Preparation of Cationic Exchange Membranes Based on Organo-Montmorillonite/Poly(vinylidene fluoride) by Two-Step Chemically Induced Grafting Method

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ABSTRACT: In this research, OMMT/PVDF-based cationic exchange membranes were prepared by two-step chemically induced grafting method. The various preparation conditions, such as alkaline treatment, initiation, and grafting conditions, and the relationship between the preparation conditions and the cationic exchange membrane performance, such as area resistance and cationic permselectivity, were investigated. The chemical and crystal changes on the membrane surface were characterized by Fourier transform infrared spectroscopy (FTIR), energy dispersive spectrum (EDS), and X-ray diffraction (XRD), respectively. Surface morphological changes were also characterized by scanning electron microscopy (SEM). The results reveal that the OMMT/PVDF-based cationic exchange membrane was successfully prepared by this method. The OMMT/PVDF-based cationic exchange membrane doped 8.5% OMMT prepared using optimum preparation parameters showed excellent basic properties. The area resistance was measured as low as 1.8 Ω cm^2, while the cationic permselectivity was as high as 93.4%. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is convincing a base material for preparation of ion-exchange membranes because of its sufficient thermal, mechanical, and chemical stability.[1] One effective method to introduce cationic conducting groups to PVDF membranes is chemically induced radical grafting polymerization.[2–10] The PVDF membranes were treated in alkaline solutions with introduction of C═C bonds to proceed radical grafting polymerization. Poly(styrene sulfonic acid) chains were then grafted to the alkaline-treated membranes serving as ion conducting parts. Chemically induced radical grafting polymerization is one promising method because of its simple grafting process, low equipment requirement, as well as low cost. This method may be of particular interest for preparation of PVDF-based cationic exchange membranes with excellent properties for various applications in chemical, biological, and biomedical fields. At present, the chemically induced grafting method used for preparing PVDF-based cationic exchange membranes commonly applied single-step induced grafting route.[3–10] A functionalized PVDF membrane was obtained by chemical dehydrofluorination with alkaline solutions followed by treatment of the resulting membrane with vinyl monomers and initiator mixture. The single-step induced grafting route produced more homopolymers since the initiator was directly exposed to the grafting monomers.[3–5] Then more solvent was required to wash and remove the homopolymers from the ion-exchange membranes, which may pollute the environment and also increase the preparation cost. Additionally, the used vinyl monomers and initiator mixture which could include the unreacted monomers and a lot of homopolymers would have to be thrown away after grafting reaction, which may further increase the economical cost and environmental contamination.[6–10] In this study, a new chemically induced grafting route was used to prepare PVDF-based cationic exchange membranes, i.e. two-step chemically induced grafting method. The breakthrough of this method is that the initiation and grafting of the alkaline-treated membranes were carried out in initiator solution and vinyl monomers solution separately. Unlike the above one-step chemically induced grafting method, this method may produce less homopolymers. What's more, the used grafting solution which could only include the unreacted monomers would be reused after further adding some monomers. Generally, a study about this method

may help confirm the merit of the two-step chemically induced grafting process as a promising alternative more economical and environmentally friendly route for preparing PVDF-based cationic exchange membranes. The development of a high selective PVDF-based cationic exchange membrane with a lower manufacture cost and in a simple preparation process is interesting and valuable from the viewpoint of practical application as well as academic research. To our knowledge, this two-step chemically induced grafting method is the first report for the grafting of vinyl monomers onto PVDF membranes.

Among the grafting monomers, the use sodium 4-styrenesulfonate (SSS, a vinyl monomer with sulfonate groups) grafting appears to be advantageous with respect to an elimination of the hazardous sulfonation reaction and subsequent cost reduction.[11] But direct graft polymerization of the vinyl sulfonate onto PVDF membranes is very difficult, because $-SO_3^-$ groups of SSS with their hydration sphere are incompatible with hydrophobic PVDF and can not diffuse onto the PVDF membranes. In this study, we used a binary mixture system, realizing the cografting of SSS and acrylic acid (AA) onto PVDF. At the beginning of the grafting reaction, AA could be grafted onto the surface of PVDF and the hydrophilicity of the surface was improved. Then SSS and AA were cografted onto PVDF, sulfonate groups were introduced onto PVDF.[12] In order to further improve the hydrophilicity of the PVDF substrate membranes, nano-sized organo-montmorillonite (OMMT) was also used to blend with PVDF to prepare OMMT/PVDF hybrid substrate membranes. OMMT made the substrate membranes more hydrophilic, consequently resulting in more SSS grafting reaction. It is expected that these OMMT/PVDF–based cationic exchange membranes may exhibit excellent physicochemical and electrochemical properties.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) (M_w = 600,000) was kindly supplied by Shanghai 3F New Materials, China. Organo-montmorillonite (1.24TL) and SSS of analytical grade were purchased from Nanocor, America and Zichuan yaodong Chemical, Zibo City, China, respectively, and used as received. Acrylic acid, analytical grade, was purchased from Sinopharm Chemical Reagent and used without further purification. Deionized water was used throughout. All the other reagents were of analytical grade and used as obtained.

Preparation of the OMMT/PVDF Substrate Membrane

A given amount of PVDF was dissolved in DMF to form a casting solution of 10 wt %. Then a required amount of OMMT was added into the solution and the mixture was stirred for 4 h at 20°C to obtain a clear homogeneous solution. The mixture was cast on a glass plate to a desired thickness and heated at 70°C for 10 h. The dried membrane was removed from the glass plate by soaking in water, and then cut into small pieces of samples (3 × 3 cm²).

Alkaline Treatment of the OMMT/PVDF Substrate Membrane

A piece of membrane sample was soaked in 30 mL KOH ethanol solution and followed by addition of 3 mg mL^{-1} phase transfer catalysis tetrabutyl ammonium bromide (TBAB) aqueous solution (V_{TBAB}:V_{KOH} = 1:20). Then, this alkaline treatment reaction was maintained at set temperature under N_2 atmosphere for at least 10 min. After the reaction, the membrane was washed with deionized water to remove residual KOH and ethanol.

Preparation of the OMMT/PVDF–Based Cationic Exchange Membrane

To a glass flask equipped with a reflux condenser were introduced 30 mL tetrahydrofuran (THF) and benzoyl peroxide (BPO) initiator. Then, the alkaline-treated OMMT/PVDF membrane was immersed in the above solution and initiated under N_2 atmosphere at set temperature for 3–5 h. The initiated OMMT/PVDF membrane was taken out and immediately submerged in nitrogen-purged AA/SSS monomers mixture. By controlling the reaction temperature and time, AA and SSS monomers were partially grafted onto the surface of the membrane. Finally, the obtained OMMT/PVDF-based cationic exchange membrane was rinsed in chloroform and then subsequently washed with deionized water to remove homopolymers.

Membrane Properties

Membrane conductance, i.e., area resistance, measurements were carried out using a clip cell. This cell was composed of two dimensional stability electrodes (DSA). The two compartments of the cell were separated by the OMMT/PVDF-based cationic exchange membrane. The active area of electrodes as well as that of membrane S was 1 cm². Before the experiments, the membrane was sandwiched in experimental 3 mol L^{-1} NaCl solution. Membrane conductance measurements were performed using an alternating low resistance meter with four-electrode mode. Membrane area resistance (r) was estimated by subtraction of electrolyte resistance (r_2) without a membrane from membrane resistance equilibrated in electrolyte solutions (r_1). The area resistance of the membrane r (Ω cm²) is calculated by eq. (1):

$$r = (r_1 - r_2) S \qquad (1)$$

The cationic permselectivity was determined from the measured membrane potentials.[1,13] The studied membrane was placed between two compartments of a diffusion cell. The geometrical area of the exposed membrane was 1 cm². A same volume of two KCl solutions of different concentrations (C_1 = 0.1 mol L^{-1} and C_2 = 0.2 mol L^{-1}), was poured in the compartments. The membrane potential that results from the difference in the concentrations in the two compartments was measured with two saturated calomel electrodes. Then, the counter-ion transport number in the membrane phase (t_+^m) can be calculated from eq. (2):

$$t_+^m = \frac{E_m + E_m^0}{2 E_m^0} \qquad (2)$$

And E_m^0 can be obtained according to eq. (3):

$$E_m^0 = \frac{RT}{F} (2t_+ - 1) \ln \frac{\alpha_1}{\alpha_2} \qquad (3)$$

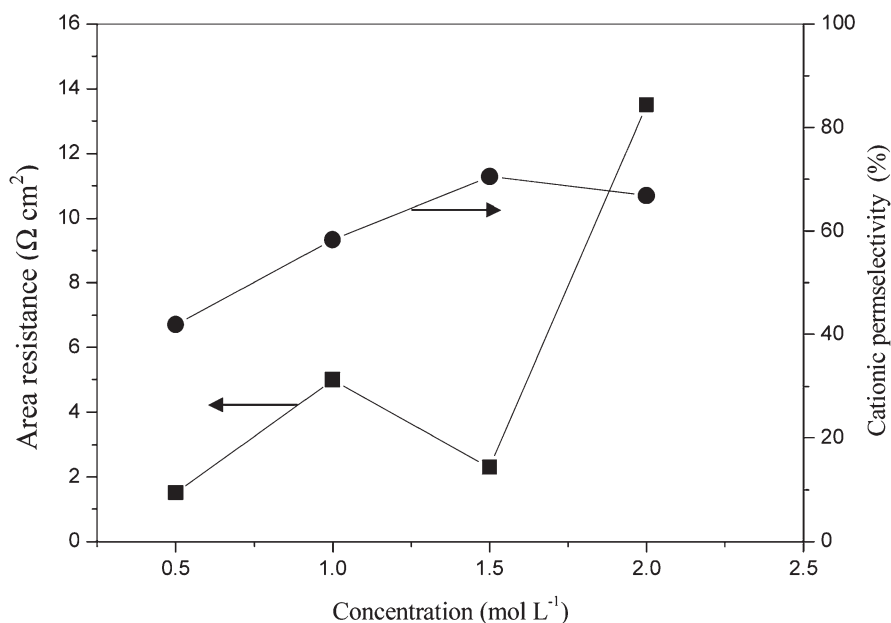Afterward, we determine the value of the cationic permselectivity with eq. (4):

Figure 1. Effect of KOH concentration on the area resistance and cationic permselectivity of the OMMT/PVDF-based cationic exchange membranes.

$$P = \frac{t_+^m - t_+}{1 - t_+} \qquad (4)$$

where E_m is the membrane potential between the compartments due to the difference in solution concentrations; E_m^0 is the ideal membrane potential between the electrodes in a same solution concentration; R is the ideal gas constant; T is the temperature; F is the Faraday constant; $\alpha_1\alpha_1$, α_2 are the activities of the electrolyte in the two solutions, respectively; t_+^m and t_+ are the counter-ion transport numbers in the membrane phase and solution, respectively.

Fourier transform infrared spectra of different membranes were obtained using FTIR spectrometer (NEXUS 470, Thermo Nicolet, America) with the reflection technique. Morphological studies were undertaken with a scanning electron microscope (PHILIPS, XL-30FEG). Samples were sputtered with a thin carbon film before SEM observation. The element distribution on the surface of the membranes was determined by energy dispersive spectrum. The changes related to the crystalline phase of the membranes were characterized by X-ray diffraction (PHILIPS, PW1700) using a CuKα radiation under 40 kV voltage.

RESULTS AND DISCUSSION

Influence of Experimental Conditions
Experimental conditions were investigated to determine some optimal preparation parameters of the OMMT/PVDF-based cationic exchange membranes by two-step chemically induced grafting method. The effect of reaction parameters including KOH concentration, alkaline treatment time and temperature (alkaline treatment conditions); initiator concentration, initiation time and temperature (initiation conditions); grafting time and temperature (grafting conditions); OMMT quantity were established in correlation with the area resistance and cationic permselectivity of the obtained cationic exchange membranes

Effect of Alkaline Treatment Conditions
When the OMMT/PVDF substrate membranes were immersed in KOH ethanol solution, H and F were stripped from the chains of PVDF, $-(CH=CF)_n-$ and $[-C(OH)=CH-C(O)-CH=CH-C(OH)=CH-C(O)-CH=CH-C(OF)-CH-]_n$ were formed on the surface of the substrate.[14,15] Then BPO was likely to initiate this substrate at $-C=C-$ and active sites were produced, so it was easy to graft vinyl monomers onto the substrate membranes.[6] In order to increase the number of $C=C$ double bonds on the PVDF membranes, various alkaline treatment conditions such as KOH concentration, alkaline treatment time, and temperature were investigated. Figure 1 shows the effect of KOH concentration on the area resistance and cationic permselectivity of the cationic exchange membranes. The reactions were performed at 60°C for 20 min. The cationic permselectivity was found to increase with increasing KOH concentration until it achieved a maximum at 1.5 mol L^{-1} beyond which it decreased with more KOH content. At the same time, a minimum value for the area resistance appeared at the same concentration as the maximum value for the cationic permselectivity. Therefore the optimum KOH concentration is 1.5 mol L^{-1}. The increase in the conductivity and cationic permselectivity of the membranes with increasing KOH content should be the result of the increase in the number of the $C=C$ double bonds, which enhanced the probability of grafting monomers. However, further increase in KOH concentration above 1.5 mol L^{-1}, the substrate membranes might be destroyed and less $C=C$ double bonds were formed on the surface, which ultimately resulted in a decrease in the conductivity and cationic permselectivity of the membranes.[16]

Figure 2 shows the effect of alkaline treatment time on the area resistance and cationic permselectivity of the membranes. The reactions were performed at 60°C with KOH concentration of 1.5 mol L^{-1}. Both the area resistance and cationic permselectivity
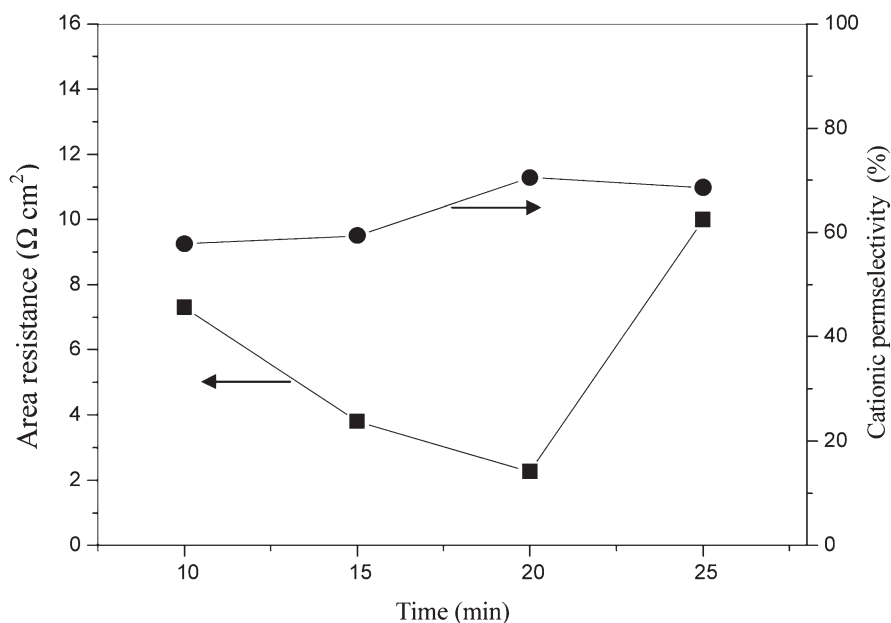
Figure 2. Effect of alkaline treatment time on the area resistance and cationic permselectivity of the OMMT/PVDF-based cationic exchange membranes.

of the membranes attained the minimum and maximum values after 20 min alkaline treatment, then increased and decreased with the increase of reaction time, respectively. This indicates that increasing alkaline treatment time was favorable for the defluorination reaction and the formation of C≡C double bonds, which resulted in the increase of grafting AA and SSS on the membranes. However, longer reaction time above 20 min might break up C≡C structures and cause cross-linking and formation of polar groups on the surface of the membranes, which decreased the conductivity and cationic permselectivity of the membranes.[15,17]

Figure 3 shows the effect of alkaline treatment temperature on the area resistance and cationic permselectivity of the membranes. It was found that the area resistance of the membranes attained the lowest value of 2.26 Ω cm^2 when the reaction temperature was 60°C. Though the value of the cationic permselectivity which appeared at the same temperature was a little lower, it was still acceptable. So 60°C for alkaline treatment temperature is the most suitable.

From the discussions above, it can be concluded that the optimum alkaline treatment parameters are 1.5 mol L^{-1} for the KOH concentration, 60°C for the temperature and 20 min for
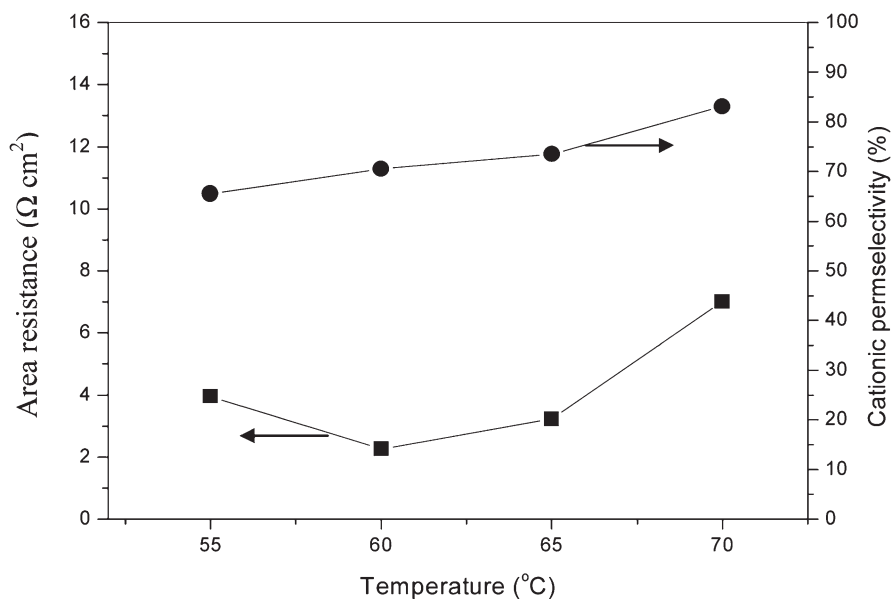

Figure 3. Effect of alkaline treatment temperature on the area resistance and cationic permselectivity of the OMMT/PVDF-based cationic exchange membranes.
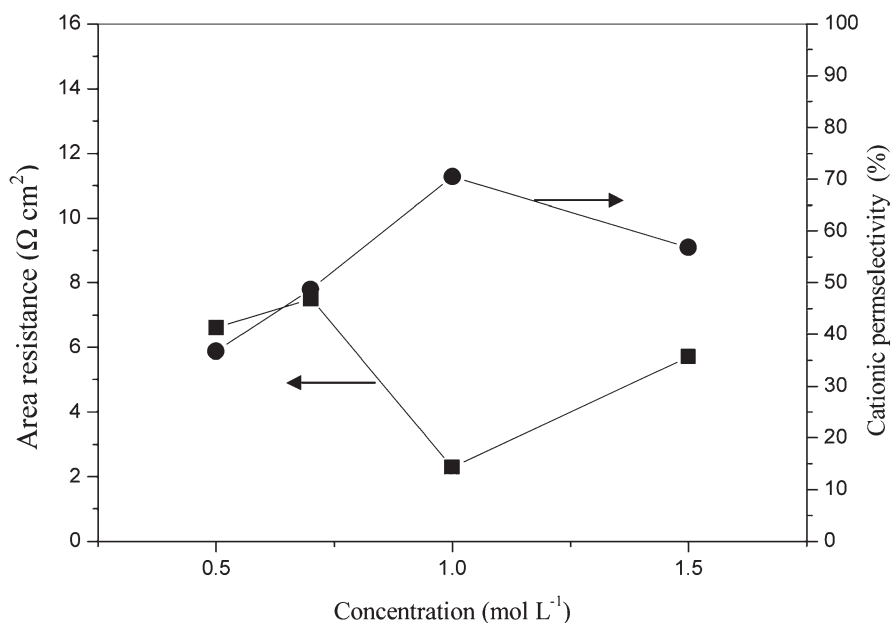
Figure 4. Effect of initiator concentration on the area resistance and cationic permselectivity of the OMMT/PVDF-based cationic exchange membranes.

the time. Therefore, the optimum alkaline treatment conditions were adopted for the following experiments.

Effect of Initiation Conditions

Figure 4 shows the effect of initiator concentration on the area resistance and cationic permselectivity of the membranes. The initiation reactions were performed at 65°C for 4 h. Both the area resistance and cationic permselectivity of the membranes attained the minimum and maximum values with initiator concentration of 1.0 mol L^{-1}, then increased and decreased with the increase of initiator concentration, respectively. It demonstrates that the optimum initiator concentration can be 1.0 mol L^{-1}.

The increasing of the conductivity and cationic permselectivity when the initiator concentration increased, was mainly because more C=C double bonds on the alkaline-treated membranes were initiated by free radicals, which yielded more active sites and gave a higher probability of being grafted by monomers to increase the conductivity and cationic permselectivity. However, more free radicals tended to couple rapidly with the active sites if further increase of BPO content above 1 mg mL^{-1}, and there may decrease the amount of the active sites on the surface. As a result, the grafting number of AA and SSS decreased, which also resulted in the decrease of the conductivity and cationic permselectivity of the membranes.
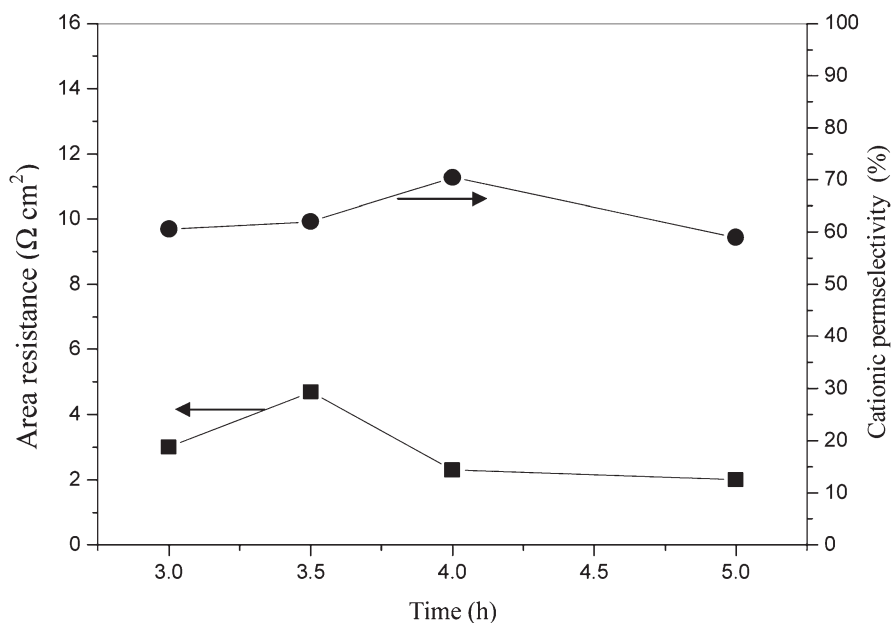

Figure 5. Effect of initiation time on the area resistance and cationic permselectivity of the OMMT/PVDF-based cationic exchange membranes.
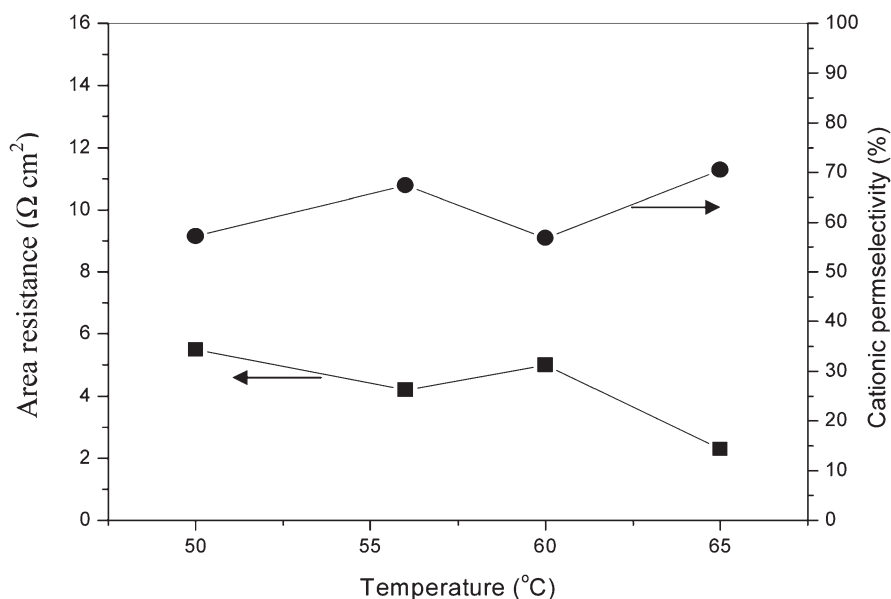
Figure 6. Effect of initiation temperature on the area resistance and cationic permselectivity of the OMMT/PVDF-based cationic exchange membranes.

The initiation temperature was 65°C and the initiator concentration was set as 1 mg mL^{-1}. Effect of initiation time on the area resistance and cationic permselectivity of the membranes were investigated. The results are shown in Figure 5. The cationic permselectivity was found to increase slowly in first 4 h and tended to decrease with further increase of time. At the same time, a very low value for the area resistance appeared at the same initiation time as the maximum value for the cationic permselectivity. Therefore the optimum initiation time can be 4 hours. Such results may be attributed to the fact that the initial initiation reaction was controlled by the diffusion rate of free radicals onto the polymer substrate. The number of trapped radicals generated on the polymer substrate increased with

initiation time. However, the trapped radicals tended to couple with free radicals diffusing onto the polymer substrate if further increase of initiation time above 4 h, which ultimately resulted in the decrease of the grafting number of monomers.

Effect of initiation temperature on the area resistance and cationic permselectivity of the membranes is shown in Figure 6. Boiling point of THF is 65°C, so the highest initiation temperature can only be set at 65°C. The initiation reactions were performed for 4 h with BPO concentration of 1 mg mL^{-1}. As can be seen in Figure 6, the area resistance and cationic permselectivity of the membranes showed the minimum and maximum values, respectively, when the initiation temperature was
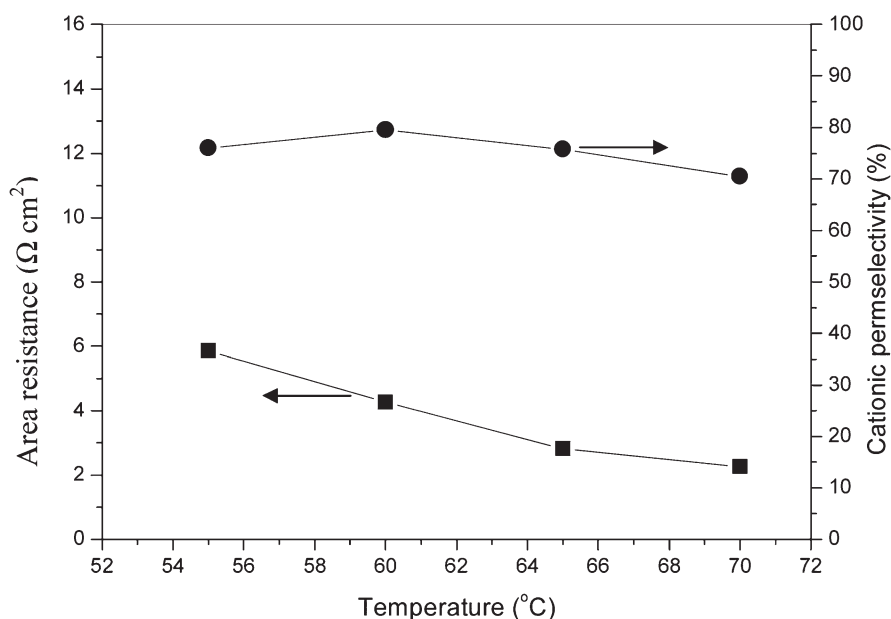

Figure 7. Effect of grafting temperature on the area resistance and cationic permselectivity of the OMMT/PVDF-based cationic exchange membranes.
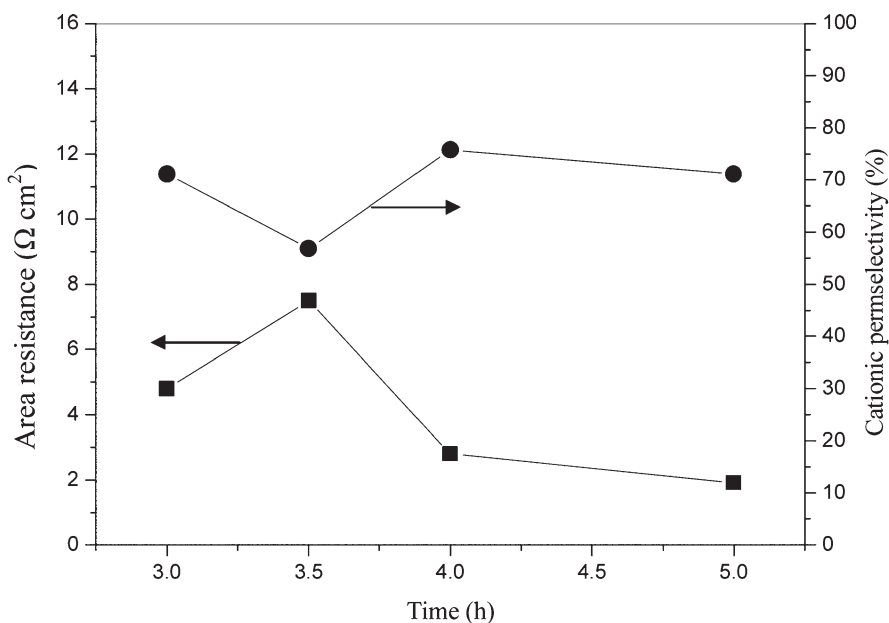
Figure 8. Effect of grafting time on the area resistance and cationic permselectivity of the OMMT/PVDF-based cationic exchange membranes.

increased up to 65°C. This was due to the rapid increase of initiator decomposition rate as well as an increase of the propagation rate constant with temperature. Both effects resulted in an increase in the cationic permselectivity and conductivity.

Generally, the optimum initiation parameters are 1 mg mL^{-1} for the initiator concentration, 65°C for the initiation temperature and 4 h for the time. For the following experiments, these optimum initiation parameters were used.

Effect of Grafting Conditions
Effect of grafting temperature on the area resistance and cationic permselectivity of the membranes is shown in Figure 7.

The increase of reaction temperature can speed up diffusion rate of monomers, but at the same time also accelerate the decay rate of the trapped radicals on the substrate. Both factors decided the behavior of the curves. The cationic permselectivity of the membranes was found to increase with increasing the temperature until it attained a maximum value at 60°C, beyond which it tended to decrease at the rest tested temperatures. On the other hand, the increase in the temperature from 55 to 70°C was also accompanied by a decrease in the area resistance. When grafting temperature was 65°C, the area resistance of the membranes showed a relatively lower value, while the cationic permselectivity was also high enough
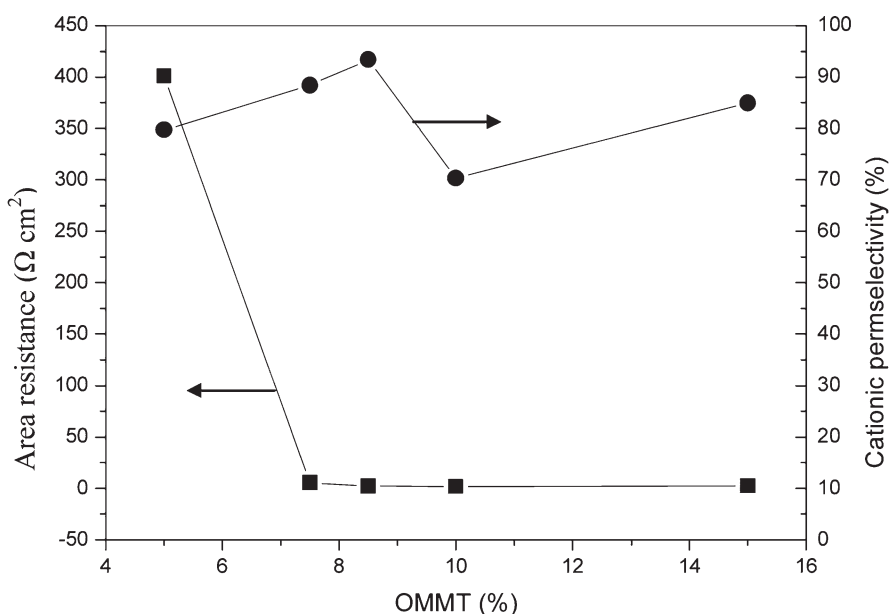

Figure 9. Effect of OMMT quantity on the area resistance and cationic permselectivity of the membranes.
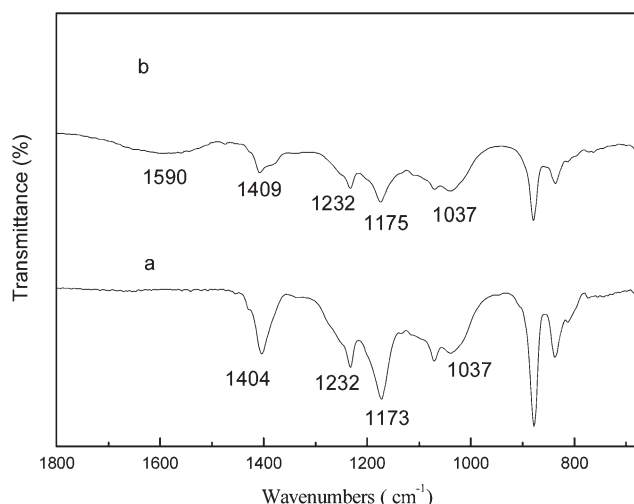
Figure 10. FTIR spectra of (a) the OMMT/PVDF substrate membrane and (b) the alkaline-treated OMMT/PVDF membrane.

for the cationic exchange membranes. So the optimum grafting temperature is 65°C.

Effect of grafting time on the area resistance and cationic permselectivity of the membranes was investigated. The results are shown as Figure 8. The increase of total grafting number of the monomers can be reasonably attributed to the monomers diffusion rate and their concentration in the grafting layers. When grafting reaction continued 4 hours, the cationic permselectivity of the membranes attained a maximum value and the area resistance also showed a very low value, indicating that more monomers reacted with the trapped radicals on the substrate, which resulted in high grafting number of the monomers. So 4 hours were chosen as the most suitable grafting time.

The optimum grafting parameters are 65°C for the grafting temperature and 4 h for the grafting time.

Effect of OMMT Quantity

PVDF with different OMMT quantity was dissolved in DMF to form 10% solutions. These solutions were then cast on glass
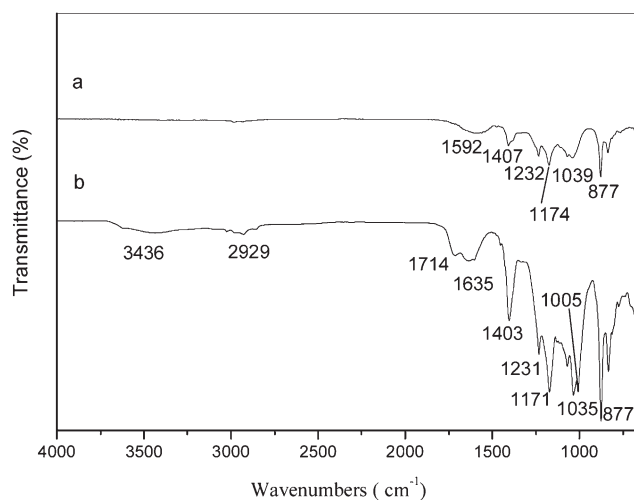

Figure 11. FTIR spectra of (a) the alkaline-treated OMMT/PVDF membrane and (b) the OMMT/PVDF-based cationic exchange membrane.
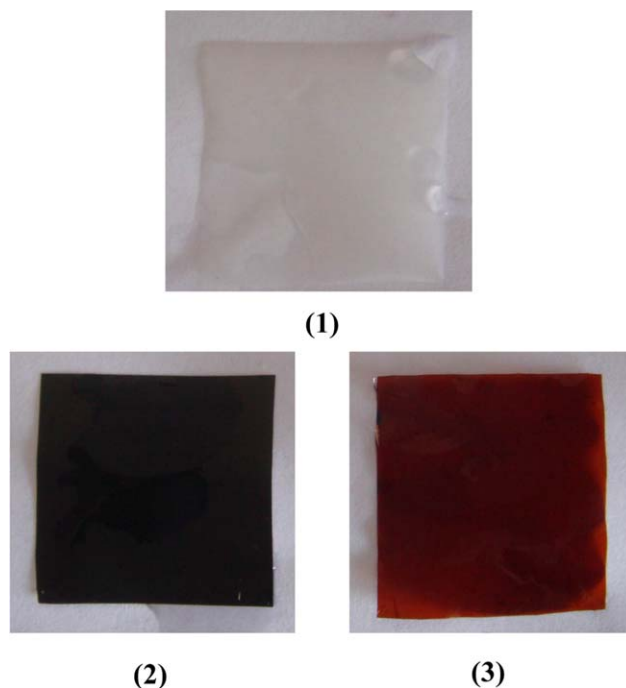

Figure 12. Pictures of (1) the OMMT/PVDF substrate membrane, (2) the alkaline-treated OMMT/PVDF membrane, and (3) the OMMT/PVDF cationic exchange membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

plates, and heated to form PVDF substrate membranes. Effect of OMMT quantity on the area resistance and cationic permselectivity of the cationic exchange membranes is shown in Figure 9. Addition of OMMT in the PVDF substrate membranes clearly improved the conductivity and cationic permselectivity of the membranes. This was mainly because OMMT improved the hydrophilicity of the PVDF substrate membranes, which made the monomers easier to diffuse and be grafted onto the PVDF membranes. When the OMMT was increased up to 8.5%, the highest cationic permselectivity of 93.4% and the low area resistance of 1.8 Ω cm^2 were achieved, respectively.

FTIR Spectroscopy Analysis

The infrared spectra in Figure 10 show the OMMT/PVdF substrate membranes prior to and after alkaline treatment. The spectra indicate the formation of carbon double bond groups (1590 cm^{-1}) on treatment with a change in the fluorocarbon groups (1000–1250 cm^{-1}). Complex changes occurred in the fluorocarbon stretching frequencies (1000–1250 cm^{-1}) in the fingerprint region of the spectrum, indicating that the fluorine groups changed with treatment. The hydrocarbon deformations 1350–1450 and 800–900 cm^{-1} did not change significantly with treatment. The peak at 1037 cm^{-1} is characteristic peak of OMMT.

Figure 11 is the infrared spectra of the alkaline-treated OMMT/PVDF membrane and OMMT/PVDF-based cationic exchange membrane. By contrast with the alkaline-treated OMMT/PVDF membrane, the infrared spectrum of the OMMT/PVDF-based cationic exchange membrane included some new characteristic peaks in the regions of 3750–3150 cm^{-1} (due to O─H and
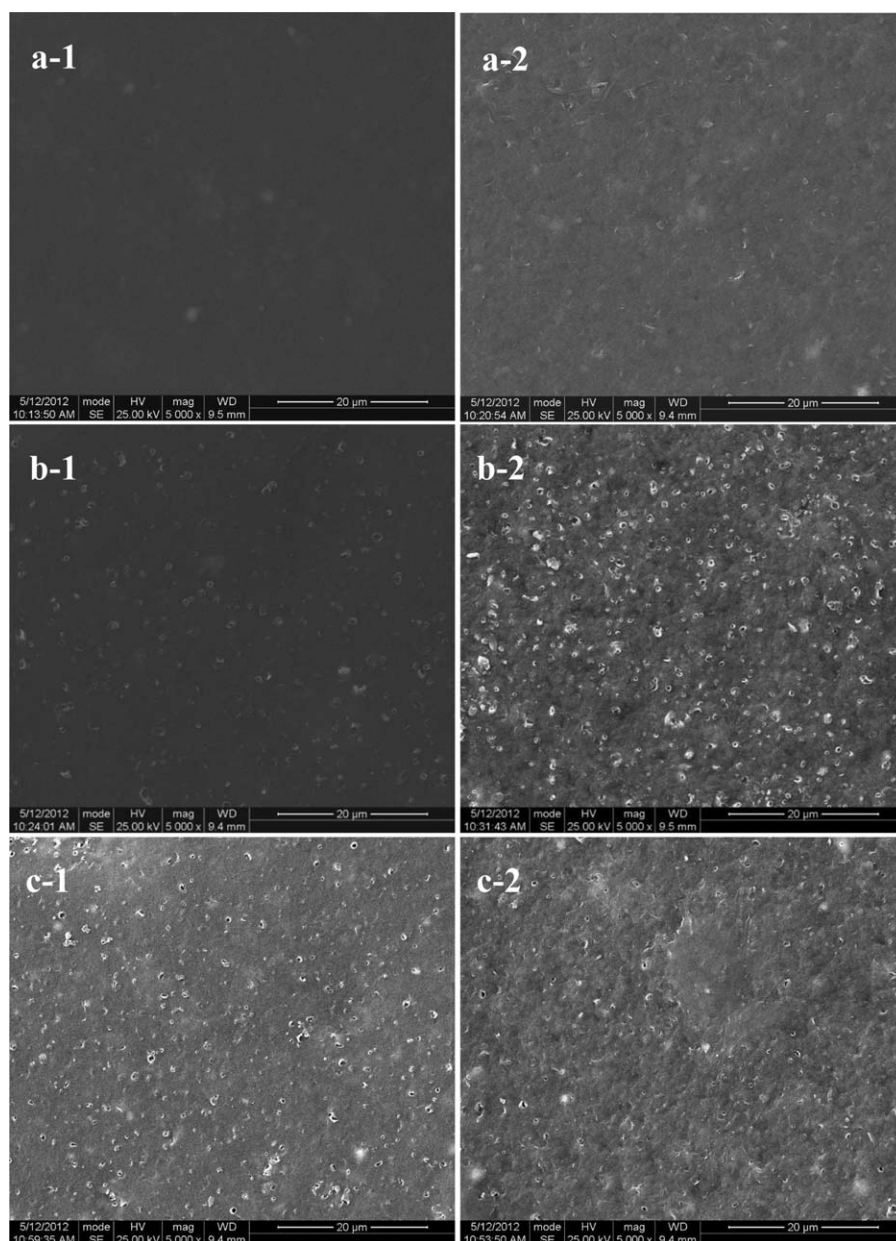
Figure 13. SEM photographs of the OMMT/PVDF substrate membrane (a-1 and a-2), the alkaline-treated OMMT/PVDF membrane (b-1 and b-2) and the OMMT/PVDF-based cationic exchange membrane (c-1 and c-2). Note: a-1, b-1, and c-1 present the membrane surface contacting glass plate; a-2, b-2, and c-2 present the membrane surface contacting air.

water which was incorporated in the hydrophilic material vibrations), 1714 cm^{-1} (due to C$=$O stretching vibrations of AA unit), 1005 cm^{-1} (due to S$=$O stretching vibrations of SSS unit), and 1635 cm^{-1} (due to aromatic C$=$C stretching vibrations). The results show that both AA and SSS have been grafted onto the OMMT/PVDF membrane. The OMMT/PVDF-based cationic exchange membrane was successfully prepared by this method.

SEM Analysis

Prior to treatment the OMMT/PVdF substrate membrane was faint translucent white in appearance. After treatment a color change was observed for all membranes, as shown in Figure 12.

The alkaline-treated OMMT/PVdF membrane was a deep black color, whereas the OMMT/PVdF-based cationic exchange membrane showed little color change, which had a deep brown color.

The surface morphologies of the OMMT/PVDF substrate membrane, the alkaline-treated OMMT/PVDF membrane and the OMMT/PVDF-based cationic exchange membrane are shown in Figure 13, respectively. The first clear observation from picture a-1 and a-2 was the difference between the two side surfaces of the OMMT/PVDF substrate membrane: the surface contacting glass plate was smooth and featureless with no obvious discernible pores, and the other side surface contacting air was rough
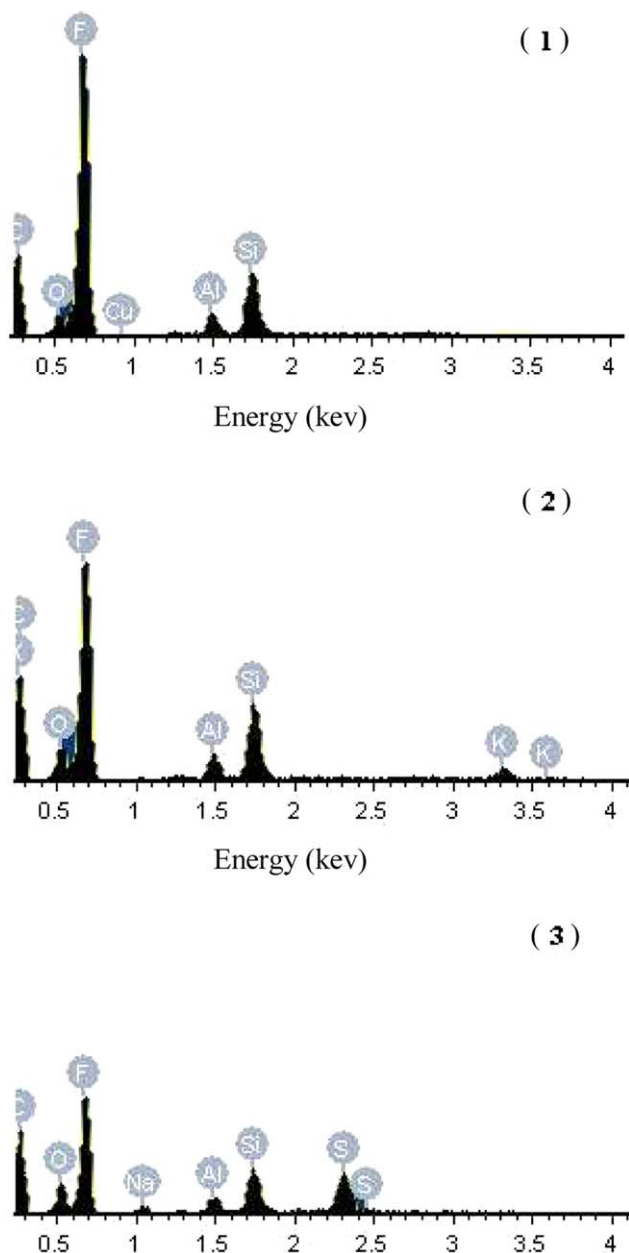
Figure 14. Elemental analysis on the surface of: (1) the OMMT/PVDF substrate membrane, (2) the alkaline-treated OMMT/PVDF membrane, and (3) the OMMT/PVDF-based cationic exchange membrane by EDS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with discernible pores and structures. In spite of these differences, the two side surfaces of the substrate membrane were both homogenous and compact, indicating that the compatibility between PVDF and OMMT was excellent. After alkaline treatment, lots of macro pores were observed on the two side surfaces of the membrane, which should be formed by chemical dehydrofluorination with alkaline solutions. When SSS and AA were grafted onto the alkaline-treated OMMT/PVDF membrane, the pores of the surfaces were filled and coated with the grafting side chains. As a result, the amount of the pores on the two

side surfaces of the OMMT/PVDF-based cationic exchange membrane tended to be less.

Elemental analysis on the surface of the OMMT/PVDF substrate membrane, the alkaline-treated OMMT/PVDF membrane, and the OMMT/PVDF-based cationic exchange membrane is shown in Figure 14. It can be seen that sulfur appeared on the OMMT/PVDF-based cationic exchange membrane, which could not be observed on both the OMMT/PVDF substrate membrane and alkaline-treated OMMT/PVDF membrane. This indicates that the grafting reactions of SSS definitely occurred on the surface of the alkaline-treated OMMT/PVDF membrane and sulfonate groups existed on the OMMT/PVDF-based cationic exchange membrane. Additionally, the distribution of sulfur and fluorine was complementary. When sulfur was more, fluorine was less relatively.

XRD Analysis

Crystallization behavior of the OMMT/PVDF substrate membrane, the alkaline-treated OMMT/PVDF membrane, and the OMMT/PVDF-based cationic exchange membrane was investigated using XRD. The results are shown in Figure 15. The OMMT/PVDF substrate membrane is a semi-crystalline structure to show several peaks centered at a diffraction angle of 20.0°, 25.4°, 30.6°, and 39.0°, which are associated with the convolution of an amorphous region and a crystalline region.[18] Alkaline treatment altered the resulting molecular structure and physical network on the surface of the substrate membrane, leading to a decrease in the crystalline peaks at 20.0°, 25.4°, and 39.0°, and a disappearance of 30.6° diffraction peak, which manifests that the crystallinity of the substrate membrane structure reduced slightly after alkaline treatment. Upon grafting of SSS and AA onto the alkaline-treated membrane, the relative intensity of the crystalline peaks at 20.0°, 25.4°, and 39.0° was further decreased, indicating more structureless amorphous morphology of the cationic exchange membrane. It may be explained by the fact that the randomness of the amorphous phase in graft copolymer was enhanced by introducing grafting
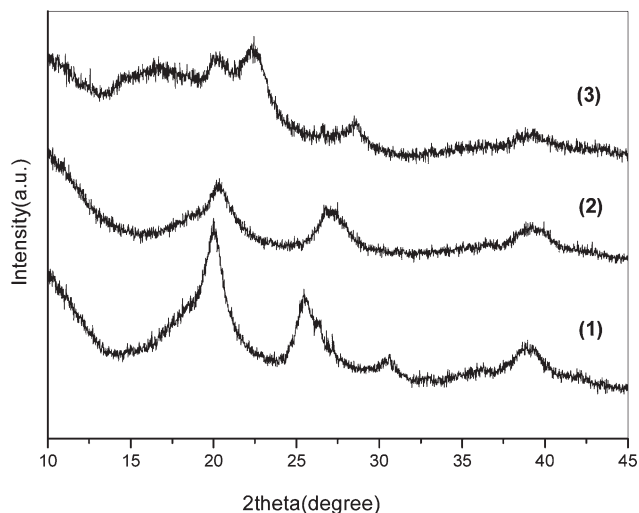

Figure 15. XRD diffraction curves of: (1) the OMMT/PVDF substrate membrane, (2) the alkaline-treated OMMT/PVDF membrane, and (3) the OMMT/PVDF-based cationic exchange membrane.

side chains, which gave rise to a perturbation of longranged spacing between the chains. The cationic exchange membrane also exhibited new broad amorphous halos centered at about 16.4° and 20.1°, which further implies that grafting side chains perturbed the microstructures of the cationic exchange membrane.

CONCLUSIONS

The OMMT/PVDF-based cationic exchange membranes were prepared successfully by the two-step chemically induced grafting method. This method could be effective for design and preparation of ionic exchange membranes based on partial fluorinated polymers with high conductivity and selectivity.

Various experimental conditions including alkaline treatment, initiation and grafting conditions were investigated to determine some optimum preparation parameters of the cationic exchange membranes. The optimum alkaline treatment parameters are 1.5 mol L^{-1} for the KOH concentration, 60°C for the temperature and 20 min for the time; the optimum initiation parameters are 1 mg mL^{-1} for the initiator concentration, 65°C for the temperature and 4 h for the time; the optimum grafting parameters are 65°C for the grafting temperature and 4 h for the time. The OMMT/PVDF-based cationic exchange membrane-doped 8.5% OMMT prepared using the optimum preparation parameters showed excellent basic properties. The values of the area resistance and cationic permselectivity reached 1.8 Ω cm^2 and 93.4%, respectively.

As compared with the OMMT/PVDF substrate membranes and alkaline-treated OMMT/PVDF membranes, the OMMT/PVDF-based cationic exchange membranes exhibited more structureless amorphous phase. The compatibility between PVDF and OMMT is excellent.

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