

Materials

Acrylate acid (AA), acrylamide (AAM), sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) were purchased from Tianhe Chemical Co., Ltd. (China). Ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and sodium sulfite (Na_2SO_3) as initiator were also purchased from the same company. Polysulfone (PS) ultrafiltration membranes with an average cut-off molecular weight of 6,000 were purchased from Vontron Technology Co., Ltd. (China). The deionized water was purchased from Wahaha Baili Food Co., Ltd. (China).

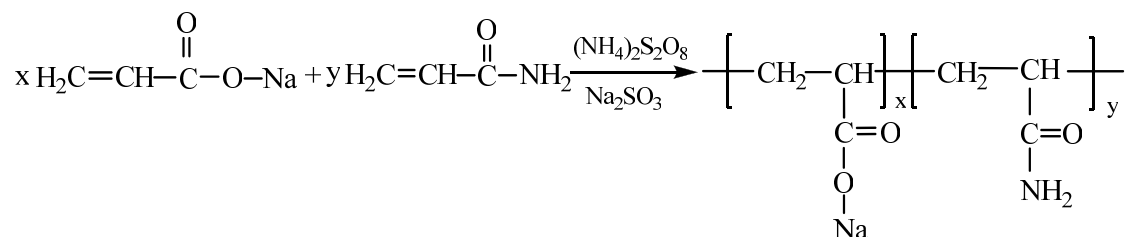
Synthesis of sodium acrylate

Sodium acrylate (AAS) was synthesized by using AA, Na_2CO_3 and NaOH. The detailed steps are as follows. A certain amount of Na_2CO_3 was added into a plastic beaker which contained some active carbon and an aqueous solution of AA, to get a 10 wt% of AAS solution. Then NaOH was added till the pH to 10. Finally, the clear solution of sodium acrylate was obtained by vacuum filtration of the mixture and was reserved in a plastic bottle.

Synthesis of the polymer

The synthesis scheme of poly(sodium acrylate-*co*-acrylamide) (P(AAS-*co*-AAM)) is presented in scheme 1. 30 g sodium acrylate solution pre-prepared, 2 g acrylamide and a certain amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and Na_2SO_3 were mixed in 68 g deionized water. Then the polymerization was carried out in a flask equipped with a stirrer at 45 ± 1 °C in water bath for 7.5 hours under N_2 atmosphere. Then the solution cooled to room temperature. After cooling, the P(AAS-*co*-AAM) solution was coagulated by slowly pouring it into a large quantity of ethanol under stirring, and white precipitated polymer was obtained. The precipitated polymer was left in ethanol for about 1 hour and then cut into small pieces. After thoroughly washed again with ethanol, the polymer pieces were dried in a vacuum oven at 40 °C for 48 hours to remove residual water and ethanol. The dried product was dissolved in deionized water, and then

filtrated with a funnel to prepare a solution with a mass concentration of 0.5%.



Scheme 1 Synthesis of P(AAS-*co*-AAM)

Preparation of the membranes

The composite membranes were prepared by casting a 0.5 wt% P(AAS-*co*-AAM) aqueous solution on the PS ultrafiltration membranes with a pre-set wet coating thickness (the gap between substrate and coating knife) by a coating applicator. After casting, the membrane was dried in a climate chamber (Climacell 222R, Germany) at 30°C and 40% relative humidity for at least 24 hours. Finally, the carboxyl group contained active layer with gas permselectivity and antioxidizability was formed on the PS support membrane.

Gas permeation measurements

The gas permeation of the membranes was measured at 25 °C by a homemade apparatus (see Fig. 1) (X. W. Yu, Z. Wang, Z. H. Wei, S. J. Yuan, J. Zhao, J. X. Wang and S.C. Wang, *J. Membr. Sci.* 2010, 362, 265-278.) using CO₂/N₂ gas mixture (15/85 by volume). The membrane was mounted in a circular stainless steel cell (effective membrane area = 19.26 cm²). Before contacting the membrane, the feed gas and the sweep gas (H₂) were both saturated with water. The composition of the permeate side gas was analyzed by a gas chromatograph (HP7890A) equipped with a thermal conductivity detector. Fluxes of CO₂ and N₂ were calculated from the flow rate and composition of the permeate side, which were average values of three data measured after steady state permeation reached. The errors from measurements were less than 2%. The feed pressure ranged from 0.11 to 1.5 MPa, while the downstream pressure was maintained at atmosphere pressure. ΔP_i is the partial pressure difference of

component i between the upstream and downstream side of the membrane. The permeance R_i is defined as the flux (N_i) divided by ΔP_i ($R_i = N_i/\Delta P_i$), and the selectivity α is defined by $\alpha_{ij} = R_i/R_j$ (the partial pressure of downstream pressure is negligible compared to that of the upstream pressure). Gas permeance unit used in this study is GPU ($1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$). All error bars present the standard errors of performances of three membranes that were prepared under the same preparation condition. In addition, it has been proved that the effect of back-diffusion of H_2 on data analysis could be neglected (X. W. Yu, Z. Wang, Z. H. Wei, S. J. Yuan, J. Zhao, J. X. Wang and S.C. Wang, *J. Membr. Sci.* 2010, 362, 265-278.).

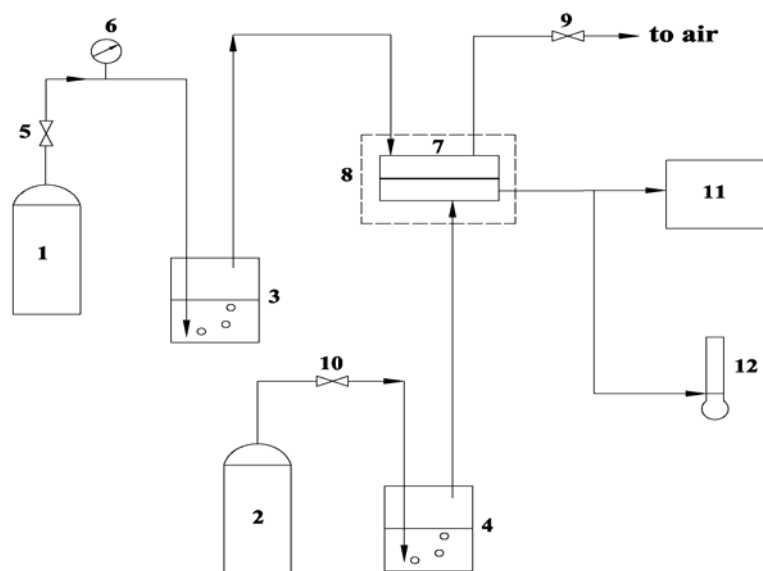


Fig. 1 Schematic representation of gas permeation apparatus: (1) feed gas; (2) sweep gas; (3)(4) humidifier; (5) pressure regulator; (6) pressure gauge; (7) membrane cell; (8) oven; (9)(10) flow regulating valve; (11) gas chromatograph; (12) soap-film flow meter.

Characterization of the membrane with the amine group as the fixed carrier

The virgin PVAm/PS membrane and the aged PVAm/PS membrane were characterized by ATR-FTIR. As shown in Fig. 2, the bands at 1290 cm^{-1} is assigned to the N=O stretching vibration of nitroso group, and the bands at 1367 cm^{-1} is assigned to the N=O stretching vibration of nitro group. The results verify the differences in the

chemical structure between the two membranes.

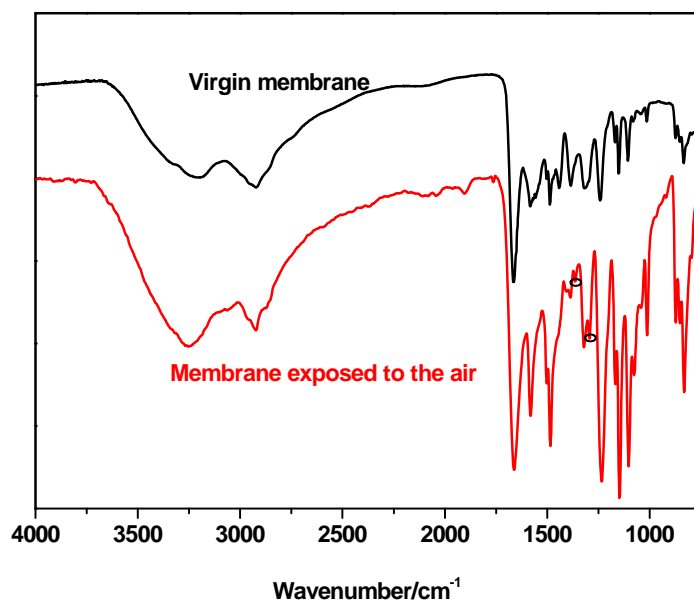


Fig. 2 ATR-FTIR spectra of the aged PVAm/PS membrane and the virgin membrane.