CHEMISTRY LETTERS, pp. 43-46, 1986.

OXYGEN PERMEATION IN THE MEMBRANE OF POLY(OCTYLMETHACRYLATE-co-4-VINYLPYRIDINE)-SALICYLALDEHYDEETHYLENEDIIMINE COBALT COMPLEX

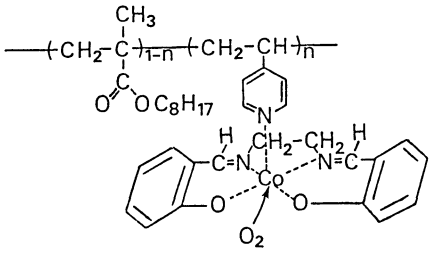
Hiroyuki NISHIDE, Masahiro KUWAHARA, Manshi OHYANAGI, Yoshitsugu FUNADA, Hiroyoshi KAWAKAMI, and Eishun TSUCHIDA*

Department of Polymer Chemistry, Waseda University, Tokyo 160

Oxygen-binding and -permeation in the membrane prepared from the poly(octylmethacrylate-co-4-vinylpyridine) complexed with salicylaldehydeethylenediimine cobalt was studied by spectroscopic and permeability measurements. The cobalt complex in the membrane effectively acted as a fixed carrier on oxygen permeation.

Gaseous molecule-binding ability of polymer-metal comlexes has been well studied and successfully applied to an oxygen transporting fluid,[1] a carbon oxide adsorbent,[2] etc. Much research has been directed toward the synthesis of permselective membranes for oxygen enrichment.[3] But the membrane prepared from the polymer-metal complex which acted as a fixed carrier on oxygen permeation has not been reported. In this communication the authors prepared the poly(octylmethacrylate-co-4-vinylpyridine)(OMP) membrane complexed with N,N'-bis(salicylidene)ethylenediamine cobalt(II)(CoS) which reversibly and rapidly bound molecular oxygen (Scheme 1). Oxygen-binding and -permeability were studied by spectroscopic and permeability measurement.

The membrane was prepared as follows. The chloroform solution of OMP(vinylpyridine residue content 7.2 mol%) and CoS was casted on Teflon plate



Scheme 1.

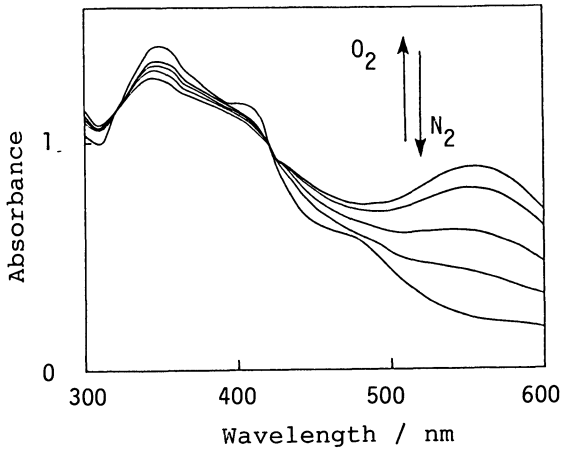


Fig. 1. UV and visible absorption spectral change in the oxygen binding to the OMP-CoS membrane at 30 °C, [Co]/[N] = 1/10, [Co] = 1.2 wt%, thickness 40 μm.

under the atmosphere without oxygen, followed by drying in vacuo, to yield a transparent and flexible membrane. Color of the membrane was changed reversibly from brown to deep violet on exposure to oxygen and nitrogen. Spectral change of the membrane shown in Fig. 1 agreed with that of the polymer-CoS complex previously reported[4]: UV and visible absorption maxima λ_{max}390, 555 nm(oxy: Co/O_2 = 1/1 adduct), λ_{max} 345, 410 nm(deoxy: five coordination), isosbestic points at 335, 425 nm. The absorbance at 555 nm in response to partial oxygen pressure $p_2(O_2)$ was measured to give the oxygen-binding and -dissociation equilibrium curve: the oxygen-binding constant was calculated to be 1.1 x 10^4 $l \cdot mol^{-1}$ at 30 °C by using Drago's equation.[5] The relationship between $p_2(O_2)$ and Y^{-1}(Y: degree of binding) shown in Fig. 2 fitted with Langmuir isotherm, which supported the Langmuir type and the reversible oxygen-binding to the membrane.

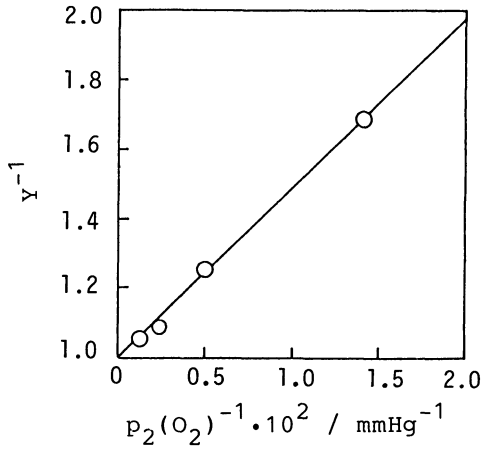


Fig. 2. Langmuir isotherm for the oxygen-binding to the OMP-CoS membrane at 30 °C, [Co]/[N] = 1/10, [Co] = 1.2 wt%, thickness 40 μm.

Time course of the oxygen-binding to the membrane was monitored spectroscopically. The oxygen-binding and -dissociation to CoS in the membrane of thickness 40 μm containing 1.2 wt% CoS attained to equilibrium within a few minutes. Rapid and reversible oxygen-binding to the CoS complex in the membrane was also confirmed by flash photolysis method (with pulse and laser flash spectrophotometer equipped with kinetic data processor). Photo-dissociation of the bound-oxygen to CoS in the membarne was successfully observed, which gave apparent oxygen-binding and -dissociation rate constants (k'_{on} = 3.85 x 10^5 $l \cdot mol^{-1}s^{-1}$, k'_{off} = 39 s^{-1}).

These results indicated that CoS acts as a binding site of Langmuir type for molecular oxygen and that oxygen-binding and -dissociation to complex are very rapid. Therefore it is expected in the oxygen permeation that the CoS complex in the membrane forms an additive pathway via the fixed carrier site of Langmuir type besides usual permeation one according to Fick's law.

Permeation coefficient of

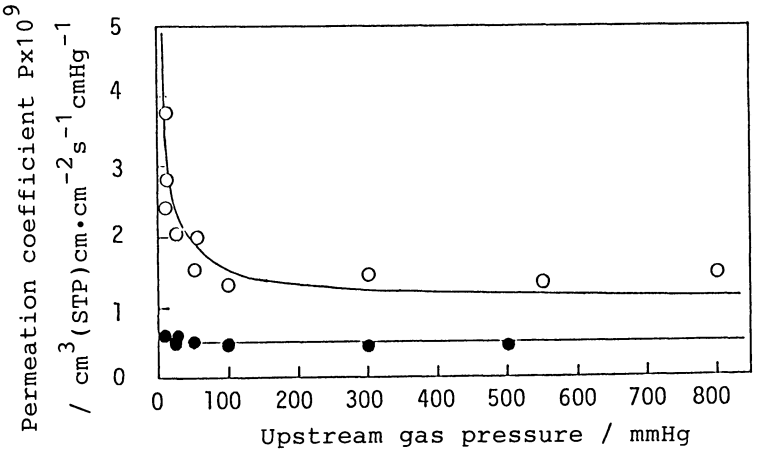


Fig. 3. Effect of upstream gas pressure on permeation coefficient for the OMP-CoS membrane at 30 °C, O: oxygen, ●: nitrogen, [Co]/[N] = 1/10, [Co] = 1.2 wt%, thickness 62 μm.

oxygen and nitrogen were measured with a low-vacuum apparatus. Permeability coefficient ratio $P(O_2)/P(N_2)$ was ca. 5 at 10 mmHg pressure of the upstream gas although it was ca. 3 at higher one. Figure 3 shows effect of upstream gas pressure(p_2) on $P(O_2)$ and $P(N_2)$ for the membrane containing 1.2 wt% CoS. $P(N_2)$ for the complex membrane and $P(O_2)$ for the octylmethacrylate homopolymer (OMA) and the OMP membranes are independent of p_2. But $P(O_2)$ increases with the decrease in $p_2(O_2)$. p_2-Dependence of P has been reported for the carbon dioxide permeation in glassy polymer membranes,[6] and dual mode transport mechanism shown by Eq. 1 was proposed.[7]

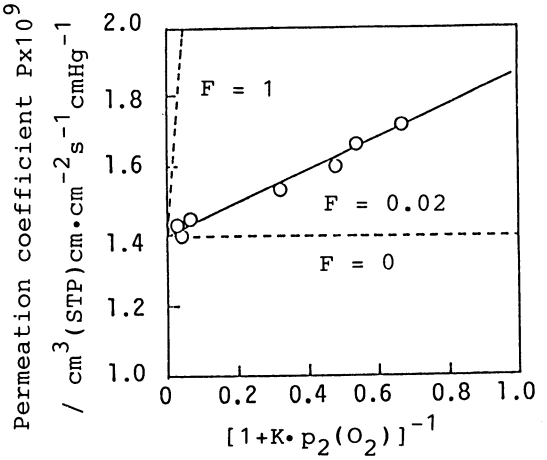


Fig. 4. Relationship between $(1 + K\ p_2(O_2))^{-1}$ and permeation coefficient in the OMP-CoS membrane at 30 °C, [Co]/[N] = 1/10, [Co] = 1.2 wt%, thickness 62 μm.

$$P = k_D \cdot D_D\ [1 + F \cdot R/(1 + K \cdot p_2)] \qquad (1)$$

$F = D_C/D_D$ $\qquad R = C_C \cdot K/k_D$

P: permeation coefficient, k_D: solubility coefficient for Henry's law, D_D and D_C: diffusion coefficient for Henry type and Langmuir type diffusion, C_C: amount of binding site or fixed carrier, K: oxygen-binding and -dissociation equilibrium constant, p_2: upstream gas pressure

That is, P is eqaul to the sum of the first term representing Henry mode and the second term for Langmuir mode which is a function of p_2. Figure 4 shows the plots for $(1+K \cdot p_2)^{-1}$ vs. P. As the linear relationship agreed with Eq. 1, $k_D \cdot D_D$ and $F \cdot R$ were determined from the intercept and the slope; F value was calculated to be 0.02. Where R was estimated to be 15 from the amount of CoS in the membrane.

On the other hand, time-lag for the dual mode transport is given as follows.[7]

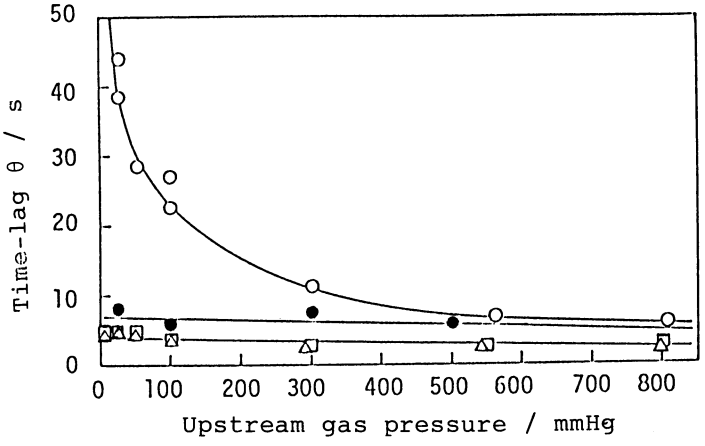


Fig. 5. Effect of upstream gas pressure on time-lag for the OMP-CoS membrane at 30 °C, ○: OMP-CoS, △: OMP, □: OMA, open plot: oxygen, cloed plot: nitrogen [Co]/[N] = 1/10, [Co] = 1.2 wt%, thickness 62 μm.

$$\theta = l^2/6D_D\ [1 + f(F, R, K, p_2)] \qquad (2)$$

l: thickness

$f(F, R, K, p_2)$ is a function which decreases with p_2.[7] Time-lag is also similarly expressed as the sum of the Henry mode and the Langmuir mode. Figure 5 shows the dependence of time-lag on p_2. Time-lag on oxygen permeation in the membrane decreases with $p_2(O_2)$ while time-lag on nitrogen permeation is independent of $p_2(N_2)$.

The above mentioned permeation behavior supported the dual mode transport of oxygen in the membrane and the pathway of oxygen permeation via the fixed carrier.

This works is partially supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan, and Asahi Glass Foundation for Industrial Technology.

References

1) E. Tsuchida, H. Nishide, M. Yuasa, E. Hasegawa, Y. Matsushita, and K. Eshima, J. Chem. Soc., Dalton Trans., 1985; E. Tsuchida, Ann. New York Acad. Sci., 446, 429 (1985); Chem. Eng. News, 14 Jan, 42 (1985).
2) H. Hirai, K. Wada, and M. Komiyama, Chem. Lett., 1983, 361.
3) T. Nakagawa and S. Yamada, "Kagaku Sosetsu", ed by the Chemical Society of Japan, the Scientific Societies Press, Tokyo(1984), No.45, p. 93.
4) E. Tsuchida, J. Macromol. Sci., Chem., A13, 545 (1979).
5) T. J. Beugelsdijk and R. S. Drago, J. Am. Chem. Soc., 97, 6466(1975).
6) W. J. Koros, D. R. Paul, and A. A. Rocha, J. Polym. Sci., Polym. Phys. Ed., 14, 687 (1976); W. J. Koros and D. R. Paul, *ibid.*, 16, 2171 (1978).
7) D. R. Paul and W. J. Koros, J. Polym. Sci., Polym. Phys. Ed., 14, 675 (1976); D. R. Paul, Ber. Bunsenges. Phys. Chem., 83, 294 (1979).

(Received October 14, 1985)