

## Stability of Acrylic Acid Grafted Poly(vinylidene fluoride) Hollow Fiber Membrane Prepared by High-Energy Electron Beam

Zhiyun Kong,<sup>1,2</sup> Junfu Wei,<sup>1,3</sup> Liang Yang,<sup>1,3</sup> Zian Luo,<sup>1,2</sup> Kongyin Zhao,<sup>1,2</sup> Xiaolei Wang<sup>1,2</sup>

<sup>1</sup>State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, Tianjin, 300387, China

<sup>2</sup>School of Material Science and Engineering, Tianjin Polytechnic University, Tianjin, 300387, China

<sup>3</sup>School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin, 300387, China

Correspondence to: J. Wei (E-mail: wjfw2013@126.com) and Z. Kong (E-mail: minikk@126.com)

**ABSTRACT:** In this article, poly(vinylidene fluoride) (PVDF) hollow fiber membrane and acrylic acid (AA) were co-irradiated by high-energy electron beam to introduce hydrophilic carboxylic groups on the membrane surface. Thermal capability, mechanical performance, pore size, and permeation property were investigated to determine the stability of the membrane pore structure before and after irradiation polymerization. The decomposition temperature, melting point, glass transition temperature, and breaking force of the PVDF-g-AA membrane increased slightly because of irradiation grafting polymerization. After 15 months of storage, the pore size distribution of the PVDF-g-AA membrane became smaller and more dispersive. The pure water flux and the rejection to bovine serum albumin of the PVDF-g-AA membrane increased significantly with the increase in hydrophilicity and decrease in pore size. The results indicated that the structure and properties of the PVDF hollow fiber membrane were stable after high-energy electron beam irradiation grafting polymerization, even after 15 months of storage. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41165.

**KEYWORDS:** grafting; hydrophilic polymers; radical polymerization

Received 26 February 2014; accepted 13 June 2014

DOI: 10.1002/app.41165

### INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is a semicrystalline membrane material that has generated widespread industrial applications and research interest since the 1960s due to its good thermal stability, chemical resistance, ultraviolet light and radiation resistance, and excellent processability.<sup>1–6</sup> As a well-known multifunctional plastic, PVDF has been widely used in petrochemical engineering, electronics, and fluorocarbon coating, especially as a membrane for microfiltration and ultrafiltration. However, the hydrophobic surfaces of PVDF membranes often give rise to protein fouling,<sup>7–10</sup> which limits their application. Therefore, PVDF membranes are often modified by chemical or physical methods to satisfy the requirements of specific applications.

Several methods for membrane surface modification including blending with hydrophilic polymer,<sup>11–15</sup> surface coating,<sup>16,17</sup> chemical modification,<sup>18</sup> and surface modification by grafting hydrophilic monomers<sup>19–21</sup> have been used to increase surface hydrophilicity. Surface grafting can conquer the instable problem completely by the grafting polymerization of monomers, which immobilizes the functional chains, brushes or layers onto the membrane surface through covalent bonding interaction.<sup>22</sup> Thus graft polymerization of specific functionalities or polymer layers has been employed as a route to tailor PVDF polymeric

membrane surfaces for different applications.<sup>23</sup> Various initiation approaches, such as plasma treatment,<sup>24</sup> UV irradiation,<sup>25</sup> ozone treatment,<sup>26</sup> gamma irradiation,<sup>27,28</sup> and electron beam irradiation,<sup>19,20</sup> have been used for surface grafting polymerization. Especially the electron beam irradiation has many advantages for the modification of PVDF membrane. The radiation-induced process is temperature independent, short irradiation time required and also it is free from contamination as no catalyst or additives are required.

Various monomers have been grafted onto the PVDF by electron beam irradiation. Acrylic acid (AA) or PAA<sup>3,29</sup> was introduced to the surface of PVDF by electron beam irradiation to improve permeability<sup>30</sup> and the water flux,<sup>31</sup> AA/sodium 4-styrenesulfonate binary monomers<sup>19</sup> was grafted onto PVDF by electron beam pre-irradiation-initiated surface grafting, and the contact angle under optimum monomer ratio and pH value decreased from 62° to 0° in only 25 s. Poly(ethylene glycol) methyl ether methacrylate (PEGMA)<sup>20</sup> was grafted onto PVDF by electron beam pre-irradiation-initiated surface grafting and caused that pure water flux increased from 180 to 226 L m<sup>-2</sup> h<sup>-1</sup>. Sodium styrene sulfonate (SSS) was grafted onto electron beam irradiated PVDF films as a single-step route for preparation of proton exchange membranes for fuel cells.<sup>32–35</sup> Proton exchange membranes were also

prepared by irradiation grafting of styrene (St) onto PVDF, followed by sulfonation;<sup>36,37</sup> 2-hydroxyethylmethacrylate (HEMA) was grafted on PVDF powder for applications for high energy density capacitors.<sup>38</sup> Poly(*N*-isopropylacrylamide) grafted PVDF membranes were prepared for controlling the permeation of high molecular weight compounds such as polynucleotides, peptides and proteins.<sup>39</sup> St and maleic anhydride was grafted on PVDF using an electron-beam-induced pre-irradiation grafting and then was sulfonated and hydrolyzed to give an ion exchange membrane for vanadium redox flow batteries use.<sup>40</sup>

However, irradiation has some drawbacks, such as thermal stability,<sup>41</sup> decrease of mechanical properties and scission of the main chain.<sup>42</sup> The PVDF films were irradiated by electron beam in air at room temperature and found that melting and recrystallization temperatures decreased with increase in the irradiation dose in the range of 100 to 1200 kGy<sup>43</sup> and the degree of crystallinity increased in the range of 20 to 500 kGy.<sup>44</sup> PVDF-based membrane reinforced with polyamide-66 fabric into deionized water was irradiated in argon and found that the mechanical properties of membrane were mainly provided by polyamide-66 fabric and PVDF in the membrane were slightly degraded by irradiation in the range of 10 to 100 kGy.<sup>45</sup> PVDF films were pre-irradiated at room temperature under helium atmosphere using electron beam irradiation in the range of 0 to 150 kGy and then AA was grafted onto PVDF films. It was found that highly grafted and expanded films are brittle than original PVDF.<sup>46</sup>

The effects of storage time and the co-irradiation of PVDF and grafting solution at low doses on the chemical and thermal stabilities of polymer matrix and grafted polymer chains have not been reported to date. In this work, the changes on thermal property, mechanical properties, permeability, and rejection percentage of PVDF hollow fiber membrane were studied before and after high-energy electron beam irradiation grafting of acrylic acid (AA). The results obtained in this study would be enlightening for researchers working on PVDF applications for industrial purposes.

## EXPERIMENTAL

### Materials

The original PVDF Hollow fiber Ultrafiltration membrane (Filtration mode: Outside-in; Outer diameter: 1200  $\mu\text{m}$ ; Inner diameter: 800  $\mu\text{m}$ ; Water permeability:  $450 \pm 50 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ), was provided by Tianjin MOTIMO Membrane Technology, Ltd. (Tianjin, China). Electrophoretic-grade BSA was obtained from the Institute of Hematology, Chinese Academy of Medical Sciences. All other chemicals, including acrylic acid, ferrous ammonium sulfate, sulfuric acid, hydrochloric acid, sodium hydroxide and hydrogen peroxide, were of analytical grade and purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). All reagents and solvents were used without further purification. Ultra-pure water with a resistivity of 17.4  $\text{M}\Omega \text{ cm}$  was used in all experiments.

### Preparation of PVDF-Grafted Membrane (PVDF-g-AA)

The high-energy electron beam irradiation equipment used was provided by Binhai South Irradiation Co., Ltd. (Tianjin, China). The irradiation dose was 20 kGy per pass. The procedure for

the preparation of hydrophilic PVDF hollow fiber membranes included the following steps.

**Monomer Loading.** The original PVDF hollow fiber membranes were first immersed in ultra-pure water for 24 h to remove glycerol. After oven drying, the membranes were weighed and moved in gas-tight PE plastic bags. Different concentrates of aqueous monomer were then filled into the bags according to a solid-to-liquid ratio of 1 : 10. Afterward, nitrogen was charged into the bags to eliminate oxygen.

**Grafting.** The prepared samples were placed on a sample platform irradiated by a high-energy electron beam.

**Washing.** The grafted membranes were finally rinsed and washed three times in an ultrasonic bath (30 s) with ultra-pure water to remove the residual monomers and homopolymers. The prepared membranes were stored in ultra-pure water before analysis. The grafting degree of the AA-grafted membranes (GD) was determined by the weight method as follows:

$$GD(\%) = \frac{W_a - W_b}{W_b} \times 100\% \quad (1)$$

where  $W_a$  and  $W_b$  are the dry weights after and before grafting, respectively.

**Storage.** The grafted membranes were soaked in 50% glycerol for 12 h and dried in the air for storage. Before analysis the prepared membranes were immersed in ultra-pure water for 24 h to remove glycerol.

### Characterization of the Membrane

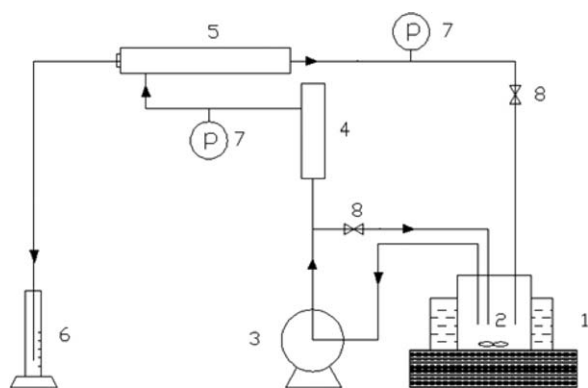
Fourier transform infrared attenuated total reflection (FT-IR-ATR) spectrometer (BRUKER German) was used to detect the chemical compositions of the membrane top surface before and after irradiation polymerization in the wave number range of 4000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$ .

SEM (QUANTA200) was employed to elucidate the membrane morphology. The membranes were cut into small pieces, cleaned with filter paper, and then immersed in liquid nitrogen for 10 min to 15 min. The frozen membranes were broken and then air dried. The dried samples were gold sputtered to produce electric conductivity. The micrographs were obtained in high-vacuum conditions at 27 kV.

The hydrophilicity of the membrane surface was evaluated by measuring the water contact angle (WCA). The process was carried out by static sessile drop method using a contact goniometer (JYSP-180, Beijing Jinshengxin Testing Machine Co., Ltd., China). The dry membranes were flattened using a scalpel, and then fixed on a glass slide using double-sided tape. To minimize experimental error, the contact angles were measured at five random locations for each sample, and the average value was reported.

The decomposition temperature of the PVDF matrix was determined using thermogravimetry (TG) (Perkin Elmer TGA-Q5000, UK). The samples were heated from 30°C to 800°C at a heating rate of 5°C  $\text{min}^{-1}$ .

The melting point of the PVDF matrix was determined using differential scanning calorimetry (DSC) (Mettler Toledo DSC 822). The samples were heated from 20°C to 220°C at 5°C  $\text{min}^{-1}$ , and



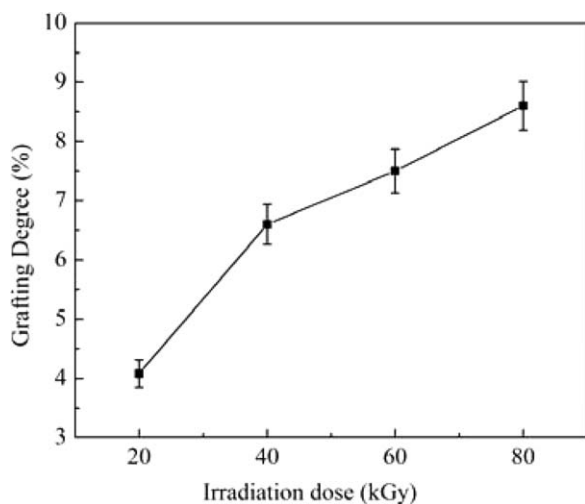
**Figure 1.** Schematic of the cross-flow filtration unit: (1) water-bath heater, (2) feed tank, (3) feed pump, (4) flow meter, (5) membrane module, (6) permeate solution, (7) pressure gauge, (8) press regulator valve.

the crystallinity percentage was calculated using the heat of fusion value for 100% crystalline PVDF,  $\Delta H_{100\%} = 102.7 \text{ J g}^{-1}$ .<sup>47</sup>

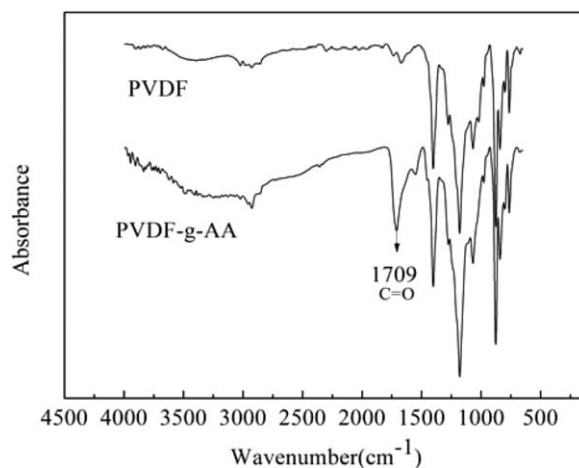
The glass transform point of the PVDF matrix was determined using dynamic mechanical analysis (DMA) (Netzsch DMA 242C, Germany) from  $-130^\circ\text{C}$  to  $30^\circ\text{C}$  at a heating rate of  $5 \text{ K min}^{-1}$ . The frequency was  $10 \text{ Hz}$ .

The tensile strength of the membranes was measured with a universal mechanical testing machine (3369, Instron). The measurements were carried out at  $20^\circ\text{C}$  and relative humidity of around 60%, with crosshead speed of  $10 \text{ mm min}^{-1}$ .

Pore size and its distribution were determined by the wetting fluid displacement technique using a capillary flow porometer (Model CFP-1100-A, Porous Materials, Inc., Ithaca, NY).<sup>48</sup> The membrane samples with 5 cm diameter were completely wet by the wetting liquid Porwick<sup>TM</sup> ( $\gamma = 16 \text{ dyne/cm}$ , Porous Materials Inc.), and gas pressure was applied on one side. The experiment then continued through step-wise increase of pressure and measurement of air flow rate at each pressure. As the pressure increased gradually, gas bubbles emerged from pores where the capillary forces were overcome.



**Figure 2.** Effect of irradiation dose on grafting degree. AA concentration : 5%.



**Figure 3.** FT-IR-ATR spectra of the original PVDF membrane and the PVDF-g-AA membrane.

### Permeation Performance Experiment

The pure water flux was measured with a filtration apparatus (Figure 1)<sup>49</sup> made by our research group. The temperature of the ultra-pure water was maintained at  $25 \pm 1^\circ\text{C}$ , and the flow rate was set at  $80 \text{ L/h}$ . Each membrane module was pre-pressurized at  $0.15 \text{ MPa}$  for 30 min before the test. After the completion of each experiment, the membrane module was rinsed with ultra-pure water, and the soaking ultra-pure water was renewed every 3 days. The pure water flux  $F$  was calculated as follows:

$$F(\text{L m}^{-2} \text{ h}^{-1}) = \frac{V}{t \times A} \quad (2)$$

where  $V$  is the volume of the salt solution through the membrane (L),  $t$  is the operation time (h), and  $A$  is the effective area of the membrane ( $\text{m}^2$ ).

The same previously mentioned setup was used for the rejection experiments with BSA. Deionized water was replaced by BSA aqueous solution with a concentration of  $1 \text{ g/L}$  as feed solution. The temperature of the feed solution, the flow rate, and the operation pressure were similar to the ones previously mentioned. The concentrations of the feed and permeate solutions were determined by ultraviolet spectrophotometer (TU-1901, Beijing PGENERAL Instrument Co., Ltd., China).

The rejection  $R$  was calculated according to the following equation:

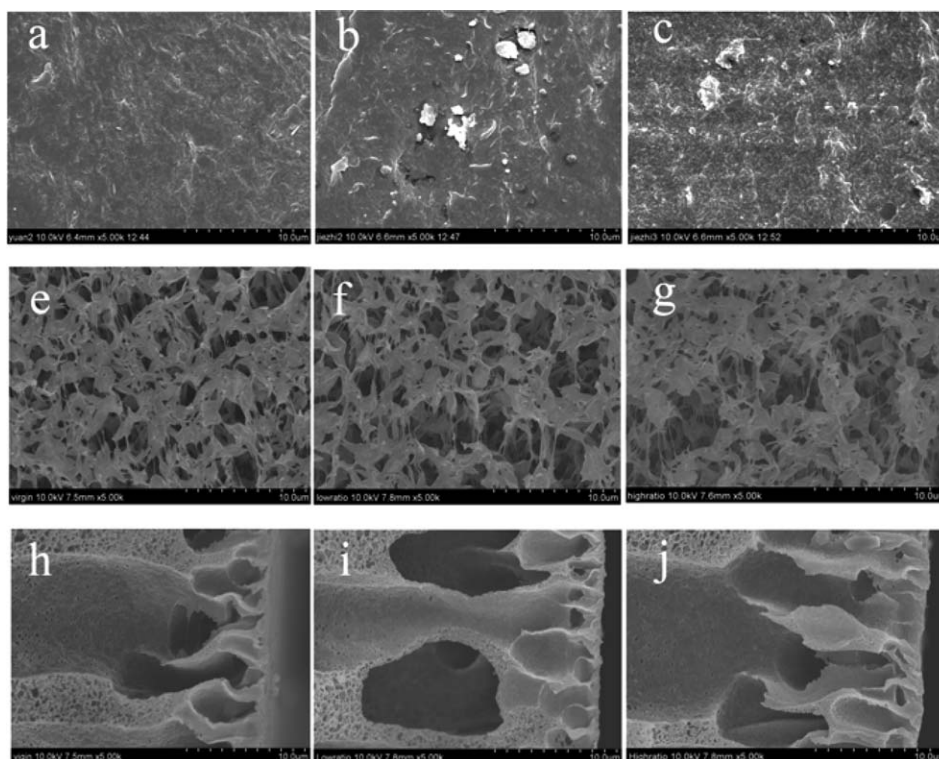
$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3)$$

where  $C_p$  and  $C_f$  are the concentrations in the permeate and feed solutions ( $\text{mg/L}$ ), respectively.

## RESULTS AND DISCUSSION

### Grafting Membrane Characterization

**Effect of Irradiation Dose on the Grafting Degree.** The effect of radiation dose on the grafting degree was investigated in the dose range of 20 to  $80 \text{ kGy}$ . The results of this study are shown in Figure 2 at monomer concentration of 5% AA. The grafting degree increased with the increase in radiation dose. This may

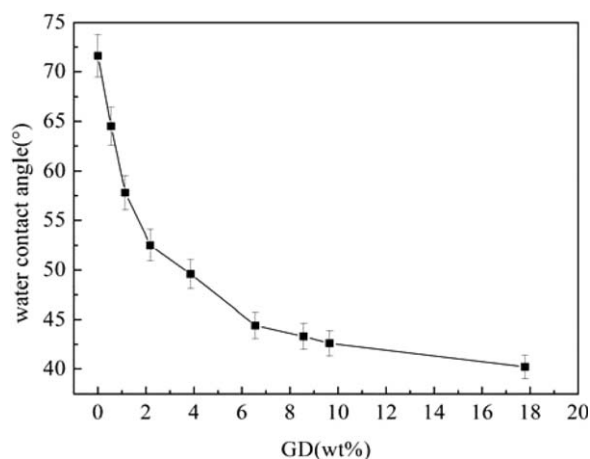


**Figure 4.** SEM graphs of the overall outer surface, inner surface, and cross-section of the original PVDF hollow fiber membrane (a, e, h), low-grafting degree PVDF hollow fiber membrane (b, f, i), and high-grafting degree PVDF hollow fiber membrane (c, g, j).

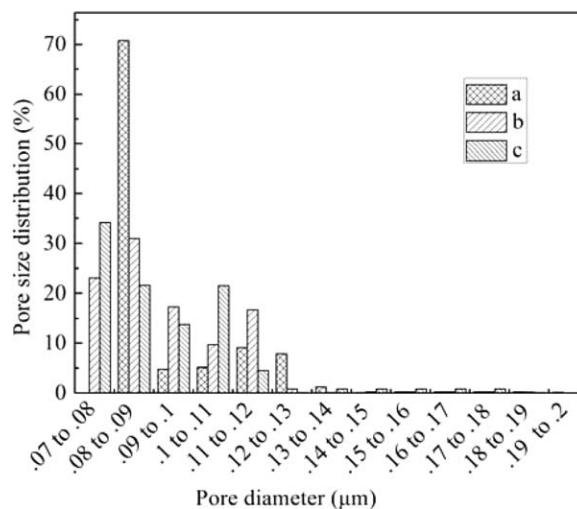
be due to increase in the number of active sites in the polymer matrix. For further investigation membrane grafted to an extent of 6.6% at a dose of 40 kGy was chosen.

**FT-IR Spectra Analysis.** The FT-IR-ATR of the original PVDF and PVDF-*g*-AA membrane is shown in Figure 3. Two types of membranes showed the main typical spectra of PVDF, namely,  $-\text{CF}_2$  deformation and stretching vibration bonds at 1402 and 1179  $\text{cm}^{-1}$ . The  $\beta$  phase vibration at 1280  $\text{cm}^{-1}$  and the amorphous phases at 876 and 840  $\text{cm}^{-1}$  indicate that the irradiation reaction in the complex would not damage the chemical structure of the PVDF. However, significant peaks around 2926 and

1709  $\text{cm}^{-1}$ , which belong to the stretching vibration peaks of  $-\text{CH}$  and  $\text{C}=\text{O}$ , respectively, were observed in the PVDF-*g*-AA membrane. Similarly, a small peak at 1670  $\text{cm}^{-1}$  was observed on the original PVDF membrane curve belongs to the stretching vibration of the  $\text{C}=\text{O}$  bond of the additional PVP, which was added in the casting solution as porogen in the spinning process, and only a small amount of residue was remained on the membrane during membrane formation process. The above

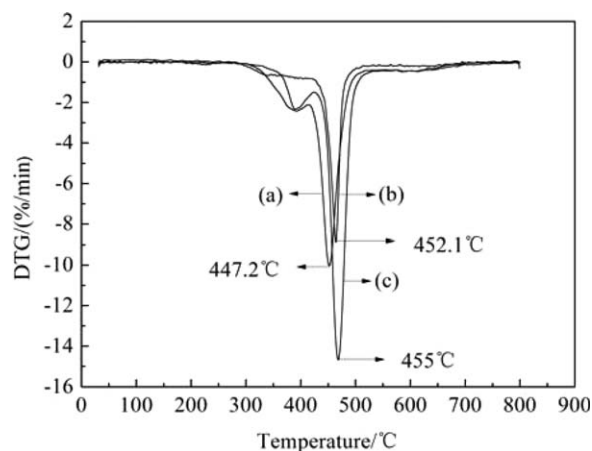


**Figure 5.** Water contact angle of different grafting degrees of PVDF membranes.



**Figure 6.** Pore size distribution of (a) the PVDF original membrane, (b) newly grafted PVDF-*g*-AA membrane (DG = 6.6%), and (c) PVDF-*g*-AA membrane grafted 15 months (DG = 6.6%).

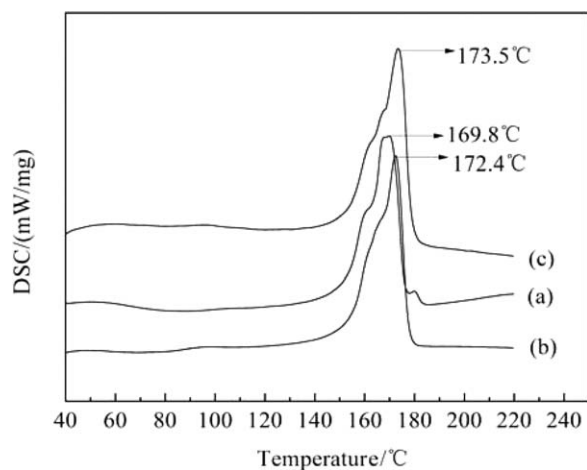




**Figure 7.** Derivative thermogravimetry curves of the (a) original PVDF membrane, (b) newly grafted PVDF-g-AA membrane (DG = 6.6%)PVDF, and (c) PVDF-g-AA membrane grafted 15 months (DG = 6.6%).

FTIR results indicated that the monomer acrylic acid was successfully grafted onto the PVDF membranes.

**Membrane Morphology.** Figure 4 shows the SEM of the surface and inner structures of the original and grafted PVDF hollow fiber membranes. The structures of the surface and the interior of the grafting-modified membranes were changed relatively. On the outer surface (b and c), some particulate matters can be observed clearly, and the particulate in the density of the high-grafting degree hollow fiber membrane (c) was larger than that of the low-grafting degree membrane (b). On the inner surfaces (e, f, g), all the membranes showed net-like structures. The low-grafting degrees of the hollow fiber membrane (f) behaved similar to the original PVDF membrane (e). The net-like pores of the high-grafting degree hollow fiber membrane (g) were denser and smaller. In the cross-section SEM (h, i, j), the finger-like pore did not change after grafting polymerization. The results indicated that low-monomer concentrate grafting polymerization occurred at the outer surface. However, with increase in



**Figure 8.** DSC curves of the (a) original PVDF hollow fiber membrane, (b) newly grafted PVDF-g-AA membrane (DG = 6.6%), and (c) PVDF-g-AA membrane grafted 15 months (DG = 6.6%).

the monomer concentrate, the grafting polymerization occurred not only at the outer surface, but also at the inner surface.

**Membrane Hydrophilicity.** Figure 5 shows the water contact angle of the membranes with grafting degree. The hydrophobic characteristic of PVDF easily leads to biological fouling. To overcome this disadvantage, improving the hydrophilic property of the PVDF membrane is necessary. The water contact angle decreased evidently with the increase of grafting degree from 0 to 6.6%. In addition, with the increase of grafting degree from 6.6 to 17.9%, the descending trend of the water contact angle decreased from 44.4 to 40.2°.

The significant improvement of the hydrophilicity is attributed to the excellent wettability of the grafted AA side chains. The hydrophilic property of the PVDF membranes was enhanced after high-energy electron beam irradiation grafting of AA.

**Pore Size.** Figure 6 shows the pore size and the distribution of the original PVDF membrane, newly grafted PVDF-g-AA membrane, and PVDF-g-AA membrane grafted 15 months. The uniform pore diameter (70% between 0.08  $\mu\text{m}$  and 0.09  $\mu\text{m}$  of the original PVDF membrane) became more disperse and smaller. The pore diameter between 0.08  $\mu\text{m}$  and 0.09  $\mu\text{m}$  decreased from 70% (original membrane) to 34% (newly grafted membrane) and 23% (after grafted membrane 15 months). A new range of pore diameter, which accounted for about 24% of all the pore size distributions, appeared between 0.07  $\mu\text{m}$  and 0.08  $\mu\text{m}$ , which was attributed to the blocking effect<sup>50</sup> of the grafted AA. The larger pores (pore diameter between 0.12 and 0.13) nearly disappeared for the same reason. Compared with the newly grafted membrane, the pore size distribution of the membrane grafted 15 months was higher at the same range of pore diameter, which was attributed to the improvement of crystallinity during irradiation.<sup>44</sup> Irradiation grafting polymerization changed the pore size distribution of the PVDF membrane, and this change remained stable even after 15 months.

#### Stability of the Polymer Matrix

**Changes in the Polymer Matrix Structure.** In this article, the decomposition temperature, melting point, and glass transform point of the PVDF were determined to investigate the structure of the PVDF and PVDF-g-AA. The resulting DTG curves are shown in Figure 7. Two thermal decomposition steps were found in the DTG curves of all three types of PVDF hollow fiber membranes. The first decomposition step belonged to the degradation of the grafted chain, whereas the second belonged to the degradation of the PVDF subject. The decomposition temperature of the original PVDF was 447.2°C; however, the decomposition temperature of the newly grafted PVDF-g-AA increased to 452.1°C, which may be due to the cross-linking<sup>42,51</sup> of the PVDF main chains caused by irradiation. The degradation temperature of the PVDF-g-AA grafted 15 months further improved to 455°C, which was attributed to the development of crystallinity.

The melting points of the original PVDF and the PVDF-g-AA membranes were measured by DSC, as displayed in Figure 8. Their crystallinity is shown in Table I. The melting point ( $T_m$ ) of the original PVDF was about 169.8°C. A slight increase of

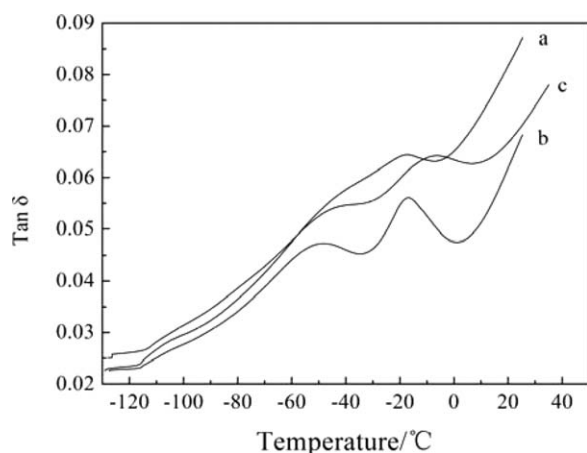
**Table I.** Crystallinity of the Original PVDF Membrane, Newly Grafted PVDF Membrane, and the Membrane Grafted 15 Months

	Original PVDF membrane	Newly grafted PVDF membrane	PVDF membrane grafted 15 months
Crystallinity(%)	51.8	53.9	56.8

the melting point ( $T_m$ ) was observed after irradiation grafting, which increased to 172.4°C for the newly grafted PVDF-*g*-AA and 173.5°C for the PVDF-*g*-AA grafted 15 months, respectively. The crystallinity of the original PVDF was 51.8%, which increased to 53.9% and 56.8% for the newly grafted PVDF-*g*-AA and 173.5°C for the PVDF-*g*-AA grafted 15 months, respectively. The results indicated that irradiation induced an increase in the crystallization of the PVDF,<sup>44</sup> and the storage could lead to the further development of crystallinity. These results also demonstrated that irradiation graft polymerization is beneficial to the stability of the PVDF matrix.

In addition, DMA was evaluated to observe the change in glass transition temperature ( $T_g$ ). The  $T_g$  value of the original PVDF was -17.3°C, and that of the newly grafted PVDF-*g*-AA and PVDF-*g*-AA grafted 15 months were -16.8 and -6.4°C, respectively (Figure 9). The increase in  $T_g$  may be due to the cross-linking caused by irradiation.<sup>42,51</sup> The finding was consistent with the results of TG and DSC. The changes in decomposition temperature, melting point, and glass transform point of the PVDF subject indicated that the stability of the PVDF matrix benefited from irradiation grafting polymerization.

**Mechanical Property.** The breaking force and elongation at break of the original PVDF hollow fiber membrane (M0) and the PVDF-*g*-AA membrane (M3) with a series of preservation times are shown in Table II. The surface of membranes modified by high-energy electron beam that initiated grafting in the aqueous solution at room temperature have stable mechanical properties at different preservation times. As shown in Table II,

**Figure 9.** DMA curves of the (a) original PVDF hollow fiber membrane, (b) newly grafted PVDF-*g*-AA membrane (DG = 6.6%), and (c) PVDF-*g*-AA membrane grafted 15 months (DG = 6.6%).**Table II.** Breaking Strength and Elongation at Break of the Original PVDF Membrane (M0) and the Grafted PVDF Membrane (M3) with a Series of Preservation Times (1, 3, 6, 12, and 15 Months)

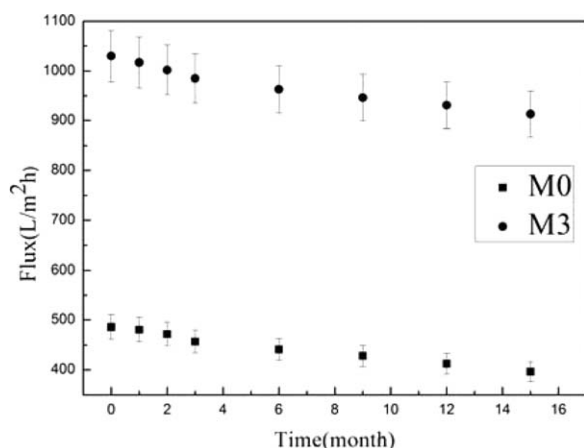
Time (mo)	Breaking strength (cN)		Elongation at break (%)	
	M0	M3	M0	M3
0	174.2	202.6	232.9	66.0
1	170.7	199.5	233.4	64.8
2	168.3	196.7	231.1	63.2
3	167.2	194.3	232.6	64.6
6	164.5	190.7	230.5	61.2
12	162.1	187.2	228.7	59.8
15	159.8	185.9	225.6	55.1

the breaking strengths of the PVDF membrane increased significantly after irradiation grafting polymerization due to the cross-linking of the PVDF main chains, but the force slightly decreased after 15 months due to the development of crystallinity. The elongation at break of the original PVDF membrane (M0) was about 232.9%, but the elongation at break of the irradiation-grafted PVDF membrane (M3) decreased to about 66%. Considering the increase of the breaking strength, the decrease of elongation at break may be explained by the cross-linking of the PVDF main chains. The elongation at break exhibited a slight decline after 15 months, which was explained by the increase of crystallinity.

**Permeation Property.** The grafting degree and pure water flux of the PVDF-*g*-AA membranes are shown in Table III. The pure water flux showed a tendency of first increasing, and then decreasing with the increase of grafting degree. The pure water flux of the original PVDF membrane was about 450 L/m<sup>2</sup>h. The pure water flux of the PVDF-*g*-AA membrane with a GD of 6.6% produced a maximum value of about 1029.5 L/m<sup>2</sup>h, which was more than twice that of the original PVDF membrane. However, the pure water flux of the PVDF-*g*-AA membrane with high GD (17.8%) was reduced to about 272.2 L/m<sup>2</sup>h, which was attributed to the competition between the hydrophilicity and the blocking effect of the grafted AA brush. The pure water flux of the PVDF-*g*-AA membrane was determined by

**Table III.** Grafting Degree and Pure Water Flux (PWF) of the PVDF Hollow Fiber Membranes with Different Monomer Grafting Degree

No.	GD (%)	PWF (L/m <sup>2</sup> h)
M0	0	450.0
M1	0.55	486.0
M2	2.18	938.2
M3	6.56	1029.5
M4	17.79	272.2
M5	8.57	858.4
M6	9.65	743.6

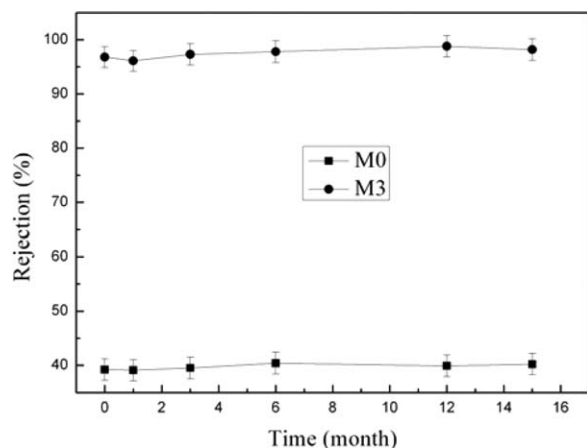


**Figure 10.** Pure water flux of the original PVDF membrane (M0) and the grafted PVDF membrane (M3) with a series of preservation times (1, 3, 6, 12, 15 months).

hydrophilicity of the grafted AA brush, with the GD approximately below 7.0%. However, the result may depend closely on the blocking of the membrane pore size when the GD is higher than about 7.0%.

Figure 10 shows the pure water flux of the original PVDF hollow fiber membranes and the PVDF-*g*-AA membrane after a series of preservation times (1, 3, 6, 12, and 15 months). Compared with the original PVDF hollow fiber membrane (M0), the pure water flux of the PVDF-*g*-AA membrane (M3) increased to more than twofold, which was attributed to the hydrophilic effect of the grafted AA brush. The pure water flux of both membranes decreased to some extent after 15 months of storage, which was consistent with the decrease of the membrane pore size.

Figure 11 shows the flux rejection rate to BSA of the original PVDF hollow fiber membranes (M0) and the PVDF-*g*-AA membrane (M3) with a series of preservation times. The initial rejection rate of the PVDF-*g*-AA membrane was twice higher than that of the original PVDF membrane. This finding could



**Figure 11.** Rejection of the original PVDF membrane (M0) and the grafted PVDF membrane (M3) with a series of preservation times (1, 3, 6, 12, and 15 months).

be explained by the improvement of hydrophilicity and the decrease of membrane pore size, which slightly increased after 15 months of storage and was attributed to the decrease of the membrane pore size. The results of pure water flux and rejection rate indicated that the permeation property of the PVDF hollow fiber membrane undergoes the test of time after irradiation grafting polymerization.

## CONCLUSIONS

PVDF-*g*-AA hollow fiber membranes with hydrophilic nature were produced through the grafting process. For the suitability of the grafting degree, the newly produced membrane exhibited high pure-water flux and rejection.

The thermal and mechanical properties of the PVDF polymer, such as thermal decomposition temperature, melting point, glass transition temperature and breaking force, were enhanced by high-energy electron beam irradiation grafting polymerization, and these changes were stable and durable. The polymer structure of the PVDF-*g*-AA hollow fiber membrane was stable.

The relatively uniform pore size distribution of the grafted PVDF membrane became dispersive due to irradiation grafting polymerization, and this change was stable even after more than one year. The pure water flux and rejection of the grafted membrane remained stable even after 15 months. The results indicated that the pore diameter and the permeation property of PVDF-*g*-AA hollow fiber membrane were stable.

## ACKNOWLEDGMENTS

The subject of research was supported by the National High Technology Research and Development Program of China (863 Program) (No.2013AA065601), the National Natural Science Foundation of China (51078264, 51103102) and ministry of education doctoral fund (20101201110001, 20111201120004).

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