PAAm (3 : 1), and PMAA (2 : 1) are higher than that in PLLA (3 : 2). These results are consistent with the surface chemical alteration after grafting copolymerization and, hence, further prove the occurrence of the surface



**Figure 4** XPS spectra for C(1S) of (a) control, (b, c) PLLA-g-PHEMA, (d) PLLA-g-PAAm, and (e) PLLA-g-PMAA. (f) Total XPS spectra of PLLA-g-PAAm. Photooxidization time was 40 min, irradiation time 1 h, and the monomer concentration was 5%, except for (c) for which it was 25%.

**Table II** XPS Analysis of Control and Modified PLLA Membranes

Sample	Area Percent of C(1S) Peak at 285.0 eV in Total C(1S) Peak, %	Area Percent of C(1S) Peak at 286.6 eV in Total C(1S) Peak, %	Area Percent of C(1S) Peak at 289.0 eV in Total C(1S) Peak, %	Mole Ratio of C to O
Control	37	26	37	1.71
PLLA-g-PHEMA <sup>a</sup>	44	29	27	1.89
PLLA-g-PHEMA <sup>b</sup>	49	29	22	2.14
PLLA-g-PAAm <sup>a</sup>	65	13	22	2.39
PLLA-g-PMAA <sup>a</sup>	58	19	23	2.05

<sup>a</sup> Monomer concentration, 5%.

<sup>b</sup> Monomer concentration, 25%.

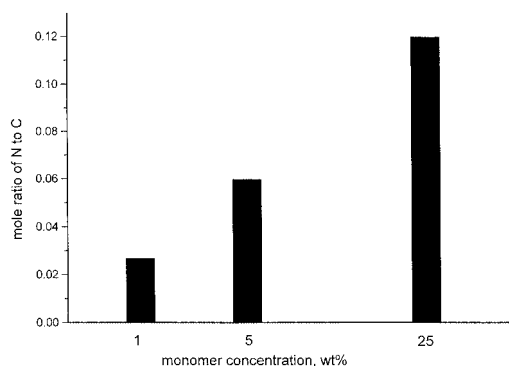
modification. Again, a higher HEMA concentration generated a higher degree of surface variation that corresponds to a higher degree of grafting. In the XPS spectrum of the membrane modified with AAm, the N (1S) peak was very obvious (see Figure 4), directly confirming the grafting of PAAm on the membrane. The mole ratio of N to C on the surface of the PLLA membranes grafted with PAAm increased with the monomer concentration, also indicating that the grafting degree increased with the monomer concentration (see Figure 5).

### Wettability

The water contact angle and water absorption ratio of the control and modified membranes are summarized in Table III. No difference existed between the photooxidized membrane and the control membrane. The water contact angles of PLLA-g-PHEMA, PLLA-g-PAAm, and PLLA-g-PMAA were lowered, whereas the water absorp-

tion ratios were increased. These results indicate that the surface wettability of the modified PLLA membranes was enhanced. When the monomer concentration was increased, the water contact angle became smaller and the water absorption ratio became larger. The lowest water contact angle was found for the membrane grafted with PMAA for both SCA and CBCA. It should be noted that a large degree of water contact angle reduction was found for CBCA compared with SCA. This result is because in air, the hydrophobic sections of the grafted hydrophilic macromolecules tend to segregate near the membrane-air surface, leaving the hydrophobic backbones face towards the air so that the surface free energy can be greatly reduced. On the other hand, the grafted hydrophilic macromolecules rearrange their conformation in water to let the hydrophilic groups face towards the water to reduce the surface free energy, as schematically represented in Figure 6.

The purpose of the modification in this study is to improve the hydrophilicity of the membrane. From the results in Table III it is evident that the water contact angle of the modified PLLA membranes decreased significantly when the monomer concentration rose from 1 to 5%, but didn't decrease or decreased only slightly when the monomer concentration rose from 5 to 25%. On the other hand, we don't expect that much grafting of hydrophilic polymers occurred on the membrane surfaces because these hydrophilic polymers are not biodegradable. The nonbiodegradable hydrophilic polymers will remain in the body, which may induce an inflammation effect for a long time. Therefore, the monomer concentration we prefer is 5%.



**Figure 5** The mole ratio of N to C on the surface of the PLLA membranes grafted with PAAm.

**Table III** Water Contact Angle and Absorption Ratio of Control and Modified PLLA-Membranes<sup>a</sup>

Sample	Monomer Concentration, %	SCA, degree <sup>a</sup>	CBCA, degree <sup>b</sup>	Water Absorption Ratio, 10 <sup>-4</sup> g/cm <sup>2</sup>
Control	—	82.0 ± 2.3	72.2 ± 2.4	1.1 ± 0.1
Photooxidized PLLA <sup>d</sup>	—	81.5 ± 2.8	71.9 ± 3.1	1.2 ± 1.2
PLLA-g-PHEMA	1	69.8 ± 5.28	42.3 ± 2.58	4.0 ± 1.2
PLLA-g-PHEMA	5	51.1 ± 5.54	40.1 ± 3.59	6.2 ± 1.5
PLLA-g-PHEMA	25	55.1 ± 3.7	37.7 ± 1.5	5.5 ± 2.2
PLLA-g-PAAm	1	70.2 ± 3.4	59.6 ± 5.1	2.1 ± 1.5
PLLA-g-PAAm	5	65.4 ± 4.01	41.8 ± 3.76	4.3 ± 1.5
PLLA-g-PAAm	25	59.3 ± 1.63	33.1 ± 4.14	7.8 ± 3.0
PLLA-g-PMAA	1	57.8 ± 4.41	42.1 ± 0.97	4.2 ± 2.5
PLLA-g-PMAA	5	51.0 ± 3.15	39.8 ± 4.41	6.2 ± 3.0
PLLA-g-PMAA	25	57.5 ± 5.49	35.4 ± 3.27	11.0 ± 2.0

<sup>a</sup> Each value was averaged from 15 measurements.

<sup>b</sup> Sessile contact angle.

<sup>c</sup> Captive bubble contact angle.

<sup>d</sup> Photooxidized PLLA membrane without further photografting.

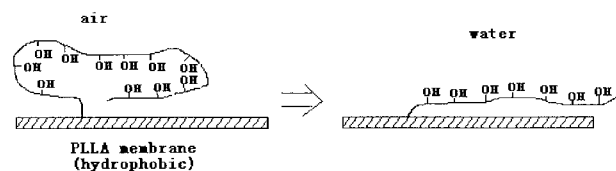
### Surface Morphology

Surface morphology has an important effect on the cytocompatibility of biomaterials. It has been reported that surface morphology plays a critical role in the adhesion process of adjacent cells and that increase of surface roughness promotes more cell adhesion.<sup>24</sup> The surface morphology of the PLLA membranes was observed by scanning electronic microscopy (SEM). As seen in Figure 7, the surfaces that face towards the air (top surface) and the surfaces that face towards the plate (bottom surface) have different morphologies. There are many ripples on the top surfaces, which were formed due to solvent evaporation in the process of the membrane preparation. After grafting with hydrophilic polymers, the membrane surfaces became smoother. When a higher monomer concentration (25 vol %) was used, small particles, which are probably composed of homopolymers that adhered too tightly on the membrane surface to be rinsed, become evident.

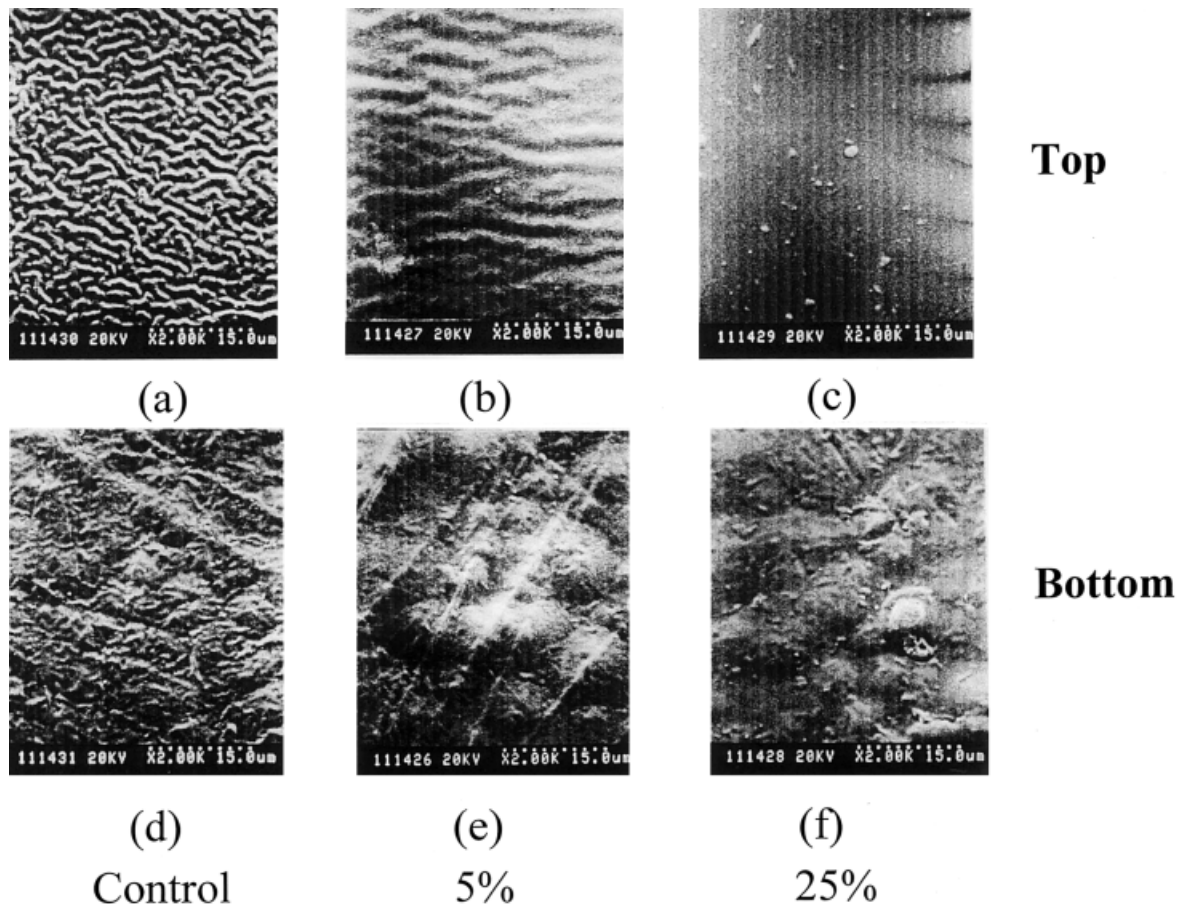
It should be noted that no pores were detected in the SEM photograph ( $\times 10,000$ ) of the PLLA membranes because the membranes were prepared at room temperature and the solvent evaporated very slowly. We don't expect there were pores on the membranes because the homopolymers could enter the pores and would be very difficult to be removed, which made the characterization of the membranes more complicated.

### CONCLUSION

Surface modified PLLA membranes (i.e., PLLA-g-PHEMA, PLLA-g-PAAm, and PLLA-g-PMAA) were obtained by grafting the corresponding monomers onto PLLA membrane surfaces. ATR-IR and XPS analysis confirmed the occurrence of the grafting. The wettability of the grafted membranes was considerably improved. For all three kinds of monomers, the best results can be obtained when the monomer concentration was 5 vol % (for AAm, 5 wt %). It is expected that the increase of the surface hydrophilicity and the alteration of the surface chemical composition may improve the cell compatibility of the material, as found for polyurethane membranes.<sup>17</sup> The functional groups, like hydroxyl and carboxyl, introduced on the PLLA surface may be used to provide a connective bridge to immobilize bioactive species, such as oligopeptides, proteins, and growth factors, and therefore, to construct a more bioactive interface.



**Figure 6** Schematic representation of the conformation of the grafted hydrophilic macromolecule in air and in water, which correspond to the lowest interfacial energy states.



**Figure 7** Morphology of the control (a, d) and PHEM-modified PLLA membranes, with a monomer concentration of (b, e) 5 vol % and (c, f) 25 vol %. The photooxidization time was 40 min, and the irradiation time was 1 h.

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## REFERENCES

- Vacanti, C. A.; Langer, R.; Schloo, B.; Vacanti, Synthetic polymer seeded with chondrocytes provide a template for new cartilage formation. *Plast Reconstruct Surg* 1991, 88, 753.
- Cao, Y.; Vacanti, J. P.; Paige, K. T. Transplantation of chondrocytes utilizing a polymer-cell construct to produce tissue-engineered cartilage in the shape of a human of ear. *Plast Reconstruct Surg* 1997, 100, 297.
- Matsuda, K.; Suzuki, S.; Isshiki, N.; Yoshioka, K.; Okada, T.; Ikada, Y. Influence of glycosaminoglycans on the collagen sponge component of a bilayer artificial skin. *Biomaterials* 1990, 11, 351–355.
- Mikos, A. G.; Lyman, M. D.; Freed, L. E.; Langer, R. L. Wetting of poly (L-lactic acid ) and Poly (DL-lactic-co-glycolic acid ) foams for tissue culture. *Biomaterials* 1994, 15, 55–58.
- van Wachem, P. B.; Beugelling, T.; Feijen, J.; Bantjes, A.; Detmers, J. P.; van Aken, W. G. Interaction of cultured human endothelial cells with polymeric surfaces of different wettabilities. *Biomaterials* 1985, 6, 403.
- Clark, P.; Moores, G. R. Cell guidance by micropatterned adhesiveness in vitro. *J Cell Sci* 1992, 103, 287.
- van Wachem, P. B.; Hoget, A. H.; Beugeling, T.; Feijen, J.; Bantjes, A.; Detmers, J. P.; van Aken, W. G. Adhesion of cultured human endothelial cells onto methacrylate polymers with varying surface wettability and charge. *Biomaterials* 1987, 8, 323.
- Nakajima, K.; Hirano, Y.; Iida, T.; Nakajima, A. Adsorption of plasma proteins on Arg-Gly-Asp-Ser peptide-immobilized poly(vinyl alcohol) and ethylene-acrylic acid copolymer films. *Polym J* 1990, 22, 985.



9. Fujimoto, K.; Tadokoro, H.; Ueda, Y.; Ikada, Y. Polyurethane surface modification by graft polymerization of acrylamide for reduced protein adsorption and platelet adhesion. *Biomaterials* 1993, 14, 442.
10. Lens, J. P.; Harmsen, P. F. H.; Terschegget, E. M.; Terlingen, J. G. A.; Engbers, G. H. M.; Feijen, J. Immobilization of functionalized alkyl-poly(ethylene oxide) surfactants on poly(ethylene) surfaces by means of an argon plasma treatment. *J Biomater Sci, Polym Ed* 1997, 8, 963.
11. Fang, Y. E.; LU, X. B.; Wang, S. Z.; Zhao, X.; Fang, F. Study of radiation-induced graft copolymerization of vinyl acetate onto ethylene-co-propylene rubber. *J Appl Polym Sci* 1996, 62, 2209.
12. Ajayaghosh, A.; Das, S. Photografting of acrylic monomers on polystyrene support. *J Appl Polym Sci* 1992, 45, 1617.
13. Bamford, C. H.; Allamee, K. G. Studies in polymer surface functionalization and grafting for biomedical and other applications. *Polymer* 1994, 35, 2844.
14. Mishra, M. K.; Tripathy, A. K. Graft copolymerization of acrylamide onto polyethylene terephthalate (PET) with potassium permanganate as initiator. *J Appl Polym Sci* 1982, 27, 1845.
15. Feng, X. D.; Sun, Y. H.; Qiu, K. Y. Selective grafting of hydrogels onto multiphase block copolymers. *Makromol Chem* 1985, 186, 1533.
16. Guan, J.; Gao, C.; Feng, L.; Shen, J. Functionalizing of polyurethane surfaces by photografting with hydrophilic monomers. *J Appl Polym Sci* 2000, 77, 2505.
17. Guan, J.; Gao, C.; Feng, L.; Shen, J. Surface photografting of polyurethane with 2-hydroxyethyl acrylate for promotion of human endothelial cell adhesion and growth. *J Biomater Sci, Polym Ed* 2000, 11(5), 523.
18. Schindler, A.; Harper, D. Polylactide. II. Viscosity-molecular weight relationships and unperturbed chain dimensions. *J Appl Polym Sci* 1979, 17, 2593.
19. Hamilton, L. M.; Green, A.; Edge, S.; Babyal, J. P. S.; Feast, W. J.; Pacynko, W.F. The surface modification of polyethylene by solution-phase photochemical grafting using short irradiation times. *J Appl Polym Sci* 1994, 52, 413.
20. Kokatnur, V. R.; Jelling, M. Iodometric determination of peroxygen in organic compounds. *J Am Chem Soc* 1941, 63, 1432.
21. Yuan, X. Y.; Sheng, J.; He, F.; Shen, N. X. Surface modification of acrylonitrile copolymer membranes by grafting acrylamide. II. Initiation by  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ . *J Appl Polym Sci* 1998, 69, 1907.
22. Gerenser, L. J.; Eiman, J. F.; Mason, M. G.; Pochan, J. M. ESCA studies of corona-discharge-treated polyethylene surfaces by use of gas-phase derivatization. *Polymer* 1985, 26, 1162.
23. Bottino, F. A.; DiPasquale, G.; Pollicino, A. XPS study on surface segregation in poly(ethylene-iso/terephthalate)-perfluoropolyether block copolymers. *Macromolecules* 1998, 31, 7814.
24. Lampin, M.; Warocquier-Clerout, R.; Legris, C.; Degrange, M.; Sigot-Luizard, M. F. Correlation between substratum roughness and wettability, cell adhesion, and cell migration. *J Biomed Mater Res* 1997, 36, 99.