Bull. Chem. Soc. Jpn., 59, 3213—3216 (1986)

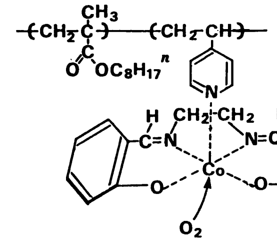
Dual-Mode Transport of Molecular Oxygen through the Membrane of the Poly(octyl methacrylate-co-4-vinylpyridine)(*N,N'*-disalicylideneethylenediaimine)cobalt(II) Complex

Hiroyuki Nishide, Manshi Ohyanagi, Hiroyoshi Kawakami, and Eishun Tsuchida*
Department of Polymer Chemistry, Waseda University, Tokyo 160
(Received May 7, 1986)

Molecular oxygen transport through a polymeric membrane was enhanced in the membrane of poly(octyl methacrylate-co-4-vinylpyridine), complexed with (*N,N'*-disalicylideneethylenediamine)cobalt(II), which forms an oxygen adduct rapidly and reversibly. The cobalt complex in the membrane effectively acted as a fixed carrier on oxygen permeation. The oxygen-binding parameters determined spectroscopically were adequate to analyze the dual-mode transport model.

Recently there has been considerable interest in the production of oxygen-enriched air by the use of permselective membranes.[1)] Metal complexes, such as iron porphyrin derivatives and cobalt Schiff base complexes, form oxygen adducts reversibly and have been successfully used for an oxygen-transporting fluid[2)] and to an oxygen-separating liquid membrane.[3)] However, an oxygen permselective membrane prepared from a polymer complexed with the metal complex acting as a fixed carrier on oxygen permeation has yet been reported. Recently the present authors preliminarily reported the preparation of polymer membranes containing the cobalt complexes as fixed carriers of oxygen which sorb and transport oxygen selectively by means of the Langmuir mode.[4,5)] Drago and Balkus also recently reported that the cobalt-*N,N*-bis[3-(salicylideneamino)propyl]methylamine complex bound to a polystyrene membrane enhances the selectivity for oxygen permeation through a polystyrene membrane at low pressures.[6)]

The present paper will describe the selective and dual-mode transport of molecular oxygen in a polymer complexed with a cobalt-Schiff base as a fixed carrier (Scheme 1). The polymer membrane was prepared by homogeneously complexing (*N,N'*-disalicylideneethylenediamine)cobalt(II) (CoS) to poly(octyl methacrylate-co-4-vinylpyridine)(POMP), whose sixth coordination site is vacant even in the solid state, to bind oxygen reversibly. Rapid and reversible oxygen binding to the polymer-bound complex (the fixed carrier) in the membrane was characterized in situ by means of spectroscopic methods. Oxygen permeation was measured in connection with the upstream oxygen pressure. The oxygen-permeation behavior through the membrane will be discussed in terms of the combination of the dual-mode transport theory and the spectroscopic data.



Scheme 1.

Experimental

Materials. (*N,N'*-disalicylideneethylenediamine)cobalt(II) (CoS) was synthesized as in the literature.[7)] Poly(octyl methacrylate-co-4-vinylpyridine) (POMP) was obtained by the radical copolymerization of octyl methacrylate and 4-vinylpyridine, with azobisisobutyronitrile as an initiator. The vinylpyridine content and the molecular weight of POMP were determined to be 15 mol% and 150000 by elemental analysis and gel-permeation chromatography (with tetrahydrofuran as the solvent and polystyrene as the standard.), respectively. The toluene solution of POMP and CoS was carefully cast on a Teflon plate under an atmosphere without oxygen, followed by drying in vacuo, to yield a transparent and flexible membrane with thickness of 60 μm and containing 2.5 wt% CoS.

Spectroscopic Measurements. Reversible oxygen binding to the POMP–CoS complex in the membrane was observed with a spectral change in the visible absorption (using a highly sensitive spectrophotometer, Shimazu UV-2000). Rapid and reversible oxygen binding to the POMP–CoS complex in the membrane was also confirmed by means of flash photolysis (using a pulse and laser flash spectrophotometer equipped with a kinetic data processor; UNISOK FR-2000). The membrane was set at 45° to the laser-flash irradiation, and perpendicularily the rapid absorption change was recorded with a contact-type photomultiplier in order to cancel the noise signals caused by the scattering light.

Permeation Measurements. Oxygen and nitrogen permeation coefficients for various upstream gas pressures were measured with a low-vacuum permeation apparatus in the chamber for stable thermostating (Rika Seiki K-315 N-03).

Results and Discussion

Oxygen Binding to the Complex in the Membrane. The visible absorption spectrum of the transparent membrane is shown in Fig. 1. The color of the membrane was changed reversibly from brown to deep violet on exposure to oxygen and nitrogen. The spectral change in the membrane agreed with that of the polymer–CoS complex previously reported[2a)]: UV and visible absorption maxima λ_{max}=555 nm (oxy: Co/O_2=1/1 adduct), λ_{max}=345, 410 nm (deoxy: five-coordina-

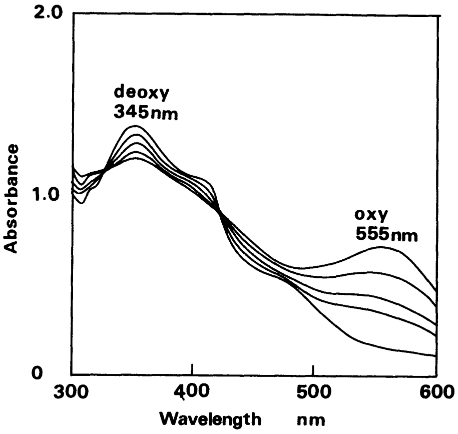


Fig. 1. UV and visible absorption spectral change in the oxygen binding to the POMP-CoS membrane at 30 °C, [CoS]=2.5 wt%.

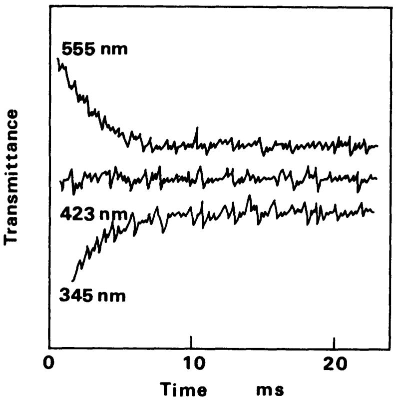


Fig. 2. Flash photolysis of the bound oxygen to the POMP-CoS membrane under exposing to air at 30 °C, [CoS]=2.5 wt%.

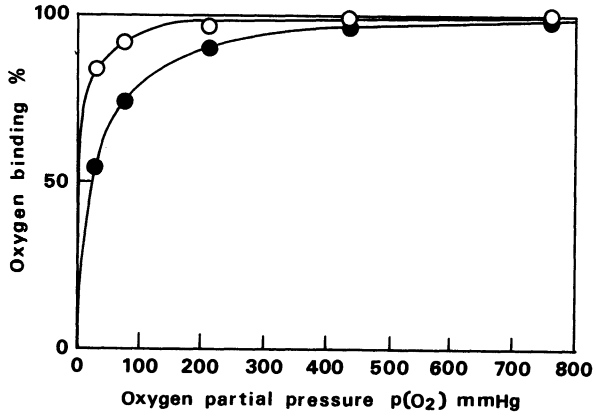


Fig. 3. Oxygen-binding equilibrium curve for the POMP-CoS membrane at ○: 25 °C, ●: 35 °C, [CoS]=2.5 wt%.

tion), isosbestic points at 335, 423 nm.

The reversible oxy-deoxy spectral change occurred rapidly; e.g., for a 60 μm-thick membrane containing 2.5 wt% CoS, the oxygen-binding equilibrium was established within several minutes after the exposure to oxygen or in vacuo at 25 °C. Although there have been several reports on the oxygen binding to a cobalt Schiff base complex or an iron porphyrin complex dispersed or bonded to the polymers in the solid state, oxygen adsorption and desorption to them occurred very slowly, even in a fine powder state with a large surface area.[8] It is important for a fixed carrier of oxygen that oxygen should be sorbed and desorbed rapidly in response to a partial oxygen pressure, even after fixation in a feasible membrane.

$$\mathrm{POMP\text{-}CoS\text{-}O_2} \xrightarrow{h\nu} \mathrm{POMP\text{-}CoS} + \mathrm{O_2} \xrightarrow{k_{\mathrm{app}}} \mathrm{POMP\text{-}CoS\text{-}O_2} \qquad (1)$$

$$\mathrm{POMP\text{-}CoS} + \mathrm{O_2} \underset{k_{\mathrm{off}}}{\overset{k_{\mathrm{on}}}{\rightleftharpoons}} \mathrm{POMP\text{-}CoS\text{-}O_2} \qquad (2)$$

The photodissociation and recombination of the bound oxygen from and to the POMP-CoS complex in the membrane (Eq. 1) was successfully observed by means of pulse and laser flash spectroscopy. The oxygen-binding and -dissociation rate constants (k_{on} and k_{off} in Eq. 2) of the CoS complexed to the POMP membrane could be determined in situ as follows. By the changing in the monitoring wavelength from 300 to 600 nm, a differential spectrum before and after the flash photolysis was measured. The positive and negative extremes in the differential spectrum, 345 and 555 nm, were selected as the monitoring wavelengths for subsequent use (Fig. 2). These wavelengths agreed with the absorption maxima of the oxygen adduct and the deoxy complex in Fig. 1. The validity of these measurements is supported further by the following results: (i) The absorbance of 423 nm is kept constant before and after flash photolysis (Fig. 2); this wavelength agrees with the isosbestic point of the oxygen adduct and the deoxy complex as it shown in Fig. 1, and (ii) the absorbance changes followed at 345 and 555 nm are symmetric (Fig. 2).

The k_{on} and k_{off} values were estimated by means of pseudo-first-order kinetics and as given in Table 1. The k_{on} and k_{off} values of the CoS complexed to the POMP membrane were similar to those of the POMP-CoS complex in a toluene solution. This means that the CoS complex is active for the oxygen binding even, in the membrane, and that it acts as an effective fixed carrier of oxygen.

The oxygen-binding equilibrium constant ($K=k_{\mathrm{on}}/k_{\mathrm{off}}$) was determined by conducting oxygen-binding and -dissociation equilibrium measurements using Drago's equation.[9] The oxygen binding curves and the K values are given in Fig. 3 and Table 1. The K values of the complex in the membrane were much larger than those in the toluene solution. This result may be explained as follows: While the axial pyridyl group-ligation is in equilibrium in the solution system, the POMP-CoS complexation is completed and/or the pyridyl ligand in POMP is immobilized to

Table 1. Oxygen-Binding Rate.[a)] Equilibrium Constant,[a)] and Its Thermodynamic Parameters[b)] for the POMP-CoS Membrane

Physical state	$10^{-5} k_{on}$	$10^{-2} k_{off}$	K	ΔH	ΔS
	$\mathrm{L\,mol^{-1}\,s^{-1}}$	$\mathrm{s^{-1}}$	$\mathrm{cmHg^{-1}}$	$\mathrm{kcal\,mol^{-1}}$	e.u.
Toluene soln.	1.8	2.7	1.1×10^{-3}	−30	−104
Membrane	4.8	0.44	4.3×10^{-1}	−16	−45

a) Data at 30 °C. b) Data for van't Hoff plots (ln K in $\mathrm{atm^{-1}}$).

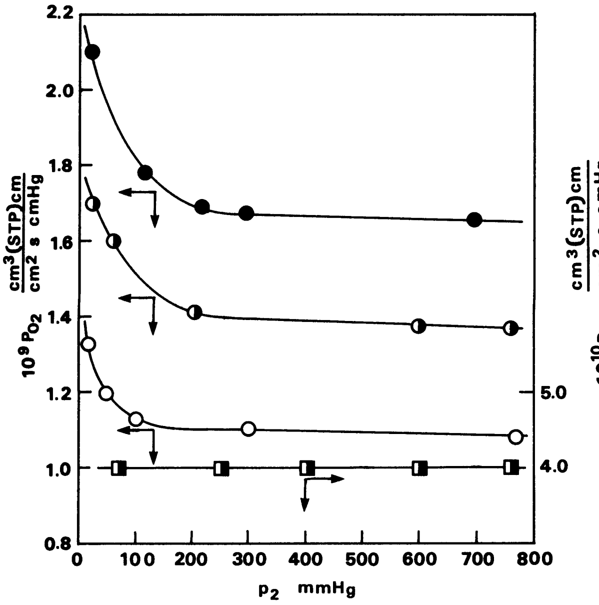


Fig. 4. Effect of upstream gas pressure on permeation coefficient for the POMP–CoS membrane. Oxygen: at ○: 25 °C, ◑: 30 °C, ●: 35 °C, Nitrogen: at ◨: 30 °C.

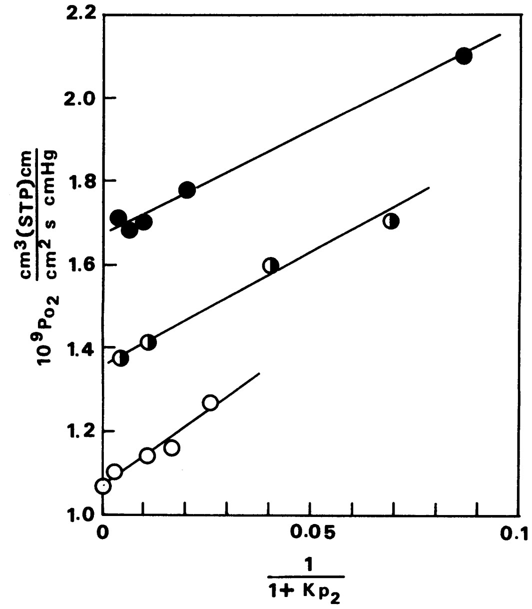


Fig. 5. Oxygen permeability in the POMP–CoS membrane plotted according to Eq. 3 at ○: 25 °C, ◑: 30 °C, ●: 35 °C.

CoS, which bring about a relatively stable oxygen adduct formation for the complex in the membrane. The thermodynamic parameters for the oxygen binding, as estimated from the temperature dependence of K, are also given in Table 1.

At any rate, the advantages of the membrane complexed with CoS are that the fixed carrier maintains its rapid and reversible binding capability of the penetrant even after fixation in the membrane and that the adsorption and desorption rates and the equilibrium constants of the penetrant to the carrier site can be evaluated in situ.

Oxygen Permeability in the Fixed Carrier Membrane. Figure 4 shows the effect of the upstream gas pressure (p_2) on the permeability coefficients (P_{O_2} and P_{N_2}) in a membrane containing 2.5 wt% CoS. Although the dependence of P on p_2 has been often reported for glassy polymers,[10)] the glass-transition temperature was −8.0 °C for the membrane containing CoS and the membrane was in a rubber state during permeability measurements. In fact, P_{N_2} was independent of $p_2(N_2)$, for the fixed carrier does not interact with nitrogen. P_{O_2} increases with a decrease in $p_2(O_2)$, which suggests that oxygen transport occurs by means of dual-mode transport[10)] (Henry mode and additive Langmuir mode). That is, P is equal to the sum of a first term, representing the Henry mode, and the second term, for representing the Langmuir mode, which is a function of p_2:

$$P = k_D D_D[1 + FR/(1 + Kp_2)] \tag{3}$$

$$F = D_C/D_D,\quad R = C_C'K/k_D$$

Here, P is the permeability coefficient, k_D is the solubility coefficient for Henry's law, D_D and D_C are the diffusion coefficients for Henry-type and Langmuir-type diffusions, C_C' is the saturated amount of oxygen reversibly bound to the binding site or the fixed carrier, K is the oxygen-binding and -dissociation equilibrium constant, and p_2 is the upstream gas pressure.

The effect of $p_2(O_2)$ on P_{O_2} was analyzed by using Eq. 3; that is, P_{O_2} was plotted against $1/(1+Kp_2)$ (Fig. 5). The plots show a linear relationship. The oxygen permeability in the membrane containing the complex as a fixed carrier can be explained in terms of the sum of the Henry mode attributed to the matrix and the Langmuir mode attributed to the fixed carrier, that is, the dual-mode theory.

The time lag (θ) for the oxygen permeation also depended on $p_2(O_2)$, as it shown in Fig. 6, in the same manner as the permeation coefficient. This behavior indicates that oxygen clearly interacts with the CoS complexed to the POMP membrane. This is further

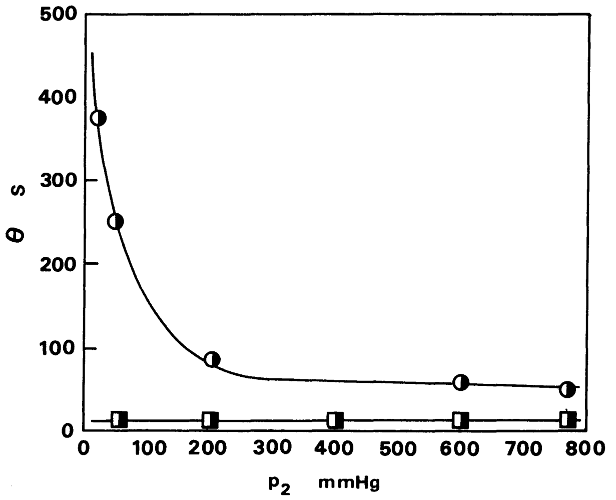


Fig. 6. Effect of upstream gas pressure on time lag for the POMP–CoS membrane. Oxygen: at ◑: 30 °C, Nitrogen: at ◨: 30 °C.

supported by the result that the value for the nitrogen permeation in the membrane containing the carrier is indepedent of the upstream gas pressures.

Although dual mode transport due to partial immobilization[10] has been reported for carbon–dioxide permeation in glassy polymers, the present authors have here verified the dual-mode transport by using a much simpler system.

This work was partially supported by a Grant-in-Aid from the Ministry of Education, Science and Culture.

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).

2) a) E. Tsuchida, *J. Macromol. Sci., Chem.*, **A13**, 545 (1979); b) E. Tsuchida, H. Nishide, M. Yuasa, E. Hasegawa, Y. Matsushita, and K. Eshima, *J. Chem. Soc., Dalton Trans.*, **1985**, 275; c) E. Tsuchida, *Ann. N.Y. Acad. Sci.*, **446**, 429 (1985); d) E. Tsuchida, *Chem. Eng. News, 14,* **1985**, 42.

3) I. C. Roman and I. W. Baker, Eur. Patent 0098731 (1983).

4) H. Nishide, M. Kuwahara, M. Ohyanagi, Y. Funada, H. Kawakami, and E. Tsuchida, *Chem. Lett.*, **1986**, 43.

5) H. Nishide, M. Ohyanagi, O. Okada, and E. Tsuchida, *Macromolecules*, **19**, 494 (1986).

6) R. S. Drago and K. J. Balkus, Jr., *Inorg. Chem.*, **25**, 716 (1986).

7) R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.*, **69**, 1886 (1947).

8) a) D. Wohrle, H. Bohlen, and C. Aringer, *Makromol. Chem.*, **185**, 669 (1984); b) E. Tsuchida, K. Honda, and S. Hata, *Bull. Chem. Soc., Jpn*, **49**, 868 (1976).

9) T. Beugelsdijk and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 6466 (1975).

10) a) D. R. Paul and W. J. Koros, *J. Polym. Sci., Phys. Ed.*, **14**, 675 (1976); b) D. R. Paul, *Ber. Bunsenges. Phys. Chem.*, **83**, 294 (1979).