

# Fouling Control in a Submerged Membrane-Bioreactor by the Membrane Surface Modification

Wei Li, Jin Zhou, Jia-Shan Gu, Hai-Yin Yu

College of Chemistry and Materials Science, Anhui Key Laboratory of Functional Molecular Solids, Anhui Normal University, Wuhu 241000, China

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**ABSTRACT:** To improve the antifouling characteristics, polypropylene microporous membranes (PPHFMMs) were surface-modified by the sequential photoinduced graft polymerization of acrylic acid and acrylamide. The grafting density and the grafting chain length, which played important roles in the antifouling characteristics, were controlled in the first and the second step, respectively. The ATR/FTIR results clearly indicated the successful modification on the membrane surface. The static water contact angle of the modified membrane reduced obviously with the increase of the grafting chain length. The contact angle of the acrylic acid modified membranes was lower than that of the acrylamide modified membrane with similar grafting chain length. The grafting chain length increased with the increase of UV irradiation time and monomer concentration. The grafting chain length of poly(acrylic acid) (PAAc) was lower than that of the polyacrylamide (PAAm) under the same polymerization conditions. Pure water flux for the modified

membranes increased with the increase of grafting chain length, and had maximums. The antifouling characteristics of the modified membranes in a submerged membrane-bioreactor (SMBR) were evaluated. The modified membranes showed better filtration performances in the SMBR than the unmodified membrane, and the acrylic acid grafted membrane presented better antifouling characteristics than acrylamide modified membranes. The results demonstrated that the surface carboxyl-containing membranes were better than the surface amido-containing membranes. The results of Pearson correlations demonstrated that the PAAc modified membranes with longer grafting chain length had higher flux recoveries, while the PAAm modified membranes with longer grafting chain length had lower flux recoveries. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2302–2309, 2010

**Key words:** fouling; membrane; modification; submerged membrane-bioreactor; wastewater treatment

## INTRODUCTION

The wide application of membrane bioreactor for wastewater treatment and water reuse processing is restricted due to membrane fouling.<sup>1–4</sup> Complex interactions between various parameters, such as membrane characteristics, feed-biomass characteristics, as well as operating conditions, all contribute to a certain extent to membrane fouling in MBRs. As to the membranes, the surface chemical and physical properties, including molecular weight cut-off (MWCO) (or pore size), surface wettability, surface charge and surface acidic/basic character, play dominant roles in determining the antifouling characteristics.

The relative size of the particles and membrane cut-off are directly related to membrane fouling. A

dynamic secondary membrane formed by large particles can be able to capture small particles and thereby slower the rate at which the latter foul the primary membrane.<sup>5</sup>

It is recognized that the antifouling characteristics for the hydrophilic membranes during the filtration of aqueous solutions are better than those for the hydrophobic ones<sup>6,7</sup>; as a result, much work has been done to endow membranes with hydrophilic surfaces.<sup>8–13</sup> Grafting of functional monomers on the membrane surface by the method of UV irradiation was widely used for its superior comprehensive properties.<sup>14–16</sup> The procedure is relatively simple, energy-efficient, and cost-effective. Most of all, when the sequential photoinduced graft polymerization method is adopted, the grafting density and grafting chain length, which play important parts in membrane permeate properties and antifouling characteristics,<sup>17,18</sup> can be regulated independently in the first and second step.

Membrane surface charge also has an important role in membrane fouling, especially when both foulant molecules and membrane surface bear the same charge due to static electric repulsion.<sup>19</sup> The weakly

Correspondence to: H.-Y. Yu (yhy456@mail.ahnu.edu.cn).

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acidic monomer, acrylic acid possesses the best ability to reduce fouling by natural organic matters among the neutral, the weakly acidic, and the strongly acidic monomers.<sup>20</sup>

Jeon<sup>21,22</sup> found that protein adsorption on surface was closely related to the balance between the attractive forces (van der Waals force and hydrophobic force) and the steric repulsive forces. The attractive forces resulted from hydrophobic interaction will become weaker with the increase of the surface hydrophilicity. The repulsive force will become stronger with the increase of grafting chain density and grafting chain length. The longer grafting chains can produce bigger repulsive force, and have higher mobility than the shorter ones, which makes higher hydrophilic layer between protein molecule and membrane surface. The membrane permeability may decrease with the increase of the grafting chain length.<sup>23</sup> Therefore, the grafting chain length and grafting density should be carefully modulated for the enhancement of membranes permeability and membrane antifouling characteristics.

Membrane bioreactor process has been deemed to be a promising technology for wastewater treatment and water reclamation.<sup>24–26</sup> However, membrane fouling is the major limitation to the large-scale application of the MBR process.<sup>27–29</sup> Many attempts have been made to address this problem and to characterize the foulants, and to investigate the possible ways of preventing or at least reducing the fouling. Unfortunately, much attention has been devoted to the control of fouling from an engineering point of view, however, in most cases, the permeate fluxes are determined by the membrane itself.

In our previous studies, PPHFMMs were surface modified by photoinduced grafting polymerization of AAc<sup>30</sup> and AAm,<sup>31</sup> the antifouling characteristic in the SMBRs have been improved to some extent. However, the photoinduced graft polymerization was performed by the one-pot method; the grafting density and grafting chain length, which play important roles in membrane fouling characteristics, were not controlled. On the other hand, the MBR system contains living microorganisms and their metabolites, the biomass biological characteristics and the physico-chemical properties of the suspension vary with the change of operating conditions; the fouling mechanism is even more complex than that of any membrane separation processes. Nevertheless, the effects of the membrane surface modifications on membrane fouling were discussed separately in our previous work.

In this work, surface modification of PPHFMMs by the sequential photoinduced grafting polymerization of AAc and AAm were carried out; grafting chain length was controlled; and the effect of grafting chain length on the antifouling characteristics in

an SMBR were investigated. The factor which mostly affected the membrane fouling among the surface chemical and physical properties was analyzed by the statistics package of social science (SPSS) software. The differences between the graft polymerization behavior of AAc and AAm and the antifouling characteristics for the PAAc and PAAm modified membranes were compared and discussed in this work.

## MATERIALS AND METHODS

### Materials

PPHFMM with a porosity of  $45.9 \pm 3.1\%$  and an average pore diameter of  $0.11 \pm 0.04 \mu\text{m}$  was prepared with a melt-extruded/cold-stretched method in our laboratory.<sup>32</sup> The inner and outer diameters of PPHFMM are 240 and 290  $\mu\text{m}$ , respectively. In this study, U-shape PPHFMM modules were carefully fabricated manually. There were 100 bundles of hollow fibers, each module with an area of about 90  $\text{cm}^2$ . Acrylic acid and acrylamide were used as received. Benzophenone (BP) was recrystallized twice from ethanol and used as photo initiator.

### Photoinduced graft polymerization

UV irradiation was conducted under argon gas environment on an UV illumination system equipped with 2 high-pressure mercury lamp ( $2 \times 300 \text{ W}$  with a wavelength range of 350–450 nm) as the light source with the strongest light emission at 365 nm. The sequential photoinduced graft polymerization method was used in the present study. In the first step, membrane samples were presoaked for 60 min in 50 mL BP solution in heptane, UV irradiation was carried out for 15 min; BP was immobilized on the membranes. In the second step, the BP immobilized membranes were immersed in acetone for 1 min, and then immersed into quartz glass tube containing 50 mL monomer solution in water. After 5 min of equilibration, UV irradiation for a given time followed.

After each step, the samples were taken out and washed with water drastically using a vibrator, dried in a vacuum oven at  $40^\circ\text{C}$  to constant weight. The grafting density ( $\sigma$ ) and grafting chain lengths of PAAc ( $\gamma_1$ ) and PAAm ( $\gamma_2$ ) on the membrane surface were calculated as the following equations<sup>33</sup>:

$$\sigma = \frac{(W_1 - W_0)MW_{BP}}{S} \quad (1)$$

$$\gamma_1 = \frac{(W_2 - W_0)/MW_{AAc}}{(W_1 - W_0)/MW_{BP}} \quad (2)$$

$$\gamma_2 = \frac{(W_3 - W_0)/MW_{AAm}}{(W_1 - W_0)/MW_{BP}} \quad (3)$$

where  $\sigma$  refers to grafting density, mol/cm<sup>2</sup>, in this work,  $\sigma$  of 0.224  $\mu$ mol/cm<sup>2</sup> was obtained under the conditions: UV irradiation of 15 min and BP concentration of 20 wt % according to the literature<sup>18</sup>;  $\gamma_1$  and  $\gamma_2$  the grafting chain length of PAAc and PAAm on the membrane surface, repeating units per chain;  $W_0$  and  $W_1$  stand for the weights of the blank and the BP immobilized membranes,  $W_2$  and  $W_3$  represent the weights of the PAAc and PAAm grafted membranes;  $S$  is the surface area of the membrane;  $MW_{BP}$  (182.22 g/mol),  $MW_{AAc}$  (72.06 g/mol), and  $MW_{AAm}$  (71.08 g/mol) are the molecular weights of BP, AAc, and AAm, respectively.

### Characterization of the membrane surface

ATR/FTIR spectra were recorded on an infrared spectrometer (FTIR-8900, Shimadzu, Japan). The ATR accessory contained a ZnSe crystal at a nominal incident angle of 45°, yielding about 12 internal reflections at the sample surface. All spectra (40 scans at 4.0 cm<sup>-1</sup> resolution and ratio to the appropriate background spectra) were recorded at 25°C.

To evaluate the hydrophilicity of the membrane surface, polypropylene flat microporous membranes with the similar pore size and porosity to PPHFMMs were treated under the same conditions. Water contact angles on these membrane surfaces were measured by the sessile drop method using a DATA Physics System (OCA20, Germany). The average values were calculated from at least five measurements for each membrane. Standard deviation between 1 to 4° was also computed.

### Filtration and antifouling characteristics measurements

Before water flux measurements, all membrane samples were wetted in 50 v/v % ethanol/water for 6 h, filtrated with 50 v/v % ethanol/water for at least 30 min, and then filtrated with pure water to precompact the membranes with the flow from out-to-in for 30 min at 60 kPa.

Before surface modification, the deionized water flux ( $J_{0,u}$ ) was measured at a trans-membrane pressure of 40 kPa. After surface modification, the de-ionized water flux ( $J_{0,m}$ ) was also obtained by the same procedure.

An SMBR was designed to characterize the filtration performance of the unmodified and modified PPHFMMs, the experimental set-up and the operation conditions have been described in detail elsewhere.<sup>34</sup> U-shaped hollow fiber membrane modules were used in the SMBR.

After about 90 hs' continuous operation in the SMBR (when 5 recorded fluxes differed by less than 2%),  $J_p$  was measured. The membranes were taken out from the SMBR and rinsed with deionized water to remove the visible cake on the membrane surface, and then the de-ionized water flux ( $J_1$ ) was measured.

The volumetric flux was determined through the timed collection of the filtrate, and adjusted to a reference temperature of 20°C in order to eliminate the effect of viscosity variations. Then  $J$  was corrected to 400 L/(m<sup>2</sup>h<sup>1</sup>) ( $J = J_{20}/J_{0,u} \times 400$ ) to normalize the filtration differences that exist between the different unmodified PPHFMMs.

$$\mu_T = \mu_{20} \times \exp(0.0239(20 - T)) \quad (4)$$

$$J_{20} = J_T \times \frac{\mu_T}{\mu_{20}} \quad (5)$$

$$J = \frac{J_{20}}{J_{0,u}} \times 400 \quad (6)$$

where  $\mu$  and  $J$  refer to the viscosity and the flux, and the subscripts  $T$  and 20 refer to the mean operating temperature at  $T$  and 20°C, respectively.  $J_{0,u}$  refers to the pure water flux of the unmodified membranes at 20°C.

The antifouling characteristics, such as reduction from the initial pure water flux, flux recovery after water cleaning and flux ratio after fouling, were described by the following equations:

Reduction from the initial pure water flux,

$$RF = \left(1 - \frac{J_p}{J_{0,u}}\right) \times 100\% \quad (7)$$

$$\text{Flux recovery after water cleaning, FR} = \frac{J_1}{J_{0,u}} \times 100\% \quad (8)$$

$$\text{Flux ratio after fouling} = \frac{J_{p,m}}{J_{p,u}} \quad (9)$$

where the subscripts  $m$  and  $u$  refer to the modified and unmodified membrane.

The statistics package of social science (SPSS, Version 11.5) was used to analyze the Pearson correlations between grafting chain length, water contact angle and reduction from the initial pure water flux, flux recovery after water cleaning, and flux ratio after fouling, respectively. The Pearson correlations ( $r_{xy}$ ) were calculated by SPSS software according to the literature.<sup>32</sup>

$$r_{xy} = \frac{\sum_{i=1}^{i=n} (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{i=n} (x_i - \bar{x})^2 (y_i - \bar{y})^2}} \quad (10)$$

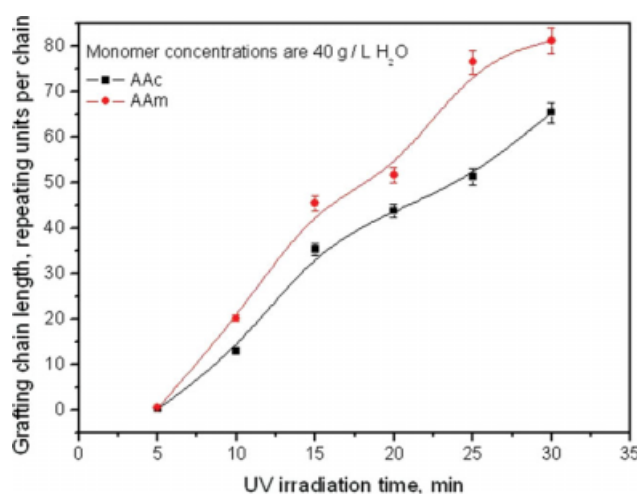
where  $x$  is observed value of grafting chain length and water contact angle;  $x_i$  is number  $i$  value of  $x$ .  $y$  is observed value of reduction from the initial pure water flux, flux recovery and flux ratio after fouling;  $y_i$  is number  $i$  value of  $y$ .

## RESULTS AND DISCUSSION

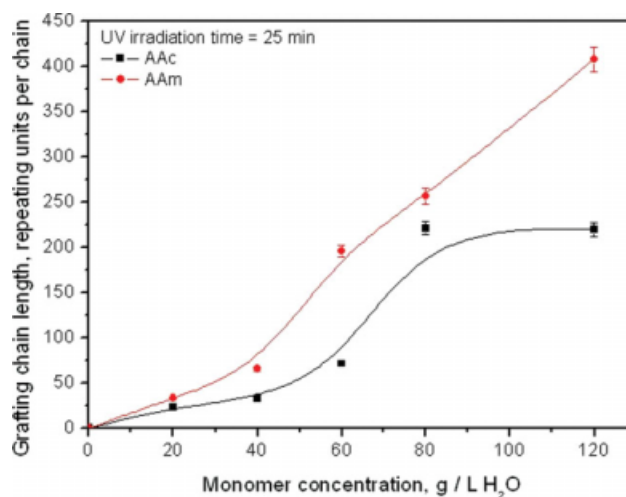
### Photoinduced graft polymerization and characterization of PPHFMMs

Figure 1 shows the effect of UV irradiation time on the grafting chain length of PAAC and PAAM on the membrane surface. It can be found that grafting chain length increases with the increase of UV irradiation time systematically because much more surface radicals generated and much more monomers got accessible to the surface radicals with the prolongation of reaction time. The grafting chain length of the PAAM is higher than that of the PAAC under the same condition. This may be due to that the solution viscosity of PAAM is higher than that of the PAAC, leading to the gel formation on the membrane surface.

The variation of grafting chain length with the monomer concentration is depicted in Figure 2, which shows that the grafting chain length increases with the rise of the monomer concentration. These results indicate that grafting chain length, which is expected to have potential advantages in surface modification for controlling membrane fouling in an MBR,<sup>18</sup> could be controlled by adjusting UV irradiation time and monomer concentration. Thus the grafting density and grafting chain length could be



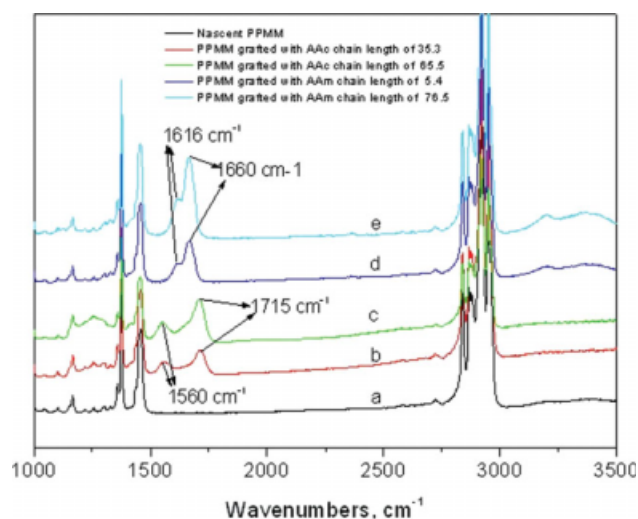
**Figure 1** Effect of UV irradiation time on the grafting chain lengths of PAAC and PAAM on the membrane surface, the monomer concentrations are set at 40 g/L. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



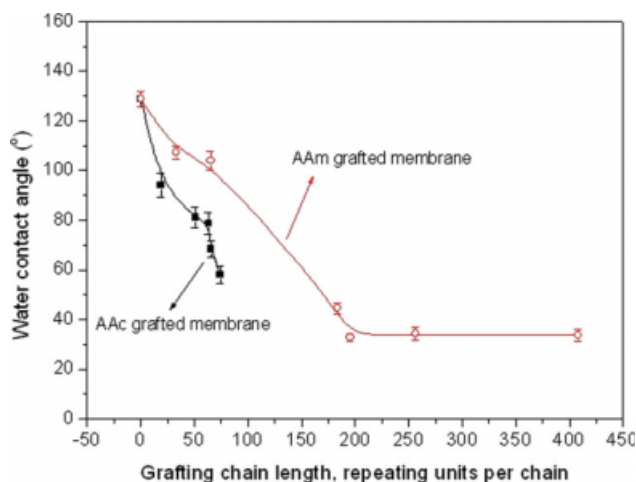
**Figure 2** Variation of the grafting chain lengths of PAAC and PAAM on the membrane surface with the monomer concentration, UV irradiation time is set at 25 min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

controlled independently in the first and second step, respectively.

The graft polymerization of AAC and AAM onto the membrane surface was confirmed by ATR/FT-IR analysis. Typical spectra for the nascent and modified membranes are depicted in Figure 3. The adsorption peaks at 1666 and 1616  $\text{cm}^{-1}$  are the characteristics of amide I and amide II, respectively. The adsorption peaks at 1715 and 1560  $\text{cm}^{-1}$ , characteristic of carbonic stretching of C=O and



**Figure 3** FTIR/ATR spectra for (a) the nascent membrane, (b,c) PAAC grafted membranes with chain lengths of 35.3 and 65.4 repeating units per chain, (d,e) PAAM grafted membranes with grafting chain lengths of 5.4 and 76.5 repeating units per chain, respectively. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



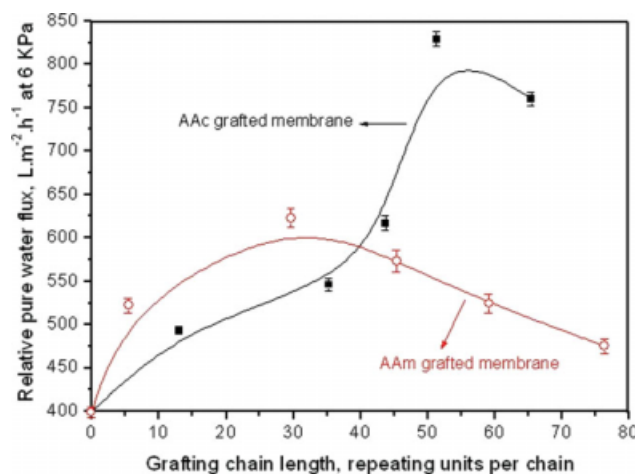
**Figure 4** Dependence of water contact angle on the grafting chain length. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

anti-symmetric stretching vibrations of carboxylate<sup>35</sup> arising from the graft polymer. These results indicate the successful graft polymerization of AAc and AAm on the membrane surface. With the increase of the grafting chain length, the intensity of these absorption bands increased.

Water contact angle was used to characterize the relative hydrophilicity or hydrophobicity of the membrane surface. Values on the membrane surface before and after surface modification are shown in Figure 4. Water contact angle on the modified membrane surface tends to decline with the increase of the grafting chain length. For example, for the PAAc modified membrane with grafting chain lengths of 65.4 and 13.0 repeating units per chain are 68° and 94.1°, respectively. Water contact angle of AAm-grafted membrane with grafting chain length of 408.4 and 33.3 repeating units per chain are 26.4° and 107.2°, which reflects that the water contact angles for the PAAc grafted membranes with the similar grafting chain length are lower than that of the PAAm grafted membranes.

#### Filtration and antifouling characteristics of the PPHFMMs

The pure water fluxes for the membranes before and after surface modification are shown in Figure 5,



**Figure 5** Variation of pure water flux with the grafting chain length. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

which displays that the pure water flux increases with the increase of the grafting chain length, then it decreases with the increase of the grafting chain length. The maximum grafting chain length for the PAAc and PAAm grafted membranes are 51.31 and 30.00 repeating units per chain, respectively. It is commonly recognized that pore size/porosity and surface hydrophilicity/hydrophobicity are the two parameters affecting pure water flux mostly. The membrane permeability increases with the increase of surface hydrophilicity and decreases with decrease of the pore size and porosity. In our cases, when the grafting chain length is shorter, the surface hydrophilicity is the dominant factor and the water flux accordingly increases with the increase of the grafting chain length despite slight pore blocking. However, pore blocking is the leading factor when the grafting chain length is too long, causing the decline of water flux.

To study the effect of surface modification on the antifouling characteristics, filtration of activated sludge in a submerged aerobic MBR was carried out. The antifouling characteristics of the studied membranes, such as RF, FR, and flux ratio after fouling, are shown in Table I (PAAc modified membranes) and Table II (PAAm modified membranes).

Table I shows that after continuous operation in the SMBR for about 90 h, RF, FR, and flux ratio after

**TABLE I**  
RF, FR, and Flux Ratio After Fouling for the Membrane Before and After Graft Polymerization of Acrylic Acid

Grafting chain length	0	0.19	12.98	35.3	43.74	51.31
RF = $(1 - J_p/J_{0,u}) \times 100\%$	98.9	97.4	98.7	98.7	97.4	97.2
FR = $(J_1/J_{0,u}) \times 100\%$	13.7	25.5	20.9	19.2	25.2	19.7
Flux ratio after fouling = $(J_p)_m/(J_p)_u$	1.00	2.36	1.18	1.20	2.39	2.52

**TABLE II**  
**RF, FR, and Flux Ratio After Fouling for the Membrane Before and After Graft Polymerization of Acryamide**

Grafting chain length	0	29.71	59.18	76.5
RF = $(1 - J_p/J_{0,u}) \times 100\%$	36.9	63.7	39.3	35.5
FR = $(J_1/J_{0,u}) \times 100\%$	74.8	66.7	71.9	69.2
Flux ratio after fouling = $(J_p)_m/(J_p)_u$	1.00	1.32	1.12	1.22

fouling for PAAc modified PPHFMMs with a grafting chain length of 51.31 are 1.7% lower, 6.0% and 152% higher than those of the nascent PPHFMM, respectively.

Table II shows that after continuous operation in the SMBR for about 90 h, FR are 74.8, 66.7, 71.9, 69.2%, flux ratio after fouling are 1.00, 1.32, 1.12, and 1.22 for the nascent and PAAm modified PPHFMMs with the grafting chain length of 29.71, 59.18, and 76.5 repeating units per chain. RF and flux ratio after fouling for PAAm modified PPHFMMs with a grafting chain length of 29.71 repeating units per chain are 26.8% and 32% higher than those of the nascent PPHFMM, respectively.

It can also be found from Table I and Table II that the surface carboxyl-containing membranes are better than the surface amido-containing membranes in the antifouling characteristics<sup>36</sup>: FR is lower, RF and flux ratio after fouling for the PAAc modified membranes are higher than those of the PAAm modified membranes. These results can be explained by the following reasons.

Extracellular polymeric substances (EPS) in MBRs are in the form of carbohydrates, proteins, humic substances, and sometimes also lipids,<sup>37</sup> and it has been reported as key membrane foulants in membrane bioreactor systems.<sup>38,39</sup> They are considered to aid in biofloculation (floc formation), enhance microbial attachment to membrane surface<sup>40</sup> and act as a diffusion barrier, retarding convective flow and transport of anti-microbial agent during membrane cleaning.

The primary forces that drive EPS protein adsorption to a membrane surface are hydrophobic dehydration resulting from the interaction between hydrophobic patches on a protein and a hydropho-

bic surface.<sup>41</sup> A general trend is that protein adsorption decreases with increasing hydrophilicity of the surface.

Proteins are composed of amino acids linked into a linear sequence by amide bonds known as peptide bonds.<sup>42</sup> These amino acids are amphoteric compounds and carry either a negative or a positive charge in solution, depending on the isoelectric point.<sup>41</sup> Both the nature colloid molecules and PAAc modified membrane surface were negatively charged at pH = 7.0,<sup>30,43</sup> the foulant can't reach the membrane surface because of electric repulsion, as a result, the PAAc modified membrane has better anti-fouling characteristics than the PAAm modified membrane.

The repulsive force, which would prevent EPS protein molecules from contacting membrane effectively, increases with the increase of the grafting chain length. Long grafting chain length could provide big repulsive force coming from conformation changes and desolvation, and has high mobility as well, which made high hydrophilic layer form between protein molecule and membrane surface. However, if the grafting chain length is too long, the membrane permeability will reduce, as a result, modified membranes with medium grafting chain length will have higher permeability and better anti-fouling characteristics.

The fouling mechanism is very complex in an MBR system, and many a factor contributes to membrane fouling. To find out which of these factor(s) affects the antifouling characteristics mostly, Pearson correlations between grafting chain length, water contact angle and reduction from the initial pure water flux, flux recovery and flux ratio after fouling for the PAAc (Table III) and PAAm (Table IV)

**TABLE III**  
**Pearson Correlations of Grafting Chain Length and Water Contact Angle with Reduction from the Initial Pure Water Flux, Flux Recovery, and Flux Ratio After Fouling for the PAAc Grafted Membranes**

	Reduction from the initial pure water flux	Flux recovery	Flux ratio after fouling
Grafting chain length	-0.458	0.195	0.463
Water contact angle	0.448	-0.136	-0.447

**TABLE IV**  
**Pearson Correlations of Grafting Chain Length and Water Contact Angle with Reduction from the Initial Pure Water Flux, Flux Recovery, and Flux Ratio After Fouling for the PAAm Grafted Membranes**

	Reduction from the initial pure water flux	Flux recovery	Flux ratio after fouling
Grafting chain length	-0.237	-0.438	0.445
Water contact angle	0.106	0.529	-0.537

grafted membranes were conducted by the SPSS software.

Table III and IV demonstrate that water contact angle is positively correlated with reduction from the initial pure water flux, and negatively correlated with flux ratio after fouling. This result indicates that membranes with lower water contact angles (more hydrophilic) have the better antifouling characteristics. However, the Pearson correlations between water contact angle and flux recovery for the AAc, AAm modified membranes are negative and positive, respectively. For both of the AAc and AAm modified membranes, the longer grafting chains, the lower water contact angles, the membrane pores would be blocked to some extent, the water flux would be affected by the combinative effect of the surface hydrophilicity and membrane pore size, and as a result, flux recovery would be affected accordingly, which has been analyzed above.

Pearson correlation ( $r_p$ ) is used to estimate linear estimations.  $r_p = -1$  and  $+1$  means the perfect correlation, while  $0$  means an absence of a relationship. Correlations are considered statistically significant at the 95% confidence interval ( $P < 0.05$ ). In the present work, Pearson correlations between grafting chain length and reduction from the initial pure water flux, flux ratio after fouling for both of the PAAc and PAAM modified membranes are negative and positive, respectively. These results indicate that membranes with longer grafting chain lengths will have lower reduction from the initial pure water flux and higher flux ratio after fouling. Nevertheless, grafting chain length is positively and negatively correlated with flux recovery for the PAAc and PAAM modified membranes. This result shows that the PAAc modified membranes with longer grafting chain length would have higher flux recoveries; while the PAAM modified membranes with shorter grafting chain length would have higher flux recoveries. These results are in good agreement with the above analysis: pure water flux increases with the increase of grafting chain length for the PAAc and PAAM modified membranes, and has a maximum value for the AAc and AAm modified membranes. The maximum value for the PAAc modified membrane is higher than that of the PAAM modified membrane.

### CONCLUSION

Polypropylene hollow fiber microporous membranes were surface-modified by the sequential photoinduced graft polymerization of acrylic acid and acrylamide to improve the antifouling characteristics in a submerged membrane-bioreactor. The grafting chain length increased with the increase of UV irradiation time and monomer concentration. The grafting chain

length of poly(acrylic acid) was lower than that of the polyacrylamide under the same polymerization conditions. ATR/FTIR analysis confirmed the successful membrane surface modification. Contact angle decreased systematically with the increase of the grafting chain length. The contact angle on the poly(acrylic acid) modified membrane surfaces was lower than that on the polyacrylamide modified membrane surfaces with similar grafting chain length.

Pure water flux for the modified membranes increased with the increase of grafting chain length up to certain values, and then it decreased continuously. The modified membranes showed better filtration behaviors in the submerged membrane-bioreactor than the unmodified membrane. The poly(acrylic acid) grafted membranes had better antifouling characteristics than the polyacrylamide grafted membranes. Results of Pearson correlations demonstrated that the poly(acrylic acid) modified membranes with longer grafting chain length would have higher flux recoveries, while the polyacrylamide modified membranes with longer grafting chain length would have lower flux recoveries.

### Reference

- Meng, F. G.; Yang, F. L.; Shi, B. Q.; Zhang, H. M. *Sep Purif Technol* 2008, 59, 91.
- Huang, X.; Wu, J. L. *J Membr Sci* 2008, 318, 210.
- Koseoglu, H.; Yigit, N. O.; Iversen, V.; Drews, A.; Kitis, M.; Lesjean, B.; Kraume, M. *J Membr Sci* 2008, 320, 57.
- Grelot, A.; Machinal, C.; Drouet, K.; Tazi-Pain, A.; Schrotter, J. C.; Grasmick, A.; Grinwis, S. *Water Sci Technol* 2008, 58, 2041.
- Kuberkar, V. T.; Davis, R. H. *J Membr Sci* 2000, 168, 243.
- Wei, X.; Wang, R.; Li, Z. S.; Fane, A. G. *J Membr Sci* 2006, 273, 47.
- Yu, H.-Y.; He, X.-C.; Liu, L.-Q.; Gu, J.-S.; Wei, X.-W. *Water Res* 2007, 41, 4703.
- Rahimpour, A.; Madaeni, S. S.; Taheri, A. H.; Mansourpanah, Y. *J Membr Sci* 2008, 313, 158.
- Kang, G.-D.; Liu, M.; Lin, B.; Cao, Y.-M.; Yuan, Q. *Polymer* 2007, 48, 1165.
- Gupta, B.; Mishra, S.; Saxena, S. *Radiat Phys Chem* 2008, 77, 553.
- Lohokare, H. R.; Kumbharkar, S. C.; Bhole, Y. S.; Kharul, U. K. *J Appl Polym Sci* 2006, 101, 4378.
- Khayet, M.; Suk, D. E.; Narbaitz, R. M.; Santerre, J. P.; Matsuura, T. *J Appl Polym Sci* 2003, 89, 2902.
- Yu, H.-Y.; Tang, Z.-Q.; Huang, L.; Cheng, G.; Li, W.; Zhou, J.; Yan, M.-G.; Gu, J.-S.; Wei, X.-W. *Water Res* 2008, 42, 4341.
- Yu, H.-Y.; He, J.-M.; Liu, L.-Q.; He, X.-C.; Gu, J.-S.; Wei, X.-W. *J Membr Sci* 2007, 302, 235.
- Kang, J. S.; Lee, S. H.; Huh, H.; Shim, J. K.; Lee, Y. M. *J Appl Polym Sci* 2003, 88, 3188.
- Ma, Z. W.; Gao, C. Y.; Juan, J.; Ji, J.; Gong, Y. H.; Shen, J. C. *J Appl Polym Sci* 2002, 85, 2163.
- Wang, Y.-Q.; Su, Y.-L.; Ma, X.-L.; Sun, Q.; Jiang, Z.-Y. *J Membr Sci* 2006, 283, 440.
- Gu, J.-S.; Yu, H.-Y.; Huang, L.; Tang, Z.-Q.; Li, W.; Zhou, J.; Yan, M.-G.; Wei, X.-W. *J Membr Sci* 2009, 326, 145.
- Gancarz, I.; Pozniak, G.; Bryjak, M. *Eur Polym J* 1999, 35, 1419.

20. Taniguchi, M.; Kilduff, J. E.; Belfort, G. *J Membr Sci* 2003, 222, 59.
21. Jeon, S. I.; Lee, J. H.; Andrade, J. D.; De Gennes, P. G. *J Colloid Interf Sci* 1991, 142, 149.
22. Jeon, S. I.; Andrade, J. D. *J Colloid Interf Sci* 1991, 142, 159.
23. Pieracci, J.; Crivello, J. V.; Belfort, G. *Chem Mater* 2002, 14, 256.
24. Pollice, A.; Giordano, C.; Laera, G.; Saturno, D.; Mininni, G. *Water Res* 2007, 41, 1832.
25. Kim, S. D.; Cho, J.; Kim, I. S.; Snyder, B. J. V. A. *Water Res* 2007, 41, 1013.
26. Zein, M. M.; Suidan, M. T.; Venosa, A. D. *Environ Sci Technol* 2006, 40, 1997.
27. Trussell, R. S.; Merlo, R. P.; Hermanowicz, S. W.; Jenkins, D. *Water Res* 2007, 41, 947.
28. Miura, Y.; Watanabe, Y.; Okabe, S. *Environ Sci Technol* 2007, 41, 632.
29. Chae, S. R.; Ahn, Y. T.; Kang, S. T.; Shin, H. S. *J Membr Sci* 2006, 280, 572.
30. Yu, H.-Y.; Xu, Z.-K.; Yang, Q.; Hu, M.-X.; Wang, S.-Y. *J Membr Sci* 2006, 281, 658.
31. Yu, H.-Y.; Xu, Z.-K.; Lei, H.; Hu, M.-X.; Yanga, Q. *Sep Purif Technol* 2007, 53, 119.
32. Yu, H.-Y.; Xu, Z.-K.; Xie, Y.-J.; Liu, Z.-M.; Wang, S.-Y. *J Membr Sci* 2006, 279, 148.
33. Ma, H. M.; Davis, R. H.; Bowman, C. N. *Macromolecules* 2000, 33, 331.
34. Yu, H.-Y.; Xie, Y.-J.; Hu, M.-X.; Wang, J.-L.; Wang, S.-Y.; Xu, Z.-K. *J Membr Sci* 2005, 254, 219.
35. Wang, L.-H.; Chen, Z.-K.; Kang, E.-T.; Zhang, W.-G.; Huang, W. *Synth Met* 2001, 118, 39.
36. Yu, H.-Y.; Liu, L.-Q.; Tang, Z.-Q.; Yan, M.-G.; Gu, J.-S.; Wei, X.-W. *J Membr Sci* 2008, 310, 409.
37. Al-Halbouni, D.; Dott, W.; Hollender, J. *Water Res* 2009, 43, 97.
38. Ye, Y.; Le Clech, P.; Chen, V.; Fane, A. G. *J Membr Sci* 2005, 264, 190.
39. Lee, S. B.; Koepsel, R. R.; Morley, S. W.; Matyjaszewski, K.; Sun, Y. J.; Russell, A. J. *Biomacromolecules* 2004, 5, 877.
40. Lim, A. L.; Bai, R. *J Membr Sci* 2003, 216, 279.
41. Nath, N.; Hyun, J.; Ma, H.; Chilkoti, A. *Surf Sci* 2004, 570, 98.
42. Her, N.; Amy, G.; Plottu-Pecheux, A.; Yoon, Y. *Water Res* 2007, 41, 3936.
43. Le-Clech, P.; Chen, V.; Fane, T. A. G. *J Membr Sci* 2006, 284, 17.