Influence of the Radiation Grafting Conditions on the Cross-Sectional Distribution of Poly(vinylbenzyl chloride) Grafted Polymer onto Poly(tetrafluoroethylene-*co*-hexafluoropropylene) Films

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ABSTRACT: Poly(vinylbenzyl chloride) (PVBC)-grafted poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) films were prepared as precursors for ion-exchange membranes with a radiation grafting technique. A scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM-EDX) instrument was used to investigate the effects of the radiation grafting conditions on the distribution profiles of the grafts in the FEP-*g*-PVBC films because the properties of the ion-exchange membranes were largely affected not only by the degree of grafting (DOG) but also by the distribution of the graft chain. These results indicate that the distribution profile of the grafts largely depended on the grafting parameters, such as the solvent, monomer concentration, film thickness, and irradiation dose. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2380–2385, 2010

Key words: diffusion; graft copolymers; radiation

INTRODUCTION

Nowadays, ion-exchange membranes attract a great deal of attention in a number of broad industrial fields, including separators, solid polymer electrolytes in batteries, sensing materials, medical applications, and fuel cells.[1–5] Among the various membrane preparation techniques, the radiation-induced grafting method[1–3,6–9] has been widely used because of its simplicity and the ability to easily control the grafting yield. The radiation grafting process can be carried out through either a simultaneous irradiation[1,3,4,9–11] or a pre-irradiation method.[1,3,11,12] Fluoropolymer films,[1,3,13–17] such as poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP), poly(tetrafluoroethylene-*co*-perfluoropropylvinyl ether) (PFA), poly(ethylene-*co*-tetrafluoroethylene) (ETFE), and poly(vinylidene fluoride) (PVDF) are often used as the base films in this process because of their excellent chemical, thermal, and mechanical properties. Acrylic acid, acrylamide, styrene, α-methylstyrene, and vinylbenzyl chloride (VBC) are generally used as grafting monomers.[1,3,10,18–20]

VBC is a very attractive monomer because it possesses two reactive functional groups, a chloromethyl group and a double bond, which can be used for nucleophilic substitution and polymerization reactions, respectively. The VBC monomer[9,21–24] has been used for various purposes, including fire-resistant polymers, photosensitive polymers, and polyelectrolytes, especially in ion-exchange-membrane applications. As shown in Scheme 1, the VBC monomer has been easily grafted onto fluoropolymer films with a radiation grafting method, either the preirradiation method[21,22,24] or the simultaneous irradiation method.[9] The chloride moiety of the prepared PVBC-grafted fluoropolymer film has been used to introduce an ion-exchangeable functional group, such as an amine[21,22,25] for anion-exchange membranes or phosphoric acid[24] for cation-exchange membranes. Recently, PVBC-grafted FEP films were used to prepare a poly(vinylbenzyl sulfonic acid)-grafted FEP polymer electrolyte membrane by modification of the benzyl chloride moiety to the benzyl sulfonic acid moiety via the formation of thiouronium salt with thiourea, base-catalyzed hydrolysis for the formation of thiol, and oxidation with hydrogen peroxide.[26]

Our previous study showed that the cross-sectional distribution profiles of poly(styrene sulfonic

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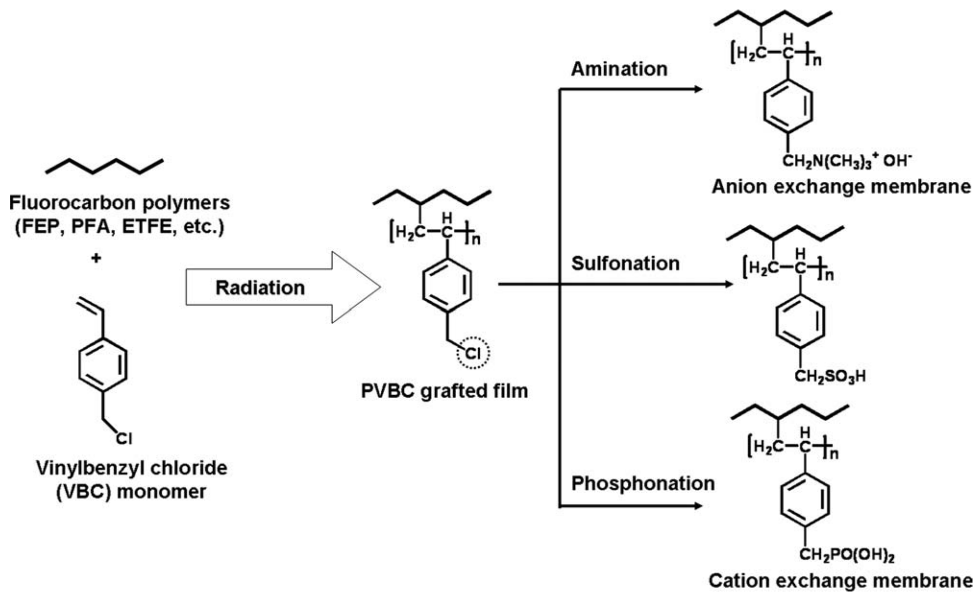

Scheme 1 Preparation of the FEP-*g*-PVBC film as a precursor for various ion-exchange membranes.

acid) graft polymers in membranes were largely affected by the grafting conditions.[27–30] The distribution profile is considered a very important factor becasue it affects ions transfer through the membrane while the fuel cell in operation.

In this study, the effects of the irradiation conditions on the PVBC graft polymers distribution in FEP-*g*-PVBC films were investigated with SEM-EDX analysis after treatment with thiourea. The distribution behaviors of the grafts were investigated with respect to the different grafting parameters, such as the solvent, monomer concentration, film thickness, and irradiation dose.

EXPERIMENTAL

Materials

FEP films 25, 50, and 100 μm thick (Universal Co. Ltd., Tokyo, Japan) were used as the base films. All reagents, including the VBC monomer (a mixture of *m* and *p* isomers, 96% purity, Acros Organics) and thiourea (99%, extra pure, Acros Organics), were used as received from the commercial suppliers.

Radiation grafting process

FEP films with various thicknesses were cut into pieces (3×4 cm^2), washed with acetone, and then dried in a vacuum oven for 6 h at 60°C. The dried FEP films were immersed in solutions containing desired ratios of VBC to chloroform. The solutions were purged with nitrogen for 10 min to remove oxygen and then irradiated with a simultaneous irradiation method, which used a γ-ray from a Co^{60} source at irradiation doses ranging from 10 to 80 kGy and a dose rate of 2 kGy/h. After the irradiation, the grafted films were washed with dichloromethane to remove residual VBC monomer and homopolymers. The grafted films were dried in a vacuum oven at 60°C for 8 h. The degree of grafting (DOG) was determined with the following equation:

$$\mathrm{DOG}(\%) = [(W_g - W_o)/W_o] \times 100$$

where W_o is the weight of the film before grafting and W_g is the weight of the film after grafting.

SEM–EDX measurements after the formation of thiouronium salt

The distribution profiles of the PVBC grafts were investigated over the cross section of the grafted PVBC films (FEP-*g*-PVBC) with SEM–EDX measurements after the benzyl chloride moiety was modified to thiouronium salt with thiourea. The PVBC-grafted FEP films were immersed in a thiourea solution (0.13*M*, in ethanol) for 6 h at 40°C to convert the chloride of PVBC to thiouronium salt. The resulting films were washed with ethanol several times and then dried at 60°C in a vacuum oven until a constant weight was achieved. The prepared poly(vinylbenzyl thiouronium salt)-grafted FEP films (FEP-*g*-PVBTS) were analyzed with SEM–EDX.[26] The SEM–EDX measurements were carried out with a 7200-H instrument (Horiba Co., Kyoto, Japan) at a working distance of 12 mm for 2200 CPS and an accelerating voltage of 15 kV. The prepared FEP-*g*-PVBTS films were broken in liquid nitrogen and then coated with osmium for the SEM-EDX analysis. The distribution profiles of the chlorine and sulfur atoms present in thiouronium salt were measured over the cross section of the FEP-*g*-PVBTS films with the SEM–EDX measurements.

RESULTS AND DISCUSSION

Figure 1 shows the effects of the monomer concentration in two different halogenated solvents (dichloromethane and chloroform) on the degree of grafting of VBC on the FEP films. As shown in the figure, DOG increased with increasing VBC monomer concentration up to a value of 60% in the dichloromethane solvent and up to a value of 50% in the chloroform solvent because of the increased monomer accessibility at the grafting sites. However, DOG decreased above these concentrations; these results were similar to those observed when styrene was used as a grafting monomer during a radiation grafting procedure presented in previous literatures.[19,20,31,32] The homopolymer formation at higher VBC concentrations caused an increase in the viscosity of the grafting solution, which limited the diffusion of the VBC monomer into the polymer matrix.[10,19,32,33]

Different grafting behaviors were observed for the two halogenated solvents because of the different radical chain-transfer constants of dichloromethane (0.15)[19,34] and chloroform (0.5).[35] A previous report showed that a solvent with a low chain-transfer constant could slow down the chain growth and chain-termination processes, which could eventually increase DOG.[36–38] From Figure 1, chloroform was a suitable solvent at a VBC concentration of 50% or lower, whereas dichloromethane was a good solvent at a VBC concentration of 60%. In this study, chloroform and a VBC concentration of 50% were chosen as the solvent and VBC concentration, respectively, for the following experiments.

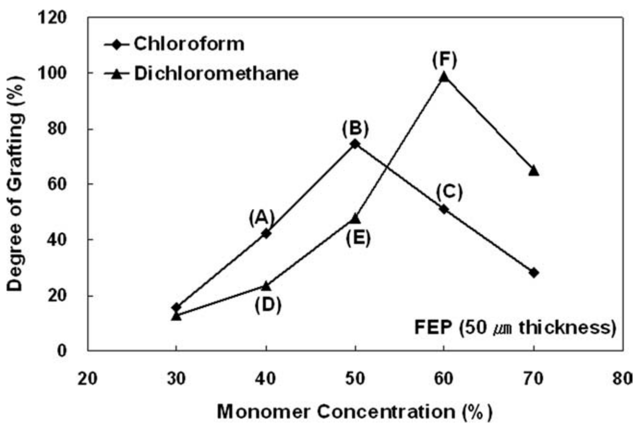

Figure 1 The degrees of grafting of VBC onto FEP films that were irradiated at various VBC concentrations in dichloromethane and chloroform solvents at a total dose of 40 kGy and a dose rate of 2 kGy/h.

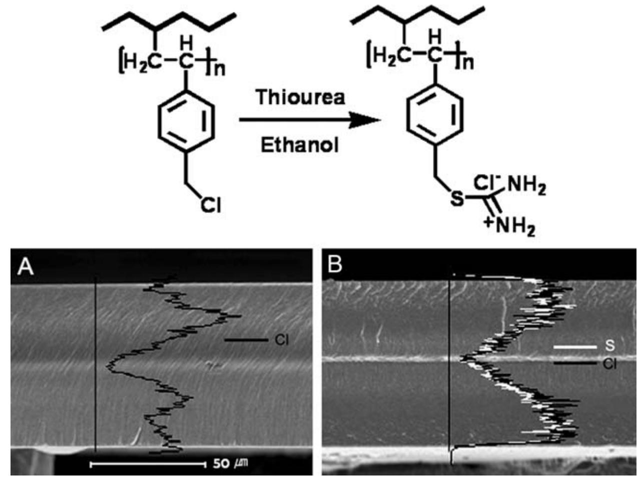

Figure 2 (A) Chloride distribution profile of the PVBC-grafted FEP film and (B) chloride and sulfur distribution profiles of the PVBTS-grafted FEP film under the same SEM–EDX conditions.

The distribution behaviors of the chlorine atoms that were present in the prepared films were observed with SEM–EDX analysis to investigate the effects of the irradiation conditions on the distribution of the grafted polymer. As shown in Figure 2(A), the EDX measurements of the chlorine atom exhibited incomprehensible distribution profiles with a relatively low distribution on the surface of the film. However, after the chloride moiety of the film was converted to thiouronium salt with thiourea, reasonable distribution profiles were obtained for the chlorine and sulfur atoms with the same EDX measurement techniques, as shown in Figure 2(B). The prepared FEP-*g*-PVBC films were converted to FEP-*g*-PVBTS films because the EDX analysis was not easily carried out for the FEP-*g*-PVBC films, and the distributions of the chlorine and sulfur atoms in thiouronium salt were analyzed over the cross section of the FEP-*g*-PVBTS films with SEM–EDX.

Figure 3 shows the distribution profiles of the graft polymer in samples that were selected from Figure 1. Figure 3(A–C) shows the cross-sectional distribution behaviors of the graft polymer in the films that were irradiated at VBC concentrations of 40, 50, and 60%, respectively, in chloroform. More chlorine and sulfur atoms were observed in the middle of the film as the VBC concentration increased from 40 to 50% [Fig. 3(A,B)]; this indicated that more VBC monomers diffused into the inner region of the films during the grafting process. However, the film that was prepared at a relatively high concentration of VBC [60%; Fig. 3(C)] exhibited a very limited diffusion of the graft chains, although it exhibited a higher DOG value (51%) than the film

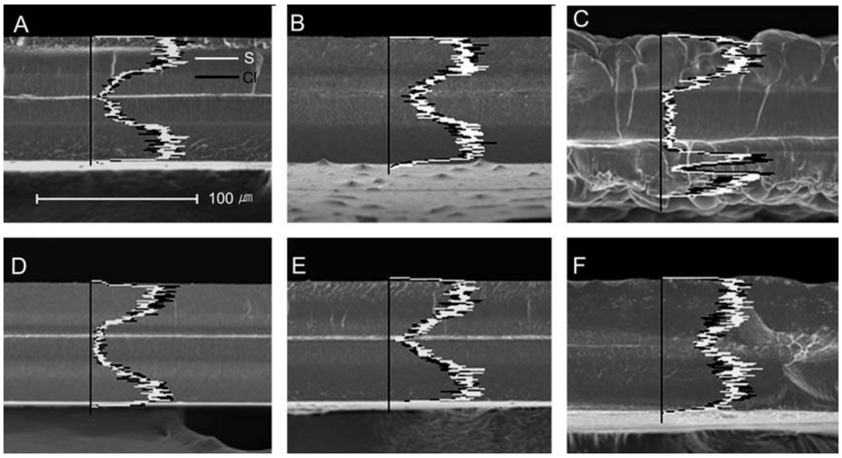

Figure 3 SEM–EDX analysis for the effects of the solvent and monomer concentration on the radiation grafting of the VBC monomer onto an FEP film (see Fig. 1 for details).

that was prepared at a VBC concentration of 40% [Fig. 3(A), 42% DOG]. Furthermore, as shown by the SEM image, the sample exhibited a very rugged surface with an increased thickness.

Figure 3(D–F) shows the SEM–EDX analysis of the samples that were prepared with 40, 50, and 60% VBC, respectively, in dichloromethane. The distribution profiles of the chlorine and sulfur atoms became uniform as the DOG values increased from 23 to 99%. Significant differences were observed in both the graft polymer distribution and the surface morphology of the two films that were prepared at the same VBC concentration and irradiation conditions but in different solvents, as shown in Figures 3(C) (51% DOG) and 3(F) (99% DOG). As previously discussed for Figure 1, these differences were attributed to the higher radical chain-transfer constant of chloroform. In the chloroform solution, the increased homopolymer formation at a VBC concentration of 60% inhibited the monomer diffusion, whereas less homopolymer was formed in dichloromethane at the same monomer concentration.

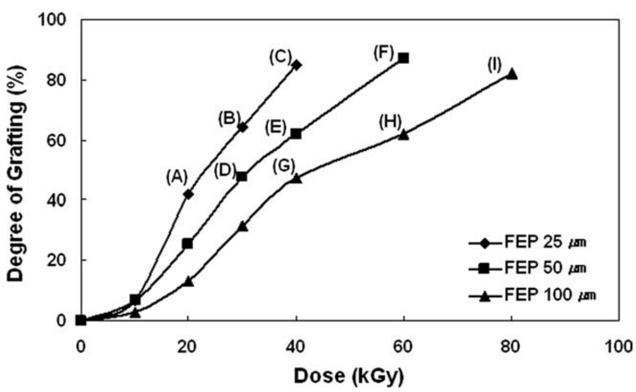

Figure 4 The degrees of grafting of the VBC monomer onto FEP films with thicknesses of 25, 50, and 100 μm. These samples were irradiated in a VBC/chloroform (50/50 v/v) solution at a dose rate of 2 kGy/h.

Figure 4 shows the variations in the DOG values of the grafted films (25, 50, and 100 μm) with respect to the irradiation doses. The grafting processes were conducted at a VBC concentration of 50% in the chloroform solution, and the total doses ranged from 10 to 80 kGy at a dose rate of 2 kGy/h. As shown in Figure 4, the DOG increased as the total irradiation dose increased, and the thinner films exhibited higher DOG values at the same dose.

Figure 5 shows the distribution profiles of the graft chains over the cross section of the grafted films that were prepared in chloroform at a VBC concentration of 50%. These films were selected from Figure 4 with various thicknesses and DOG values between 40 and 80%. These results indicate that the distribution profiles became more uniform as the DOG values increased. Furthermore, a higher DOG was required as the film thickness increased to obtain a uniform distribution.

The uniformity of the cross-sectional distribution of the PVBC graft polymer across the grafted film would be very important if the PVBC-grafted film were used as a precursor for an ion-exchange membrane (either a cation- or an anion-exchange membrane) of a fuel cell because ions pass through the membrane while the fuel cell is in operation. Under these grafting conditions, DOG values of 60 and 80% were required to obtain a uniformly grafted membrane with 25 and 50 μm thick FEP films, respectively, and a higher DOG was required for a 100 μm thick FEP film. FEP-*g*-PVBC films are currently being investigated as precursors for the preparation of ion-exchange membranes (either cation- or an anion-exchange membranes).

CONCLUSIONS

In this study, the effects of the irradiation parameters, such as the solvent, monomer

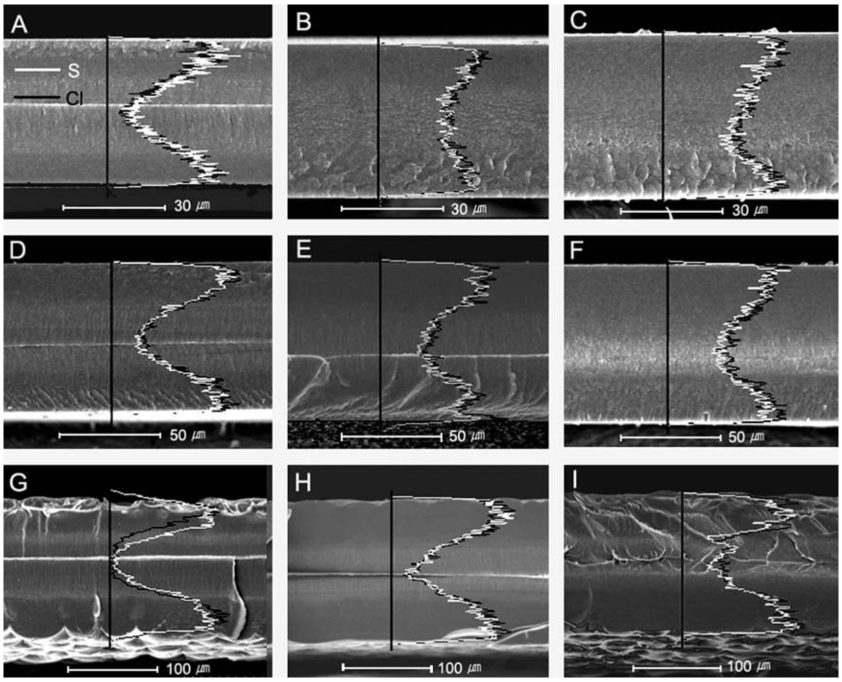

Figure 5 SEM–EDX analysis of the effects of the film thickness and DOG on the radiation grafting of the VBC monomer onto an FEP film (see Fig. 4 for details).

concentration, film thickness, and irradiation dose, on the distribution behaviors of PVBC were investigated over the cross section of FEP-*g*-PVBC films with SEM–EDX measurements after chloride was modified to thiouronium salt with thiourea. In this study, two halogenated solvents, chloroform and dichloromethane, were compared at various monomer concentrations. The simultaneous irradiation grafting polymerization of the VBC monomer onto FEP films, with various thicknesses, was performed at a VBC concentration of 50% in a chloroform solvent, and the grafted films were subjected to SEM–EDX analysis to investigate the distribution behaviors of the grafts. Under these grafting conditions, these results indicate that DOGs of 60 and 80% were required to obtain uniformly grafted membranes with 25 and 50 μm thick FEP films, respectively. Additionally, a higher DOG was required to obtain the 100 μm thick FEP film. This research, regarding the effects of the radiation grafting conditions on the distribution of grafts, provided valuable information for the ion-exchange membrane research community.

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