



# Graft polymerization of acrylic acid and methacrylic acid onto poly(vinylidene fluoride) powder in presence of metallic salt and sulfuric acid

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## ABSTRACT

Poly(vinylidene fluoride) (PVDF) powder was grafted with acrylic acid (AAc) or methacrylic acid (MAA) by the pre-irradiation induced graft polymerization technique. The presence of graft chains was proven by FT-IR spectroscopy. The degree of grafting (DG) was calculated by the acid–base back titration method. The synergistic effect of acid and Mohr's salt on the grafting kinetics was examined. The results indicated that adding sulfuric acid and Mohr's salt simultaneously in AAc or MAA solutions led to a strong enhancement in the degree of grafting. The grafted PVDF powder was cast into microfiltration (MF) membranes using the phase inversion method and some properties of the obtained MF membranes were characterized.

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## 1. Introduction

PVDF is one of the major materials used for preparation membranes due to its favorable properties including good thermal stability, chemical resistance, excellent membrane forming properties and high weathering resistance (Hashim et al., 2009; Betz and Begue, 2003; Clochara et al., 2004).

Under ionizing radiation from  $\gamma$ -rays or electron beams, free radicals are produced in fluoropolymers. Therefore, a convenient method of getting modified fluoropolymers is by use of the radiation-induced graft polymerization technique (Dargaville et al., 2003; Nasef and Hegazy, 2004). In this way, functional membranes, which possess selective mass transfer properties, such as proton exchange membranes (PEMs) and antifouling microfiltration (MF) membranes, can be fabricated by grafting monomers containing the desired functional groups (Li et al., 2004, 2005a, 2005b, 2006a, 2006b, 2006c).

Many works have been reported concentrating on the grafting of monomers onto membranes directly (Hashim et al., 2009; Betz and Begue, 2003; Clochara et al., 2004; Boributh et al., 2009). Recently, we reported the modification of polymer powder by pre-irradiation induced graft polymerization and then fabrication of the grafted polymer into membranes (Deng et al., 2008, 2009, 2010; Li et al., 2010). This new routine has the advantage of improving the evenness of the distribution of the graft chains.

Hydrophilic filtration membranes are usually obtained by grafting hydrophilic monomers such as AAc and MAA onto the

hydrophobic membranes. An interesting phenomenon reported by Nho and Jin (1998) was that by adding sulfuric acid and Mohr's salt simultaneously to the AAc or MAA grafting solutions led to an unusual enhancement in the DG of grafted PE membranes. This is very valuable for increasing the monomer conversion.

Here, a study of the grafting kinetics for the pre-irradiation induced graft polymerization of AAc and MAA onto PVDF powder is reported. Hydrophilic MF membranes were prepared from AAc and MAA grafted PVDF powder using the phase inversion method.

## 2. Experimental

### 2.1. Materials

PVDF (Mw=420,000) in powder form with diameter of 0.1 mm was purchased from Solvay Chemicals Company, Belgium. AAc, MAA, 1-methyl-2-pyrrolidone (NMP), poly(vinyl pyrrolidone) (PVP) K30 (Mw=50,000), sulfuric acid and ferrous ammonium sulfate hexahydrate were purchased from Sinopharm Reagent Co. Ltd., Shanghai. All of the materials mentioned above were used without further purification.

### 2.2. Pre-irradiation induced graft polymerization

PVDF powder was irradiated to 15 kGy in air using  $\gamma$ -ray from a <sup>60</sup>Co source at room temperature, and then stored at  $-24\text{ }^{\circ}\text{C}$  in a refrigerator before use.

70 mL deionized water, 5 g of irradiated PVDF powder and 30 mL of AAc or MAA were added to a 150 mL Erlenmeyer flask

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successively. The flask was then bubbled with nitrogen for 15 min to remove oxygen. After that, it was sealed, and graft polymerization was started at 60 °C under continuous stirring.

After a defined period, graft polymerization was stopped, and the grafted PVDF powder was filtered and washed. Then it was washed with 1 M NaOH solution at 60 °C under stirring for 2 h. During the wash, NaOH solution was replaced three times to remove all of the homopolymer completely. After that the powder was filtered and recovered by washing with an excess of 1 M HCl solution. Then the powder was washed repeatedly with deionized water until the pH value of the exhausted liquid was 7.0. Finally, the PVDF-g-PAAC or PVDF-g-PMAA powder was dried to constant weight at 60 °C in a vacuum oven.

The DG values of PVDF-g-PAAC or PVDF-g-PMAA powder were determined by acid–base back titration. The details of acid–base back titration were described in our previous papers (Deng et al., 2008, 2009, 2010).

### 2.3. Infrared spectroscopy of pristine and grafted PVDF powder

Pristine and grafted PVDF powders were pressed into pellets with KBr. Then FT-IR spectra were taken using a Nicolet Avatar 370 FT-IR spectrometer by the accumulation of 32 scans at a resolution of 4 cm<sup>-1</sup>.

### 2.4. Membrane preparation

MF membranes were cast from NMP solution of pristine PVDF powder or grafted PVDF powder using the phase reverse method with PVP as the pore former as follows.

Pristine or grafted PVDF powder and PVP were dissolved in NMP at 70 °C with a weight ratio of 12.5:3:84.5 for 6 days. Before casting, the solution was ultrasonicated for 30 min to eliminate bubbles. After that, the solution was cast onto a glass plate. Then, the new-born membrane was immersed in deionized water at 25 °C. The membranes were let stand in the coagulation bath for 3 days and then they were taken out and rinsed with deionized water 3 times to thoroughly remove any remaining solvent and then kept in fresh deionized water before further characterization.

A clear solution is required for membrane preparation; however, when the DG exceeded 30%, the solubility of the grafted PVDF powder became poor and the solutions were cloudy, even when heated for more than 7 days at 70 °C. Therefore, in this work only grafted PVDF powder with a DG lower than 30% were cast into MF membranes and then characterized.

### 2.5. Water uptake measurement

The water uptake (WU) of the MF membranes was determined by the weight change after soaking in deionized water.

MF membranes were rinsed with deionized water, and then dried in a vacuum oven at 60 °C for 24 h. After that, the dried membranes were immersed in deionized water for at least 24 h. Then the swollen membranes were taken out, and the excess water on the surfaces gently removed by a blotter. The swollen membrane weights were then quickly measured before drying the membranes under vacuum at 60 °C for 24 h. The dried membranes were quickly weighed and the WU was calculated according to the following relationship:

$$\text{Water uptake (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where  $W_s$  and  $W_d$  were the weight of the swollen and dry MF membranes, respectively.

## 3. Results and discussion

### 3.1. FT-IR spectra

PAAC and PMAA homopolymers are water-soluble acidic polymers and can be removed efficiently from the grafted PVDF powder by hot alkaline solution extraction. Therefore, the characteristic absorption attributed to the carboxyl groups in FT-IR spectra proves that AAC or MAA were successfully grafted onto the PVDF powder.

FT-IR spectra of PVDF-g-PAAC and PVDF-g-PMAA are shown in Figs. 1 and 2, respectively. All FT-IR spectra in Figs. 1 and 2 were normalized according to the absorption peak of CH<sub>2</sub> stretching mode located at 1411 cm<sup>-1</sup>. In the spectrum of pristine PVDF powder, the characteristic absorption bands at 1168 and

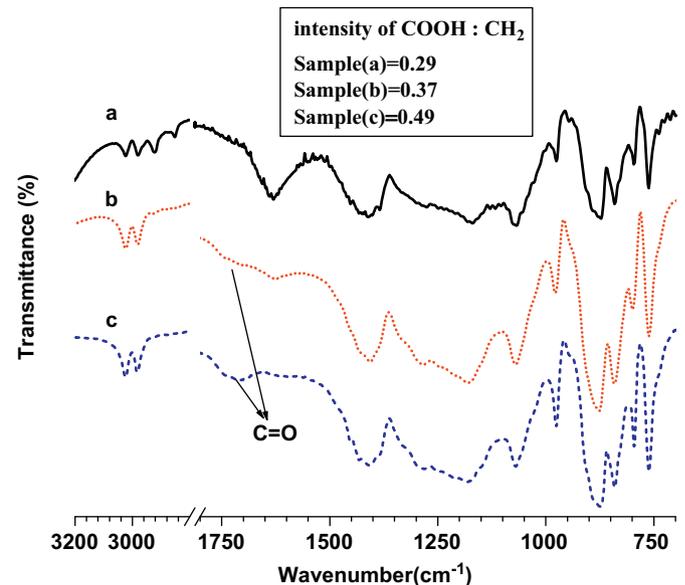


Fig. 1. FT-IR spectra of pristine PVDF (a) and PVDF-g-PAAC powder with DG of (b) 23.7% and (c) 47.1%.

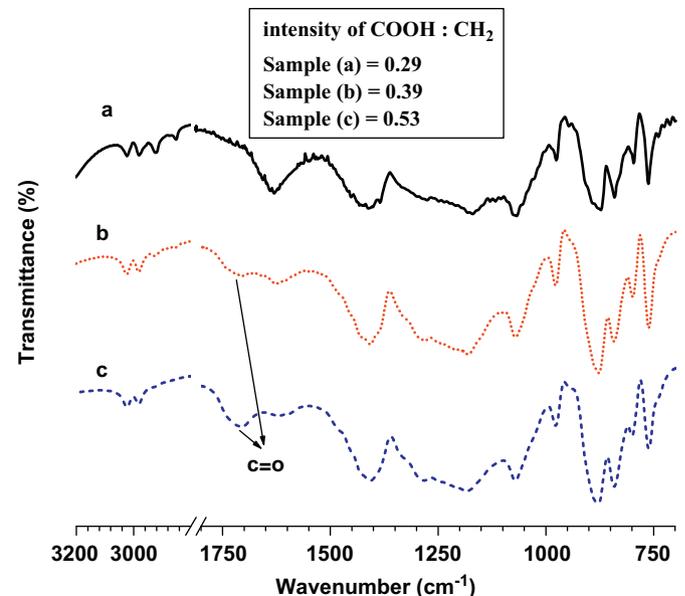


Fig. 2. FT-IR spectra of pristine PVDF (a) and PVDF-g-PMAA powder with DG of (b) 24.3% and (c) 48.4%.

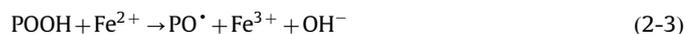
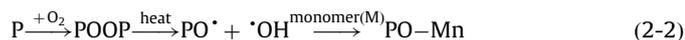
1411  $\text{cm}^{-1}$  are due to the absorption peaks of  $\text{CF}_2$  stretching and  $\text{CH}_2$  stretching modes, respectively (Boributh et al., 2009). The observed stretching vibration of  $\text{C}=\text{C}$  at 1631  $\text{cm}^{-1}$  and the weak stretching vibration of  $\text{C}=\text{O}$  at 1726  $\text{cm}^{-1}$  can be attributed to partial oxidation of the PVDF powder during storage as reported (Clocharda et al., 2004). The asymmetric and symmetric stretching vibrations of the  $\text{CH}_2$  group in the pristine PVDF are located, respectively, at 3024 and 2982  $\text{cm}^{-1}$  (Betz and Begue, 2003; Betz et al., 2003).

The spectra of PVDF-g-PAAc or PVDF-g-PMAA powders revealed a more intense absorption band at about 1725  $\text{cm}^{-1}$  due to the stretching vibration of carbonyl groups, which indicate the existence of the PAAc or PMAA chains. Moreover, the absorbance at about 1725  $\text{cm}^{-1}$  increased with increase in DG according to the ratio of peak intensities of the  $\text{C}=\text{O}$  (at 1725  $\text{cm}^{-1}$ ) to the  $\text{CH}_2$  (at 1631  $\text{cm}^{-1}$ ). That is to say, the higher the percentage of PAAc or PMAA graft chains, the higher the DG. Meanwhile, the  $\text{CH}$  stretching of the PVDF structure located at 2921 and 2852  $\text{cm}^{-1}$  weakened with increase in DG, consistent with more PAAc or PMAA graft chains in the grafted PVDF powder.

### 3.2. Kinetics study

Figs. 3 and 4 shows the effect of reaction time on the degree of grafting of acrylic acid and methacrylic acid into PVDF powder in the presence and absence of sulfuric acid, respectively.

Typical grafting reactions utilize peroxide free radicals can be represent as follows (Nho and Jin, 1998; O'Neill, 1972):



From Figs. 3 and 4, the high initial grafting rates and long radical lifetimes result in a much higher saturated DG in the presence of acid for both AAC and MAA graftings.

The sulfuric acid accelerates the decomposition of hydroperoxide in the presence of  $\text{Fe}^{2+}$  to form radicals, which can initiate a grafting reaction in the presence of sulfuric acid. Also the accumulated  $\text{OH}^-$  can be consumed by the sulfuric acid. Therefore,

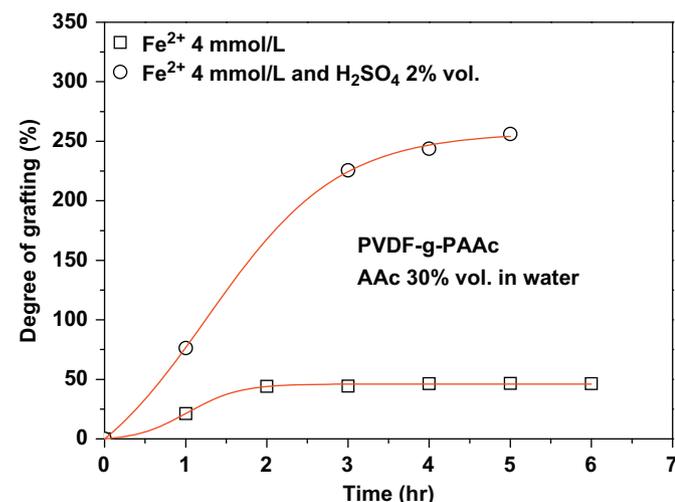


Fig. 3. Effect of reaction time on the grafting of AAC for 15 kGy irradiated PVDF powder in 30% aqueous solution containing  $4 \times 10^{-3}$  M Mohr's salt at 60 °C with  $\text{H}_2\text{SO}_4$  (○) (2% vol.) and without  $\text{H}_2\text{SO}_4$  (□).

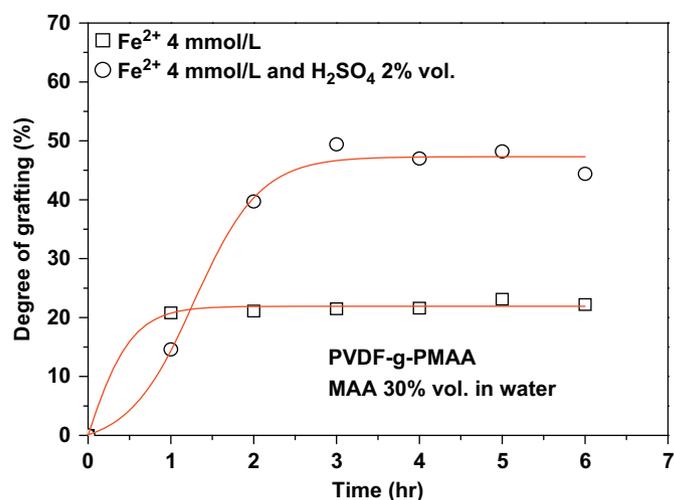


Fig. 4. Effect of reaction time on the grafting of MAA for 15 kGy irradiated PVDF powder in 30% aqueous solution containing  $4 \times 10^{-3}$  M Mohr's salt at 60 °C with  $\text{H}_2\text{SO}_4$  (○) (2% vol.) and without  $\text{H}_2\text{SO}_4$  (□).

reactions (2-3) can be progressed and consequently a higher saturated DG results (Nho and Jin, 1998).

As we know, the methyl group of MAA can activate the double bond, which makes MAA more reactive than AAC (Nho and Jin, 1998). Thus, the DG is higher using MAA as monomer than AAC in most cases under the same reaction conditions, except for the monomer type.

But Figs. 3 and 4 revealed an abnormal phenomenon in that the DG for MAA (about 20%) was lower than that for AAC (only 15%) after 1 h without the acid.

This is similar with grafting AAC or MAA onto polypropylene membrane at 50 °C, which was reported by Nho and Jin (1998). The most likely reason for this is the difference in the reaction temperature.

As mentioned above in Section 2.4, the DG of the modified PVDF powder should be controlled to below 30% w/w to allow fabrication of the MF membranes successfully. So we also investigated the effect of the concentration of the Mohr's salt on the DG in the presence of  $\text{H}_2\text{SO}_4$  in order to keep the DG of the grafted PVDF powder below 30%.

The kinetics curves in Fig. 5 represent the effect of the Mohr's salt concentration on the DG of grafted PVDF-g-PAAc powder in the presence and absence of sulfuric acid. From Fig. 5, it can be found that the degree of grafting for a given monomer concentration and reaction time decreases with increase in salt's concentration, with or without sulfuric acid. And it can also be found from Fig. 5 that the addition of sulfuric acid and appropriate concentration of  $\text{Fe}^{2+}$  can greatly enhance the grafting, which is in accord with the results in Fig. 3.

### 3.3. MF membranes casting and their water uptake

MF membranes were cast from NMP solution of pristine PVDF powder or grafted PVDF powder using the phase reverse method with a weight ratio of 12.5:3:84.5 for PVDF, PVP and NMP, respectively.

Water uptake of the MF membranes cast from PVDF-g-PAAc and PVDF-g-PMAA at different DG is plotted in Fig. 6. From Fig. 6 we can see that although PVDF is hydrophobic and the water absorption by PVDF is negligible, water can be stored in the numerous pores in the MF membranes cast from virgin PVDF.

The average pore diameters of MF membranes were measured by the bubble point method, as described in our previous papers

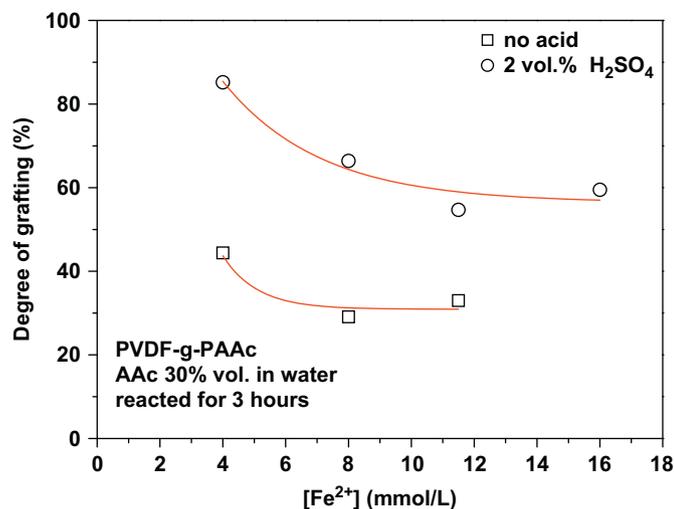


Fig. 5. Effect of  $\text{Fe}^{2+}$  concentration on the grafting of AAC for 15 kGy irradiated PVDF powder in 30% aqueous solution with  $\text{H}_2\text{SO}_4$  (○) (2% vol.) and without  $\text{H}_2\text{SO}_4$  (□) at 60 °C.

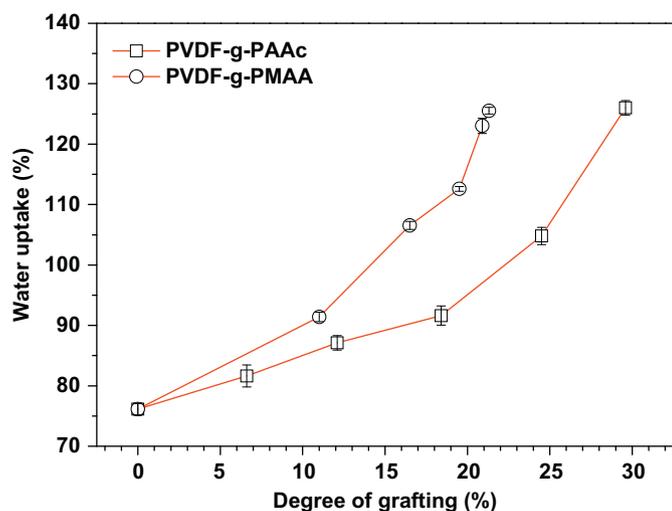


Fig. 6. Water uptake of MF membranes cast from PVDF-g-PAAc and PVDF-g-PMAA at different DG.

Table 1

Average pore diameters of MF membranes cast from PVDF-g-PAAc and PVDF-g-PMAA at different DG, measured by the bubble point method.

DG of PVDF-g-PAAc	0	6.6	12.1	18.4	24.5	29.6
Pore diameters ( $\mu\text{m}$ )	0.15	0.17	0.18	0.18	0.19	0.19
DG of PVDF-g-PMAA	0	11.0	16.5	19.5	20.9	21.3
Pore diameters ( $\mu\text{m}$ )	0.15	0.17	0.17	0.18	0.18	0.19

(Deng et al., 2008, 2009, 2010). The average pore diameters of the MF membranes cast from grafted PVDF powder at different DG are listed in Table 1, and showed little difference.

As reported (Abdiyev et al., 2003) the strengthening of the intra- and intermolecular hydrophobic interactions in macromolecules of PMAA polycomplex in the presence of  $\alpha$ -methyl groups in PMAA resulted in the higher hydrophilicity of PMAA than PAAc.

That is to say, with the improved hydrophilicity due to the presence of PAAc or PMAA grafts, the WU of the modified MF membranes increased mainly because of the enhancement of the hydrophilicity of membrane material.

#### 4. Conclusions

PVDF powder was grafted with AAC or MAA using the pre-irradiation induced graft polymerization method. The existence of grafted PAAc or PMAA in PVDF powder was demonstrated by FT-IR spectroscopy. The synergistic effect of acid and Mohr's salt can lead to an unusual enhancement in the DG of PVDF-g-PAAc or PVDF-g-PMAA powder, and the  $\text{OH}^-$  produced in the reaction medium can be consumed by the  $\text{H}_2\text{SO}_4$ . This can increase monomer conversion ratio thereby lowering the cost of production. MF membranes were cast from modified PVDF powder and the increased hydrophilicity of the MF membranes was proved by the increased water uptake.

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