Modified polysulfone membranes. IV. Gas separation with aminated polysulfone membranes

Yoshikawa, Masakazu; Niimi, Akio; Guiver, M. D.; Robertson, G. P.

National Research Council Canada   Conseil national de recherches Canada

Canada

Transaction

Modified Polysulfone Membranes. IV.
Gas Separation with Aminated Polysulfone Membranes[#]

Masakazu Yoshikawa,[*1] Akio Niimi,[*1] Michael D. Guiver,[*2] and Gilles P. Robertson[*2]

[*1] Department of Polymer Science and Engineering, Kyoto Institute of Technology,
Matsugasaki, Kyoto 606-8585, Japan

[*2] Institute for Chemical Process and Environmental Technology, National Research
Council of Canada, Ottawa, Ontario K1A 0R6, Canada

ABSTRACT: Novel gas permeation membranes were prepared from polysulfones and amine-modified polysulfones.   The introduction of the primary amine moiety into polysulfone membranes led to an increase in permselectivity toward CO_2 in CO_2/N_2 separation and a significant increase in that toward O_2 in O_2/N_2 separation.

1. Introduction

Polysulfone (PSf) is known to have thermal stability combined with mechanical strength and membrane-making qualities.   It has a stable backbone onto which functional moieties can be introduced and is a good candidate material for specialty polymeric membranes.   Modified polysulfones have been prepared for a variety of membrane applications including ultrafiltration (UF),[1-7] nanofiltration and reverse osmosis (RO),[3,6,8,9] gas separation,[3,10-13] pervaporation,[10,11,14-16] affinity separation,[17] electromembrane processes,[18,19] and chiral separation.[20]

Separation or removal of CO_2 or enrichment of O_2 is an important subject in membrane separation in connection with developing environmentally friendly and energy efficient technologies.   Consequently, we studied gas separation of CO_2/N_2 and O_2/N_2 mixtures through modified polysulfone membranes in order to determine the effect of the primary amine functional group on permselectivity of these gases.

2. Experimental

2.1 Materials

2.1.1 Synthesis of Polysulfone (ortho-sulfone

(OSDA)) and Polysulfone (ortho-ether diamine (OEDA))

Polysulfone amines were prepared by a lithiation/azidation route according to the method previously reported.[21,22] The degree of substitution (DS) of each polymer was 2.0, determined by NMR spectroscopy.

2.1.2 Synthesis of Aminomethyl Polysulfone (AMSF)

Aminomethylated polysulfone was prepared by a two step procedure adapted from ones reported previously.[23,24] In the first step, a phthalimidomethylated derivative was prepared by reaction of polysulfone with chloromethyl-phthalimide.[23]

Udel polysulfone (22.12 g, 50 mmol) was dissolved in 1,2-dichloroethylene (DCE, 200 cm^3) by stirring in an inert atmosphere overnight. n-Octanol (4.4 cm^3) and chloromethylphthalimide (24.45 g, 125 mmol) were added to the clear polymer solution, followed by tin (IV) chloride (5.7 cm^3, 49 mmol) in DCE (40 cm^3) which was added dropwise using an addition funnel over a period of 20 minutes. During tin chloride addition, the colour changed to dark red-brown. The mixture was stirred at 45 °C overnight, then precipitated into an agitated mixture of methanol (2.5 dm^3) containing water (100 cm^3) and conc. HCl (50 cm^3). The resulting polymer was washed twice by stirring it in fresh ethanol (95%) for several hours, then washed once more with water. The recovered red polymer was dried in a vacuum oven.

The conversion of the phthalimido-methylated derivative to aminomethylated polysulfone was carried out by hydrazinolysis.[24]

The phthalimidomethylated polymer resulting from the previous reaction was dissolved in a mixture of THF (600 cm^3) and ethanol 95% (200 cm^3) and under inert atmosphere in a 2 dm^3 flask heated to 74 °C. Hydrazine hydrate (50 cm^3) was poured quickly into the reaction mixture under vigorous stirring, and a white solid precipitated shortly afterwards. The heterogeneous mixture was stirred for 1 hour at 74 °C and 48 hours at room temperature. The volume of reaction mixture was reduced to approximately 400 cm^3 using a rotary evaporator. The mixture was precipitated into well stirred ice-cold isopropanol in a large beaker. The fine white powder was filtered, then washed by stirring again in fresh cold isopropanol. The polymer was then washed with a solution of sodium bicarbonate (40 g) in cold water for several hours in order to remove byproducts. The product was washed with fresh cold water, then cold isopropanol and filtered. The white aminomethylated polysulfone product was dried initially under an inert atmosphere, then vacuum dried at room temperature. The yield of polymer was 90%. The polymer contained aminomethyl groups on the bisphenol portion of the repeat unit at the ortho-ether site, and the DS was determined by NMR to be 1.5.

2.1.3 Synthesis of the 6F-Polysulfone (6FSF)

6F-Polysulfone was prepared by condensation polymerization from 2,2-bis(4-hydroxyphenyl)-hexafluoropropane (PCR Inc., USA) and bis(4-hydroxyphenyl)sulfone (Aldrich) and K$_2$CO$_3$ in 1-methylpyrrolidinone (NMP) using the conditions reported previously.[25] Both monomers were purified by crystallization prior to use. The M$_n$ was estimated to be 52,600 from GPC calibrated

with monodisperse polystyrene standards. [η] = 0.98 using NMP as the solvent.

2.1.4 Synthesis of the 6F-Polysulfone Amine (6FSA)

A dilute solution of 6F-polysulfone (12.5 g, 23 mmol) in THF (1.25 dm^3) was prepared and cooled to -25 °C. A large magnetic stirring bar was used because of a viscous gel formation during the lithiation process. The polymer solution was lithiated using 2.95 mol equiv. n-butyllithium (10.0 mol dm^{-3} solution, 6.70 cm^3, 67 mmol), introduced slowly and dropwise into the mixture via a syringe pump. The 0.95 molar excess of butyllithium is necessary since the 6F moiety appears to form a complex with the reagent. A thick gel formed immediately after addition of n-butyllithium was started, and there was a colour change from yellow to red. During addition, the gel changed to a less viscous solution. Five minutes following addition of butyllithium, the temperature of the mixture was reduced to -60 °C prior to the electrophile addition. Tosyl azide (17.9 g, 13.8 cm^3, 91 mmol), diluted in THF (20 cm^3), was cooled and poured promptly into the reaction flask. A less viscous yellow suspension formed, and this was gradually warmed to -50 °C and stirred for 30 min. An ethanol-water mixture (100 cm^3 - 10 cm^3) was poured into the mixture to quench the reaction. The cooling bath was removed and the mixture was stirred at room temperature for 1 h. Approximately 900 cm^3 of THF was evaporated on a rotary evaporator to concentrate the polymer solution. The resulting diazide polymer was recovered by precipitation from ethanol 95% and washed. The DS was slightly higher than 2.0 as determined by ^{1}H-NMR analysis of the aromatic region. The ^{1}H-NMR

spectrum shown in Fig. 1 illustrates that most of the repeat units were identical and contained two azide groups per repeat unit as shown by the five major signals. In the 6F-bisphenol ring, there are two 4H coupled doublets. In the azide-substituted ring, the upfield signal (H12) shielded by the azide is narrowly split by meta-coupling to H8, whereas H8 is a doublet of doublets from coupling to both H12 and to H9. IR: strong absorption 2114 cm^{-1} (azide); ^{1}H-NMR (CDCl$_3$): δ = 8.23, 2H doublet, H-ortho-sulfone; δ = 7.44, 4H doublet, H-6F ring; δ = 7.08, 4H doublet, H-ortho ether 6F ring; δ = 6.85, 2H doublet of doublets ortho and meta coupling, H-ortho-ether; δ = 6.79, 2H doublet of doublets meta coupling, H-ortho-azide.

The diazide was reduced to 6F-polysulfone diamine following a procedure similar to one reported previously.[22] In this case, the polymeric diazide was dissolved in THF (500 cm^3) containing ethanol (50 cm^3) and reduced with sodium borohydride (8.6 g, 10 mol equiv.) at -50 °C, followed by stirring at room temperature for 12 h. The diamine polymer (12.06 g, 91% yield) was recovered by precipitation into 95% ethanol and washed with hot water. The structure was confirmed by NMR spectroscopy. The ^{1}H-NMR spectrum shown in Fig. 2 illustrates clean reduction of the azide derivative to the primary amine as shown by the absence of the azide signals and the presence of five new major aromatic-H signals and an additional NH$_2$ singlet. The aromatic-H signals have the same splitting pattern as those of the azide but have different chemical shifts due to the electronic environment of the amine. ^{1}H-NMR (DMSO-d$_6$): δ = 7.78, 2H doublet, H-ortho-sulfone; δ = 7.37, 4H doublet, H-6F ring; δ = 7.19, 4H doublet, H-ortho ether 6F ring; δ = 6.37, 2H broadened singlet, H-ortho-amine; δ = 6.30, 2H broadened doublet, H-ortho-ether; δ = 6.16, 4H

broadened singlet, D_2O exchangable, NH_2.

2.2 Preparation of Polymeric Membranes for Gas Permeation

Polymer solutions were filtered through a course glass frit and poured on a leveled mirror glass surface having a circular retaining wall of 10.0 cm diameter, or onto mercury (membranes OSDA and OEDA). The solvent was evaporated over a one day period at ambient temperature under a slow stream argon atmosphere in a stainless steel vented vessel. The membranes were removed from the glass by immersion in water and by cutting around the periphery. The membranes were sandwiched between two glass plates with small Teflon spacers, then dried in a vacuum oven initially at ambient temperature. The membranes were subsequently heated in incremental stages under vacuum. For example, OEDA was heated at 70 °C for 48 h, 100 °C for 24 h. 130 °C for 8 h, 150 °C for 16 h, and 175 °C for 24 h. Final heating temperatures and times for other membranes were as follows: OSDA 215 °C for 16 h, AMSF 80 °C for 72 h, 6FSF 205 °C for 1 h, 6FSA 150 °C for 72 h. AMSF was not heated to a high temperature because of a tendency to crosslink at higher temperatures. Membrane thickness measurements were taken at 12 evenly spaced points on the disk, and averaged.

2.3 Permeation Experiment

The permeation of CO_2, O_2, and N_2, through membranes, were measured at 25 °C. From the steady-state straight line of the permeation curve, the permeability coefficients was evaluated.[26]

Table 1   Polymer structure and glass transition data

Polymer	X	R^1	R^2	DS	Tg^a / °C
6FSA	CF_3-C-CF_3	H	NH_2	2.0	232.8
6FSF	CF_3-C-CF_3	H	H	2.0	201.2
AMSF	CH_3-C-CH_3	CH_2NH_2	H	1.5	—[b]
OSDA	CH_3-C-CH_3	H	NH_2	2.0	210.5
OEDA	CH_3-C-CH_3	NH_2	H	2.0	230.4

[a] Determined by DSC on polymer powders.

[b] Above degradation point at 200 °C.
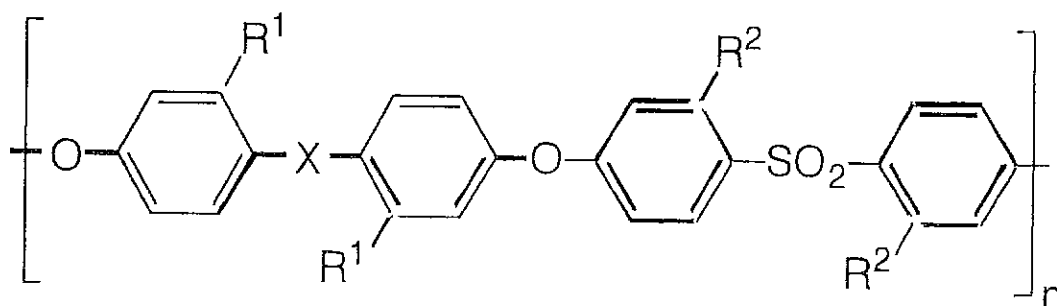
3. Results and Discussion

The steady state permeability coefficients of various gases in 6FSA membrane are presented in Fig. 3 as a function of upstream driving pressure p. The permeability coefficients of O_2 and N_2, were independent of upstream pressure. In contrast with O_2 and N_2, the permeability coefficient of CO_2 showed a slight dependence on upstream pressure. P_{CO2} increased with a decrease in upstream driving pressure, as shown in Fig. 3. The 6FSF membrane, which is the parent polymer of 6FSA, also showed a similar dependence on upstream pressure. On the other hand, OSDA and OEDA membranes, which contain isopropylidene rather than the 6F-isopropylidene linkage in the polymer chain, did not show upstream pressure dependence. In other words, the steady state permeability coefficients of various gases in OSDA and OEDA membranes were independent on upstream pressure for the experimental pressure range of 10 - 76 cmHg. The gas permeation behavior for AMSF was anomalous because permeation of CO_2 was experimentally insignificant, while O_2 and N_2 permeation were independent of upstream pressure in similarity with the other membranes. In selecting aminated polymer membranes for this study of gas permeation, we anticipated that the interaction of a basic primary amine in the membrane with an acidic gas such as carbon dioxide might have interesting effects in changing the permeability coefficients of those interacting gases while having a much lesser effect on non-interacting gases. In the case of the AMSF membrane, it is probable that the interaction between CO_2 and the most strongly basic aminomethyl moiety in AMSF membrane was too strong for CO_2 to diffuse in the membrane. That is, CO_2 might be immobilized on the aminomethyl sites in AMSF membrane resulting in virtually no CO_2 permeation being observed through AMSF membrane.[27,28] This property could possibly be exploited to make a membrane permeable to gases other than CO_2.

Permselectivities between two kinds of gases were evaluated theoretically. Ideal separation factors $\beta_{CO2/N2}$ and $\beta_{O2/N2}$ were defined by[29]

$$\beta_{CO2/N2} = P_{CO2} / P_{N2}$$

$$\beta_{O2/N2} = P_{O2} / P_{N2}$$

Fig. 4 shows the ideal separation factors for CO_2/N_2 and O_2/N_2 as a function of CO_2 and O_2 partial pressures respectively. The experimental
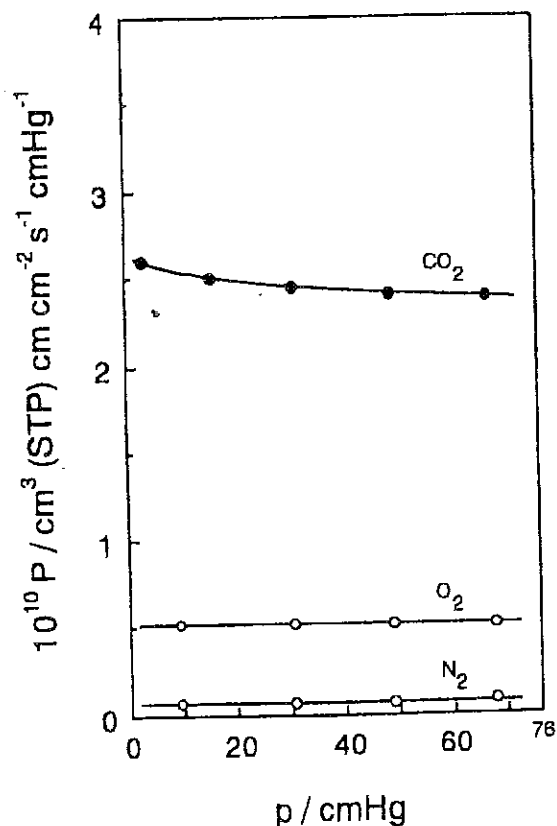
Fig. 3   Pressure dependence of the permeability coefficients of CO_2, O_2, and N_2 through 6FSA membrane at 25 °C.

conditions were that the total upstream pressure was 76 cmHg (1 atm) and the downstream pressure was assumed to be negligibly small.

The ideal separation factor towards CO_2 between CO_2 and N_2 for 6FSA membrane increased with decrease in partial pressure of CO_2 as shown in Fig. 4. As expected, $\beta_{CO2/N2}$ for 6FSF membrane gave a similar CO_2 partial pressure dependence. Other membranes gave constant separation factors, $\beta_{CO2/N2}$ and $\beta_{O2/N2}$ independent of partial gas pressures. $\beta_{CO2/N2}$ and $\beta_{O2/N2}$ for all the membranes studied in the present article are summarized in Table 2. The permeability coefficients of CO_2 for 6FSA and 6FSF at 66.8 and 69.8 cmHg upstream pressure respectively were adopted to evaluate the ideal $\beta_{CO2/N2}$ values for the membranes. From Table 2 and gas permeation data for polysulfone, which is the parent polymer of OSDA and OEDA,[30] it is clear that the introduction of primary amine groups into polysulfone led to a significant increase in permselectivity toward CO_2 in CO_2/N_2 separation and toward O_2 in O_2/N_2 separation. One reason for enhanced permselectivity of CO_2 for CO_2/N_2 separation may be due to a specific interaction between primary amine moiety and CO_2. However, a large increase in permselectivity of O_2 for O_2/N_2 separation is also observed. This is suggestive of an additional or alternative mechanism for permselectivity. The presence of many primary amine groups spaced regularly along the polymer backbone would allow strong interchain hydrogen-bonding interactions. These interactions would result in reduced segmental motion, thus giving higher permselectivity. Although the aminated polysulfone membranes gave higher permselectivities toward CO_2 in CO_2/N_2 separation and O_2 in O_2/N_2 separation, there was an expected trade-off in reduced

permeability coefficient. For aminated polysulfone membranes to have commercial utility for gas separation, it is important to increase flux values. In order to make the barrier layer as thin as possible for maximum gas permeance, an asymmetric membrane structure or a thin-film composite membrane format would be required for gas purification or other separation processes.
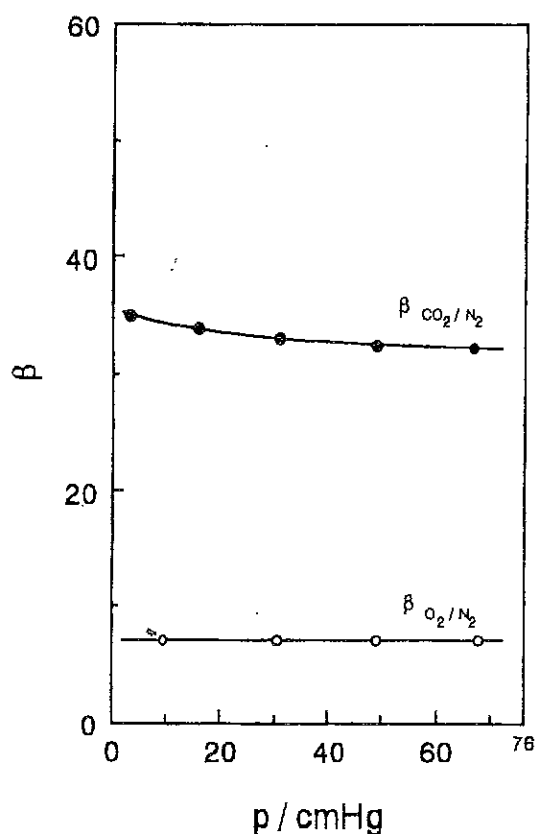

Fig. 4   Ideal separation factor for CO_2 relative to N_2 and that for O_2 relative to N_2 as a function of partial pressure of CO_2 or O_2 for the case of a negligible downstream pressure at 25 °C for 6FSA membrane. The total upstream pressure was 76.0 cm

Table 2   Gas permeation data and ideal selectivities for polymer dense membranes

Membrane	P_{CO_2} [a]	P_{O_2} [a]	P_{N_2} [a]	β_{CO_2/N_2} [b]	β_{O_2/N_2} [c]
6FSA	2.39×10^{-10} [d]	5.22×10^{-11}	7.34×10^{-12}	32.3	7.0
6FSF	2.63×10^{-9} [e]	5.10×10^{-10}	9.33×10^{-11}	28.2	5.5
AMSF	—[f]	4.73×10^{-11}	6.48×10^{-12}	—[f]	7.3
OSDA	5.41×10^{-11}	1.19×10^{-11}	1.18×10^{-12}	45.8	10.1
OEDA	8.76×10^{-11}	2.04×10^{-11}	2.20×10^{-12}	39.8	9.3

[a] $cm^3(STP)$ cm cm^{-2} s^{-1} $cmHg^{-1}$

[b] $\beta_{CO_2/N_2} = P_{CO_2} / P_{N_2}$

[c] $\beta_{O_2/N_2} = P_{O_2} / P_{N_2}$

[d] P_{CO_2} was evaluated at the 66.8 mmHg of upstream pressure.

[e] P_{CO_2} was evaluated at the 69.8 mmHg of upstream pressure.

[f] CO_2 permeation was scarcely observed.

References

1. L. Breitbach, E. Hinke, and E. Staude, Angew. Makromol. Chem., **184**, 183 (1991).

2. E. Hinke and E. Staude, J. Appl. Polym. Sci. **42**, 2951 (1991).

3. M. D. Guiver, G. P. Robertson, M. Yoshikawa, and C. M. Tam in Membranes Formation and Modification; I. Pinnau, and B. Freeman, Eds.; ACS Symposium Series **744**; American Chemical Society: Washington, DC; 1999, Chap. 10.

4. C. M. Tam, A. Y. Tremblay, M. D. Guiver, and M. M. Dal-Cin, Can J Chem. Eng., **69**, 1348 (1991).

5. A. Y. Tremblay, C. M. Tam, and M. D. Guiver, Ind. Eng. Chem. Res. **31**, 834 (1992).

6. M. D. Guiver, in Proceedings of the Eleventh Annual Membrane Technology/Separations Planning Conference; Business Communications Co. Inc. and Filterex Inc.: Newton, MA, October 11-13, 1993.

7. M. D. Guiver, C. M. Tam, S. Ball, T. A. Tweddle, M. M. Dal-Cin, A. Kumar, in Proceedings of Euromembrane 95, Vol. 1; R. Bowen, R. W. Field, and J. A. Howell, Eds; Anthony Rowe Ltd.: Chippenham, UK, 1995; pp. 345-348.

8. M. D. Guiver, A. Y. Tremblay, and C. M. Tam, in Advances in Reverse Osmosis and Ultrafiltration; T. Matsuura, and S. Sourirajan, Eds.; National Research Council: Ottawa, Canada 1989; pp. 53-70.

9. M. D. Guiver , A. Y. Tremblay, and C. M. Tam, U.S. Pat. 4,894,159, 1990.

10. Y. Nagase, A. Naruse, and K. Matsui, Polymer, **30**, 1931 (1989).

11. Y. Nagase, A. Naruse, and K. Matsui, Polymer, **31**, 121 (1990).

12. B. Bickson, J. K. Nelson, and G. Götz, U.S. Pat. 5,071,448, 1991.

13. H. C. Park, J. Won, Y. S. Kang, I. W. Kim, J. Y. Jho, M. D. Guiver, and G. P. Robertson in Proceedings of the 5th Pacific Polymer Conference, Kyongju, Korea, Polymer Society of Korea, October 26-30, 1997.

14. M. Yoshikawa, H. Hara, M. Tanigaki, M. Guiver, and T. Matsuura, Polymer , **33**, 4805 (1992).

15. M. Yoshikawa, H. Hara, M. Tanigaki, M. Guiver, and T. Matsuura, Polymer J., **24**, 1049 (1992).

16. M. Yoshikawa, K. Tsubouchi, M. D. Guiver, and G. P. Robertson, J. Appl. Polym. Sci., **74**, 407 (1999).

17. K. Rodemann, and E. Staude, J. Membr. Sci., **88**, 271 (1994).

18. J. Kerres, W. Cui, R. Disson, and W. Neubrand, J. Membr. Sci., **139**, 211 (1998).

19. J. Kerres, W. Cui, and M. Junginger, J. Membr. Sci., **139**, 227 (1998).

20. M. Yoshikawa, J. Izumi, T. Ooi, T. Kitao, M. D. Guiver, and G. P. Robertson, Polym. Bull., **40**, 517 (1998).

21. M. D. Guiver, and G. P. Robertson, Macromolecules, **28**, 294 (1995.

22. M. D. Guiver, G. P. Robertson, and S. Foley, Macromolecules, **28**, 7612 (1995).

23. N. Kahana, R. Arad-Yellin, A. Deshe, and A. Warshawsky, J. Polym. Sci: Part A: Polym. Chem., **28**, 3303 (1990).

24. F. H. Roos, W. H. Daly, M. N. Aniano-Ilao, and I. I. Negulescu, J. Macromol. Sci. Pure Appl. Chem., **A33**, 275, (1996).

25. D. K. Mohanty, and J. E. McGrath, Polym. Sci. Tech., **31**, 113 (1985).

26 T. Nakagawa, Maku (Membrane), **6**, 197 (1981).

27. D. R. Paul, W. J. Koros, J. Polym. Sci.,
    Polym. Phys. Ed., **14** 675 (1976).

28. W. J. Koros, and D. R. Paul, J. Polym. Sci.,
    Polym. Phys. Ed., **16**, 2171 (1978).

29. W. J. Koros, R. T. Chern, V. Stannett, and H.

B. Hopfenberg, J. Polym. Sci., Polym. Phys.
Ed., 19, 1513 (1981).

30. K. Ghosal, R. T. Chern, B. D. Freeman, W. H.
    Daly, and I. I. Negulescu, Macromolecules, 29,
    4360 (1996).