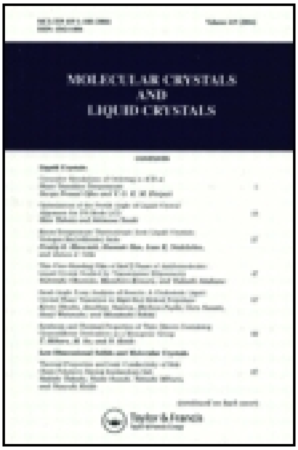

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High Oxygen-Binding Affinity of Poly(4-Vinylimidazole-*co*-octylmethacrylate)-Cobaltporphyrin Complex: Effect of Hydrogen-Bond at the Imidazole Residue

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The oxygen-binding affinity of the cobalt-picketfence-porphyrin (CoP) ligated with imidazole was enhanced in the presence of an additive which forms a hydrogen-bond with the ligated imidazole. The CoP complex with poly(4(5)-vinylimidazole-*co*-octylmethacrylate) rapidly and reversibly bound oxygen and showed very high oxygen-binding affinity: The oxygen transport in the CoP-polymer membrane was efficiently facilitated.

Keywords: cobaltporphyrin; polymer complex; oxygen binding; polymer ligand

INTRODUCTION

The authors have been studying metalloporphyrins as an efficient oxygen carrier and applied them to oxygen-permselective membranes.[1,2] Among them, the authors have demonstrated selective oxygen transport in the solid polymer membranes containing the cobalt-picketfence porphyrin[3] (*meso*-tetrakis(α, α, α, α-*o*-pivalamidophenyl)-

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* (CREST Investigator, JST)

porphyrinatocobalt(II): CoP in CHART 1). The CoP complexed with a solid polymer-ligand acted as a fixed carrier of oxygen and facilitated the transport of oxygen relative to components such as nitrogen in a feed stream. This specific and reversible oxygen-binding reaction established a steep gradient in the oxygen concentration across the membrane from the feed stream side to the product stream side and yielded the facilitated or the carrier(cobaltporphyrin)-mediated oxygen transport (CHART 2).[2,4] The oxygen permeation coefficient through the polymer membranes depends on the solubility of oxygen in the membranes: Selective enhancement of the oxygen solubility into the membrane ascribed to the oxygen-binding reaction of CoP leads higher oxygen permeation and selectivity. That is, the high oxygen-binding affinity of CoP is essential to increase the oxygen permeability for the facilitated transport membrane.

It has been described that the oxygen-binding affinity of CoP correlates to the basicity of a nitrogeneous ligand which coordinates to the 5th position of Co:[2] *E.g.*, an imidazole ligand gives higher oxygen affinity of CoP in comparison with a pyridine ligand. Valentine *et al.* reported,[5] in connection with the ligand basicity, more negative shifts of the redox potential for ironporphyrin complexes which contain a hydrogen-bond at the imidazole ligands. In this paper, the authors succeeded in enhancing both the oxygen-binding affinity of CoP and the facilitated oxygen transport by preparing the membrane of CoP

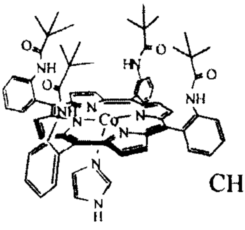


CHART 1

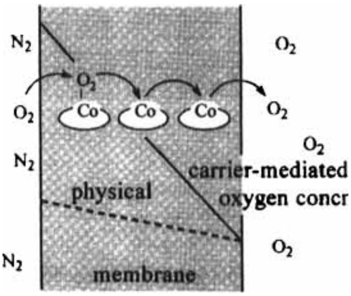


CHART 2

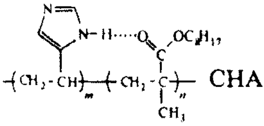


CHART 3

complexed with poly(4(5)-vinylimidazole-*co*-octylmethacrylate) (CHART 3) which contains a hydrogen-bond at the imidazole residue.

RESULTS AND DISCUSSION

The oxygen-binding affinity of the CoP complexes with various aromatic nitrogeneous ligands was evaluated, by measuring the oxy-deoxy visible spectral change (λ_{max}=550 and 532 nm for oxy and deoxy, respectively) of the toluene solution of the CoP complexes (FIGURE 1). The oxy (binding) equilibrium curves obeyed the Langmuir isotherms to give the oxygen-binding affinities p_{50} (oxygen partial pressure at which half of the CoP binds with oxygen) summarized in TABLE 1. The CoPs ligated with imidazoles have a stronger affinity (smaller p_{50} values) than the CoPs with pyridine and aniline; the affinity relates to the basicity of the axial aromatic nitrogeneous ligand of CoP.

The strong oxygen affinity of the CoP-imidazole complex was further increased by adding a small excess of hydrogen-accepting molecules involving a carbonyl group to the CoP solution (TABLE 2). A typical example to induce the affinity increase was methacrylate, which is assumed to externally form a hydrogen-bond with the hydrogen of the CoP-ligated imidazole and to increase the basicity of the imidazole.

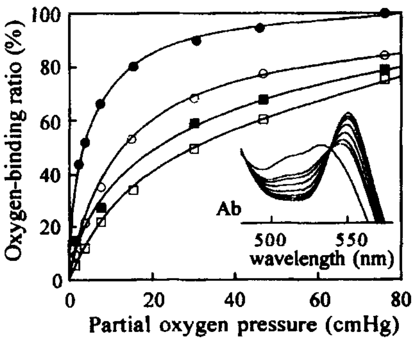


FIGURE 1 Oxy (binding) equilibrium curves for the CoP complexes ligated with poly(4-vinylimidazole-*co*-octylmethacrylate)(●), imidazole(○), 1-methylimidazole(■), and pyridine(□) in the toluene solution at 25°C. Inset: Visible absorption spectral change at different prtial oxygen pressure from 0 to 76 cmHg for the CoP complex.

TABLE 1 Oxygen-binding affinity (p_{50}) of the CoP complexes[a]

ligand	p_{50}/cmHg
1-benzylimidazole	4.2
lithium imidazolium	7.5
1-methylimidazole	14
1-vinylimidazole	19
imidazole	21
pyridine	28
aniline	230

a: toluene solution, [CoP]= 20 μM, [ligand]/[CoP] =10, at 25°C

TABLE 2 Oxygen-binding affinity of the CoP-imidazole complex in the presence of additives[a]

additives	p_{50}/cmHg
none	21
ethyl urea	13
pyrrolidone	12
octylmethacrylate	8.6

a: toluene solution, [CoP]= 20 μM, [imidazole]/[CoP]= 10, [additive]/[imidazole]= 10, at 25 °C

A copolymer of 4(5)-vinylimidazole and octylmethacrylate (CHART 3) was designed and synthesized as a polymer-ligand of CoP. 4(5)-Vinylimidazole was prepared by decarboxylation of urocanic acid,[6] and octylmethacrylate was selected because of not only its hydrogen-accepting capability but the rubbery nature of its polymer.

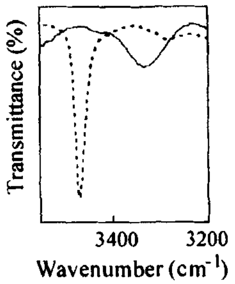


FIGURE 2 IR spectra of the poly(4-vinylimidazole-*co*-octylmethacrylate)(—) and the dilute imidazole(······) in chloroform.

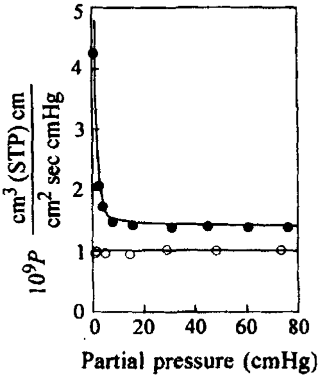


FIGURE 3 Permeation coefficient of oxygen(●) and nitrogen(○) for the membrane of the CoP-poly(4-vinylimidazole-*co*-octylmethacrylate) complex at various partial oxygen(●) and nitrogen(○) pressure of the feed stream. [CoP]=10 wt%, at 25°C.

The copolymer (mol. wt. = 8.3 x 10^4, the imidazole content: *m* in CHART 3 = 26 mol%, glass transition temperature = 19°C) was soluble in common solvents such as chloroform and toluene. IR spectroscopy (FIGURE 2) shows $\nu_{N\text{-}H}$ = 3320 and 3488 cm^{-1} for the copolymer and the dilute imidazole in chloroform, respectively, and that the copolymer contains an intra-(or inter-)molecular hydrogen-bond $N\text{-}H\cdots O{=}C$ between the imidazole hydrogen and the methacrylate carbonyl group.

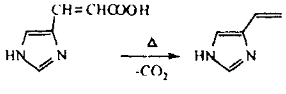
The membrane of the CoP-copolymer complex was homogeneously and deeply red colored and was still flexible even after the CoP complexation and the hydrogen-bonding formation in the copolymer. The membrane piece reversibly displayed a rapid oxy-deoxy spectral change in response to the partial oxygen pressure of the atmosphere. The oxy equilibrium curve of the CoP-copolymer complex locates at the lower partial oxygen pressure in FIGURE 1: The p_{50} value was 3.6 cmHg and the oxygen affinity of CoP was significantly augmented for the CoP-copolymer complex.

FIGURE 3 shows the permeation coefficients of oxygen and nitrogen (P_{O2} and P_{N2}) for the CoP-copolymer membrane. P_{O2} is larger than P_{N2} and steeply increases with a decrease in the feed stream partial oxygen pressure. These results indicate that the CoP fixed to the membrane facilitates oxygen transport and that the CoP-copolymer complex with very high oxygen affinity acts more efficiently for a feed stream at extremely low partial oxygen pressures.

EXPERIMENTAL SECTION

Materials. CoP was synthesized as in the literature.[3] 4(5)-Vinylimidazole was prepared by decarboxylation of urocanic acid upon heating (SCHEME)[6]: 5g of urocanic acid was heated at 230°C and recrystallized from water to yield 4(5)-vinylimidazole (mp 84°C). Yield 1.9g (57%).

The copolymerization procedure was as follows. 0.10 g (1.1 mmol) of 4(5)-vinylimidazole and 0.89 g (4.5 mmol) of octylmethacrylate were dissolved in 2 ml of benzene, and 1 μg of azobisisobutyronitrile was added. This was degassed, sealed, and then heated at



SCHEME

80°C for 6 hr. The reaction mixture was added dropwise in a large amount of methanol. The precipitate was dissolved in chroloform and purified by reprecipitation. Yield 0.37g (37%). Molecular weight of the copolymer was determined to be $M_w = 8.3 \times 10^4$ and $M_w/M_n = 1.3$ by a light-scattering moleclar weight analyzer Tosoh LS-8000. The copolymer composition was determined to be 26 mol% by elemental analysis.

Membrane Preparation. The chloroform solution of the copolymer and CoP were mixed to ligate the imidazole residue of the copolymer to the 5th coordination site of CoP. The solution was cast on a Teflon plate under an oxygen-free atmosphere, followed by drying in vacuo, to yield a deeply red-colored membrane with a thickness of 2–60 μm and containing 2–10 wt% CoP.

Permeation Measurement. Oxygen and nitrogen permeation coefficients for various feed stream gas pressures were measured with a low-vacuum permeation apparatus (Rika Seiki Inc. Model K-315 N-03).

Acknowledgement

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