Gas Permeable Membranes Composed of
Carboxylated Poly(vinyl chloride) and Polyurethane

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Gas-permeable polymeric membranes containing carboxyl groups which are suitable for enzyme immobilization were investigated in order to use them as gas electrode membranes in biosensors. Carboxylated polyurethane (CPU) was synthesized via a reaction between 2,2-bis(hydroxymethyl)propionic acid as a chain extender and prepolymers prepared from polycarprolactone (Mn=2,000) and 4,4'-diphenylmethane diisocynate. It was difficult to prepare membranes from the pure CPU because of its high elasticity and cohesion. However, transparent free-standing membranes were easily prepared from the blend solutions of CPU and carboxylated poly(vinyl chloride) (CPVC) in tetrahydrofuran. Both elasticity and cohesion of the CPU/CPVC membranes were decreased with increasing the content of CPVC. DSC experiment suggests that CPU and CPVC may be well mixed. Permeability coefficients for O_2 and CO_2 (P_{O2} and P_{CO2}) in the membranes increased as the proportion of CPU increased. The addition of dioctyl phthalate (DOP), a plasticizer, significantly enhanced the P_{O2} and P_{CO2} which were 4.4 and 30 Barrer, respectively, in the CPU/CPVC (80/20 wt/wt) membranes containing 20% of DOP at 25 °C and 100 psi. Thus this type of membranes may have a potential for the use as gas electrode membranes in biosensors.

Introduction

A biosensor is a device incorporating a biological sensing element connected to a transducer.[1] The biological sensing component could be enzyme, microorganism, tissue materials, and antibody, etc. Since the first enzyme biosensor was described by Clark and Lyons in 1962,[2] a great deal of researches have been reported in this field.[3] In biosensors, three different membranes are usually employed for construction of an electrode.[4-7] Typically, a gas electrode is covered with a gas-permeable membrane such as poly(tetrafluoroethylene), polyethylene or Cellophane. A layer of enzyme is placed over this and held in place with a second membrane such as cellulose acetate. Finally, the electrode is wrapped with a dialysis membrane. If only one membrane instead of the two or three membranes is used, the response time and sensitivity of the biosensors will be improved, and the manufacture process will be also simplified. In this case, the membrane should be gas-permeable, enzyme-immobilizable, and biocompatible if the device is for medical applications. Water, however, should not permeate through the membrane, otherwise the electrolytes in the electrode can not be protected.

Various types of polymers such as Teflon, polypropylene, polystyrene and polyethylene have been employed in preparing the O_2 electrode membranes. Among these polymers, Teflon is most frequently used since the other polymeric membranes are not very stable to heat.[8,9] Teflon, however, is not appropriate for immobilization of enzymes without any chemical modification which seems to be very difficult. Polysulfones have properties such as good reproducibility, good mechanical strength and chemical inertness, and thus

have been studied for the use of a membrane-covered O_2 electrode system.[10-15] However, the polysulfone membranes show rather low permeability coefficients for O_2 even though the ideal gas separation factor between O_2 and N_2 is relatively high.[16] Most of the other polymeric membranes being used in biosensors are prepared from graft or block copolymers, but they still have some limitations.

Over the past decade or more, remarkable researches have been performed in the field of gas separation through polymer membranes to yield an extensive body of experimental data on permeation of gases for a variety of glassy polymers. Most of this research has focussed on the relationship between gas permeability and polymer structure because of an interest in developing better gas separation membranes.[17,18] Recently, Park and Paul reported correlation and prediction of gas permeability in glassy polymer membranes via a free volume based group contribution method, which significantly improves the accuracy of correlation and of prediction.[19]

In a biosensor, the biological element such as enzyme, antibody, nucleic acid, and receptors should be properly attached to the transducer. There are several methods of this immobilization such as adsorption, microencapsulation, entrapment, cross-linking, and covalent bonding.[20] In general, the lifetime of the biosensor is greatly enhanced by proper immobilization, and the covalent bonding is the most effective among the immobilization methods.[1] Some functional groups in an enzyme which are not essential for the catalytic activity of the enzyme can be covalently bonded to a support containing reactive groups such as -NH_2, -OH, -COOH, or -SH.

We are investigating polymeric membranes that are gas-

permeable and enzyme-immobilizable, and can be used as electrode membranes in constructing biosensors. In this paper, we report synthesis of carboxylated polyurethane (CPU) and characterization of membranes prepared from CPU and carboxylated poly(vinyl chloride) (CPVC) in various ratios.

Experimental Section

Reagents. CPVC (carboxyl content 1.8 wt%), dioctyl phthalate (DOP), 2,2-bis(hydroxymethyl propionic acid) (DMPA), polycarprolactone diol (PCL, Mn=2,000), and 4,4'-diphenylenemethane diisocynate (MDI) were purchased from Aldrich. PCL was dried in a vacuum oven at 90 °C for 12 h before its use. Tetrahydrofuran (THF) was used as received.

Instrumentation. Infrared spectra were obtained with a FT-IR 300E spectrometer (Jasco Co). Thermal transitions of polymer samples were observed with a DSC 2910 differential scanning calorimeter (TA Instruments Co.) at a heating rate of 10 °C/min. Gel permeation chromatography (GPC) data were obtained with a Waters 440 HPLC calibrated with polystyrene in THF.

Preparation of CPU. A mixture of MDI (12.5 g, 50 mmol) and PCL (50.0 g, 25 mmol) was stirred at 75-80 °C under nitrogen atmosphere to prepare prepolymers as represented in Scheme 1. The content of -NCO groups was determined by titration with di-*n*-butylamine.[21] A solution of DMPA (3.35 g, 25 mmol) in THF (30 mL) and a catalytic amount of dibutyltin dilaurate were added to the prepolymers, and the mixture was stirred until the -NCO group was not detected any more. The reaction mixture was used for preparation of membranes without further purification.

Preparation of membranes. CPU and CPVC were dissolved in THF (4 wt %), and the solution was stored in a refregerator for longer than 12 h in order to remove foams and simultaneously to reduce the amount of solvent evapo-

rated. The polymer solution was cast on a Teflon plate, and dried in air for 5 h and further dried at 160 mmHg and 50 °C for 30 h.

Measurement of gas permeability coefficient. The permeabilities for O_2 and CO_2 in the polymeric membranes were determined using the apparatus as shown in Figure 1. The pressure of the upstream side was maintained to be constant during the experiment while the pressure in the downstream side was monitored. The effective membrane area was 9.6 cm². The temperature of the permeation apparatus was maintained to be 30 °C by using a thermostatic water bath. The volume of permeated gas through the membrane was calculated from the flow speed of 1-propanol in the micro-tube.

$$\wp = \frac{J_s L}{p_1 - p_1}, \quad J_s = \frac{\pi d^2}{4A}\left(\frac{273.15 p_b}{76 T}\right)\left(\frac{dh}{dt}\right)$$

The permeability coefficient, *P*, was calculated by empolying the above equations. In the first equation, J_s [cm³(STP)/cm².sec] is the volume of permeated gas for a certain period at STP condition at steady state and *L* [cm] is the thickness of the membranes. The p_1 and p_2 represent the pressure in the upstream and downstream side, respectively. In the second equation, *d* [cm], *A* [cm²], p_b [Hg], *T* [K], and *dh/dt* represent the diameter of the micro-tube, the area of the permeation cell, the barometric pressure, the experiment temperature, and the flow speed of 1-propanol in the micro-tube, respectively. The P is usually expressed in Barrer which is corresponding to 10^{-10} cm³ (STP)·cm/cm²·sec·cmHg.

Results and Discussion

CPU was synthesized as described in the experimental section, and the IR spectra of the starting materials and CPU are presented in Figure 2. The -NCO group in MDI and the
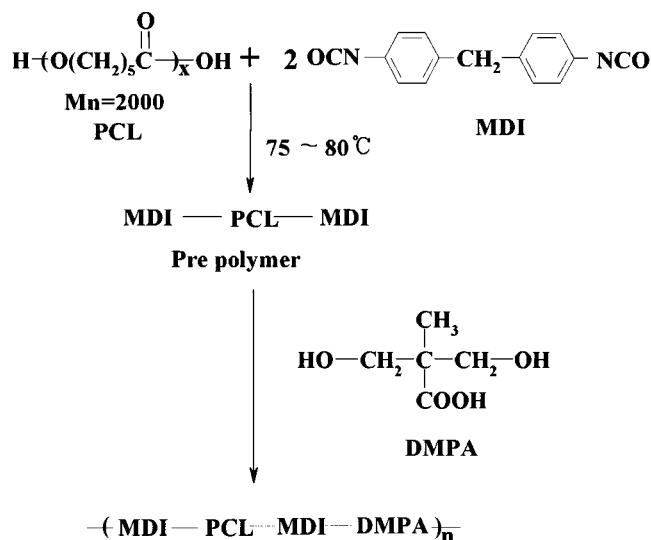
Scheme 1. A schematic route for synthesis of carboxylated polyurthane (CPU).
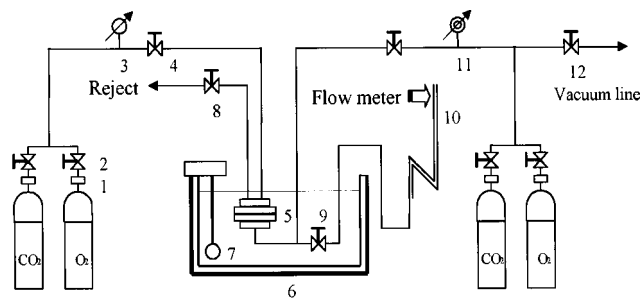
1.	Needle valve	7	Thermometer
2.	On/Off valve	8	Needle valve
3.	Pressure gauge	9	3-Way valve
4.	On/Off valve	10.	Capillary tube
5.	Permeation cell	11.	Vacuum gauge
6.	Water bath	12.	On/Off valve

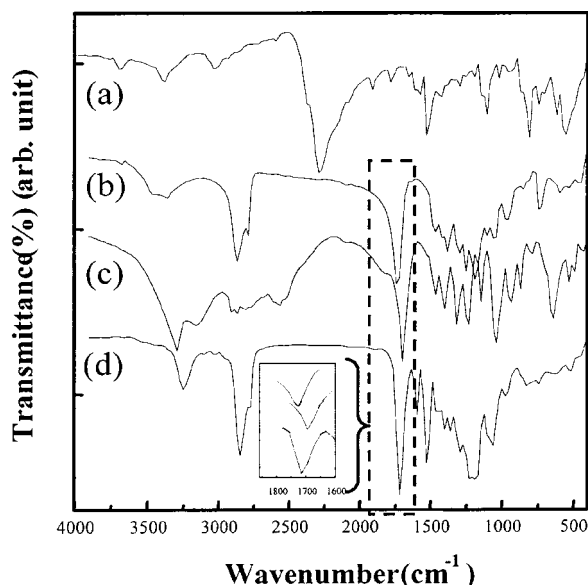**Figure 1**. The experimental apparatus for permeability measurement.

Figure 2. FT-IR spectra of (a) MDI, (b) PCL, (c) DMPA, and (d) CPU. Inset shows C=O stretching bands for PCL, DMPA, and CPU from the top.

Figure 3. DSC thermograms for blends of CPU/CPVC: (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80, and (f) 0/100.

-OH group in PCL appear at 2265 and 3400 cm^{-1}, respectively. These two bands disappeared almost completely in CPU, and instead a new band for -NH appears at 3340 cm^{-1}. Furthermore, a strong and broad band appears at 1700-1725 cm^{-1} where a strong band originated from the carbonyl of -NH-COO group is overlapped largely with a band originated from -COOH group as shown in the inset. This result indicates that the polymerization was complete and the polymer contains carboxyl groups. GPC experiment indicated that the number- and weight-average molecular weight of the CPU were about 97,000 and 280,000, respectively.

It was attempted to prepare CPU membranes employing the solution casting method using THF. However, the thin film was too cohesive and elastic to be peeled off from the Teflon plate to form a free standing film. The high elasticity and cohesion of CPU were expected since these properties are commonly observed from PUs consisting of the soft segments of high molecular weights.[22,23] PCL with lower molecular weights would give CPUs which are less cohesive and elastic.[24] The cohesion and elasticity of the membrane, however, were reduced greatly when CPU was blended with CPVC. Thus free-standing films were easily prepared when CPVC was added to the CPU solution at least about 20% or greater by weight.

DSC experiment was carried out for CPU, CPVC, and blends of CPU/CPVC, and the results are presented in Figure 3 where the thermograms were obtained from the first heating scans. The thermal transitions at -39 and 25 °C in Figure 3a are probably due to the glass and melting transition of the soft segments in CPU, respectively. No evidence of a transition attributable to the hard segments of CPU was observed from the thermogram traces, which is typical for PUs. CPVC undergoes a glass transition at 62 °C as shown in Figure 3f. The CPU/CPVC membranes were transparent. They also show only one glass transition, whose temperature
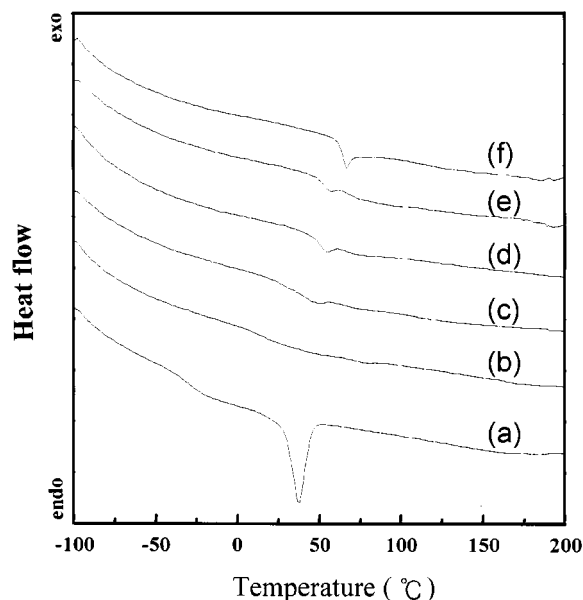
is dependent on the relative ratios of each component and lies between the T$_g$s of CPU and CPVC.[25] Actually, the thermoplastic polyurethane is used as a plasticizer for poly(vinyl chloride), being compatible in any ratio.[26] Thus it can be concluded that CPU and CPVC are reasonably mixed in the membranes. The T$_g$s of the membranes approach to the T$_g$ of CPU as the proportion of CPU increases. This result suggests that the membranes become more rubbery as increasing the content of CPU.

The P$_{CO2}$ and P$_{O2}$ in the membranes were determined as a function of gas pressure in the upstream side, and the results are presented in Figure 4 and 5. At constant pressure, the P$_{CO2}$ and P$_{O2}$ increase as the content of CPU in the mem-
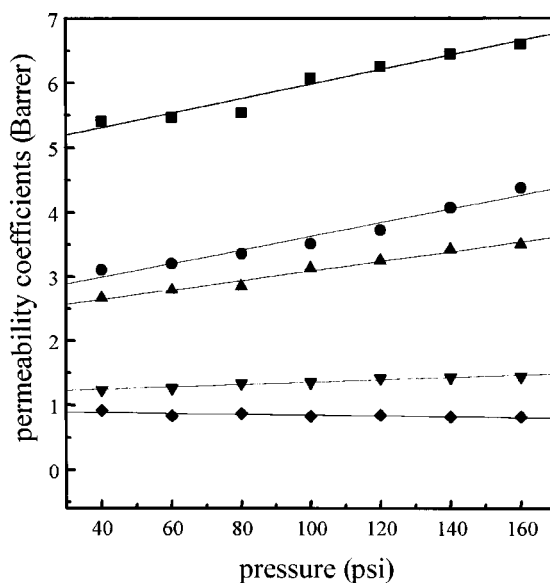

Figure 4. Dependence of P$_{CO2}$ on the pressure at 25 °C in the membranes composed of CPU/CPVC: ■80/20, ●70/30, ▲60/40, ▼ 40/60, and ◆ 20/80.
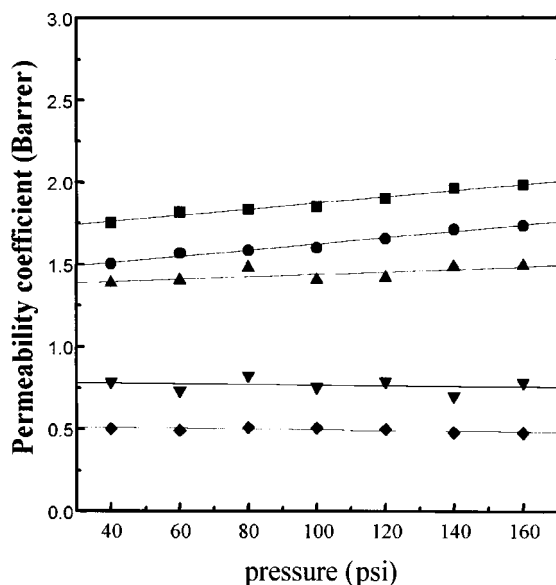
Figure 5. Dependence of P_{O_2} on the pressure at 25 °C in the membranes composed of CPU/CPVC: ■80/20, ●70/30, ▲60/40, ▼ 40/60, and ◆ 20/80.

Figure 6. Ideal separation factors between CO_2 and O_2 (P_{CO_2}/P_{O_2}) in the CPU/CPVC membranes containing various proportions of CPU.

brane increases. This result is understandable since according to the DSC experiment, the CPU/CPVC membranes become more rubbery at room temperature as the proportion of CPU in the membranes increases.

The solubility coefficient of CO_2 in some rubbery polymers such as poly(trifluoropropyl methyl siloxane) was reported to be significantly high at certain temperature and was attributed due to a specific penetrant/polymer interactions.[27] The solubility coefficient of CO_2 in the polymer increased linearly with pressure at the temperature.[28] On the other hand, the solubility coefficient of CO_2 in the rubbery polymer was decreased with temperature, and the permeability coefficient was decreased accordingly. In this case the permeability coefficient was almost independent of the pressure at the higher temperatures.

The permeability coefficients of CO_2 in CPU/CPVC (80/ 20, 70/30, and 60/40) membranes are relatively high at 25 °C, and increased linearly with the upstream pressure. On the other hand, the permeability coefficients of CO_2 in CPU/ CPVC (40/60 and 20/80) membranes are relatively low, and independent of the upstream pressure. In this research, contributions of solubility and diffusivity coefficient to the permeability coefficient of CO_2 were not estimated, but both of the two factors could affect the pressure dependence. A similar explanation may be applied to the pressure dependence of the permeability coefficient of O_2 in these membranes. However, the dependency of the permeability coefficient of CO_2 on the upstream pressure is more noticeable than that of O_2. This result may be attributable to the fact that CO_2 is more condensable gas.

The ideal separation factors between CO_2 and O_2 (P_{CO_2}/P_{O_2}) at 100 psi and 25 °C were calculated based on the data described above, and the results are shown in Figure 6. The separation factor increases rapidly as the content of CPU in the CPU/CPVC membranes increases, and reaches to 3.2
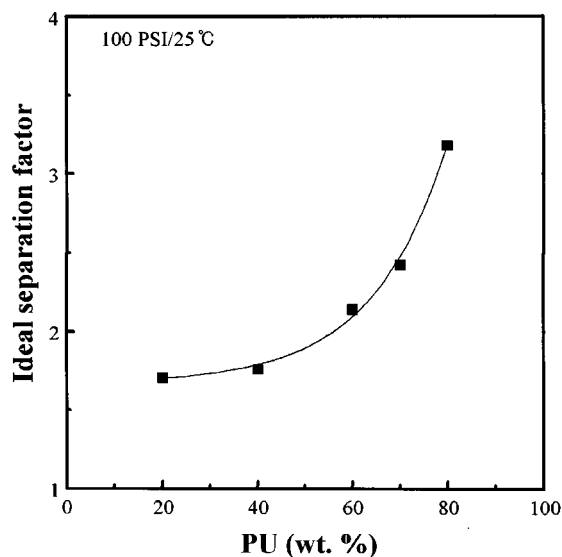
when the content of CPU is increased to 80%. This results from the fact that the P_{CO_2} increases more rapidly than the P_{O_2} as the content of CPU in the membrane increases.

It was difficult to prepare free-standing membranes containing CPU more than 80% due to high cohesion and elasticity of the blends. The P_{CO_2} and P_{O_2} in the CPU/CPVC (80/ 20) membranes containing various amount of DOP which is a typical plasticizer were determined, and presented in Figure 7. The addition of DOP to the membranes enhances significantly the P_{O_2} and P_{CO_2}, and the degree of enhancement increases with increasing the amount of DOP added. The effect of DOP on the gas permeability is more effective toward CO_2 than O_2. For example, the P_{CO_2} and P_{O_2} in the membrane containing 20% DOP at 25 °C and 100 psi are about 30 and 4.4 Barrer, respectively. The DOP dispersed in the membrane probably increases the free volume in the
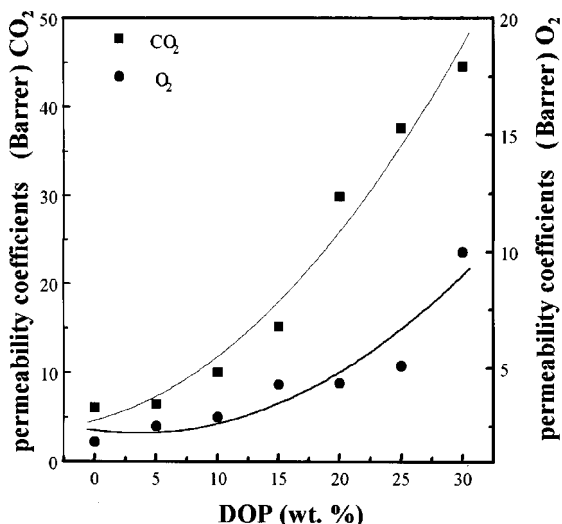

Figure 7. Dependence of P_{O_2} and P_{CO_2} in the CPU/CPVC (80/20) membranes on the content of DOP at 25 °C and 100 psi.

polymers, resulting in the enhancement of the P values.

Summary

   Prepolymers were obtained from PCL (Mn=2,000) and MDI, and reacted with DMPA to yield CPU. Transparent free-standing membranes were easily prepared from the blend solutions of CPU and CPVC in THF, while the pure CPU was not able to form the free-standing membranes due to its high elasticity and cohesion. CPU and CPVC may be well mixed since the blend membranes are transparent and show only one glass transition in any ratio. The P_{O2} and P_{CO2} in the CPU/CPVC membranes increased as the proportion of CPU increased, and the highest P_{O2} and P_{CO2} in the CPU/ CPVC membranes were obtained when the proportion of CPU in the blend was 80%. The addition of DOP enhanced significantly the P_{co2} and P_{o2} in the CPU/CPVC membranes. Thus the blends of CPU and CPVC containing appropriate amount of DOP may be used in preparing a gas electrode membranes in biosensors.

References

1. Eggins, B. R. *Biosensors: an Introduction*; John Wiley & Sons and B. G. Teubner: 1996.
2. Clark, Jr., C.; Lyons, C. *Ann. N.Y. Acad. Sci.* **1962**, *102*, 29.
3. Yim, H.-S.; Kibbey, C. E.; Ma, S.-C.; Kliza, D. M.; Liu, D.; Park, S.-B.; Torre, C. E.; Meyerhoff, M. E. *Biosensors & Bioelectronics* **1993**, *8*, 1.
4. Hall, E. A. H. *Biosensors*; Open University Press: Milton Keynes, 1990.
5. Park, I.-S.; Kim, J.-H.; Kim, T.-J.; Noh, B.-S. *Food Biotechnol.* **1995**, *4*, 61.
6. Watanabe, E.; Takagi, M.; Takei, S.; Hoshi, M.; Shu-Gui, C. *Biotechnol. Bioeng.* **1991**, *38*, 99.
7. Jurng, T.-H.; Hong, S.-I.; Kim, T.-J. *J. of Korean Ind. & Eng. Chemistry* **1996**, *34*, 489.
8. Linek, V.; Vacek, V.; Sinkule, J. *Measurement of Oxygen by Membrane-Covered Probes*; John Wiley & Sons: New York, 1988.
9. Borkowski, J. D.; Johnson, M. J. *Biotechnol. Bioeng.* **1967**, *9*, 435.
10. Henis, J. M. S.; Tripoi, M. K. *Sep. Sci. Tech.* **1980**, *15*, 1059.
11. Noshay, A. *J. Appl. Polym. Sci.* **1976**, *20*, 1885.
12. Brown, D. W.; Rowry, R. E. *J. Polym. Sci. Polym. Chem. Edn.* **1976**, *20*, 1885.
13. Johnson, B. C.; Trans, C. *J. Polym. Sci. Polym. Chem. Edn.* **1984**, *22*, 721.
14. Chuldzinski, P. J.; Fickett, A. P. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1971**, *12*, 276.
15. Guiver, M. D.; Apsimon, J. W.; Kutowy, O. *U. S. Patent 4,797,457*, 1989.
16. Hong, S. I.; Kim, H. J.; Park, H. Y.; Kim, T. J. Jeong, Y. S. *J. of Korean Ind. & Eng. Chemistry* **1996**, *7*, 877.
17. Kawakakami, Y. *Prog. Polym. Sci.* **1994**, *19*, 203.
18. Dhingra, S. S.; Marrand, E. *J. Membrane Sci.* **1998**, *141*, 45.
19. Park, J. Y.; Paul, D. R. *J. Membrane Sci.* **1997**, *125*, 23.
20. Takemoto, K.; Inaki, Y.; Ottenbrite, R. M. *Functional Monomers and Polymers*; Marcel Dekker, Inc.: New York and Basel, 1987; pp 461-539.
21. Meares, P. *Polymers: Structure and Bulk Properties*; Van Nostrand: London, 1965; pp 321-326.
22. Bruins, P. F. *Polyurethane Technology*; Interscience Publishers, John Wiley & Sons, Inc.: 1969.
23. Oertel, G. *Polyurethane Handbook*, 2nd Ed.; Hanser/ Gardner Publications, Inc.: Cincinnati, 1993.
24. Sanchezadsuar, M. S.; Pastorblas, M. M.; Martinmartinez, J. M.; Villenave, J. J. *Intl. J. Adhesion & Adhesives* **1997**, *17*, 155.
25. Olabisi, O.; Robinson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic Press: New York, 1979; Chap. 6.
26. Hupburn, C. *Polyurethane Elastomers*; Elsevier Science Publishers: New York, 1991; p 263.
27. Stern, S. A.; Shah, U. M.; Hardy, B. J. *J. Polym. Sci. Polym. Phys.* **1987**, *25*, 1263.
28. Shah, V. M.; Hardy, B. J.; Stern, S. A. *J. Polym. Sci. Polym. Phys.* **1986**, *24*, 2033.