PVDF Hollow fiber Membrane with High Flux and High Rejection Ratio Prepared by Irradiation Induced Grafting of PAA

Wei Junfu,[*1,2] *Zhao Kongyin,*[1,2] *Wang Lei,*[2] *Zhang Huan,*[1] *Chen Li,*[2] *Zhang Zhengpu*[3]

Summary: A modified poly (vinylidene fluoride) (PVDF) hollow fiber membrane with higher flux and flux recovery rate was prepared by γ-radiation induced grafting of acrylic acid (AA). The influence of radiation dose and monomer concentration on the grafting degree was investigated. The results indicated that the grafting degree increased in the lower monomer volume fraction until the monomer volume fraction exceeded 20%. The grafting degree increased with the increase of radiation dose. Structural and morphological of the original and grafted membrane surface were characterized by FT-IR, scanning electron microscopy (SEM). The results indicated that acrylic acid was grafted onto PVDF hollow fiber membrane and the grafted membrane was more hydrophilic than original PVDF. There was a slight increase of breaking strength and yield stress with the increase of the grafting degree of AA. The pure water flux increased initially but decreased subsequently with the raise of grafting degree. When the grafting degree was 4.4%, the maximum pure water flux reached 1496.3 $L/m^2 \times h$, 1.79 times of original membrane. The pure water flux, flux recovery rate and rejection ratio for bovine serum albumin could improve simultaneously in a low grafting degree ($<$4.4%).

Keywords: acrylic acid; filtration; flux; high pure water flux; irradiation induced grafting; PVDF hollow fiber membrane; rejection ratio

Introduction

Among all water treatment technologies, membrane technology seems to be the most promising. Poly (vinylidene fluoride) (PVDF) membranes are widely used in microfiltration and ultrafiltration due to their excellent chemical resistance, well-controlled porosity and good thermal properties.[1] However, the application of PVDF membranes is limited by the hydrophobic nature of their surfaces. In recent years, polymer membranes with pore structures and specifically functionalized surfaces attract more and more attention.[2] As the result of the charged groups introduced onto the membrane interface, the membrane becomes more hydrophilic. The negative charge is capable of minimizing adsorption of negatively charged foulants and increasing the rejection of dissolved salts.[3]

The hydrophilic and antifouling properties of the PVDF membrane can be improved by introducing hydrophilic groups into the surface of PVDF. There is widespread concern about the modification of PVDF by grafting of acrylic monomers like acrylic acid,[4] methacrylic

[1] The State Key Laboratory Cultivation Base of Hollow Fiber Membrane Materials and Membrane Process, Tianjin Polytechinic University, Tianjin 300160, China
Fax: (+86) 022 24528451;
E-mail: jfwei@tjpu.edu.cn
[2] School of Material Science and Engineering, Tianjin Polytechinic University, Tianjin 300160, China
Fax: (+86) 022 24528454;
E-mail: zhaokongyin@tjpu.edu.cn
[3] The State Key Laboratory of Adsorption & Separation of Functional Polymer Materials, Nankai University, Tianjin 300071, China

acids and 4-vinylpyridine[5] to increase membrane hydrophilicity and fouling resistance properties. Among the various modification techniques, grafting of the acrylic acid polymer onto PVDF membranes is a good way to improve the hydrophilic properties of the membrane.[6] Besides, acrylic acid and vinyl amine grafted PVDF membranes were found to have temperature sensitivity.[7] The membranes undergo a discontinuous phase transition and change their configuration in response to temperature changes.

Radiation-induced graft polymerization is a valuable method for the modification of the chemical and physical properties of polymer surfaces. Betz N et al.[8] reported acrylic acid grafted PVDF by ionizing radiation induced copolymerization. Saito Betz N et al.[9] prepared a strongly acidic cation-exchange porous hollow-fiber membrane with high water permeability and high affinity for sodium ion. The cation-exchange membrane immobilizing uncross-linked graft chains exhibited a negligible pure water flux, whereas that immobilizing cross-linked graft chains with a degree of cross-linking of 6% had a 1.2-fold higher pure water flux than the original hollow-fiber membrane.

Although the functional PVDF membrane prepared by radiation grafting has received more and more attention, the γ-ray radiation grafted PVDF hollow fiber membrane with high water flux, high rejection ratio and flux recovery rate has seldom been reported.

In our previous literature a weakly acidic cation exchange fiber have been prepared by ^{60}Co irradiation grafting with acrylic acid onto the polytetrafluoroethylene (PTFE) fiber.[10] The aim of this work is to prepare a modified PVDF hollow fiber membrane by γ-radiation induced grafting of acrylic acid onto PVDF. The influence of preparation conditions such as radiation dose and monomer concentration on the grafting degree of PVDF will be discussed. PVDF-g-AA with different grafting degree (9%-22%) was prepared and the grafted membranes were characterized by FT-IR and scanning electron microscopy (SEM). The pure water flux, flux recovery rate and rejection ratio for bovine serum albumin were investigated.

Experimental Part

Reagents and Materials

The poly (vinylidene fluoride) (PVDF) fiber was from Motianmo Co., Ltd., Tianjin, China. Glycerol and ethanol was purchased from Pharmaceutical Company in Tianjin. Bovine serum albumin (BSA) was obtained from the Institute of Hematology, Chinese Academy of Medical Science, electrophoretic grade. Acrylic acid (AA) and eight hydrated ferrous ammonium sulfate were from Kewei Chemical Reagent Company and used without further purification. All the other reagents used in this research were an analytical grade (AR).

Preparation of Acrylic Acid Grafted PVDF Hollow Fiber Membrane (PVDF-g-AA)

The PVDF hollow fiber membrane was immersed in ethanol for 48h, and then dried in a vacuum oven at 60 °C for 4h and weighed. The treated membrane was joined into a glass tube, containing acrylic acid in aqueous solution with different concentrations (0.1%-40%, v/v), 2wt % Mohr's salt and 0.2wt% sulfate acid. The reactant mixtures in the glass flask were aerated by bubbling nitrogen gas for 10 min and sealed with silica gel membrane. The mixture was irradiated by ^{60}Co γ-ray at room temperature with a dose rate of 1kGy/h-2kGy/h and the total radiation dose ranged from 10kGy-25kGy. The resulting AA grafted PVDF (PVDF-g-AA) fibers were washed with plenty of ethanol and water to remove the unreacted monomer and homopolymer.

Characterization of PVDF-g-AA

Infrared spectra were obtained with VECTOR22 Spectrometer (BRUKER Co. Ltd.) equipped with a continuum microscope and an ATR objective.

The dry hollow fiber samples were immersed in liquid nitrogen and fractured,

and then sputtered with platinum. SEM micrographs of PVDF and PVDF-g-AA were obtained with QUANTA 200 scanning electron microscope.

The grafted PVDF membrane was dried in a vacuum oven at 70 °C for 48h and weighed. The degree of grafting (G) was obtained using the following formula:

$$G = \frac{W_g - W_0}{W_0} \times 100\% \quad (1)$$

where W_o and W_g is the weight of the original and grafted fiber, respectively.

Amount of 0.2 g of PVDF hollow fiber was immerged in the water to be fully wetted. The surface of water on the fiber was adsorbed and the wet fiber was weighed. Then the wet fiber was vacuum dried at 60 °C to constant weight and weighed. The overall porosity (Pr) of the PVDF hollow fiber can be calculated as

$$P_r = \left(1 - \frac{m_d/\rho_{PVDF}}{(m_w - m_d)/\rho_w + m_d/\rho_{PVDF}}\right) \times 100\% \quad (2)$$

where m_d and m_w are the mass of dried and wet PVDF hollow fiber, respectively. ρ_{PVDF} and ρ_w are the densities of PVDF (1.78g/cm^3) and water (1.00g/cm^3), respectively.[11]

Performance Measurement

The maximal diameter of the pores of hollow fiber membrane (d) was measured by bubble point technique.[12] COULTER POROMETER with a measurement range of 0.05∼300 μm was used to investigate the maximal pores of the grafted membrane according to the ASTM F-316-80 procedure.[13] One end of the membrane is immersed in ethanol (surface tension 22.32 dynes cm^{-1}) and nitrogen gas is aerated from another side. The pressure of nitrogen is gradually increased until the nitrogen gas goes through the wall of the hollow fiber membrane. Then the nitrogen pressure at this time is recorded as the pressure at the beginning bubble point. The maximal diameter of the pore (d, μm) is calculated from the following formula:

$$d = \frac{2\sigma\cos\theta}{P} \quad (3)$$

where P is the pressure of beginning bubble point (MPa), σ is the surface tension of liquid, and θ is the contact angle between the liquid and hollow fiber membrane.

In this experiment, the contact angles were measured using a flat sheet membrane prepared with the same condition as PVDF hollow fiber membrane at Y82 contact angle meter. The deionized water was dropped on the membrane surface at 5 different points and the average of measured values was taken as its water contact angle.

The pure water flux (L/m^2 × h) and Flux Recovery rate (%) was measured according to the reference with the pressure of 0.1 MPa.[9] The rejection ratio (R) (%) for bovine serum albumin (BSA) was carried out using 2000 mL of 1 g/L BSA solutions. Under a constant pressure of 0.1 MPa after equilibrium, every 5 minutes the concentration of BSA in solutions before and after permeating the membrane was detected by an UV spectrophotometer (UV2450) at 280 nm. The rejection ratio (R) is calculated like this

$$R = \frac{A_{in}£ - A_{out}}{A_{in}} \times 100\% \quad (4)$$

where A_{in} and A_{out} is the UV absorbance of BSA in solutions before and after permeating the membrane, respectively.

The breaking strength, yield strength and elongation at break of PVDF and PVDF-g-AA membrane were measured by an Electronic Single Fiber Strength Tester (PC/LLY06).

Results and Discussion

Preparation of PVDF-g-AA

The γ-radiation could cleave the C–H bond of the surface PVDF to form surface radicals and the monomer would react with surface radicals. Thus, the desired polymer chains were grafted onto PVDF hollow

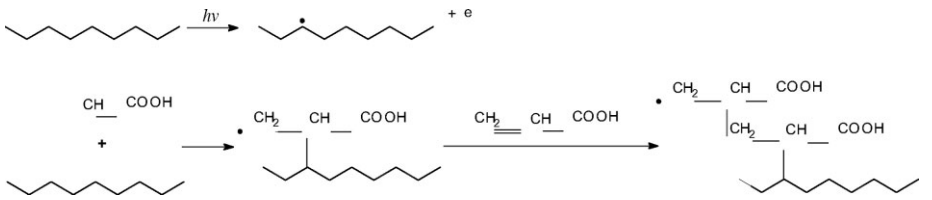

Figure 1.
Schematic diagram of γ-radiation induced grafting polymerization.

fiber membrane by radical polymerisation of AA. The mechanism for the preparation of PVDF-g-AA is as follows:

The mass of covalently bound AA on the PVDF depends upon the γ-ray dose, the monomer concentration and grafting time. Figure 2 shows the grafting degree of PVDF-g-AA prepared with different radiation doses. It is found that, for the same dose rate and concentration of monomer, the grafting degree increased with the increase of radiation dose from 10 kGy to 25 kGy. Because the concentration of peroxide increased with the raise of radiation dose, the grafting degree increased with the increase of radiation dose.

It is found in Figure 3 that the grafting degree increased initially but decreased subsequently with the increase of the monomer concentration. The maximal grafting degree of AA reached 22.03% when the concentration of AA was 20% (v/v). In a low concentration of AA (<20%, v/v), the grafting polymerization proceeded satisfactorily with the increase of the monomer concentration. However, when the concentration of AA was greater than 20% (v/v) in solutions, the homopolymer yield increased along with a sharp rise in the grafting degree.[4] In this case, it was very difficult to wash out the gelatinous poly (acrylic acid) from PVDF. So the concentration of AA was usually controlled to below 10% (v/v).

Characterization of PVDF-g-AA

Figure 4 shows the FT-IR spectra of original and the grafted PVDF membrane. Compared to original PVDF, new band appeared at 1725 cm^{-1} and 3500-2900 cm^{-1} in the grafted PVDF due to the stretching vibrations of C = O and O-H. The bands at 1454 cm^{-1} was corresponding to the bending vibration of O-H. The broad adsorption band at 3500-2900 cm^{-1} expressed the existence of carboxylic acid groups. These

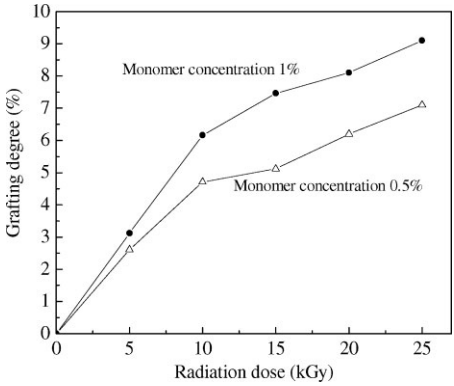

Figure 2.
grafting degree of PVDF-g-AA prepared with different radiation dose. The sample was prepared with a dose rate of 1kGy/h.

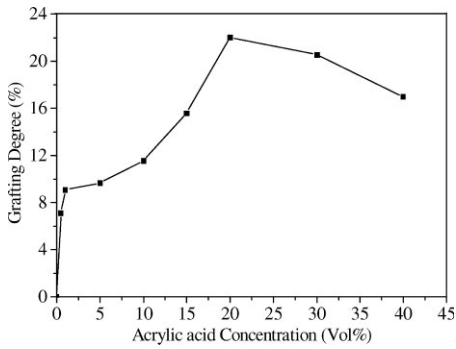

Figure 3.
grafting degree of PVDF-g-AA prepared with different monomer concentration. The samples were prepared with a dose rate of 1kGy/h and the total radiation dose was 25kGy.

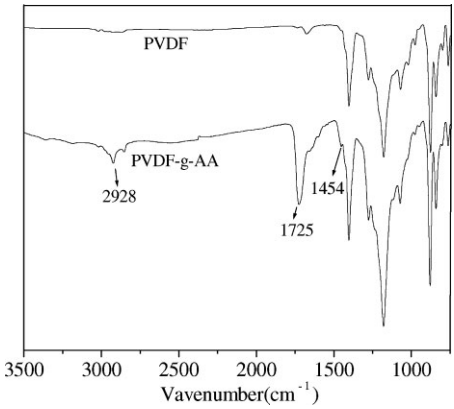

Figure 4.
FT-IR spectra of PVDF and PVDF-g-AA. (the grafting degree is 9.11%).

evidences proved that the acrylic acid have been grafted onto the PVDF fiber.[14]

Figure 5 shows the SEM images of PVDF and PVDF-g-AA. In Figure 5 (a), (b) a thin layer of film can be observed on outer surface of PVDF-g-AA membrane. The grafted poly (acrylic acid) covered and closed parts of smaller holes on the outer surface of the membrane. It is reported in the literature that for the modified membrane with a grafting degree of 7.46 wt.%, the grafted polymer covered the membrane matrix. And slightly less changes were seen for the modified membrane with a grafting degree of 0.21 wt.%.[9] In this experiment the grafting degree of PVDF hollow fiber membrane is 9.11 wt.% and it is found that the change is evident. The porosity and pore size of PVDF-g-AA of the membranes will be discussed in the next section.

It can be observed in Figure 5 (c) and (d) that there are many white dots on the inner surface of grafted PVDF, indicating that AA was grafted to the internal PVDF hollow fiber membrane. The γ-radiation has a strong energy and can cause internal graft polymerization of PVDF. Both the outer and inner surfaces of PVDF-g-AA became coarser than the surfaces of PVDF. There was no significant difference between the cross-section SEM images of the main structure of original and grated PVDF membrane in a low magnification. But the edge of the outer surface of PVDF-g-AA became denser as the grafted PAA covered and closed parts of smaller holes.

Porosity and Pore Size of PVDF-g-AA

The porosity and maximum pores of PVDF-g-AA prepared with different radiation dose (kGy) are shown in Table 1. It is found that the porosity of PVDF increased slowly with the increase of radiation dose. The reason for this phenomenon is as following: (1) Parts of PVDF hollow fiber membranes were destroyed to a certain extent in the process of radiation due to the fracture or re-integration of PVDF molecular chain. The injury especially the destroy of PVDF crystalline may form porous structure and the porosity will increase with the raise of radiation dose. (2) The damage of macromolecular additives in PVDF by radiation also resulted in the increased porosity. It is also found that the maximum diameter of the PVDF membrane pores decreased with the increase of radiation dose.

Unlike the PVDF, the porosity and maximum pores of PVDF-g-AA decreased with the increase of radiation dose, especially in a high dose ($>$10 kGy). It is the increase of grafting degree that reduced porosity and maximum pores on PVDF-g-AA membrane. In a low radiation dose ($<$5 kGy) the grafting degree of PVDF-g-AA is no more than 3.12%. The grafted poly (acrylic acid) had little influence on the porosity and maximum pores of PVDF-g-AA. On the other hand, the porosity of PVDF increased slowly with the increase of radiation dose. So the difference for the porosity of PVDF-g-AA and PVDF was not so much when the radiation dose was below 5 kGy. However, the maximum pores decreased rapidly with the continuous improvement of radiation dose because the increasing grafting degree of PVDF-g-AA.

Water Contact Angles of PVDF-g-AA

Membrane hydrophilicity was studied by measuring contact angles of the membranes at room temperature. The data of water

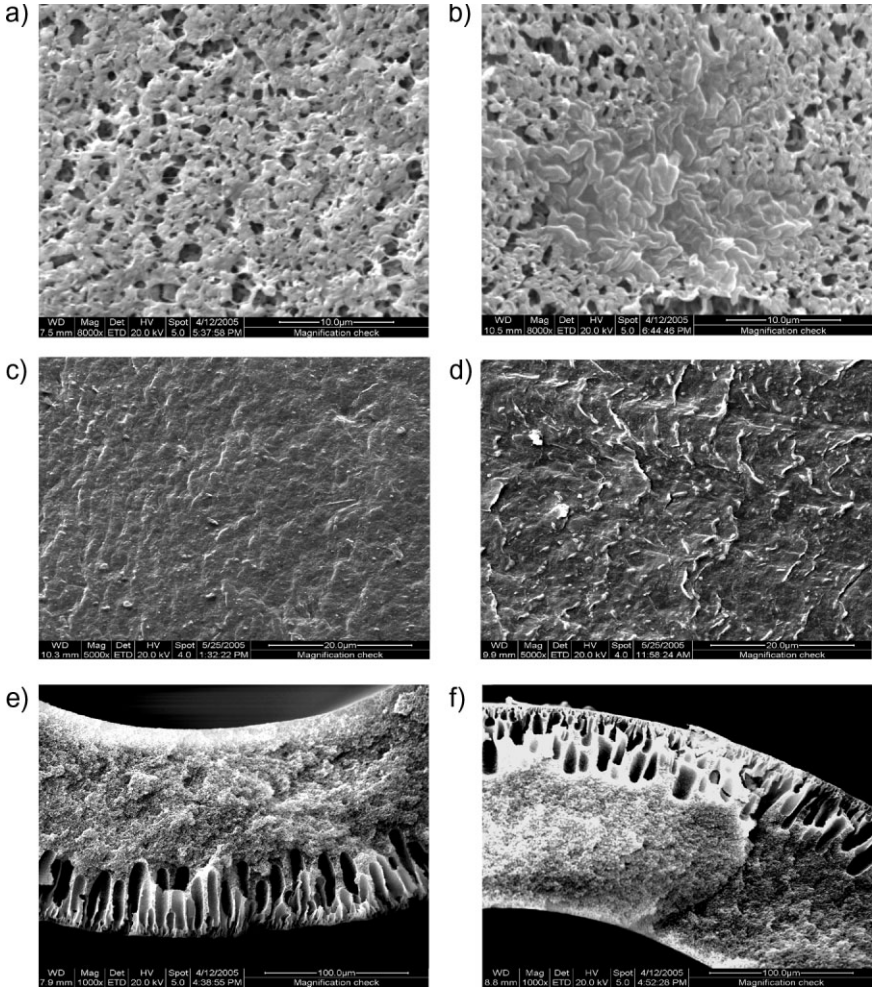

Figure 5.
SEM images of the internal PVDF membrane surfaces. (the grafting degree is 9.11%).(a) Outer surface of PVDF (b) Outer surface of PVDF-g-AA (c) Inner surface of PVDF (d) Inner surface of PVDF-g-AA (e) Cross-section of PVDF (f) Cross-section of PVDF-g-AA.

contact angle on the surfaces of PVDF and PVDF-g-AA membrane are shown in Figure 6. It is found that the water contact angle decreased with the increase of the grafting degree, indicating that the grafted PVDF membrane became more hydrophilic than the original one. The contact angle of PVDF-g-AA membrane with a grafting degree of 4.4% is 29.8°, while the contact angle of PVDF membrane is $75 \pm 4.3°$. When the grafting degree was more than 10% it was impossible to measure the water contact angle because of the rapid wetting of grafted membrane. The data of contact angle for PVDF membrane are different from the contact angle values reported in the literature.[15] The authors claimed that the external rough surface of the porous PVDF membrane exhibited greatly enhanced apparent contact angle values ($112 \pm 3°$) with water, compared to $85 \pm 2°$ of a dense PVDF membrane. The reason why the water contact angle on the rough and porous PVDF is smaller than the

Table 1.
The porosity and maximum pores of PVDF-g-AA under different grafting degree

Radiation dose (kGy)	0	5	10	15	20	25
Porosity of PVDF (%)[a]	78.8	78.3	79.29	79.68	81.6	81.75
Maximum diameter of PVDF pores (nm)	350 ± 8.5	352.5 ± 6.5	371.3 ± 8	378.4 ± 4.8	382.8 ± 6.3	384.2 ± 5.7
Porosity of PVDF-g-AA (%)[b]	78.8	77.9	75.2	70.4	68.2	67.3
Maximum diameter of PVDF-g-AA pores (nm)[b]	350 ± 8.5	340.5 ± 10	306.8 ± 9.3	293.2 ± 6	287.7 ± 5.3	277.6 ± 9.5
Grafting degree (%)	0	3.12	6.16	7.46	8.1	9.1

[a]The PVDF was radiated under different radiation dose without AA.[b]The PVDF-g-AA was prepared with 1% (v/v) AA.

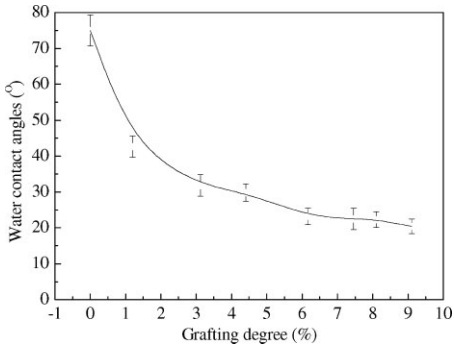

Figure 6.
Water contact angles of PVDF-g-AA with different grafting degree.

literature reported is not clear. The porosity of the membranes used for contact angle measurements was listed in Table 1. Maybe it is the radiation-induced crosslinking of PVDF molecular chain that made the membrane denser. Anyway, the hydrophobic PVDF membrane can be hydrophilized via the grafting polymerization of AA in order to improve the permeation and antifouling properties.

Pure Water Flux, Flux Recovery Rate and Rejection Ratio of PVDF-g-AA

The permeation and antifouling properties of PVDF-g-AA were characterized by testing the pure water flux and flux recovery rate of PVDF-g-AA. Table 2 shows the pure water flux, flux recovery rate and rejection ratio for bovine serum albumin (BSA) under different grafting degrees.

The pure water flux increased with the increase of grafting degree and reached the maximum when the grafting degree was 4.4%. The maximum pure water flux was 1496.3 $L/m^2 \times h$, 1.79 times of PVDF. But the pure water flux decreased with the sequential increase of grafting degree. In a low grafting degree (<4.4%) the grafted poly (acrylic acid) (PAA) had little influence on the porosity and maximum pores of PVDF-g-AA and the grafted PAA made the PVDF matrix more hydrophilic. From Figure 6 we know that the hydrophilicity of PVDF-g-AA increased with the increase of grafting degree. So the pure water flux of PVDF-g-AA increased with the increase of grafting degree in a low value. However, with the sequential increase of grafting degree, the longer comb-like grafted PAA chain could block the pores on the membrane. The porosity of the membrane decreased as part of holes on the membrane was block and lead to the decrease of pure water flux.

The antifouling characteristics for the PVDF-g-AA and PVDF were assessed by

Table 2.
Pure water flux, flux recovery rate and rejection ratio for BSA.

Grafting degree (%)	0	1.2	3.36	4.4	4.74	6.65	8.12	9.11
Pure water flux ($L/m^2 \times h$)	834	893.9	1295.7	1496.3	1444.7	1381	1245.1	1127.3
Flux Recovery rate (%)	87.3	91.2	93.3	94.5	95.1	95.6	95.9	96.1
Rejection ratio (%)	5.2	10.6	21.2	27.1	28	28.9	31.6	32.9

the filtration of bovine serum albumin (BSA). It is founded in Table 2 that the flux recovery rate increased with the increase of grafting degree and then reached the equilibrium when the grafting degree was about 4.74%. The hydrophilicity of PVDF membrane surface increased with the increase of grafting degree as a result of the introduction of -COOH hydrophilic group. It was difficult for BSA to adhere to the surface of PVDF and improved the antifouling properties of PVDF membrane.[16]

It is also found in Table 2 that the rejection ratio of PVDF-g-AA for BSA improved with the increase of grafting degree. The increase of the grafting degree reduced the size of maximum pores on PVDF membrane and increased the amount of charged carboxyl groups. In this way, more proteins were excluded outside the membrane via the electrostatic repulsion and the rejection ratios for BSA were improved. The pure water flux, flux recovery rate and rejection ratio for BSA could improve simultaneously in a low grafting degree (<4.4%). There are many factors that had an effect on the water flux and the rejection ratio for BSA, such as pH values, ionic concentration and temperature. These factors are now under investigating and will be reported in our future paper.

Mechanical Properties of PVDF-g-AA

The mechanical properties of PVDF and PVDF-g-AA hollow fiber membrane were tested by an Electronic single fiber strength tester. Samples were prepared in the same radiation conditions with a dose rate of 1kGy/h and the total radiation dose was about 15 kGy. The results are listed in Table 3 and it is found that there was a slight increase of breaking strength and yield stress with the increase of the grafting degree. However, the elongation at break increased initially but decreased subsequently with the increase of the grafting degree.

The physical cross-linking point is formed as a result of grafted PAA chains connecting the molecule of PVDF. With the increase of the grafting degree, the number of grafting chain and the degree of entanglement of them also increased. When the membrane was stretched, the graft chain of PVDF-g-AA could share some part of the stress, leading to an increased breaking strength, yield stress and elongation at break for membrane. Anyway, there is little difference for the mechanical properties of PVDF-g-AA membranes with different grafting degree in our experimental conditions.

Table 3.
The mechanical properties of PVDF and PVDF-g-AA membranes.

Grafting degree (%)	Breaking strength(cN)	Elongation at break (%)	Yield stress (cN)
0	157.6	317.4	107.2
1.0	160.1	343.5	115.4
1.8	166.6	353.1	121.8
2.8	167.7	305.4	121.3
3.6	170.2	293.0	126.8
4.4	169.5	315.7	126.6

Conclusion

A modified PVDF hollow fiber membrane was performed by γ-radiation induced grafting of acrylic acid (AA) from water solution. The grafting degree increased with the increase of radiation dose from 10 kGy to 25 kGy. The grafting degree increased initially but decreased subsequently with the increase of the monomer concentration. FT-IR and scanning electron microscopy (SEM) indicated that AA had been successfully grafted onto PVDF membrane. The water contact angle of PVDF-g-AA decreased with the increase of the grafting degree, indicating that PVDF-g-AA became more hydrophilic than PVDF. The porosity and maximum pores of PVDF-g-AA decreased with the increase of radiation dose. The pure water flux increased with the increase of grafting degree and reached the maximum when the grafting degree was 4.4%. The pure water flux, flux recovery rate and the rejection ratio for protein could improve

simultaneously when the grafting degree was below 4.4%. Future study will optimize the PVDF hollow fiber structure and environmental conditions to increase the pure water flux and the rejection ratio for proteins.

Acknowledgements: The authors thank the special program for key research of Chinese national basic research program (2008CB417202), the project of Science and Technical Development of China (2007AA03Z533), Tianjin colleges science and technology development fund (2006ZD40) and Tianjin basic applied and forefront technology research projects (09JCZDJC23200) for supporting this research work.

[1] D. L. Wang, K. Li, W. K. Teo, *J. Membr. Sci.* **1999**, *163*, 211.
[2] A. Rahimpour, S. S. Madaeni, S. Zereshki, Y. Mansourpanah, *Appl. Surf. Sci.* **2009**, *255*, 7455.
[3] A. E. Childress, M. Elimelech, *Environ. Sci. Technol.* **2000**, *34*, 3710.
[4] M. M. Nasef, E. A. Hegazy, *Prog. Polym. Sci.* **2004**, *29*, 499.
[5] T. Tarvainen, T. Nevalainen, A. Sundell, B. Svarfvar, *J. Control. Release.* **2000**, *66*, 19.
[6] H. Iwata, I. Hirata, Y. Ikada, *Macromolecules* **1998**, *31*, 3671.
[7] H. Iwata, M. Oodate, Y. Uyama, H. Amemiya, Y. Ikada, *J. Membr. Sci.* **1991**, *55*, 119.
[8] N. Betz, J. Begue, M. Goncalves, K. Gionnet, G. Deleris, Le. Moel, *Nucl. Instrum. Meth. Phys. Res. B* **2003**, *208*, 434.
[9] H. Y. Yu, Z. K. Xu, Q. Yang, M. X. Hu, S. Y. Wang, *J. Membr. Sci*, **2006**, *281*, 658.
[10] J. F. Wei, Z. P. Wang, J. Zhang, Y. Y. Wu, Z. P. Zhang, C. H. Xiong, *React. Funct. Polym.* **2005**, *65*, 127.
[11] Y. W. Kai, T. S. Chung, G. Marek, *Chem. Eng. Sci.* **2008**, *63*, 2587.
[12] ASTM Prcoedure No. ASTM F316-80, American Society for Testing and Materials, Philadelphia, PA, 1980.
[13] K. Venkataraman, W. T. Choate, E. R. Torre, *J. Membr. Sci.*, **1988**, *39*, 259.
[14] S. Kaori, S. Kyoichi, S. Kazuyuki, *Ind. Eng. Chem. Res*, **2002**, *41*, 5686.
[15] P. Mao, H. B. Li, L. J. Wu, Q. Zheng, Y. Chen, W. F. Gu, *J. Appl. Poly. Sci.* **2005**, *98*, 1358.
[16] D. S. Wavhal, E. R. Fisher, *Langmuir* **2003**, *19*, 79.

