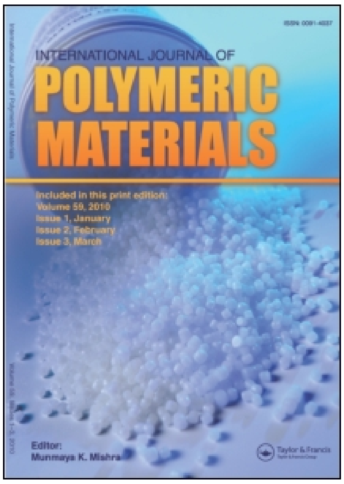

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Separation of Gases by Polymer Membranes

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INTRODUCTION

Synthetic polymer membranes for gas separation continue to be the object of intensive research in the fields of physical and polymer chemistry, and chemical engineering. Investigation of separation coefficients of various gases is the most primitive method of evaluating membrane properties. However, the ratios of permeability coefficients of different gases are used for separation coefficients, since other measurements are so complicated. The gas permeability coefficients of dense membranes are functions of solubility and diffusion coefficients. Therefore measurements of sorption isotherm, diffusion and permeability coefficients are important in the understanding of the fundamentally properties of polymer membranes for gas separation.

Recently, many investigations concerned with gas separation membrane for oxygen and nitrogen have been performed. Oustanding problems with this type of membrane are that the separability is reduced when the membrane has a high flux or vice versa. These contradictions have been explained by the uncertain fact that low polymer density introduces a high flux and low solubility of gases. There have been several attempts to solve this problem.

Facilitated transport of oxygen was investigated by K. Okabe *et al.* (E 1223) using a liquid membrane. Several metal complexes which are composed of cobaltous Shiff-base were synthesized as oxygen carrier. The highly selective and permeable membranes for oxygen enrichment were formed with cobaltdihistidine and amminecobalt which showed an ideal selectivity coefficient for O_2/N_2 at about 80. Permeabilities of oxygen through these membranes decreased after a short time. The deterioration in the permeability was caused by the water and oxygen. Deteriorated carriers were regenerated by contact with zinc at an elevated temperature. Even if these problems are solved a high flux cannot be expected. Immobilization of such carriers in the membrane has been tried, to avoid destruction of a liquid membrane by an external solution. A cobaltporphyrin containing polymer is considered as one of the oxygen enrichment membranes. The transport mechanism of oxygen for this membrane was investigated by H. Kawakami *et al.* (E 1589). They explained the transport mechanism of oxygen through this membrane using 6 different parameters. This idea is based on a modified dual sorption model using more than three parameters. The use of equations which include many unknown parameters can however explain every kind of phenomenon. Since the gas permeability coefficient of this membrane is so low research effort has been carried out to increase it. The application of poly(organophosphazene) as the base polymer increases the oxygen permeability because it has a large free volume as shown by K. Tsuda *et al.* (E1225). Studies have also been made on porous glass by Y. Sasame *et al.* (E1224). Vycor glass was dipped in dilute acid for a few days, and then washed well with pure water, followed by activation by heat treatment in vacuo. Porphyrin/Vycor composite membrane was prepared by immersing the activated Vycor glass in a dichloromethane solution of cobalt-porphyrin complexed with 1-methylimidazole or poly(alkylmethacrylate-covinylimidazole) under an oxygen-free atmosphere for a few days, and drying in vacuo. The nitrogen permeability coefficient (P_{N2}) is independent of the nitrogen upstream pressure. On the other hand, P_{02} for the Vycor/CoP composite membrane depends on the oxygen upstream pressure P_{02} and P_{02}/P_{N2} at $P_{02} = 2.6\,\mathrm{cmHg}$ were 4.2×10^{-6} barrer and 4.7, respectively.

Poly[1-(trimethylsily)-1-propynel](PMSP) has an extremely high gas permeability coefficient. Much attention has been paid because of its potential utilization in industrial applications and its unusual permeation behaviour. In spite of the high permeability, PMSP has a low separation factor and low durability. In order to modify these properties *T.* Nakagawa *et al.* (E1145) investigated the effects of plasma treatment, γ-ray irradiation and successive treatments of plasma and γ-ray irradiation on the permeability and selectivity of PMSP membranes. The effect of the total dose of γ-ray irradiation of the membranes pretreated by plasma on the permeability coefficients and the ideal separation factor of O_2 and N_2, tells us that the permeability coefficients show a maximum at 2 Mrad of dose, and separation factor shows a minimum at the same dose. Plasma-polymerization is also one of the methods of obtaining membranes which have high permeation rates. Among polymeric materials, fluoro polymers have attracted much interest because of their high affinity to oxygen. H. Kita *et al.* (E1146) reported plasma polymerization of perfluoroalkanes such as $n\text{-}C_6F_{14}$, C_2F_6 and CF_4 and gas permeation through plasma polymerized membranes. The membrane which was prepared from $n\text{-}C_6F_{14}$ showed high separation characteristics. The largest ratio of oxygen permeation rates to nitrogen gas was 4.4. It is considered that the permeation rate should be increased if this membrane is to be commercialized. I think this is one of the shortest routes to obtaining the ideal oxygen enrichment membrane. Poly(4-methyl-1-penten: TPX) film has been used as an oxygen enrichment membrane for medical application. Y. Taru *et al.* (1590) modified the surface of TPX using fluorine to improve the separation factor of oxygen and nitrogen. The selectivity was altered by changing the fluorine exposure time. The selectivity increased from an initial value of 3.3 to about 6.5 after 15 minutes of fluorine exposure. Siloxane-imide blockcopolymers(Six-PI) with various siloxane contents were investigated to improve the separation factor of siloxane polymer by Y. Tsujita *et al.* (E1568). The selectivity was developed and permeability decreased with increase of polyimide content.

Separations of different gases apart from nitrogen and oxygen are also an important project from the viewpoint of energy saving and environmental disruption. Recently several gases such as H_2, CH_4, CO_2 have been studied. H. Kita *et al.*

(E1146) and Y. Taru *et al.* (E1590) investigated gas separation of H_2/CH_4 using a plasma-polymerized membrane of perfluoroalkanes and the partially fluorinated poly(4-methyl-1-pentene), respectively. Taru *et al.* showed that the selectivity increased from an initial value of 7 to about 80 after 15 minutes of fluorine exposure.

Separation of CO_2 from gas mixture is also an important problem. However sorption and diffusion of gases through polymers include several problems because the diffusion and solubility coefficients strongly depend on the CO_2 concentration. There are several efforts to avoid these effects because such problems reduce the separability and membrane strength. Y. Tsujita *et al.* (E1586) also investigated the CO_2 permeabilities through siloxane-imide blockcopolymers (Six-PI). This polymer shows the micro phase separation. Sorption isotherm and permeability coefficient were analysed in terms of the dual sorption model. The sorption and diffusion of CO_2, N_2 and He below latm were measured for polyimide films prepared from benzophenoneteteracarboxylicdianhydride (BTDA) with 3, 5-diaminotoluenetrifluoride (DATF), 2, 4-diaminotoluene (DAT), m-phenylenediamine (MPD), and diaminotoluenetrifluoride (DATF), 2, 4-diaminotoluene (DAT), m-phenylenediamine (MPD), and diaminobenzoicacid (DABA) by a volumetric sorption method and permeation method by K. Toi *et al.* (E1584). Non linear isotherms obseved for CO_2 sorption were successfully interpreted in terms of the dual mode sorption model in glassy polymers. Linear isotherms observed for N_2 and He seemed to obey Henry's law. Diffusion coefficients are measured from the short-time and long-time methods from sorption, and time lag method and activation energy of diffusion were also measured. These diffusion coefficients increase with an increase in the free space, which is calculated by the method of Bondi using the density data. These results suggest that the substituents act as spacers for the polymer chains, and control their gas diffusivities by influencing the polymer chain packing. The activation energies of diffusion increase with increases in cohesive energy density of these polyimides. Sorption and transport of CO_2 in several polyimides containing CF_3 groups were investigated and compared with those for other glassy polymers by K. Tanaka *et al.* (E1585). Fluorinated polyimides have higher fractions of free space as compared with non-fluorinated polyimides because of weak molecular interaction and steric effect caused by CF_3 groups. Sorption isotherms were analyzed according to the dual-mode sorption model. Correlations between the values of sorption parameters and physical properties such as free space, concentration of functional groups and glass transition temperature, are almost in agreement with those observed for other glassy polymers, with the exception of the constant of Henry's law k_D. Fluorinated polyimides have larger values of k_D than those predicted from the correlation. Y. Kamiya *et al.* (E1587) investigated sorption and dilation behaviour for N_2, CH_4, and CO_2 in poly(ethylene-co-vinyl acetate) (EVAc), and determined partial molar volumes of the gases in the polymer as functions of temperature and pressure. From the temperature and pressure dependence, the thermal expansivity and compressibility by the dissolved gases were estimated. Sorption isotherms for N_2 and CH_4 followed Henry's law at every temperature, whereas the isotherms for CO_2 were convex toward the pressure axis and well described by the Flory-Huggins equation. Dilation isotherms for the gases were obtained as pressure dependence of the elongation $l_s = (L - L_0)/L_0$, where L was the length at pressure $p = p$ and L_0 the length at $p = 0$. The isotherms were very similar in shape to the corresponding sorption isotherms. From the sorption and dilation isotherms, partial molar volumes of the gases in the polymer were determined as a function of temperature and pressure. From slopes of the temperature- and pressure-dependent curves, the expansivity and compressibility of the dissolved gases were estimated to be about $2 \times 10^{-3}\,{}^{\circ}C^{-1}$ and 3×10^{-3} atm^{-1}, respectively, on average. These volumetric properties are compared with those for liquid CO_2, organic liquids, and dissolved CO_2 in polybutadiene. From the comparison, it may be concluded that each gas molecule dissolving in rubbery polymers behaves like a molecule of liquid.

Polyimide has been expected to be a suitable material for gas separation membrane because of its dense structure. Hollow fiber formation of this polymer is necessary to develop it on an industrial scale. Hollow fibers made of an alicyclic polyimide were prepared using various spinning conditions and the microstructures of the hollow fibers obtained were observed by A. Kaneko *et al.* (E1220). Further, the flux and rejection of liquid and gas for the hollow fibers were determined and related to the processing conditions. Hollow fibers with skin layer on the inside were prepared from 20 wt% polyimide solution in DMF. A dry-wet jet spinning technique was employed, using a Tube-in orifice nozzle. The parameters in the spinning process such as the flow rates of polymer solution and the internal coagulant, the air gap between the nozzle and the coagulant surface, and the take-up velocity were kept constant. The composition of the internal coagulant was taken as a main variable. Unfortunately, the hollow fiber which has a dense skin lay or suitable for gas separation was not obtained from the polyimide solution in DMF. Currently, the gas separation for the hollow fibers prepared from polyimide solution in γ-bytyrolactone, which is expected to have lower diffusion rate, is under estimation.