

Simultaneous Radiation Grafting of Vinylbenzyl Chloride onto Poly(tetrafluoroethylene-co-hexafluoropropylene) Films

Junhwa Shin, Geng Fei, Sung-A Kang, Beom-Seok Ko, Phil-Hyun Kang, Young Chang Nho

Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeongeup-si, Jeollabuk-do, Republic of Korea

Received 18 November 2008; accepted 17 February 2009

DOI 10.1002/app.30264

Published online 1 May 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, we demonstrated that vinylbenzyl chloride (VBC), a versatile monomer with reactive a chloromethyl group could be grafted onto a poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) film without a degradation of the chloromethyl group during a simultaneous irradiation process. The effects of various irradiation conditions such as the total dose, dose rate, solvent, and

VBC concentration on the degree of grafting of VBC onto a FEP film were also investigated. The prepared PVBC-grafted films were characterized using FTIR, TGA, and SEM EDX. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2858–2862, 2009

Key words: VBC; FEP; radiation; grafting

INTRODUCTION

Vinylbenzyl chloride (VBC) is a dual functional monomer that consists of a polymerizable double bond and a chloromethyl group that can undergo a reaction with various nucleophiles. A modification of the chloromethyl group can be performed either before or after a polymerization. VBC has been widely used as a valuable precursor for the preparation of various polyelectrolytes (e.g. ion exchange resins), polymeric supports for solid peptide synthesis, fire-resistant polymers, and photosensitive polymers etc.^{1–5} Among them, several ion exchange membranes have been prepared by a radiation grafting of VBC onto a polymer film. In this process, a polymer film is exposed to radiation to generate reactive radicals on a polymer backbone prior to the introduction of a VBC grafting monomer (pre-irradiation method) and the prepared polyvinylbenzyl chloride (PVBC)-grafted film is then modified by a chemical treatment to prepare ion exchange membranes.^{6,7} Especially, VBC is a valuable precursor for anionic exchange membranes which have usually been prepared by a reaction with an amine after a grafting or a polymerization of VBC.^{6–8}

Radiation grafting is a very convenient and effective way to provide a novel functionality to existing commercialized polymers and is performed by either a simultaneous irradiation or a pre-irradiation method. These two methods have their own advantages and disadvantages. It is known that a simultaneous irradiation method has such advantages as a one-step process and a simple irradiation procedure requiring a lower total dose and temperature, compared to the pre-irradiation method.⁹ This method also has a serious disadvantage arising from the high level of homopolymer formation. However, this problem could be overcome by adopting suitable irradiation conditions such as a solvent, the concentration, dose rate, and total dose etc.¹⁰

Even with the advantages of the simultaneous irradiation mentioned earlier, only the pre-irradiation method has been applied for the grafting of VBC onto commercialized films and reported in the literature as far as we are aware.^{6–8,11} We assume that this could be due to a concern about a reactive chloromethyl group that might be labile at a simultaneous irradiation condition. No detailed investigations for the compatibility of VBC at a simultaneous irradiation grafting condition have also been reported.

In this study, ¹H-NMR spectrometer was applied to demonstrate the stability of the chloromethyl group of VBC at simultaneous irradiation conditions up to a total dose of 80 kGy. VBC was grafted at various simultaneous irradiation conditions onto a FEP film that has drawn wide attention due to its excellent radiation stability.¹² The correlations between the

Correspondence to: Y. C. Nho (ycnho@kaeri.re.kr).

Contract grant sponsors: Nuclear R&D Program of the Ministry of Education, Science & Technology of Korea.

degree of grafting and the irradiation parameters such as the solvent, concentration, dose rate, and total dose were also established. The prepared films were characterized using FTIR, TGA, and SEM EDX.

EXPERIMENTAL

Materials

VBC (mixture of *m*- and *p*-isomers, 96%) was purchased from Acros Organics and used as received. Other chemicals including the solvents were of reagent or higher grade and used without further purification. A FEP film of a 25- μm thickness was supplied by Universal Company (Japan) and washed with dichloromethane (DCM) before subjecting it to a grafting reaction.

$^1\text{H-NMR}$ study for the radiolytic polymerization of VBC in CDCl_3

NMR spectroscopy (JEOL, 500 MHz for $^1\text{H-NMR}$) was used to monitor the radiolytic polymerization of VBC in CDCl_3 . VBC and CDCl_3 were mixed in small vials prior to a nitrogen purging. The mixtures (VBC : CDCl_3 , 10 : 0, 5 : 5, volume ratio) were exposed to γ -ray irradiation for 20 h at dose rates of 2 and 4 kGy/h. Small portions of the irradiated samples were diluted with CDCl_3 for the $^1\text{H-NMR}$ analysis. When pure VBC (10 : 0) was exposed to γ -ray, it became very rigid so it could not be dissolved in CDCl_3 .

Simultaneous radiation grafting of VBC onto FEP films

Generally, a FEP film (25 μm thickness) cut into 2 cm \times 3 cm, was immersed in a vial containing a VBC monomer and CHCl_3 with a 1 : 1 volume ratio. A series of mixture samples containing a FEP film, VBC, and CHCl_3 was purged with nitrogen gas for 10 min to remove the oxygen, and then subjected to a γ -ray irradiation up to a total dose of 40 kGy at dose rates of 1, 2, and 4 kGy/h for the grafting of VBC onto the FEP films. The PVBC-grafted FEP films were washed with DCM three times to remove the unbound homopolymers and the excess VBC monomer. After drying the films in a vacuum oven at 60°C overnight, the degrees of grafting (DOG) of the grafted films were calculated as shown below. (W_o : original sample weight, W_g : grafted sample weight).

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

Characterization of the PVBC-grafted FEP films

IR spectra of the PVBC-grafted FEP films were obtained by using the FTIR spectrometer Tensor-37 (Bruker, Germany) at ambient conditions in the

transmittance mode. The spectra were measured in a wave number range of 400–4000 cm^{-1} . The thermal property of the PVBC-grafted FEP films was investigated by a thermogravimetric analysis (TGA). The samples were heated from 40 to 650°C at a rate of 10°C min^{-1} under a dry nitrogen atmosphere. SEM EDX (SIRION, FEI Company) measurement was conducted to investigate the distribution of the PVBC grafting polymer on the cross-section of the FEP-g-PVBC films. The grafted films were broken in liquid nitrogen and placed between two silicon wafers. These samples were coated with platinum and subjected for a SEM EDX analysis. The SEM EDX operating conditions were set as follows: accelerating voltage with 20 kV, spot size of 4, and a working distance of 5–10 mm for obtaining CPS: 1500. In the EDX mode, the relative content of the chlorine atom over the cross-section of the FEP-g-PVBC films presented in a diagram.

RESULTS AND DISCUSSION

$^1\text{H-NMR}$ study of the polymerization of VBC in CDCl_3

To investigate the possibility for the use of VBC in simultaneous irradiation conditions, mixtures of VBC monomer and CDCl_3 (1 : 1 volume ratio) were exposed to γ -ray up to 80 kGy at a dose rate of 4 kGy/h. Small amounts of the irradiated samples which became viscous were diluted with CDCl_3 prior to the $^1\text{H-NMR}$ analysis. The $^1\text{H-NMR}$ spectra of the pure VBC and the irradiated VBC samples are illustrated in Figure 1. The multiplets at 7.25–7.44 ppm correspond to four aromatic hydrogens of VBC and the three peaks at 5.28, 5.76, and 6.70 ppm correspond to three hydrogens at the C=C double bond of VBC, respectively. A sharp singlet observed at 4.59 ppm can be assigned to the methylene peak of the chloromethyl group of VBC. As shown in Figure 1(B,C), new broad peaks resulting from the polymerization of VBC appeared at around 1.4, 1.7, 4.4, 6.5, and 7.0 ppm and the intensities of the peaks increased as the radiation dose increased. These spectra show that the peaks from the aromatic hydrogens of VBC were slightly shifted to 6.5 and 7.0 ppm, whereas the peaks from the hydrogens at the C=C double bond of VBC were significantly shifted to a downfield region (1.4 and 1.7 ppm) due to a change of the C=C double bond to a single bond. These spectra also show that the methylene peak resulting from the chloromethyl moiety of VBC was shifted from 4.59 ppm to 4.4 ppm with a line broadening response. By comparing the integral values of the peaks arising from VBC and PVBC, it can be concluded that the chloromethyl moiety of VBC is fairly stable at the given irradiation conditions (up

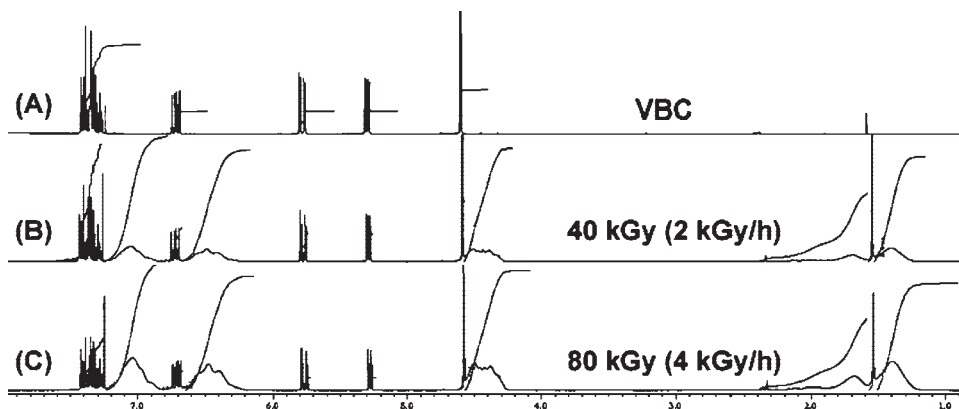


Figure 1 The $^1\text{H-NMR}$ spectra of pure VBC (A) and the irradiated VBC samples (50% VBC in CDCl_3) at total doses of 40 kGy (B) and 50 kGy (C), respectively.

to 80 kGy) and therefore could be applied for a simultaneous radiation grafting onto a polymer film.

Simultaneous radiation grafting of VBC onto FEP films

It is well known that the usage of a suitable solvent for a simultaneous irradiation grafting polymerization could not only improve the grafting efficiency but also minimize the homopolymerization.^{13,14} This can be attributed to the facts that the diffusion of the monomer onto the grafting sites is largely determined by the swellability of the polymer in a solvent, and furthermore, the reactivity and lifetime of the radicals generated during an irradiation are also affected by a solvent.¹⁵

Several solvents including halogenated, aromatic, and aliphatic hydrocarbon solvents were tested to find a suitable solvent for the grafting of VBC onto a FEP film. A piece of FEP film was immersed in a mixture containing VBC and a solvent at a ratio of 1 : 1 (v/v), and then irradiated at total doses of 20 and 40 kGy with a dose rate of 2 kGy/h. The DOG of the samples irradiated in various solvents are calculated and shown in Figure 2. Among the used solvents, hexane, methanol, and isopropanol are excluded from this figure since too much insoluble VBC homopolymer was formed in these solvents at the given irradiation conditions. The homopolymer formation increases the viscosity of the grafting solutions and therefore it also reduces the monomer diffusion onto a polymer film.¹⁶ As shown in Figure 2, higher grafting efficiencies were observed from the halogenated solvents with the exception of carbon tetrachloride. For the VBC grafting onto FEP, chloroform was found to be a better solvent than dichloromethane which has normally been used as a solvent for a simultaneous irradiation grafting of polystyrene (PS) into a polymer film.¹³ Although a moderate grafting efficiency was observed from toluene, the film grafted in toluene was found to be brittle

and broke easily. On the basis of this solvent effect study, chloroform was selected as the solvent for a simultaneous irradiation grafting of VBC onto a FEP film.

Figure 3(A) shows the variation of the degree of grafting with the irradiation dose at various VBC concentrations (30, 40, and 50% v/v in CHCl_3) during a simultaneous irradiation grafting of VBC onto a FEP film. The VBC grafting solutions containing FEP film were irradiated at total doses of 10, 20, 30, and 40 kGy with a dose rate of 2 kGy/h. As shown in the figure, the degree of grafting increases as the radiation dose and VBC concentration increases. This behavior can be explained easily by considering the increase in the radical yield with the irradiated dose and the enhancement in the accessibility of VBC monomers near graft sites, which subsequently lead to an increase of the graft yields. To investigate the effects of the dose rate on a simultaneous irradiation grafting of VBC, the grafting samples containing a FEP film and a mixture of VBC and CHCl_3 (50 : 50 volume ratio) were irradiated at dose rates of 1, 2, and 4 kGy/h. As shown in Figure 3(B), the degree

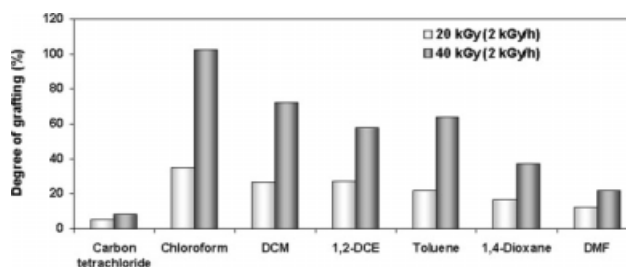


Figure 2 The degree of grafting of the PVBC-grafted FEP films prepared in various solvents; carbon tetrachloride, chloroform, DCM (dichloromethane), 1,2-DCE (1,2-dichloroethane), toluene, 1,4-dioxane, DMF (*N,N*-dimethylformamide). Each sample containing a FEP film and a VBC/solvent (1 : 1 v/v) mixture was irradiated at total doses of 20 and 40 kGy with a dose rate of 2 kGy/h.

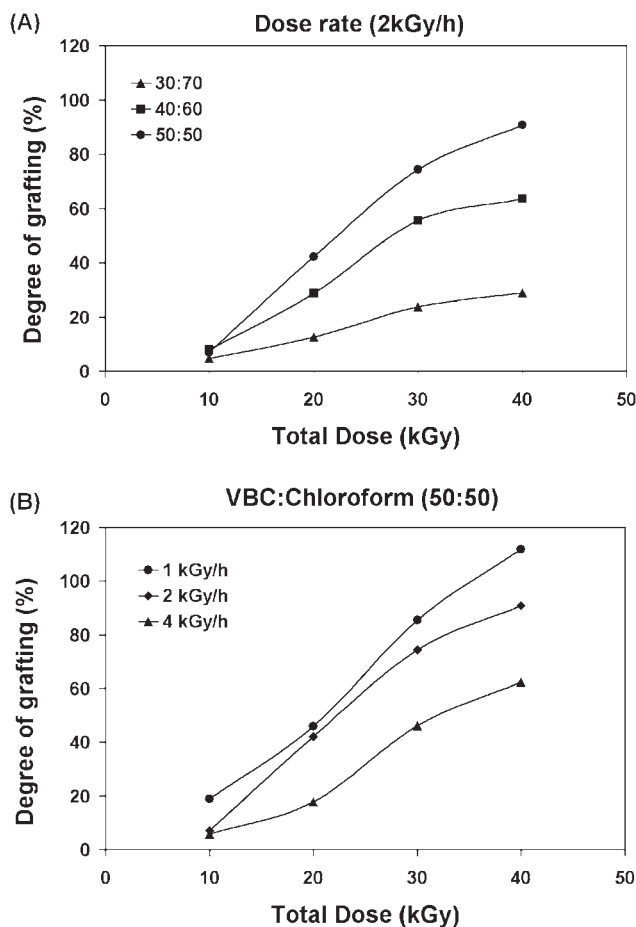


Figure 3 A: The degree of grafting vs. the total dose at different VBC concentrations (2 kGy/h dose rate). B: The degree of grafting vs. the total dose at different dose rates (VBC : chloroform 50 : 50 (v/v)).

of grafting decreases with an increasing dose rate when the same irradiation dose is employed since a prolonged irradiation time at a low dose rate can provide a sufficient time for a survival of the radicals and a polymer chain growth. The PVBC-grafted FEP films prepared at the conditions shown in Fig-

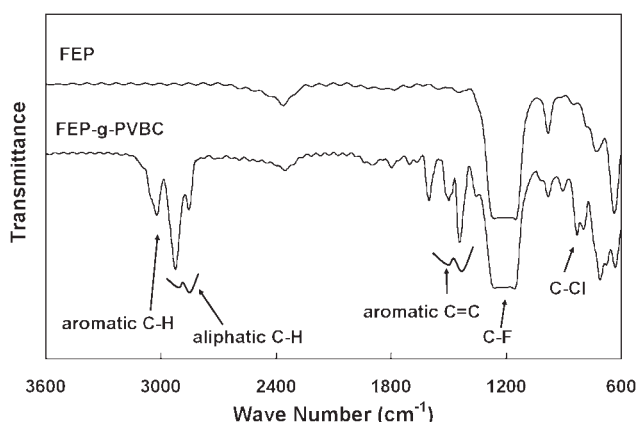


Figure 4 The FTIR-ATR spectra of the original FEP film and the FEP-g-PVBC film.

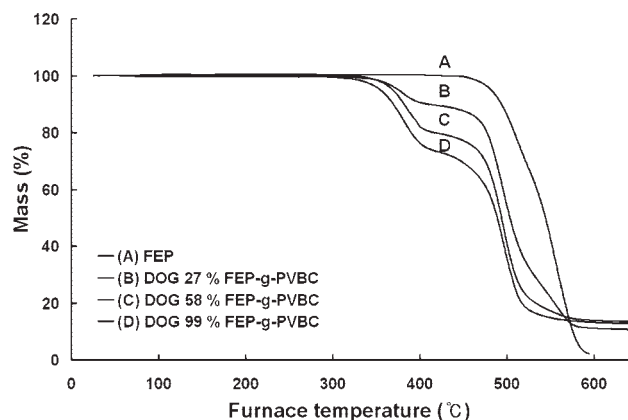


Figure 5 TGA thermograms of the PVBC-grafted FEP films with different degrees of grafting: FEP-g-PVBC with (A) ungrafted FEP, (B) 27% DOG, (C) 58% DOG, and (D) 99% DOG.

ure 3 are flexible and have a good shape while the grafted films prepared in a high VBC concentration solution (70%) at a dose rate of 4 kGy/h are somewhat brittle. At high VBC concentration conditions, a significant formation of homopolymer, resulting in a lower grafting efficiency was also observed. Therefore, these grafting studies, presented in Figure 3 and discussed here, suggest that 40–50% of VBC in chloroform (v/v) at dose rates of 1–2 kGy/h seem to be suitable conditions for the grafting of VBC onto a FEP film.

Characterization of the PVBC-grafted FEP Films

The FTIR-ATR spectrum of the original FEP film (Fig. 4) showed strong bands at 1150–1250 cm^{-1} and a sharp band at around 980 cm^{-1} arising from the $-\text{C}-\text{F}$ stretching vibration of the FEP polymer.¹⁵ The spectrum of the FEP-g-PVBC film showed all the signals assignable to the FEP base film and the new absorption bands arising from the grafted

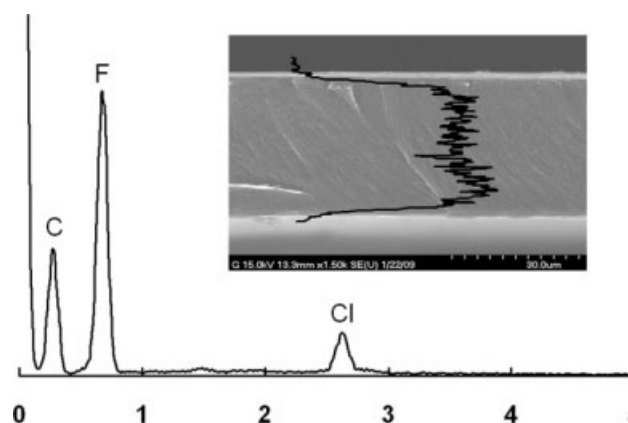


Figure 6 Cross-sectional SEM micrograph image of the grafted FEP film (64% DOG) with the chlorine distribution profile and the EDX spectrum of the grafted FEP film.

PVBC components, indicating a successful grafting of VBC onto a FEP film.^{17,18} The aromatic absorption bands of the grafted PVBC appeared at 3050 cm^{-1} ($=\text{C}-\text{H}$ stretching vibration) and at $1450\text{--}1600\text{ cm}^{-1}$ ($\text{C}=\text{C}$ stretching vibrations), respectively. The aliphatic absorption bands were observed at $2800\text{--}2900\text{ cm}^{-1}$ ($-\text{C}-\text{H}$ stretching vibration) and a characteristic band of the chloromethyl group ($-\text{C}-\text{Cl}$ stretching vibration) of the grafted PVBC was also observed at 820 cm^{-1} .¹⁹

Figure 5 shows the TGA thermograms of the ungrafted FEP film and the grafted (FEP-*g*-PVBC) films. The grafted FEP-*g*-PVBC films were found to undergo a two step degradation at 360 and 490°C , whereas the ungrafted FEP film exhibited a one-step degradation where it maintains a temperature up to 490°C . These results indicate that the incorporation of PVBC grafts in the FEP matrix does not bring about any changes to the inherent decomposition of the FEP backbone and the mass loss of the PVBC decreases with the extent of the radiation grafting of the PVBC.^{19,20}

To observe the distribution profile of the PVBC grafts over the cross-section of a FEP film, the SEM EDX technique was utilized in this study. EDX result in Figure 6 shows three major peaks: carbon, fluorine, and chlorine atoms. Among those atoms, the chlorine atom was chosen for the distribution study of the PVBC grafts since it only exists in the PVBC grafts. This means that the distribution profile of the chlorine atoms corresponds to that of the PVBC grafts. The SEM EDX data shows that chlorine atoms are uniformly distributed over the cross-section of a grafted FEP film with a 64% DOG, indicating that the VBC monomer was evenly grafted from the surface to the inner of a FEP film by a simultaneous radiation method.

CONCLUSIONS

In this article, we demonstrated that a simultaneous irradiation method could be applied for the grafting of VBC onto FEP films without a noticeable degradation of the chloromethyl group. It is also concluded that chloroform is a more effective solvent than the other solvents including dichloromethane during a radiation grafting of VBC onto a FEP film. Our stud-

ies showed that the degree of grafting of the FEP-*g*-PVBC increased with an increasing irradiation dose and the monomer concentration increased. The optimum radiation grafting conditions were also determined to be in the ranges of $1\text{--}2\text{ kGy/h}$ for the dose rate and $40\text{--}50\%$ (v/v) for the VBC concentration in chloroform. Several instruments such as FTIR, TGA, and SEM EDX were utilized to characterize the prepared FEP-*g*-PVBC films and the results support a successful grafting of VBC onto a FEP film via a simultaneous irradiation method. We strongly believe that this simple and easy radiation grafting method for VBC can be very useful for the preparation of many valuable grafted materials including ion exchange membranes.

We would like to thank the KBSI, Jeonju Center for the help of SEM EDX measurements.

References

1. Schwarz, S.; Jaeger, W.; Paulke, B.-R.; Bratskaya, S.; Smolka, N.; Bohrisch, J. *J Phys Chem B* 2007, 111, 8649.
2. Gong, M. S.; Lee, C. W. *Mater Chem Phys* 2002, 77, 719.
3. Görtz, V.; Ritter, H. *Macromolecules* 2002, 35, 4258.
4. Renil, M.; Meldal, M. *Tetra Lett* 1996, 37, 6185.
5. Kaledkowski, A.; Trochimczuk, A. W. *React Funct Polym* 2006, 66, 957.
6. Herman, H.; Slade, R. C. T.; Varcoe, J. R. *J Membr Sci* 2003, 218, 147.
7. Danks, T. N.; Slade, R. C. T.; Varcoe, J. R. *J Mater Chem* 2002, 12, 3371.
8. Slade, R. C. T.; Varcoe, J. R. *Solid State Ion* 2005, 176, 585.
9. Horsfall, J. A.; Lovell, K. V. *Eur Polym J* 2002, 38, 1671.
10. Nasef, M. M.; Hegazy, E. S. A. *Prog Polym Sci* 2004, 29, 499.
11. Holmberg, S.; Holmlund, P.; Wilén, C.-E. *J Polym Sci* 2002, 40, 591.
12. Gupta, B.; Büchi, F. N.; Scherer, G. G.; Chapiro, A. *J Membr Sci* 1996, 118, 231.
13. Dargaville, T. R.; George, G. A.; Hill, D. J. T.; Whittaker, A. K. *Prog Polym Sci* 2003, 28, 1355.
14. Cardona, F.; George, G. A. *Macromolecules* 2002, 35, 355.
15. Nasef, M. M. *Polym Int* 2001, 50, 338.
16. Cardona, F.; George, G. A.; Hill, D. J. T.; Perera, S. *J Polym Sci* 2002, 40, 3191.
17. Danks, T. N.; Slade, R. C. T.; Varcoe, J. R. *J Mater Chem* 2003, 13, 712.
18. Choi, Y. J.; Kang, M. S.; Cho, J.; Moon, S. H. *J Membr Sci* 2003, 221, 219.
19. Park, K. R.; Kang, P. H.; Nho, Y. C. *React Funct Polym* 2005, 65, 47.
20. Nasef, M. M.; Saidi, H.; Nor, H. M.; Foo, O. M. *J Appl Polym Sci* 2000, 76, 1.