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# pH Sensitive polypropylene porous membrane prepared by grafting acrylic acid in supercritical carbon dioxide

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## Abstract

pH sensitive membrane was prepared by grafting acrylic acid (AA) on the porous polypropylene (PP) membrane using supercritical (SC) $CO_2$ as a solvent. The monomer (AA) and the initiator (benzyl peroxide, BPO) were impregnated into the PP substrate with the aid of SC $CO_2$, and were grafted onto the microporous PP substrate. The grafted membranes were characterized by Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), and the water permeability of the virgin and grafted membranes were determined at different pH values. It was demonstrated that the grafting degree (Dg) could be easily controlled by varying operating conditions, such as the monomer concentration, pressure, and temperature during the soaking process. The water permeation of the virgin membrane is nearly independent of pH. However, the water permeation of grafted membranes decreases dramatically with pH as the pH varies from 3 to 6 because the conformation of the PAA changes significantly with the pH of the contacting solution.

*Keywords:* pH Sensitive; Membrane; Supercritical carbon dioxide

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## 1. Introduction

Environmental sensitive membranes can rapidly response to a minor stimulus from their surrounding environment. Their permeability, selectivity or hydrophobicity can be tuned by altering the easily controlled parameters such as pH value [1–5], temperature [6–8], ionic strength [1,9], and others [10]. So these membranes have found many potential applications ranging from separations to controlled-released systems [11]. As an important member of environmental sensitive membranes, pH sensitive membrane has been extensively studied [1–5] and it was found that some polyelectrolytes could change from a random coil to compact helix by tuning the pH value of the contacting solution [12]. This can be accomplished by introducing 'sensitive' monomers like acrylic acid (AA) and methacrylic acid onto the surface of porous membrane substrates. Many methods, such as UV [13,14], plasma [15], electron-beam [2] and glow discharge [1,16] have been used to graft monomers onto porous substrates, resulting in sensitive membranes.

Supercritical fluids (SCFs) have many unique properties and they can be applied in many processes [17,18]. Utilization of SC $CO_2$ is the most attractive because it is nonflammable, nontoxic, relatively inexpensive, and has moderate critical parameters ($T_c = 31.1$ °C, $P_c = 7.38$ MPa). In recent years there has been increasing interest in using supercritical carbon dioxide as a solvent and/or a swelling agent in polymer processing and polymer chemistry [19,20]. SC $CO_2$ has been widely applied in polymer sciences, such as synthesis of different kinds of polymers [21–28], preparing fibers [29,30], generation of fine particles [31–34], producing foam materials [35–38], and polymer fractionation [39–41]. SC $CO_2$ has strong ability to dissolve small organic compounds. It can also swell many polymers, but most polymers are not soluble in SC $CO_2$. These unique properties of $CO_2$/polymer systems have been applied to impregnate different additives into polymer matrices [42–44]. Using SC $CO_2$ as a solvent and

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swelling agent, some polymer composites have been fabricated by impregnating polymer substrates with monomers and initiators, and then initiating polymerization in the substrates [45–49]. This principle can also be used to graft monomers onto some polymer backbones, and grafting of maleic anhydride onto poly (4-methyl-1-pentene) [50], isocyanato-isopropyl groups onto poly(ethylene-*co*-vinylalcohol) [51], 2-hydroxyethyl methacrylate, AA onto isotactic polypropylene (PP) [52,53], and maleic anhydride onto PP [54] have been accomplished. However, to the best of our knowledge, study on modification of microporous membranes by grafting polymerization in SC $CO_2$ has not been reported in the literature.

It is known that the density of SC $CO_2$, and thus its solvent strength, is continuously tunable from gas-like to liquid-like by changing pressure and/or temperature. Moreover, SC $CO_2$ has low viscosity, high diffusivity, and near zero surface tension. Therefore, the monomers and initiator can diffuse into the substrates in shorter time and distribute more uniformly. Moreover, since $CO_2$ is gas at ambient conditions, removal of the solvent from the final product is extremely facile. All these advantages of SC $CO_2$ may be favorable to modifying porous membranes effectively by grafting functional monomers on the substrates. In this work, grafting AA onto porous PP membrane has been investigated. The results indicate that the grafting level can be tuned easily by controlling pressure, temperature, and monomer concentration during the soaking process, and pH sensitive membranes has been prepared. This work combine the two novel approaches that have been demonstrated: (1) using SC $CO_2$ as a solvent and carrier to graft polar monomer onto PP; (2) grafting of pH sensitive AA onto PP.

## 2. Experimental

### 2.1. Materials

Celgard 2400(Daicel Chemical Industries, Ltd) microporous PP membrane was used as the grafting substrate. Its pore size was 125 nm × 50 nm with a thickness of 25 μm and a porosity of 38%. They were cut into 5 cm × 5 cm pieces and rinsed in acetone for about 24 h, and then dried in a vacuum oven at 70 °C. Acrylic acid (AA, Beijing Chemical Reagent Company, A.R. grade) was vacuum distilled. Benzoyl peroxide (BPO, Beijing Chemical Plant) was recrystallized twice from methanol. $CO_2$ with a purity of 99.95% was purchased from Beijing Analytical Instrument Factory and used as received.

### 2.2. Grafting procedure

In a typical experiment, suitable amount of PP membrane was placed into a stainless steel autoclave of 20 ml. Desired amount of AA/BPO solution (1 wt% BPO) was charged into the autoclave, and the air in autoclave was removed. Then the autoclave was placed into a constant-temperature water bath controlled by a HAAKE D3 temperature controller. $CO_2$ was then charged using a syringe pump (DB-80, Beijing Aircrafts) to a desired pressure. During charging $CO_2$, the autoclave was shaken by hand to promote the dissolution of monomer and initiator in SC $CO_2$. After soaking for 2 h, the autoclave was transferred into a constant temperature oven of 80 °C to initiate the grafting polymerization. After a desired reaction time, the sample was taken out, washed with hot water and then Soxhlet-extracted with boiling ethanol for 24 h to remove AA homopolymer. After drying, the extracted sample was re-extracted. Such procedure was repeated two or three times until the sample weight was constant. It was assumed that the unreacted monomer and homopolymer had been removed completely.

### 2.3. Characterization

FTIR spectra of original and grafted PP membranes were recorded using a Bruker Tensor 27 FTIR spectroscopy. The morphological characteristics of the original and grafted samples were observed using field emission scanning electron microscopy (JSM6301F), and the samples were sprayed with gold before observation.

A dead-end cell filtration cell with an active membrane area of 10.75 $cm^2$ was employed to characterize water permeability of the grafted and original membranes. All filtration measurements were carried out at a constant transmembrane pressure of 0.3 MPa and at 18 °C, and the membranes were wetted with ethanol before the measurements. The pH value of the distilled water was adjusted by HCl or NaOH. Prior to the measurement, the sample was equilibrated in the test solution under pressure until a stable flux was achieved. The flux was calculated easily from the mass of water collected, the filtration time, and the area the membrane.

## 3. Results and discussion

### 3.1. Grafting

In this work, the soaking experiments were conducted under conditions at which $CO_2$, AA, and BPO existed in a single phase, which was known by simulating experiments using an optical cell used previously [55]. In order to optimize the operation conditions, the effects of monomer concentrations, soaking pressure and temperature, and polymerization time on the degree of grafting Dg were studied. The Dg was calculated from the following equation.

$$\text{Dg}\ (\%) = 100(W_1 - W_0)/W_0$$

where $W_0$ stands for the weight of original PP membrane and $W_1$ is the weight of grafted membrane after removal of homopolymer and unreacted AA.

Fig. 1 shows the effect of monomer (AA) concentration

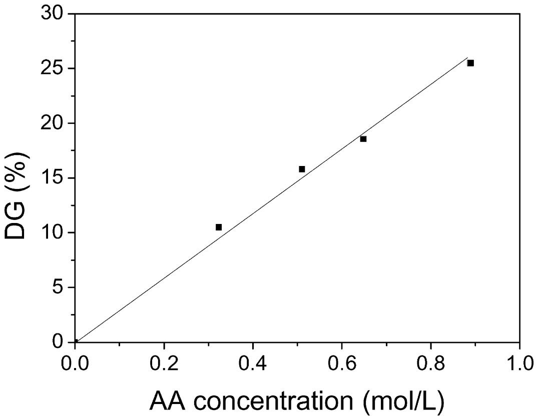

Fig. 1. Effect of the monomer (AA) concentration during the soaking process on grafting degree (soaking condition: 35.0 °C and 9.00 MPa; reaction condition: 80 °C for 24 h).

on the degree of grafting. The soaking temperature and pressure are 35.0 °C and 9.00 MPa, respectively. The Dg increases linearly with monomer concentration in the concentration range studied. This is easy to understand because the monomer distributes between the SC $CO_2$ phase and PP solid phase during the soaking process. The monomer concentration studied in this work is relatively low ($<1.0$ mol/l), and saturation adsorption of AA cannot be reached. Increasing monomer concentration favors the adsorption of the monomer on the surface of PP substrate. Thus, more monomer can be grafted onto PP backbone. It can be concluded that the grafting level can be controlled by the concentration of the monomer in the fluids phase.

Fig. 2 shows the effect of reaction time on the Dg. It is evident that the Dg increases initially with reaction time and levels off in 24 h. This is because all the initiator BPO are consumed and/or all the monomers are polymerized after 24 h.

Fig. 3 shows the dependence of Dg on soaking pressure at 55 °C. It can be seen that there is a significant rise as the pressure drops. The Dg decreases from 8.6 to 61.4% as pressure is decreased from 15.00 to 9.00 MPa. This can be explained by the remarkable change of solvency of SC $CO_2$ with the change of pressure. At higher pressure, SC $CO_2$ has stronger solvent power, and thus more monomer exists in the $CO_2$ phase. In other words, more monomer is extracted from the PP membrane by SC $CO_2$ when pressure increases. As a result, the amount of monomer and initiator adsorbed on PP substrate is reduced. This indicates that the Dg of the can also be controlled easily by tuning soaking pressure. In previously work [53], we grafted AA on nonporous PP substrate. The Dg on the porous PP (Fig. 3) is more sensitive to pressure than that on the nonporous substrate. One of the reasons is that the former has larger surface area.

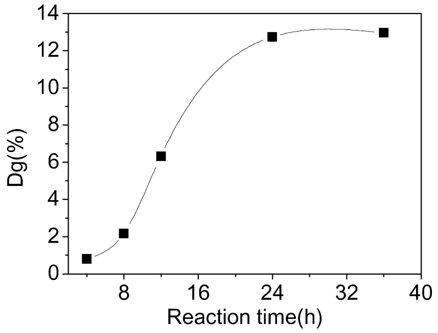

Fig. 2. Effect of reaction time on degree of grafting degree (soaking condition: 35 °C, 8.00 MPa, [AA] = 0.19 mol/l).

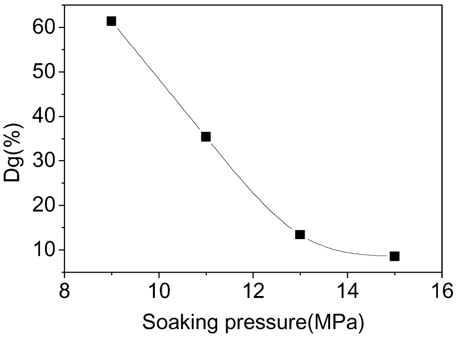

Fig. 3. Effect of soaking pressure on grafting degree at 55.0 °C with monomer concentration of 0.22 mol/l (reaction time: 24 h).

Fig. 4 illustrates the dependence of grafting degree on soaking temperature. Dg increases monotonously with the rise of soaking temperature. This can also be explained by the change of the solvency of SC $CO_2$. It is well known that the density of $CO_2$ decreases with increasing temperature at fixed pressure. Therefore, the solvent power of $CO_2$ is enhanced as the temperature is reduced. As a result, more monomer exists in $CO_2$ phase at the lower temperature, which diminishes the amount of monomer in the PP phase. Consequently, the samples prepared at the lower soaking temperature have lower grafting level.

### 3.2. Characterization

After grafting, AA chains were anchored on the surface of the PP membrane, which can be confirmed by FTIR spectroscopy analysis. Fig. 5 demonstrates the IR spectra of virgin PP and the grafted PP samples. It can be seen from

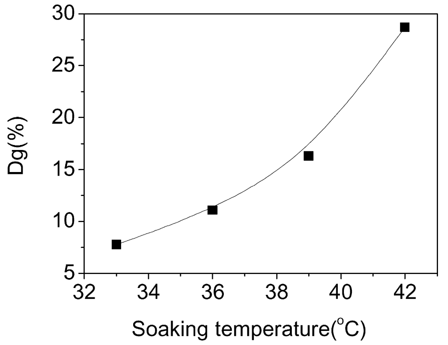

Fig. 4. Effect of soaking temperature on grafting degree at 9.00 MPa with monomer concentration of 0.32 mol/l (reaction time: 24 h).

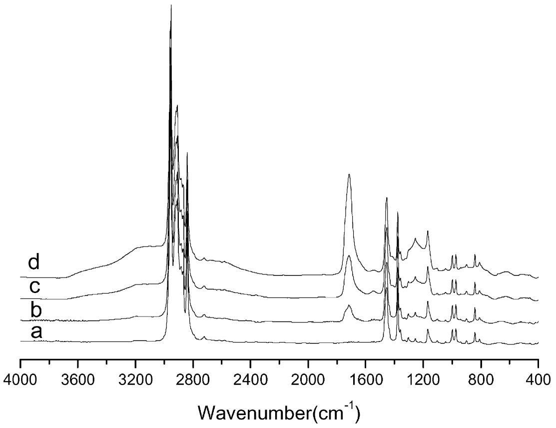

Fig. 5. FTIR Spectra of original PP (a) and 3.39% (b), 17.20% (c) and 35.37% (d).

this figure that there is an absorption peak around 1725 cm$^{-1}$ in the spectra of the grafted samples, which cannot be observed for the virgin PP sample. This peak is assigned to the stretch of the C=O group. This was an indication that the AA chains were grafted onto the PP because the unreacted monomer and the homopolymer could be removed in the Soxhlet-extraction process, as discussed. As expected, the strength of the characteristic peak (at 1725 cm$^{-1}$) of the grafted samples increases with the increase of the grafting degree. For each grafted sample, we scanned at 8–10 different points, and the difference of the spectra was not noticeable, suggesting the uniform grafting of the samples in SC $CO_2$. In addition, when the grafted sample with relatively high Dg (e.g. $>10\%$) obtained in SC $CO_2$, which was opaque in dry state, was immersed in water, it became transparent because of the inclusion of water in membrane pores for the sample got hydrophilicity after AA grafting. And it should be noted that the whole membrane throughout its full size became transparent, indicating the uniformity of grafting in SC $CO_2$. The uniformity of grafting in SC $CO_2$ can be attributed to special properties of SC $CO_2$. SC $CO_2$ has high diffusivity and low viscosity comparing with liquids, and near zero surface tension [18]. Thus, the monomer and the initiator molecules can diffuse into any space in the PP matrix with a faster rate, provided that the size of the space is larger than that of the molecules. Therefore, the monomer and the initiator are more uniformly distributed in the matrix before polymerization.

FE-SEM was employed to compare the change of the surface structure of the original and grafted membranes, and the SEM micrographs are shown in Fig. 6. The figure shows clearly that the original PP membrane has a number of flat or elliptical pores (It should be noted that the membrane only treated with SC $CO_2$ and without the graft procedure has almost the same morphology as the virgin membrane for there is no significant interaction between the SC $CO_2$ and PP under the pressure and temperature adopted in the present work). Obviously, the density and pore size are reduced after the AA is grafted on the PP backbones. The number of the pores and their size decrease with the increase in grafting level, and only the larger pores are left as the grafting level is very high. In addition, by comparing Fig. 6(e) and (f), we can see that the size of pores in the cross section of the grafted membrane also decreased compared with the virgin un-grafted sample, indicating that the grafting in SC $CO_2$ also occurred in the deep regions from the surface of membrane due to the good diffusive and penetrating properties of SC $CO_2$.

### 3.3. The pH sensitive property

The pH-dependent water permeability of some AA grafted membranes with different grafting degrees and the virgin PP membrane were examined at various pH values, and some of the results are demonstrated in Fig. 7. The flux of the original PP membrane is nearly constant in the entire pH range studied, which is similar to that of the commercial porous poly(vinylidene fluoride) films [5]. However, like other pH-sensitive porous membranes [1–5], the water permeability of grafted membranes depend strongly on pH value. The grafted membranes with different Dg have a similar trend in their pH-flux relation, which can be divided into 3 sections: $\mathrm{pH} < 3.5$(i), $\mathrm{pH} > 6$(ii) and $3.5 < \mathrm{pH} < 6$(iii). In section (i), the flux is nearly independent of pH value. In section (ii), the flux decreases sharply with pH value until pH reaches 6. After the curve steps into section (iii), the flux is not sensitive to pH. The flux change with pH results from the response of the PAA chains grafted on the PP substrate to the $H^+$concentration in environment. As a weak polyelectrolyte, PAA molecules adopt coiled or stretched conformation depending upon the degree of dissociation or protonation, which is controlled by the $H^+$strength of the surrounding solution [56]. The conformation of the PAA chains changes from coiled at lower pH to more stretch at higher pH. The stretched conformation will plug the pores partly or even completely provided that the grafted chains are enough and/or longer enough, which results in the decrease in the active pore size, and therefore the permeating flux is correspondingly reduced. In the range of pH $<3$, the conformation of the grated PAA is not sensitive to pH, probably because the acidity of the solution is strong enough. In section (ii), the PAA changes from coil to stretch, and the conformation is very sensitive to the acidity of the solution. Thus, an increase in pH results in dramatic decrease in the flux. When the pH rises to a certain value, the PAA chains have stretched almost to the limit. Therefore, change in the flux not considerable after pH $>6$.

Fig. 7 also shows dependence of the flux on the grafting degree. The grafted membrane with 7.8% Dg has the largest flux of about 27 kg/m$^{-2}$ h$^{-1}$at pH = 3, which is very close to that of the original PP membrane. This is another evidence of uniform grafting. However, the maximum flux is only about 7 kg/m$^{-2}$ h$^{-1}$ for the grafted membrane of

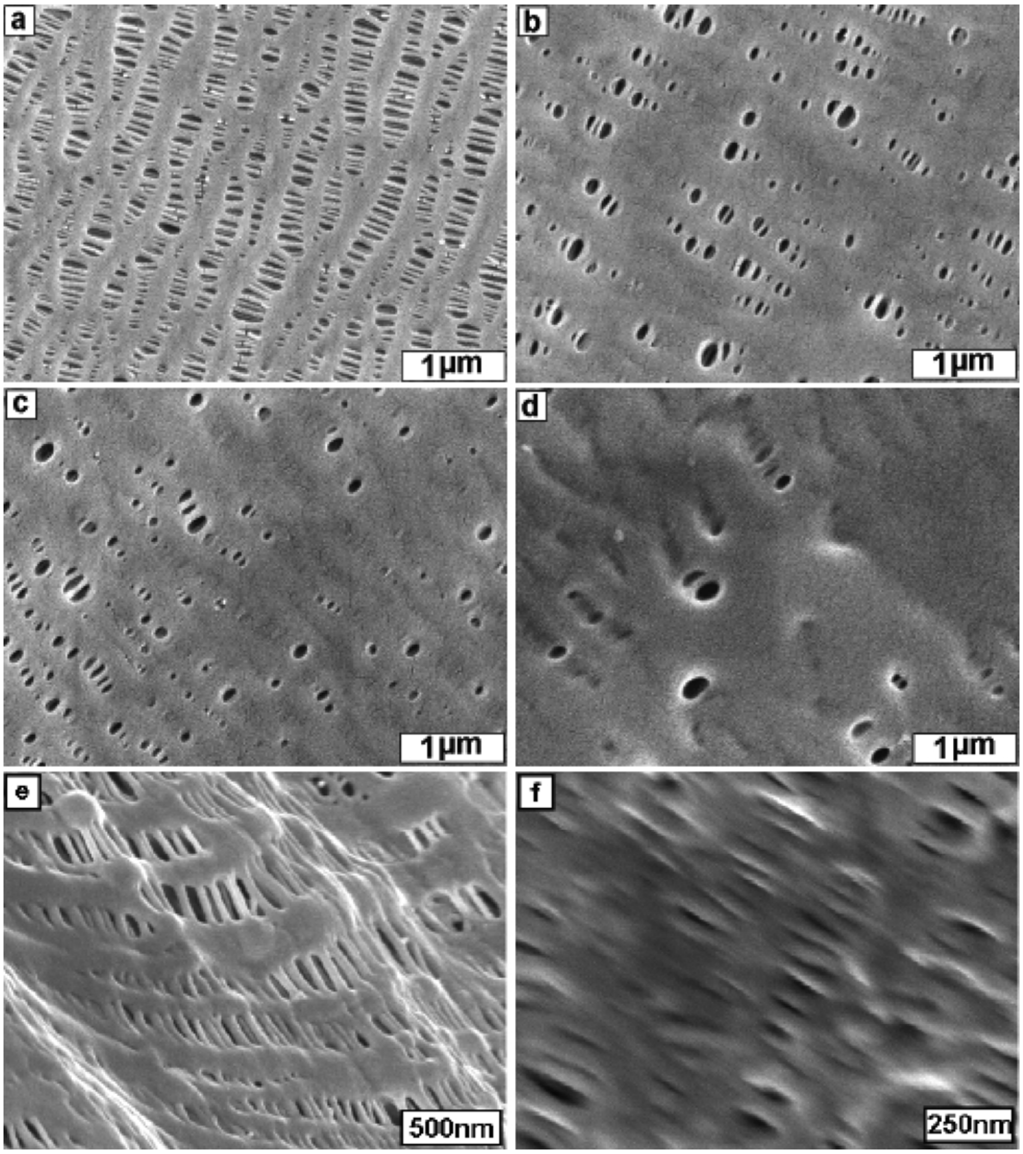

Fig. 6. FE-SEM images of outer surface of virgin PP membrane (a) and the grafted membranes with grafting degrees of 7.8% (b), 16.0% (c), 25.5% (d); and the cross section of the virgin PP membrane (e) and the 30% grafted membrane (f).

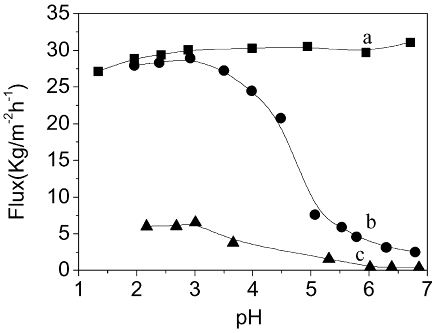

Fig. 7. pH dependence of virgin PP membrane (a) and 7.8%(b), 22.6%(c) grafted membranes.

22.6% Dg. It is caused by the blocking effect of the PAA grafts anchored onto the PP substrate. Heavily grafted membranes possess more PAA grafts and their average chain length may be longer, and as a result the active pore size is blocked to a greater degree compared with the lightly grafted ones. This demonstrates that controlling the Dg is crucial for the pH sensitive membranes. As discussed above, by using SC $CO_2$, the Dg can be easily tuned by changing pressure and monomer concentration during the soaking process.

## 4. Conclusions

Acrylic acid can be grafted onto microporous PP membrane using SC $CO_2$ as solvent, resulting in uniformly grafted membrane. This method is simple, and the grafting percentage can be controlled by altering the monomer concentration, pressure, and temperature during the soaking process. The water permeation of the virgin membrane is nearly independent of pH. However, the water permeation of grafted membranes decreases dramatically with pH as the pH varies from 3 to 6 because the conformation of the PAA changes significantly with the pH of the contacting solution.

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