

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Facilitated Transport of Molecular Oxygen in Membranes of Macromolecular Cobalt-Porphyrin Complex: Modification of Dual-Mode Transport Model

E. Tsuchida^a; H. Nishide^a; M. Ohyanagi^a

^a Department of Polymer Chemistry, Waseda University, Tokyo, Japan

To cite this Article Tsuchida, E. , Nishide, H. and Ohyanagi, M.(1988) 'Facilitated Transport of Molecular Oxygen in Membranes of Macromolecular Cobalt-Porphyrin Complex: Modification of Dual-Mode Transport Model', *Journal of Macromolecular Science, Part A*, 25: 10, 1327 – 1338

To link to this Article: DOI: 10.1080/00222338808053424

URL: <http://dx.doi.org/10.1080/00222338808053424>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

FACILITATED TRANSPORT OF MOLECULAR OXYGEN IN MEMBRANES OF MACROMOLECULAR COBALT-PORPHYRIN COMPLEX: MODIFICATION OF DUAL-MODE TRANSPORT MODEL

E. TSUCHIDA,* H. NISHIDE, and M. OHYANAGI

Department of Polymer Chemistry
Waseda University
Tokyo 160, Japan

ABSTRACT

Transport of molecular oxygen is facilitated in poly(butyl methacrylate) membranes containing the cobalt(II)- $\alpha, \alpha', \alpha'', \alpha'''$ -*meso*-tetrakis(*o*-pivalamidophenyl)porphyrin-1-methylimidazole (CoPIIm) complex which forms oxygen adduct rapidly and reversibly. The facilitated transport of oxygen is studied by modifying a dual-mode transport model for gas permeation. The diffusion coefficient of oxygen via the fixed CoPIIm complexes (Langmuir mode) is assumed to depend on oxygen concentration, and the modified dual-mode transport equation is described for the permeation steady state. The modified equation represents the effect of upstream oxygen pressure on the permeability. The oxygen permeation behavior through the macromolecular-metal complex membrane is discussed.

*To whom correspondence should be addressed.

INTRODUCTION

Oxygen permselective polymer membranes have been fairly widely studied for the production of oxygen-enriched air [1]. Recently, polymer membranes containing a metal complex that interacts specifically and reversibly with a gaseous molecule have been noted as facilitated transport membranes for the gas molecule. The concept is successfully applied first to oxygen separation by a liquid membrane containing hemoglobin [2], then to a liquid membrane containing a cobalt Schiff base complex [3]. Oxygen exhibited high permeability in the membrane. However, the liquid membrane itself cannot be used under a differential gas pressure and the liquid medium containing the metal complex evaporates in use. Thus, it is difficult to employ a liquid or wet membrane as an oxygen-enriching membrane from air. Therefore, attention has been attracted to study of a dry polymer membrane containing such a metal complex as a fixed carrier of oxygen.

The authors recently succeeded in preparing poly(alkyl methacrylate) membranes containing a cobaltporphyrin complex or a cobalt Schiff base complex with reversible oxygen-binding ability and found facilitated oxygen transport attributed to the cobalt complexes fixed in the polymer membranes [4]. The membrane containing the cobalt(II)- $\alpha,\alpha',\alpha'',\alpha'''$ -*meso*-tetrakis(*o*-pivalamidophenyl)porphyrin-1-methylimidazole (CoPIIm) complex is assumed to sorb oxygen by a dual mode: Henry's law sorption to the polymer domain and additional Langmuir sorption to the complex. Oxygen ad- and desorption to the CoPIIm complex in solution are known to be very rapid and reversible. If the CoPIIm complex is fixed in the membrane with preservation of its oxygen-binding ability, oxygen interacts with the fixed CoPIIm complex rapidly and reversibly and is not immobilized by it during passage through the membrane. In fact, oxygen transport was accelerated by the additional Langmuir mode besides the Henry mode. Although the facilitated oxygen transport could be discussed in terms of the dual-mode transport model, the facilitation of oxygen transport was remarkably enhanced at extremely low upstream pressure, and the permeability coefficient deviated from the values estimated by the dual-mode transport model.

In the present paper the dual-mode transport model is modified to represent the oxygen permeation behavior in the CoPIIm membrane even under low upstream oxygen pressure. The diffusion coefficient of oxygen via the fixed cobalt complex according to the Langmuir mode in the dual-mode model is assumed to depend on the oxygen concentration in the membrane. The effect of oxygen upstream pressure on oxygen permeation is analyzed by the equation modified for the permeation steady state.

EXPERIMENTAL

Materials

[$\alpha, \alpha', \alpha'', \alpha'''$ -*meso*-Tetrakis(*o*-pivalamidophenyl)porphinato] cobalt(II) (CoP) was synthesized as in the literature [5] and complexed with 1-methylimidazole (Im) in toluene under a nitrogen atmosphere. Toluene solutions of the CoPIm complex and poly(butyl methacrylate) (PBMA) (MW 320 000) were mixed, and the mixed toluene solution was carefully cast on a Teflon plate under an oxygen-free atmosphere, followed by drying *in vacuo*, to yield a transparent, wine-red membrane with a thickness of 60–65 μm containing 2.5 wt% CoPIm. A blank membrane containing an inert Co(III)PIm complex with no oxygen-binding ability was prepared by the same procedure.

Permeation Measurements

Oxygen permeation coefficients for various upstream gas pressures were measured with a low-vacuum permeation apparatus (Rika Seiki Inc. Model K-315 N-01), as reported in previous papers [4].

RESULTS AND DISCUSSION

Effect of Oxygen Upstream Pressure on Permeability in the Macromolecular-Metal Complex (CoPIm/PBMA) Membrane

Figure 1 shows the effect of upstream gas pressure, p_2 , on the oxygen permeation coefficient, P_{O_2} , in the membrane containing 2.5 wt% CoPIm. Although the dependence of P on p_2 has been reported for glassy polymers [6], in this case the glass-transition temperature is 20°C for the CoPIm/PBMA membrane, and the membrane was in a rubbery state at the temperatures of the permeability measurement. In fact, P_{O_2} is independent of $p_2(\text{O}_2)$ for the blank Co(III)PIm/PBMA membrane [the Co(III)PIm complex does not interact with oxygen], but P_{O_2} obviously increases with decreasing $p_2(\text{O}_2)$ in Fig. 1.

The enthalpy change for oxygen binding of the CoPIm complex in the PBMA membrane has been estimated to be -14 kcal/mol [4], and the oxygen-binding constant K of the complex decreases with temperature. Thus, it is assumed that the contribution of the Langmuir population decreases with temperature. However, $p_2(\text{O}_2)$ is enhanced at higher temperature as is seen in Fig. 1. This means that for CoPIm, the oxygen-binding kinetics predomi-

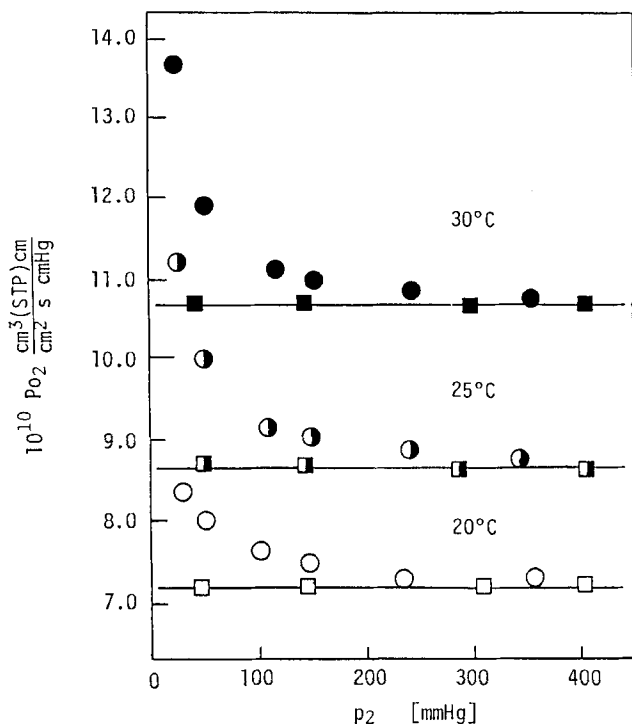


FIG. 1. Effect of upstream oxygen pressure on the permeation coefficient for the CoPIIm (or blank Co(III)PIIm)/PBMA membrane (circles: CoPIIm; squares: blank Co(III)PIIm).

nantly influence the oxygen transport rather than the oxygen-binding equilibrium.

The time course of gaseous molecule permeation through membranes often shows an induction period (time lag) followed by permeation with a constant slope (steady state). For a macromolecular-metal complex membrane, the time lag in the permeation-time course should be enhanced because the fixed complex interacts with the penetrant and retards its diffusion into the membrane. The oxygen permeation time lag for the CoPIIm/PBMA membrane is also governed by both the Henry and the Langmuir modes.

The time lag (θ) for oxygen permeation also depends on $p_2(O_2)$, as shown

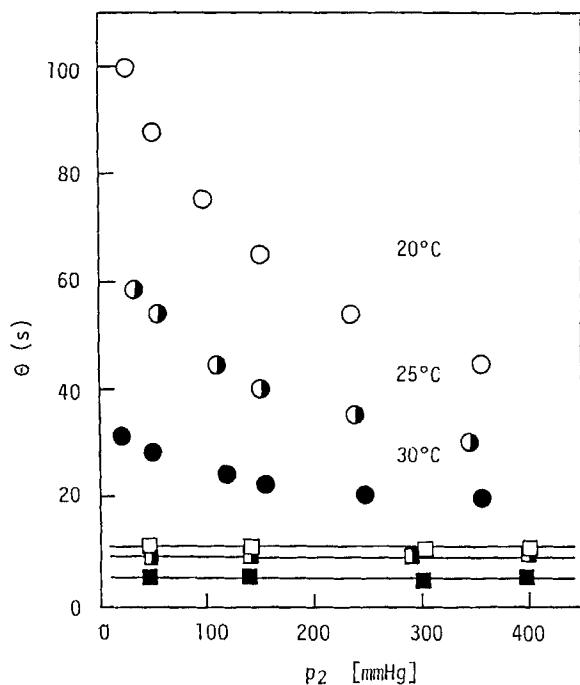


FIG. 2. Effect of upstream oxygen pressure on the time lag for the CoPIIm (or blank Co(III)PIIm)/PBMA membrane (circles: CoPIIm; squares: blank Co(III)PIIm).

in Fig. 2, in the same manner as the permeation coefficient. This behavior indicates that oxygen clearly interacts with the CoPIIm complex in the membrane. This is further supported by the results that θ is independent of the upstream gas pressure for oxygen permeation in the blank Co(III)PIIm/PBMA membrane. Notice in Fig. 2 that θ_{O_2} and the $p_2(O_2)$ dependence of θ_{O_2} decrease with temperature. θ_{O_2} and the $p_2(O_2)$ dependence of θ_{O_2} are both based on oxygen binding to the fixed complex and enhanced at lower temperature because K of the fixed complex increases and the dissociation rate constant of bound oxygen from the complex, k_{off} , decreases with decreasing temperature [4].

Analysis of Oxygen Permeability through the Macromolecular-Metal Complex Membrane According to the Dual-Mode Transport Model

The membrane containing the CoPIIm complex as a fixed carrier is assumed to sorb molecular oxygen by a dual mode: Henry's law sorption to the polymer domain, C_D , and additional Langmuir sorption to the complex, C_C , is represented by

$$C = C_D + C_C = k_D P_2 + C_C' K p_2 / (1 + K p_2). \quad (1)$$

Here, k_D is the Henry's law solubility coefficient, C_C' is the saturated amount of oxygen reversibly bound to the fixed complex, K is the oxygen-binding and dissociating equilibrium constant of the fixed complex, and p_2 is the upstream gas pressure.

The oxygen transport through the macromolecular-metal complex membrane can be described by the following expression for the total mass flux, N , of oxygen, as has been previously reported [4],

$$N = -D_D \frac{\partial C_D}{\partial x} - D_C \frac{\partial C_C}{\partial x}, \quad (2)$$

where D_D and D_C are taken as constants and interpreted as diffusion coefficients for the oxygen molecules in the physically dissolved and the reversibly complex-bound modes, respectively. With the assumption that the local oxygen-exchanging equilibrium between the two modes is rapidly established, C_D and C_C are related by

$$C = C_D + C_C = C_D + R C_D / (1 + \gamma C_D), \quad (3)$$

where $R = C_C' K / k_D$ and $\gamma = K / k_D$. Then the permeability is given by

$$P = k_D D_D [1 + FR / (1 + K p_2)], \quad (4)$$

where $F = D_C / D_D$. The effect of upstream oxygen pressure on the permeation coefficient in Fig. 1 is analyzed according to Eq. (4) in Fig. 3. The permeation coefficients in the blank Co(III)PIIm membrane which has no oxygen-binding ability are used as the intercepts. Notice in Fig. 3 that the facilitation of oxygen transport is appreciable at extremely low upstream pressure and the permeability coefficient deviates from the straight lines based on the dual-mode transport model.

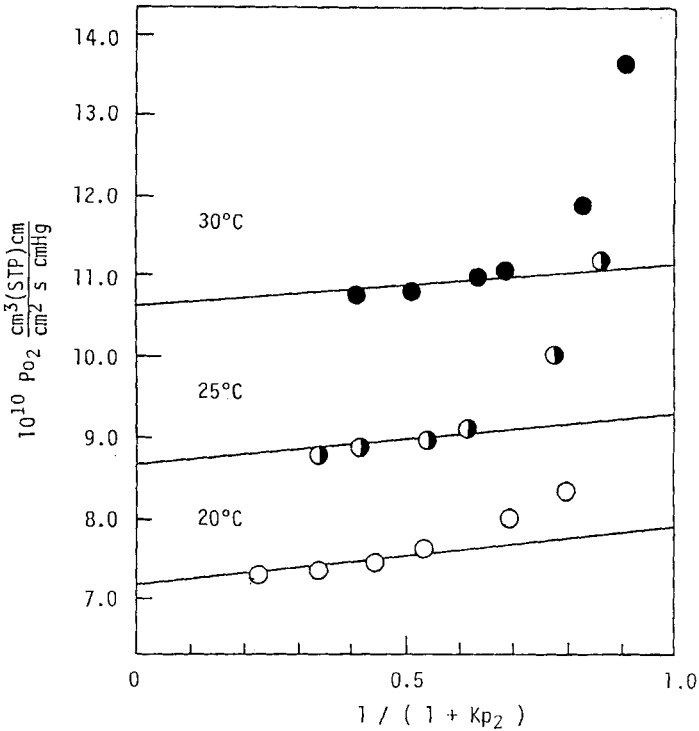


FIG. 3. Oxygen permeation coefficient in the CoPIIm/PBMA membrane analyzed according to dual-mode transport model (Eq. 4).

Empirically Modified Equation of the Dual-Mode Transport Model

For oxygen permeation in the macromolecular-metal complex membrane, the following two assumptions will be used: 1) There are complexes uniformly distributed and fixed in position throughout the macromolecular matrix; 2) local equilibrium between the two modes (the physically dissolved and the complex bound) is very rapidly established.

The oxygen-permeation rate, V_D , through the matrix in the macromolecular-metal complex membrane can be described by

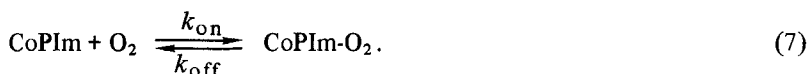
$$V_D = Ap_2, \tag{5}$$

where A is a constant and p_2 is the upstream or external pressure. Equation (5) is supported by the following well-known equation:

$$Q_s = k_D D_D p_2 / L, \quad (6)$$

where Q_s is the same as V_D , and L is the thickness of the membrane.

On the other hand, the oxygen-binding and -dissociating equilibrium reaction is as follows in the macromolecular cobaltporphyrin complex membrane.



Here, k_{on} and k_{off} are oxygen-binding and -dissociating kinetic constants. Then the oxygen-dissociating rate, V_{off} , can be described by

$$\begin{aligned} V_{\text{off}} &= k_{\text{off}} [\text{CoPIIm-O}_2] \\ &= k_{\text{off}} \frac{C_C' K p_2}{1 + K p_2}. \end{aligned} \quad (8)$$

As the concentration gradient is constant in the steady state of the oxygen permeation, the diffusion via the complex may be represented as an increasing function of V_{off}/V_D :

$$V_{\text{off}}/V_D = k_{\text{off}} C_C' K / A (1 + K p_2), \quad (9)$$

$$D_C = f(V_{\text{off}}/V_D). \quad (10)$$

Accordingly, we assign different diffusion coefficients to the oxygen molecules sorbed by each of the two mechanisms and obtain the following expression for the flux rather than Eq. (2) of the original model.

$$N = -D_D \frac{\partial C_D}{\partial x} - D_C (C_D) \frac{\partial C_C}{\partial x}. \quad (11)$$

Here, it is assumed that the total oxygen concentration may be divided into a mobile part with a diffusion coefficient D and concentration C_m , while the remainder, $C - C_m$, is totally immobilized. Furthermore, we assume that all of the oxygen previously associated with C_D as well as a fraction F of that

associated with C_C has this finite mobility, while the remaining fraction, $1 - F$, of C_C has zero mobility. This leads to

$$N = -D_D \frac{\partial C_m}{\partial x}, \tag{12}$$

where

$$C_m = C_D + FC_C \quad [F = D_C(C_D)/D_D]. \tag{13}$$

If we assume D is constant and set $p_1 = 0$ (and thus $C_{m1} = 0$), we obtain at the steady state

$$C_m = C_{m2}(1 - x/L). \tag{14}$$

Here, p_1 and C_{m1} are the downstream pressure and concentration, respectively, and p_2 and C_{m2} are the upstream pressure and concentration, respectively. From Eqs. (12), (13), and (14), we see that the permeability is given by

$$P = k_D D_D + \frac{C_C' K D_C(C_D)}{1 + K p_2}. \tag{15}$$

From Eqs. (9), (10), and Fig. 3, we take the following empirical equation for the diffusion based on the original model of dual-mode transport:

$$D_C(C_D) = \frac{D_C^\circ}{(1 + K p_2)^{\beta-1}}, \tag{16}$$

where D_C° and β are constant at any given temperature. If β is 1, $D_C(C_D)$ is independent of C_D ($= k_D p_2$), which means that Eq (11) reduces to the original model. Equation (15) is converted to the following equation by substituting Eq. (16) in it:

$$P = k_D D_D + \frac{\alpha}{(1 + K p_2)^\beta} \quad (\alpha = D_C^\circ C_C' K). \tag{17}$$

TABLE 1. Permeability Parameters for Eq. (17)

$T, ^\circ\text{C}$	α	β	$(\alpha + k_D D_D)/k_D D_D$
20	1.8×10^{-10}	1.8	1.3
25	4.3×10^{-10}	4.3	1.5
30	6.4×10^{-10}	9.3	1.6

Analysis of the Oxygen Permeation Behavior by an Empirically Modified Equation

Equation (17) is converted for easier analysis of oxygen permeation according to the empirically modified equation as follows:

$$\ln(P - k_D D_D) = \ln \alpha - \beta \ln(1 + K p_2). \quad (18)$$

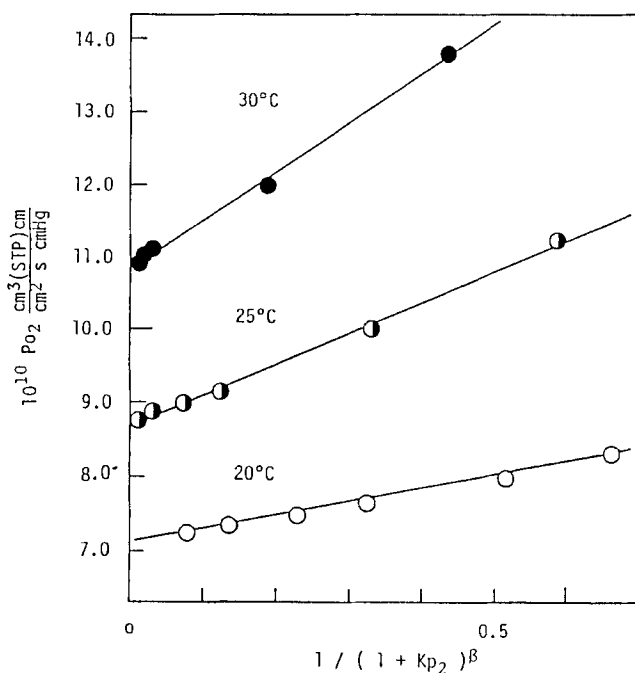


FIG. 4. Oxygen permeation coefficient in the CoPIm/PBMA membrane analyzed according to the empirical equation (Eq. 17).

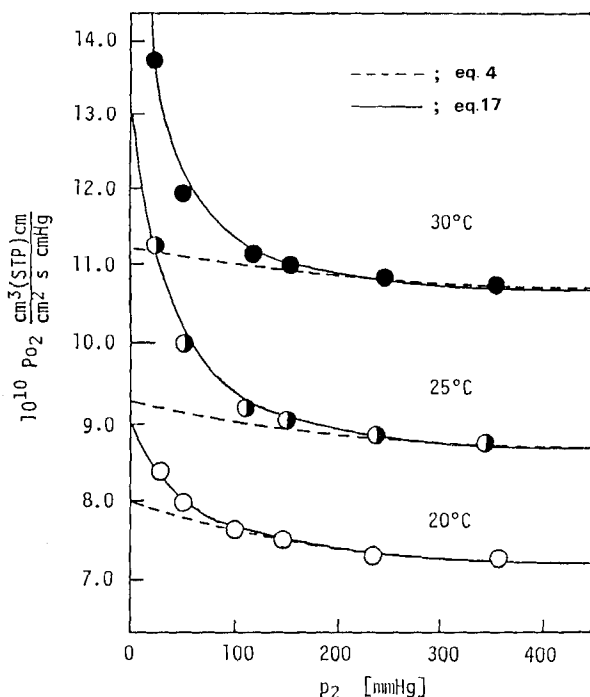


FIG. 5. Oxygen permeation coefficient dependence on the partial pressures represented by the parameters of the dual-mode transport model (Eq. 4) and the empirical equation (Eq. 17).

Here, the oxygen permeation coefficients through the blank Co(III)PIm/PBMA membrane are used as the values of $k_D D_D$. When $\ln(P - k_D D_D)$ is plotted against $\ln(1 + Kp_2)$ according to Eq (18), α and β are determined from the intercept and the slope of the linear relationship and listed in Table 1. The efficiency of the facilitated oxygen transport is represented as $(\alpha + k_D D_D)/k_D D_D$ and is also listed in Table 1. The value increases with temperature, which suggests that an increase in k_{off} is effective.

Calculated α and β values are substituted into Eq. (17) and P is plotted against $1/(1 + Kp_2)^\beta$ in Fig. 4, which shows good linear relationships. P is plotted against p_2 using Eq. (17) and substituting the values of α and β , which is compared with the represented curves using parameters calculated by the dual-mode transport model in Fig. 5. The oxygen permeation behaviors in the macromolecular-metal complex membrane were found to be well-explained in terms of the empirically modified equation in this work.

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area of "Macromolecular Complexes" from the Ministry of Education, Science and Culture, Japan.

REFERENCES

- [1] (a) W. Pusch and A. Walch, *Angew. Chem., Int. Ed. Engl.*, **10**, 81 (1982). (b) W. J. Schell, *J. Membr. Sci.*, **22**, 217 (1985). (c) J. Comyn (ed.), *Polymer Permeability*, Elsevier, New York, 1985. (d) R. E. Kesting, *Synthetic Polymeric Membranes*, 2nd ed., McGraw-Hill, New York, 1985.
- [2] (a) P. F. Scholander, *Science*, **131**, 585 (1960). (b) E. Hemmingsen and P. F. Scholander, *Science*, **132**, 1379 (1960).
- [3] B. M. Johnson, R. W. Baker, S. L. Matson, K. L. Smith, I. C. Roman, M. E. Tuttle, and H. K. Lonsdale, *J. Membr. Sci.*, **31**, 31 (1987).
- [4] (a) H. Nishide, M. Ohyanagi, O. Okada, and E. Tsuchida, *Macromolecules*, **19**, 494 (1986). (b) H. Nishide, M. Ohyanagi, O. Okada, and E. Tsuchida, *Ibid.*, **20**, 417 (1987). (c) E. Tsuchida, H. Nishide, M. Ohyanagi, and H. Kawakami, *Ibid.*, **20**, 1907 (1987). (d) H. Nishide, M. Ohyanagi, Y. Funada, T. Ikeda, and E. Tsuchida, *Ibid.*, **20**, 2312 (1987). (e) H. Nishide, M. Kuwahara, M. Ohyanagi, Y. Funada, H. Kawakami, and E. Tsuchida, *Chem. Lett.*, p. 43 (1986). (f) H. Nishide, M. Ohyanagi, H. Kawakami, and E. Tsuchida, *Bull. Chem. Soc. Jpn.*, **59**, 3213 (1986). (g) H. Nishide, M. Ohyanagi, O. Okada, and E. Tsuchida, *Polym. J.*, **19**, 839 (1987).
- [5] J. P. Collman, J. I. Brauman, K. M. Coxsee, T. R. Halbaert, S. E. Hayes, and K. S. Suslick, *J. Am. Chem. Soc.*, **100**, 2761 (1978).
- [6] D. R. Paul and W. J. Korros, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 675 (1976).

Received January 21, 1988