Irradiation-Induced Grafting of Polyacrylamide onto the Sulphonated Poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) Films as Well as Its Use as Catalytical Layer in a Bipolar Membrane

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ABSTRACT: The sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) was modified by γ-ray irradiation-reduced grafting of polyacrylamide. The grafting reaction was proved by the elemental composition of grafted SPPO, which was determined by XPS data. The influences of both the irradiation dose and the concentration of polymerization inhibitor on grafting copolymerization rate were investigated and the effect of graft rate on water content of SPPO film was fully discussed. Bipolar membranes were prepared by using these grafted SPPO as the cation exchange layers (and thus the grafted polyacrylamide is used as interfacial layer) and their I–V curves were studied. The results showed that γ-ray irradiation-reduced grafting copolymerization of acrylamide was one of the most efficient methods to improve the properties of a bipolar membrane. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1447–1453, 2008

Key words: Irradiation-reduced grafting; sufonated poly (2,6-dimethyl-1,4-oxide) (SPPO); grafting rate; polyacrylamide; bipolar membrane

INTRODUCTION

Since their invention in 1950s,[1] ion-exchange membranes have deserved special attentions because of their excellent performances such as higher ion permselectivity, low energy consumption, etc., and been widely used in such industrial processes as the desalination of brackish water by electrodialysis,[2,3] the treatment of industrial wastewater,[4,5] the production of organic acid and base by bipolar membrane electrodialysis,[6–9] and fuel cell separators,[10,11] etc.

With the rapid development of ion-exchange membrane technology, the performances of ion-exchange membranes have highly been improved. Among the preparing methods, modification is regarded as one of the most effective and convenient techniques to improve membrane's characteristics.[12,13] As one important class of ion-exchange membranes, bipolar membranes have attracted especial attentions due to their important applications in the cleaning separation and production.[7] In the investigation of bipolar membranes, it is found that their natures are highly impacted by the interfacial layer between the anion and cation-exchange membranes.[14] Therefore, the exploration of interfacial layer is significantly important.

Recently, in our laboratory, some efforts have been made to develop the interfacial layer of bipolar membranes.[15–19] In most cases, these interfacial layers have been introduced by modification of anion exchange layer. Our continuing interests in such investigations drive us to do more jobs. It is well known that poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a good engineering plastic material and possesses excellent flexibility. It can be easily sulfonated and the sulfonated product (SPPO) is of high conductivity, which is often used as cationic conductor such as proton conductive membrane or conventional cation exchange membranes.[20–22] In our previous researches, SPPO is also used as the cation exchange layers of bipolar membranes where the performance is improved by optimizing the composition of anion exchange layers or by modifying the anion exchange layers.[23,24] To continue the series job of bipolar membranes preparation in our lab, herein, new bipolar membrane will be prepared by the modification of cation exchange layer so that the modified substance can be acted as catalytical layer

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simultaneously when SPPO is used as cation exchange layers. The modification of SPPO was conducted by γ-ray irradiation induced acrylamide grafting copolymerization. Different affecting factors of the grafting degree including irradiation dose, inhibitor concentration, and contact time were investigated and the performance of bipolar membranes prepared from grafted SPPO will be elucidated.

EXPERIMENTAL

Materials

Sulfonated poly(phenylene oxide) (SPPO) was commercially obtained from Shangdong Ocean Chemical Industry Scientific Research Institute (Weifang City, Shandong Province, China) with an ion-exchange capacity of 2.1 mequiv/g-dry. Acrylamide (AM), *N*,*N*-methene-biacrylamide (crosslinker, MBAM) and $CuSO_4 \cdot 5H_2O$ (inhibitor) were all of analytical grades. They were obtained from commercial way and used as received.

Grafting of polyacrylamide on SPPO and the preparation of bipolar membranes

The grafting process of polyacrylamide on sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) can be described as follows.

First, the SPPO films were cut into 5×5 cm^2 slices and washed by ethanol, then they were dried to a constant weight (labeled as W_0) to produce the explored membrane slices. Subsequently, a piece of filter paper with the same size as the above-prepared membrane slice was dipped into a monomer solution, which was prepared from the acrylamide aqueous solution mixed with crosslinker MBAM and inhibitor $CuSO_4 \cdot 5H_2O$. Then the filter paper adsorbed the monomer solution was adhered tightly to the surface of SPPO film; followed, both the membrane slice and filter paper, which were nipped by two pieces of glass plate, were put into a γ-ray resource room to irradiate for stipulated time. After being irradiated at a certain dose rate for a desired dose, the membrane slices were taken out and washed by 20% methanol aqueous solution in a Soxhlet fat extractor for 4 h so as to remove the homopolymer and other impurities. Finally, these membrane slices were dried to constant weight in an oven at 50°C for about 10 h. The grafting rate can be calculated via the following formula:

$$\text{Grafting}\,\% = \frac{w_1 - w_0}{w_0} \times 100\% \quad (1)$$

where w_0 is the dry weight of SPPO and w_1 is the dry weight of SPPO grafted polyacrylamide.

The preparation of bipolar membranes was conducted as follows. Quaternary ammonium halide poly(2,6-dimethyl-1,4-phenylene oxide) solutions in dimethyl formamide(DMF) of the same concentration and volume were cast on the polyacrylamide side of different grafting rate SPPO film, respectively. When DMF was naturally evaporated in air, bipolar membranes containing different grafting rate polyacrylamide acting as the interfacial layers were prepared, respectively.

Sample characterizations

FTIR spectra of the step reaction samples were recorded with a Bruker Equinox-55 FTIR spectrometer in the region of 400–4000 cm^{-1}.

C/O/S/N elemental compositions of the step reaction samples were determined by X-ray photoelectron spectroscopy(XPS), which was performed in a VG ESCALAB MK II system equipped with a hemispherical electron analyzer, using Mg Kα radiation ($h\nu$ = 1254.6 eV) operated in the constant pass energy mode at 20 kV and 20 mA. The size of the analyzed area was 5×5 mm^2.

The water content of grafted SPPO film was determined by conventional process, in which the water content of the membranes was calculated from the difference of wet grafted membrane (w_2) and dried grafted membrane (w_1).

$$w\% = \frac{w_2 - w_1}{w_1} \times 100\% \quad (2)$$

The measurement of current-voltage (I–V) curves of the bipolar membranes was carried out with an experimental set-up reported in a previous paper.[15] The key element of this experimental set-up is the conical-shape measurement cell. The DC power system (PPE-3323, Good Will Instrument Co., Taiwan), amperometer (ZW1419, Qingdao Qingzhi Instruments Co., Qingdao City, Shandong Province, China), and voltmeter (ZW1418, Qingdao Qingzhi Instruments Co., Qingdao City, Shandong Province, China) were linked to a computer through communication interface, so that each experimental point was not taken until the fluctuation in the measured value was lower than a prefixed tolerance level. In the experiments, 0.5*M* aqueous Na_2SO_4 solution was used as the electrolyte solution and the temperature of the thermostatic bath was set at 25°C.

RESULTS AND DISCUSSION

FTIR spectra and the confirmation of grafting reaction

To have an insight into the structural difference of SPPO and the grafted SPPO, their FTIR spectra were conducted and shown in Figure 1.

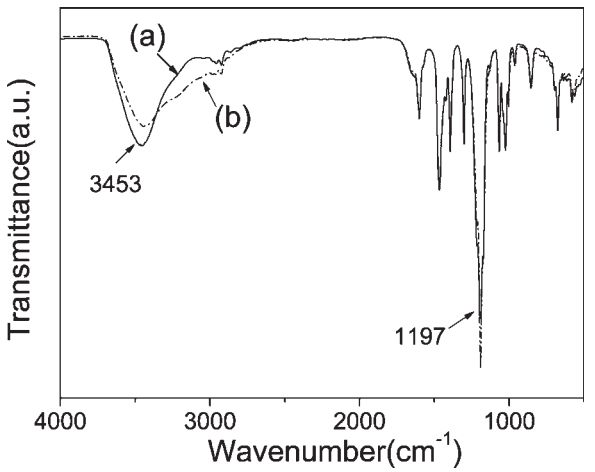


Figure 1 FTIR spectra of (a) SPPO and (b) SPPO grafted polyacrylamide.

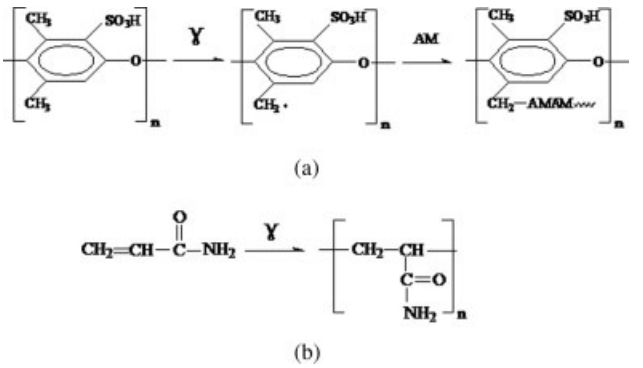
As can be seen in Figure 1(a), the absorption band situated at 3450 cm^{-1} was in the region of —NH— and —OH groups stretching vibration. The significant absorption peak located at 1197 cm^{-1} can be ascribed to the —C—N— stretching vibration.

By comparing the FTIR curve 1(a) with curve 1(b), it is interesting to find that the two curves have the same shape except a significant difference of adsorption peak appeared at around 3453 cm^{-1} and 1197 cm^{-1}. The sharp peak at around 3453 cm^{-1} of the SPPO changes into broad one after the occurrence of grafted reaction. Meanwhile, the intensity of peak at 1197 cm^{-1} was highly increased. The theoretical interpretation to this trend is that after the γ-ray irradiation, the polyacrylamide was successfully grafted on SPPO. The amount of amine groups in SPPO is thus increased. As a result, the peaks of —NH— and —C—N— groups appeared in the FTIR spectra. Because of the overlapping of —NH— and —OH groups stretching vibration, the peak shape located at near 3450 cm^{-1} changes into broad. Based on these changes in the adsorption peaks, it can be concluded that the reaction of irradiation grafting presented in Scheme 1(a) has happened.

Surface elemental compositions(C/O/S/N) of membranes by XPS spectra

To further confirm the occurrence of graft copolymerization, the elemental compositions of both SPPO membrane (ungrafted) and the grafted SPPO membrane (acrylamide-grafted side) were determined by XPS and the data were listed in Table I.

By comparing the composition of C and S in the ungrafted SPPO membranes with those in the grafted SPPO, it can be seen that the data decrease slightly; meanwhile the composition of O and N in the grafted SPPO increased a little after the occurrence of grafting. It seems to indicate different change trend, especially the C content in the investigated samples. However, if the relative content of O, N and S to C was calculated and compared in the ungrafted SPPO with the grafted one, the change trend will be clearly revealed. The relative content of O and N to C for the ungrafted SPPO membrane is 26.2% and 2.04%; whereas such values are increased to 33.4% and 2.95% for the grafted SPPO membrane, demonstrating an increasing trend. In contrast, the relative content of S to C demonstrates a decreasing trend.



Scheme 1 The possible reactions of acrylamide polymerization. (a) The grafting copolymerization; (b) The homogeneous polymerization.

To explain the above phenomenon, special attention will be paid to the grafting of acrylamide on the SPPO. It is well accepted that the composition of acrylamide mainly dominated by O, N, and C (the relative content of O and N to C in acrylamide is 44.4% and 38.9%, respectively); its grafting on SPPO primarily increases the O, N, and C. As a result, the relative content of O and N to C for the grafted SPPO membrane reveals an increasing trend. Moreover, acrylamide does not contain S, thus the grafting of acrylamide on the SPPO doesn't make any contribution to enhance the ingredient of S in the grafted SPPO. Consequently, the relative content of S to C exhibits a decreasing trend as discussed above. Based on these findings, it can be deduced that the grafting copolymerization has occurred during γ-ray irradiation-reduced, which further verifies the reaction illustrated in Scheme 1(a).

TABLE I
Elemental Composition Determined by XPS

	Elemental compositions (%)							
Membranes	C	O	S	N	Others	O/C	S/C	N/C
Ungrafted SPPO	74.1	19.43	3.06	1.41	1.9	26.2	4.13	2.04
Grafted SPPO	68.86	23.01	1.86	2.03	4.24	33.4	2.70	2.95

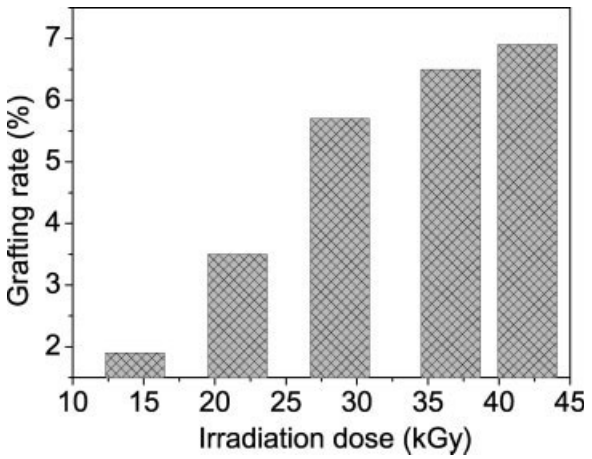


Figure 2 The effect of irradiation dose on grafting rate, in which the concentration of Cu^{2+} = 0.15% (weight), the concentration of MBAM = 0.2%, and dose rate = 60 Gy/min, respectively.

The effect of irradiation dose on grafting rate

In the case of keeping the irradiation dose rate, the concentrations of crosslinker and inhibitor at fixed values, the effect of different irradiation dose on grafting rate was investigated. The results were shown in Figure 2.

It can be seen in Figure 2 that the grafting rate increased with the increasing irradiation dose. When the irradiation dose arrived at 30 kGy, such increasing trend became very slowly. The theoretical interpretation to this trend can take our eyes to the grafting polymerization. As shown in Scheme 1(a) and (b), there are two possible reactions. One is the graft polymerization of acrylamide on SPPO film (Scheme 1a), which is similar to the grafting reaction of *N*-isopropylacrylamide (NIPAAm) onto the brominated poly(2,6-dimethyl-1,4-phenylene oxide) BPPO discussed in our previous investigation.[25] The other is the homogeneous polymerization of acrylamide [Scheme 1(b)]. When the irradiation begins, the two reactions proceed very rapidly, and the reaction velocities are very fast due to enough monomers in the reacting box; therefore, the grating rate increases with an increase in irradiation dose. However, with the proceeding of polymerization, the monomers are consumed gradually; the reaction rate is thus decreased with the consumption of the monomers. In addition, the grafting rate will be also affected by the deposition of the grafted polyacrylamide on the membrane surface. Because the deposition of grafting product will decrease the effective area of irradiation, correspondingly inhibits the occurrence of grafting polymerization. These results are consistent with the basic theory of polymerization reactions. As a result, the grafting rate increases slowly when the irradiation dose increases to some extent.

The influence of inhibitor concentration on the grafting rate

Figure 3 illustrates the effect of inhibitor concentration on grafting rate at the case of irradiation dose = 40 kGy, MBAM% = 0.2, dose rate = 60 Gy/min. It can be seen that with an increase in inhibitor concentration, grafting rate first increases and then decreases. There exists a maximum in the plot at the concentration of Cu^{2+} = 0.2% acrylamide weight.

The above phenomenon can be explained as follows: it is well accepted that acrylamide is an active monomer. Its homogeneous polymerization rate is much higher than that of copolymerization. When the homogeneous polymer is produced, it will inhibit the diffusion of monomer from solution to the membrane's surface. So grafting rate is very low at the lower concentration of Cu^{2+}. However, when the concentration of Cu^{2+} increases, the concentration of Cu^{2+} in solution is higher than that on the membrane surface, thus the homogeneous polymerization will be prevented. Consequently, the increase of copolymerization rate is larger than that of homogeneous polymerization rate. Accordingly the grafting rate is increased. But when the concentration of Cu^{2+} in the solution increases to some extent, the concentration of Cu^{2+} on the membrane surface will also increase; thus both the homogeneous polymerization and copolymerization will be inhibited. As a result, grafting rate is decreased and thus the grafting rate reaches the maximum at some concentration of Cu^{2+} say 0.2% (weight).

The contact time between the membrane slice and filter paper

In the case of keeping the irradiation dose rate, irradiation dose, concentration of $CuSO_4 \cdot 5H_2O$, and the

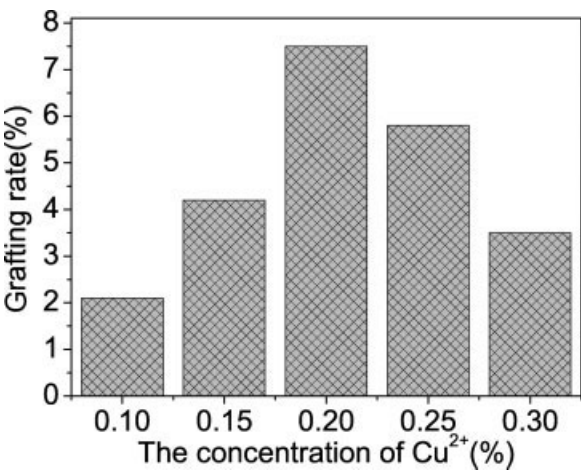


Figure 3 The effect of inhibitor concentration on grafting rate, in which irradiation dose = 40 kGy, the concentration of MBAM = 0.2% (weight), dose rate = 60 Gy/min.

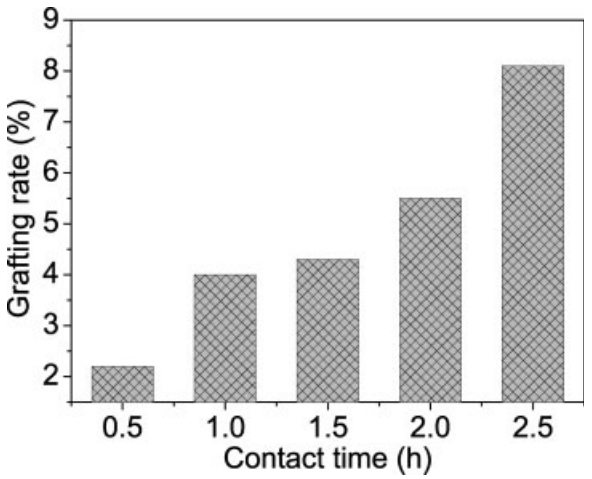


Figure 4 The effect of contact time of membrane slice with filter paper on grafting rate, in which irradiation dose = 40 kGy, $CuSO_4 \cdot 5H_2O\%$ = 1.5 (m/m), the concentration of MBAM% = 0.2, dose rate = 60 Gy/min.

concentration of MBAM constant, some efforts are made to investigate the effect of contact time between the membrane slice and filter paper on the grafting rate. The results were shown in Figure 4.

As expected, the grafting rate increased with an increase in the contact time. As well known, SPPO is a hydrophilic polymer and possesses high affinity to some polar molecules, such as water or acrylamide solution. So an increase in contact time will correspondingly increase the sorption amount of acrylamide monomer Furthermore, the acrylamide can be easily polymerized and crosslinked; meanwhile, the production of polymerization cannot be expediently removed via extraction method. As a result, with the elapsed contact time between the membrane slice and filter water, more amount of acrylamide penetrated into the membrane slice, the grafting rate was thus increased accordingly.

The grafting rate versus the water content of SPPO film

To have an insight into the properties of SPPO, the grafting rate against the water content of SPPO film was tested and the corresponding results were shown in Table II. For comparison, Table II also listed two membranes with grafting rate = 0 : 1 is the untreated SPPO film and the other is the grafted SPPO film in the same manner but using pure water instead of acrylamide monomer solution. Obviously, the water content of these two cases shows close consistence. It suggests that irradiation (without acrylamide monomer) does not affect the nature of SPPO film, that is, the water change of grafted SPPO film is mainly because of the grafting polymerization.

When the grafted membranes were compared, it is interesting to find that with an increase in grafting rate, the water content firstly increased and then slightly decreased after attaining a maximal value 214% at 6.5% grafting rate. The phenomena can be ascribed to the uptake water of polyacrylamide as mentioned earlier. As well known, polyacrylamide is more hydrophilic than SPPO and its ability for water uptake is extremely high. So when the amount of polyacrylamide in the membrane reaches a certain value, the water content of the modified membrane is mainly dominated by grafted polyacrylamide. In general, two chief factors can affect the water content of the grafted polyacrylamide. The first one is its structure (linear or crosslinking), which determines the absorbing water ability per unit mass of polyacrylamide; the other is the total amount of the grafted polyacrylamide. When the amount of irradiation dose is lower, linear molecular polyacrylamide will be formed, thus the absorbing water ability per grafted membrane is lower. Meanwhile, the low amount of the total grafted polyacrylamide will also allow low water content. However, when the irradiation dose increases, the increases in grafting rate (i.e., the total amount of grafted polyacrylamide) will correspondingly increase the water content. Meanwhile, the molecular structure of polyacrylamide tends to gradually change from linear structure to crosslinked one, which will highly improve its ability of absorbing water per grafted amount. In this case, both the absorbing water ability per polyacrylamide and total grafted polyacrylamide will favor the water content. When the irradiation dose increases to some extent, the grafting rate will keep constant but the crosslinking degree of the polyacrylamide will increase continuously. According to Flory formula for water absorbents,[26] when the crosslinking degree reaches a certain value, the ability of absorbing water of a material decreases with the increase of crosslinking degree. This may be the rea-

TABLE II
The Effect of Grafting Rate on SPPO Film Water Content

Grafting rate (%)	Water content (%)	Irradiation dose (kGy)
0[a]	56.6	0
0[b]	56.3	22.2
3.5	135	22.2
5.7	183	31.1
6.5	214	39.4
6.9	189	44.8

[a] Untreated SPPO film.
[b] The filter paper was filled with pure water.

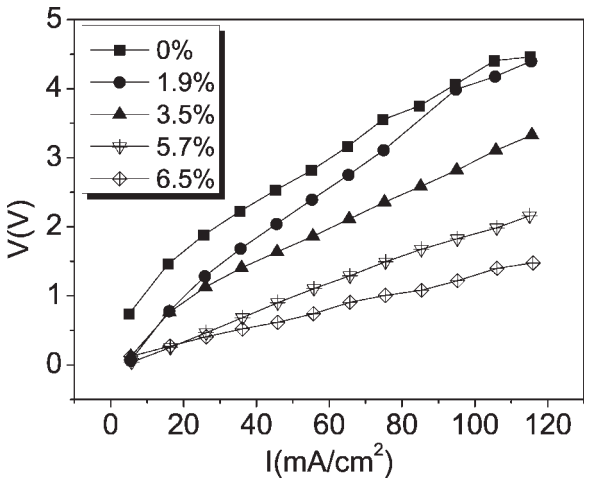


Figure 5 I–V curves of bipolar membranes, in which the SPPO grafted polyacrylamide was used as interfacial layer.

son why the water content tends to decrease a little when the grafting rate increases further.

The I–V curves of bipolar membranes using SPPO grafted polyacrylamide as interfacial layer

A bipolar membrane is a kind of composite membrane consists of both anion-exchange and cation-exchange layers as well as a hydrophilic junction layer.[27] The function of the junction layer is the catalysis of water dissociation and the most important requirement is that it should possess high water uptake ability. As discussed earlier, after grafting, the SPPO film has higher water uptake because of the extremely high affinity ability of grafted polyacrylamide to water. Hopefully, the grafted polyacrylamide can effectively catalyze the water dissociation if a bipolar membrane is prepared from the grafted SPPO film. As a try, a series of bipolar membranes were prepared with the grafted SPPO films of different grafted ratios as the cation-exchange layers (and correspondingly, the grafted polyacrylamide acts as the junction layer). Figure 5 showed the fundamental properties (current–voltage curves) of these bipolar membranes.

Obviously, with an increase in grafting ratio, the voltage at given current density is appreciably decreased. Compared with the bipolar membranes using un-grafted SPPO as cation-exchange layer, all the bipolar membranes prepared from the grafted SPPO possess lower voltage. These improvements in bipolar membrane's performance are no doubt to origin from the grafted polyacrylamide, which has two positive effects for water dissociation: one is that it has high water affinity and thus can provide more hydrophilic points for water dissociation as discussed intensively in literatures;[14,28,29] the other is that it is a weak base and can catalyze the water dissociation according to the following conventional proton transfer reaction:[30]

$$\begin{aligned} B + H_2O &\rightleftharpoons BH^+ + OH^- \\ BH^+ + H_2O &\rightleftharpoons B + H_3O^+ \end{aligned} \qquad (3a, b)$$

where ''B'' represents the grafted acrylamide. Obviously, the reactions of protonation and deprotonation will be accelerated with the availability of acrylamide.

CONCLUSIONS

The γ-ray irradiation-reduced grafting of polyacrylamide onto the sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) membranes were initiated, which was confirmed by the elemental composition of grafted SPPO determined by XPS data. Some important affecting parameters on the grafting processes were discussed. It was shown that the grafting rate increased with both the increasing irradiation dose and the elapsed contact time between the membrane slice and the filter paper. As for inhibitor concentration, the grafting rate firstly increases and then decreased after reaching a plateau value at about 0.2% $CuSO_4 \cdot 5H_2O$ concentration. The water content of the grafted SPPO was largely determined by the nature of polyacrylamide. It firstly increases and then decreases with an increase in grafting rate. When the grafting rate is equal to 6.5%, the water content arrived at maximum.

A series of bipolar membranes were prepared with the grafted SPPO of different ratios as the cation exchange layers. Correspondingly, the grafted polyacrylamide acts as the junction layer. The results show that with an increase in grafting ratio, the voltage at given current density is appreciably decreased. These improvements in bipolar membrane performance are mainly due to the two positive effects of grafted polyacrylamide for water dissociation: one is its high water affinity and the other is its weak base characteristics, which can catalyze the water dissociation by proton transfer reaction.

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