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Characterization of Surface Modified Polysulfone Membranes with Various Fluorine Chemicals

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Abstract : The surface of polysulfone membranes has been modified using the fluorine chemicals, ITFE (2-iodo-1,1,1-trifluoro-ethane F.W.=209.94) and PFPI (1H,1H-pentafluoro-n-propyl iodide F.W.=259.95), and PFI (1H,1H,2H,2H-perfluorohexyl iodide, F.W.=373.99) based on Friedel-Crafts reaction mechanism with varying reaction temperatures, reaction time, and catalysis types. The resulting membranes were characterized through mainly the contact angle measurement and pure water permeability. The smaller reactant shows the larger contact angles. $FeBr_3$ catalyst is more effective than $AlCl_3$. Typically, the PS film treated with ITFE at 25℃ under $FeBr_3$ catalyst showed the contact angle 78.5° which indicated 10% over the value of unreacted PS films. More than 50% of pure water flux, 8.0 g/m^2hr, reduced at reaction time 10 min relative to the original flux, 3.49 g/m^2hr.

Keywords *: polysulfone, modification, ITFE, PFPI, PFI, contact angles, pure water permeability*

Introduction

Surface fluorination has been described for the modification of various homogeneous solid films of polyethylene [1], substituted polypropylenes, such as poly[1-(trimethylsilyl)propyne] [2-4], poly(4-methyl-1-pentene) [5-8], ethyl cellulose, polystyrene, aromatic polyesters, and certain copolymers [9].

Polysulfone repeat unit has four aromatic rings as well as the methyl groups in the isopropylidene. It seems that direct fluorination is diffusion controlled with the reaction proceeding from the surface inward since fluorine is extremely reactive. In most cases, the fluorinated polymeric membranes show intrinsically less permeable but more selective than the untreated material. Therefore, fluorination throughout the entire membrane thickness may lead to an undesirably large decreases in permeation rates whereas a fluorinated layer that comprises too small fraction of the total thickness may not yield an improvement in permselectivity. Careful control to achieve the maximum potential benefit is needed. In addition, the direct fluorination of elemental fluorine to polymers is highly exothermic and may lead to explosions or degradation of polymers at early attempts. The release of energy has to be controlled or dispersed through the reduction of reaction rate or rapid removal of excess energy during fluorination so that the intermediate fluorination reactions may occur sequentially rather than simultaneously [10]. Not only broader range of usefulness but also the difficult control of direct fluorination reaction described above are the motivations for this work. And the other motivation may be that the previous results of the modified PS

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membranes by pentafluoropropionic anhydride and tri-deca-fluoro-8-iodoctane were not satisfied [11].

In this work, the surface reaction between polysulfone and fluorine chemicals based on Friedel-Crafts reaction mechanism has been tried with varying reaction temperatures, reaction time, catalysis and reactant types which molecular weights are smaller than those used in [11]. The resulting membranes were characterized through the analysis of the contact angle measurement and pure water permeability.

Experimental

Materials

The commercial Polysulfone (PSf) Udel was supplied by Amoco, Augusta, GA. Iodo-trifluoroethane (ITFE, F.W.=209.94), pentafluoro-n-propyl iodide (PFPI, F.W.=259.95), perfluorohexyl iodide(PFI, F.W.=373.99) were purchased from Aldrich Chemical Co. and used without any further purification. 1-Methyl-2-pyrrolidinone (NMP) and carbon tetrachloride were analytical grade from Aldrich Chemical Co. and SHOWA Chemical Co. Ltd. (Tokyo, Japan), respectively. Aluminum chloride ($AlCl_3$) and iron bromide ($FeBr_3$) used as catalysts were from Junsei Chemical Co. (Tokyo, Japan) and Aldrich Chemical Co., respectively. Ethanol was also analytical grade from Ducksan Pure Chemical Co. (Seoul, Korea).

Membrane Preparations

10 wt.% of PSf solution in NMP was filtered and then cast onto a glass plate using a Gardner knife. The cast films were dried in a thermostated oven at 60℃ for 6 hrs. The films were peeled off from the glass plate. The resulting membranes ranged from 1 5~20 μm. Since CCl_4 solution contains the small of amount of water which could produce the side reaction with the catalyst, such as $AlCl_3$, the neutralization has to be carried out before the reaction between the films and fluorine chemicals. The proper amount of catalyst and fluorine chemicals was dissolved in CCl_4 and stirred for 1 hr. The films were then immersed and stirred very slowly for the desired reaction time. The treated films were washed with pure ethanol solution, and then dried and stored in vacuum oven for further use.

Contact Angle Measurements

The water contact angle, an indicator of the wettability of surfaces, was measured at room temperature using a contact angle goniometer (Model 100-0, Rame-Hart, Inc., U.S.A.). More than three different specimens for modified PSf samples were prepared at several different parts for each specimen. For each part, 3 μL of a drop of purified water was deposited onto the surface. 5~10 times were measures for each specimen and then averaged.

Pure Water Flux Measurements

In this study, the pervaporation experiment was carried out to measure pure water flux for modified PSf membranes at 60℃. Details of schematic diagrams of apparatus and membrane cell can be referred in ref. [12].

Results and Discussion

Contact Angle Measurements

The water contact angle is explained as an indicator of the wettability of film surfaces. It is well known that the increase of the contact angles means the reduction of the hydrophilic properties of surfaces whereas the decrease indicates the increase of that properties.

To elucidate the effect of the concentration of the reactant and the catalysts, contact angles were measured with varying the concentration of ITFE for $AlCl_3$ and $FeBr_3$ as the catalysts. As illustrated in Figs. 1 and 2, the effects of the reactant concentrations are considered almost none since the contact angles are identical for both reactant concentrations. However, it shows that the contact angles of $FeBr_3$

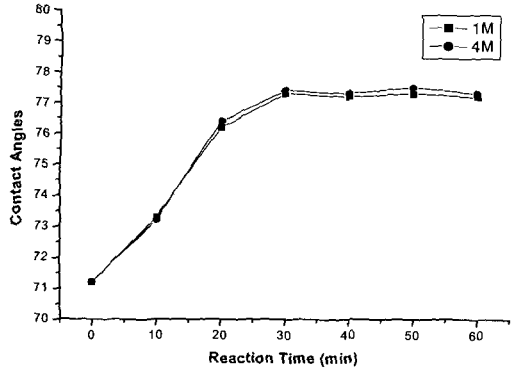

Fig. 1. Effect of concentration of 2-Iodo-1,1,1-trifluoro-ethane on the contact angles of PS films. (Reaction Temp. : 25℃, Catalyst : $AlCl_3$)

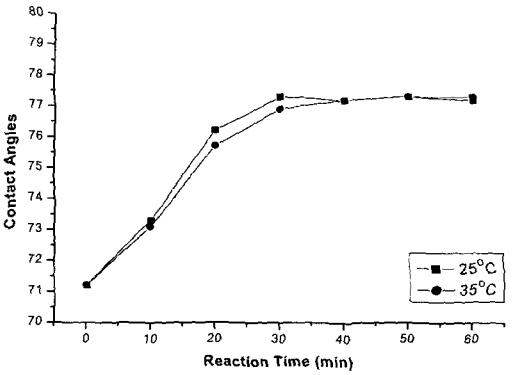

Fig. 3. Effect of reaction temperature on the contact angles of PS films. (1 M 2-Iodo-1,1,1-trifluoro-ethane, Catalyst : $AlCl_3$)

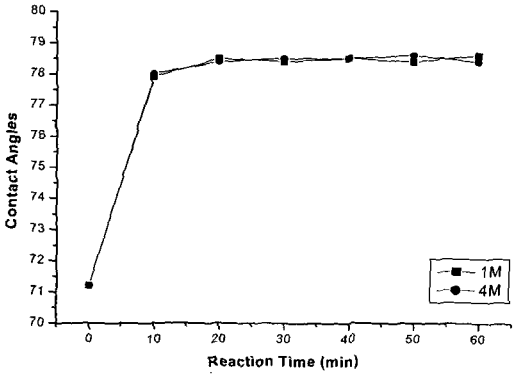

Fig. 2. Effect of concentration of 2-Iodo-1,1,1-trifluoro-ethane on the contact angles of PS films. (Reaction Temp. : 25℃, Catalyst : $FeBr_3$)

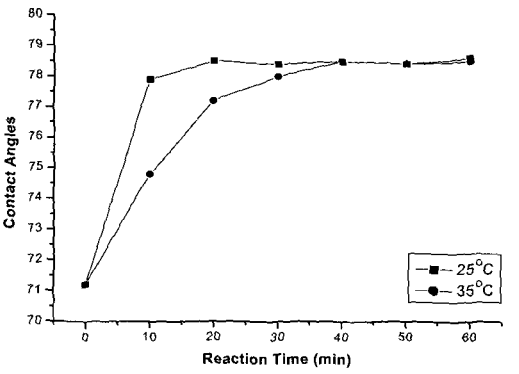

Fig. 4. Effect of reaction temperature on contact angles of PS films. (1 M 2-Iodo-1,1,1-trifluoro-ethane, Catalyst : $FeBr_3$)

are better than those of $AlCl_3$. And the contact angle at 10 min. for $FeBr_3$ is 78.2 while 72.9 for $AlCl_3$, so the former's reaction rate is faster than the latter's case. After 10 min. for $FeBr_3$, the contact angles maintain constant.

Next Figs. 3 and 4 show the effect of the reaction temperatures, 25 and 35℃ for ITFE. In case of $AlCl_3$, it seems that there is no effect of reaction temperatures. However, for $FeBr_3$, there is no change in contact angles as the reaction time passes over 40 min. At initial reaction time between 0 and 30 min., the contact angles obtained at lower temperature, 25℃, are higher than those at 35℃. Therefore, it could be said that the optimum reaction temperature is 25℃.

Figs. 5 and 6 illustrates the effect of catalysts on contact angles. As explained above, the $FeBr_3$ is more effective than $AlCl_3$ at both reaction temperatures, 25 and 35℃.

Fig. 7 shows the contact angles at 25℃ for the reactant, PFPI, which formula weight of 259.95 is larger than 209.94 of ITFE. It shows that the reaction rate for $FeBr_3$ is faster than for $AlCl_3$. And the reaction is stabilized after 20 min. for the case of $FeBr_3$. The contact angles obtained are lower than ITFE. Since the molecular weight of PFPI is larger than that of ITFE, PFPI could not penetrate and react with PS easier than ITFE.

Fig. 8 gives the effect of larger molecular weight, PFI, than PFPI. As expected, the contact angles are

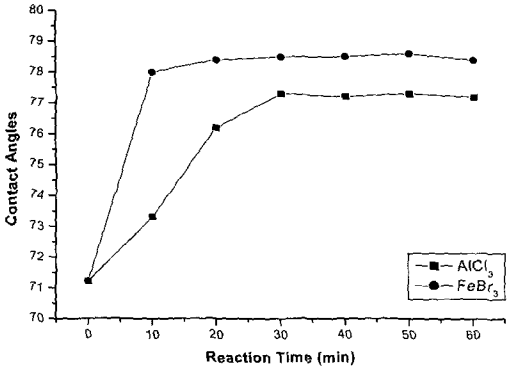

Fig. 5. Effect of catalysts on contact angles of PS films. (1 M 2-Iodo-1,1,1-trifluoro-ethane, Reaction Temp. : 25℃)

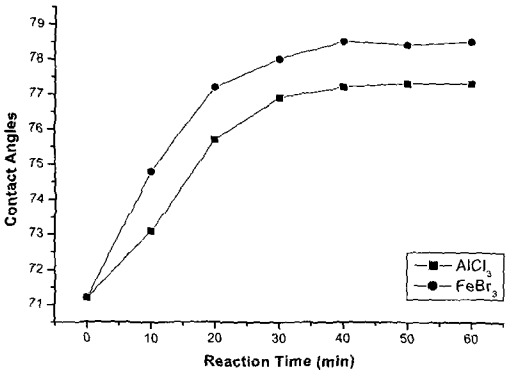

Fig. 6. Effect of catalysts on contact angles of PS films. (1 M 2-Iodo-1,1,1-trifluoro-ethane, Reaction Temp. : 35℃)

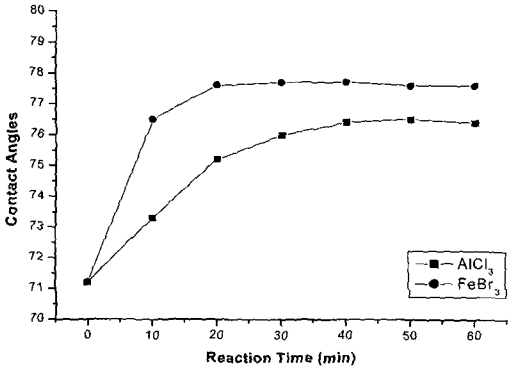

Fig. 7. Effect of catalysts on contact angles of PS films. (1 M, 1 H, 1 H-pentafluoro-N-propyl iodide, Reaction Temp. : 25℃)

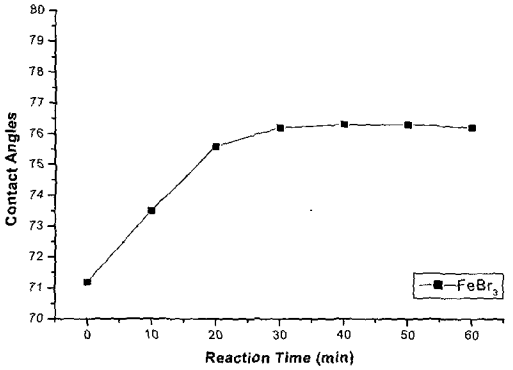

Fig. 8. Contact angles of reacted PS films with 1 M 1 H, 1 H, 2 H, 2 H-Perfluorohexyl iodide. (Reaction Temp. : 25℃, Catalyst : $FeBr_3$)

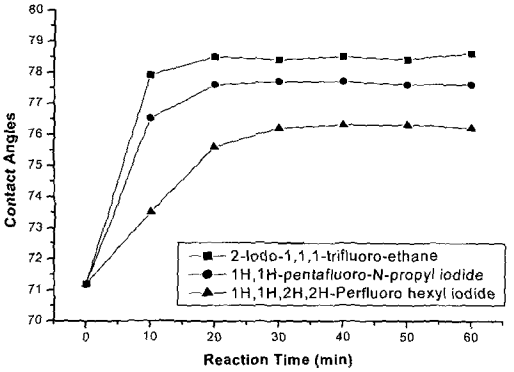

Fig. 9. Effect of fluorination agents on contact angles of PS films. (Concentaration : 1 M, Reaction Temp. : 25℃, Catalyst : $FeBr_3$)

less than the case of PFPI. In Fig. 9 we summarize the effect of three kinds of fluorine chemicals in question in this study at 25℃. The smallest molecular weight, ITFE indicates the highest contact angles, i.e. the highest hydrophobicity.

Pure Water Flux Measurements

The following Fig. 10 shows the pure water flux measured from pervaporation apparatus at 60℃ for PS membrane reacted with ITFE at 25℃ under $FeBr_3$ catalyst. As the reaction time increases, the pure water flux decreases as expected since the hydrophobic properties of PS films increase. More than half of original flux reduced at reaction time 20 min.

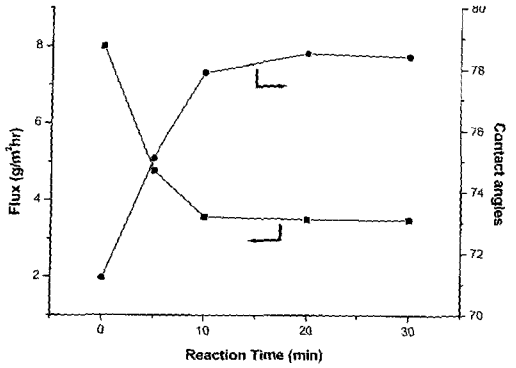

Fig. 10. Comparison between flux and Contact angles. (Membrane = 1 M 2-Iodo-1,1,1-trifluoro-ethane, Reaction Temp. : 25℃, Catalyst : $FeBr_3$ Pervaporation Process = Temp. : 60℃, 1Torr)

Conclusion

The surface of PS membranes has been modified using the fluorine chemicals, ITFE, PFPI and PFI. Treated PS membranes were characterized through contact angle and pure water flux measurements. From this investigations, the following conclusion can be drawn:

(1) For the contact angle measurement, the contact angles increase at which the reaction temperature is 25℃ rather than 35℃. And the smaller molecular weight of fluorine chemical shows the faster reaction rate. For ITFE, the contact angles remain constant after 10 mim of reaction time. $FeBr_3$ catalyst is more effective than $AlCl_3$. The PS film treated with ITFE at 25℃ under $FeBr_3$ catalyst showed the contact angle 78.5° which indicated 10% over the value of unreacted PS films.

(2) More than 50% of pure water flux, 8.0 g/m^2hr, reduced at reaction time 10 min relative to the original flux, 3.49 g/m^2hr.

(3) The resulting membranes may be used in membrane contactor and deoxygenation from water, etc. It will be appeared in next paper.

References

1. C. L. Kiplinger, D. F. Persico, R. J. Lagow, and D. R. Paul, *J. Appl. Polym. Sci.*, **31**, 2617 (1986).
2. M. Langsam, U.S. Patent 4,657,564 (1987).
3. M. Langsam, M. Anand, and E. J. Karwacki, *Gas Sep. Purif.*, **2**, 162 (1988).
4. M. Langsam and L. M. Robeson, *Polym. Eng. Sci.*, **29**, 44 (1989).
5. J. M. Mohr, D. R. Paul, T. E. Mlsna, and R. J. Lagow, *J. Membrane Sci.*, **55**, 131 (1991).
6. J. M. Mohr, Ph.D. Dissertation, University of Texas at Austin (1990).
7. J. M. Mohr, D. R. Paul, Y. Taru, T. Mlsna, and R. J. Lagow, *J. Membrane Sci.*, **55**, 149 (1991).
8. J. M. Mohr, D. R. Paul, Y. Taru, T. Mlsna, and R. J. Lagow, *J. Appl. Polym. Sci.*, **42**, 2509 (1991).
9. C. C. Chiao, U.S. Patent 4,828,585 (1989).
10. J. D. Le Roux, D. R. Paul, J. Kampa, and R. J. Lagow, *J. Membrane Sci.*, **94**, 121 (1994).
11. J. W. Rhim, J. R. Kim, Y. I. Park, and K. H. Lee, *J. Ind. Eng. Chem.*, Vol. 7, No. 5, pp. 299-304 (2001).
12. J. W. Rhim and Y. K. Kim, *J. Appl. Polym. Sci.*, Vol. 75, pp. 1699-1707 (2000). *J. Appl. Polym. Sci.*, **75**, 1699 (2000).