

## Preparation and Oxygen Binding Properties of Ultra-Thin Polymer Films Containing Cobalt(II) meso-Tetraphenylporphyrin via Plasma Polymerization

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**Abstract :** Ultra-thin polymer films containing cobalt(II) meso-tetraphenylporphyrin(CoTPP) have been prepared by vacuum codeposition of the metal complex and *trans*-2-butene as an organic monomer using an inductively coupled RF glow discharge operating at 7-9 Watts. The polymer films were characterized by sorption measurements. Sorption data obtained for polymer films containing CoTPP indicate that the CoTPP molecules are capable of reversibly binding oxygen molecules. It was found that the adjacent CoTPP molecules in the aggregated metal complex phase could irreversibly share the oxygen molecules. A dispersion of the metal complex molecules in the polymer matrix was made to maintain the reversible reactivity of the metal complex molecules with oxygen in the polymer films via vacuum evaporation process. The Henry mode solubility constant, the Langmuir mode capacity constant, the amount of binding oxygen, and the dissociation equilibrium in the dual mode sorption theory were discussed.

**Keywords :** ultra-thin polymer film, metal complex, oxygen uptake, polymer/metal composite film.

### Introduction

In recent years there has been considerable interest in plasma and/or conventional polymer films containing metal complexes. Some works have concentrated exclusively on the production of films containing metal particles as discrete entities or as semi-continuous phases found mainly in the conventional polymer films.<sup>1-3</sup> The sublimation of low vapor pressure metal chelates into a plasma and codeposition onto a substrate has been attempted to make plasma polymer films containing metal complexes.<sup>4-8</sup> In general, plasma polymer/metal composite films can be widely applied to bio-medical applications due to their good biocompatibility<sup>9,10</sup> such as tissue replacement,<sup>11</sup> tissue reinforcement and organ transport, the minimal access surgery,<sup>12</sup> the replacement of ligaments,<sup>13</sup> and the shape memory microvalve to control drug delivery precisely.<sup>14</sup> Plasma polymer/metal composite films can be prepared by plasma polymerization of volatile organometallic compounds or by plasma polymerization accompanying metal evaporation. The latter method is preferred for the simultaneous incorporation of metal atoms/metal complexes into the polymer films and the compositional control of polymer matrix.

The metal complex is capable of reversibly binding oxygen, thereby promoting oxygen solubility in polymer matrix

resulting in considerable mass transport and/or adsorption of oxygen through the polymer matrix.<sup>15,16</sup> Oxygen adduction with transition metal complexes has been studied in order to gain an understanding of the nature of the metal-oxygen bond, for such applications as synthetic blood substitutes, solid phase oxygen sorbents, homogeneous catalysts for organic oxidation reactions, and models for the mono- and dioxygenase enzymes.<sup>6,7</sup> Many different environments are known to bind oxygen molecules. This sorption behavior has been described using the dual mode sorption theory originally developed for glassy polymers.<sup>4</sup> Metal complex is considered as the Langmuir site in the dual mode sorption theory. The objective of this paper is to prepare plasma polymer films containing metal complex and to get better understanding of reversible oxygen binding in the system as well as to achieve better dispersion of metal complexes in the prepared polymer matrix via a vacuum evaporation process.

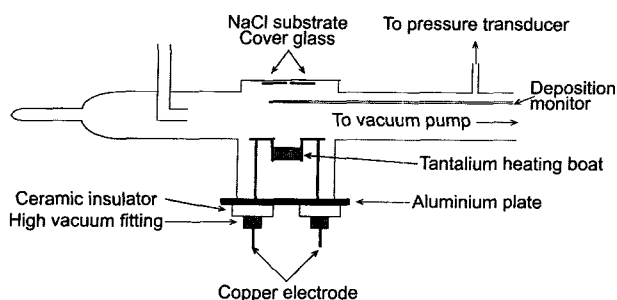
### Experimental

**Materials.** CoTPP (Cobalt(II) meso-tetraphenylporphyrin, Strem Chemicals, Inc.) as a metal complex and *trans*-2-butene (Matheson Gas Products, Inc.) as a comonomer were used as received.

**Metal Complex Sublimation.** Metal complex sublimation was carried out in the cylindrical reactor (inside diameter = 50 mm), as shown in Figure 1. An aluminium plate was used to seal the bottom of the reaction chamber by means of

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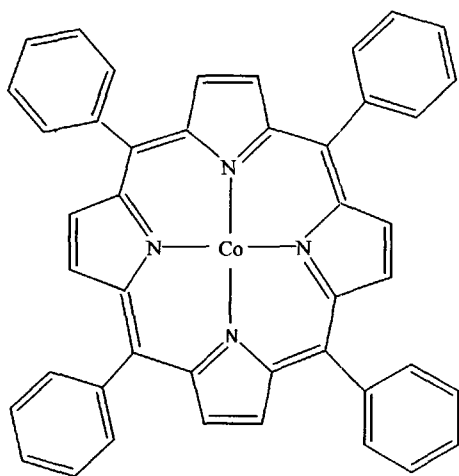
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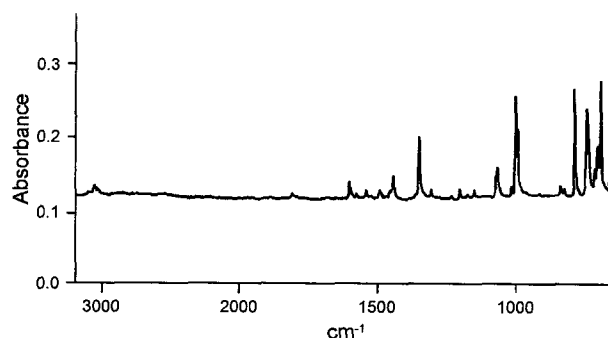
**Figure 1.** Schematic diagram of a reactor for metal chelate sublimation.

a viton O-ring. A tantalum heating boat, connected to two copper electrodes and covered with the lib which has a number of tiny holes, was placed inside the reactor. Two copper electrodes passed through two vacuum tight ports in the aluminium plate were connected to the heating power supply. Electrical insulation of the copper electrodes from the aluminium plate was provided by using two threaded ceramic plugs in the aluminium plate. A metal flag could be movable over the heating boat. Metal complex sublimation into the reactor and onto the substrate for spectroscopy sampling and a cover glass for sublimation rate measuring were placed on the inside top of the reactor right above the heating boat. As an alternative way of measuring the sublimation rate of metal complex, the deposition monitor was employed. CoTPP (Cobalt(II) meso-tetraphenylporphyrin) as a metal complex is stable in air and the chemical structure is shown in Figure 2. The weight difference before and after metal complex sublimation onto the cover glass was measured to get the mass thickness (sublimed film weight per unit area) of plasma polymer on the substrate.

**In-situ Plasma Polymerization.** Metal complex containing plasma polymer films were prepared in an inductively coupled cylindrical plasma reaction chamber under a con-



**Figure 2.** Structure of cobalt(II) meso-tetraphenylporphyrin.



**Figure 3.** FTIR spectrum of a 5% CoTPP-loaded plasma polymer film.

tinuous monomer flow, which has the same configuration as used for metal complex sublimation. Plasma polymer films were prepared from *trans*-2-butene. When a polymerizable plasma supporting gas is used, it is referred to as a "comonomer" with the metal complex, CoTPP. A FTIR spectrum for 5% CoTPP-loaded plasma polymer film is shown in Figure 3. The C=C stretching vibrations of *trans*-2-butene at 1000  $\text{cm}^{-1}$  and the aromatic stretching vibrations of CoTPP at 750, 1475, and 1600  $\text{cm}^{-1}$  appeared in a FTIR spectrum. The aromatic structure of CoTPP was preserved in the plasma polymer film according to two experimental evidences, FTIR peak assignment and oxygen uptake measurements. Typical experimental parameters are: RF power = 7.0~12 W (continuous power), monomer flow rate = 0.3~0.4 sccm, reactor pressure (no plasma) = 7.0~8.0 mTorr, reactor pressure (with plasma) = 9.0~14.0 mTorr, and heating boat current = 48~65 amps.

**Sorption Measurements.** Sorption data were obtained out to determine sorption isotherms using the sorption measurement apparatus, which consists of a cylindrical aluminium chamber and deposition monitor sensor. A cylindrical chamber was designed to sustain up to 10 atmospheric pressure. To measure the sorption amount, CoTPP/*trans*-2-butene plasma polymer was deposited onto the surface of the gold crystal (sensor) with maintaining a constant temperature of 35  $^{\circ}\text{C}$ , followed by evacuating for 24 h. High pressure(100~5,000 torr) was then introduced and oxygen binding was monitored.

## Results and Discussion

**Incorporating Metal Complex into Polymer Matrix.** Plasma polymer films were prepared using *trans*-2-butene as a comonomer. This comonomer supports the plasma for plasma polymer films and therefore provides the bulk of molecular fragments in the plasma, as well as the material for the plasma polymer matrix. The pressure in the glow discharge ( $P_g$ ) was monitored for each polymerization. The value of this pressure was found to decrease with increasing loading percent of complex in the polymer film, as shown in

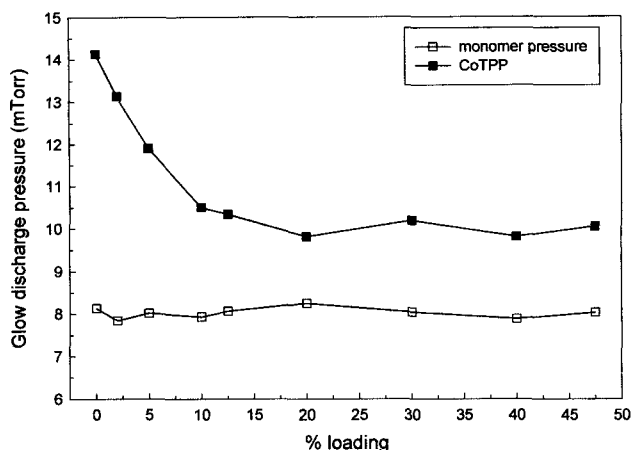


Figure 4. Plot of reactor pressure during glow discharge.

Figure 4. For CoTPP/*trans*-2-butene polymerization, the glow discharge pressure was the highest when no complex was being polymerized. The fact of decreasing glow discharge pressure with increasing loading percent of CoTPP supports that the bulk fragments of *trans*-2-butene in the plasma react with the functional groups of metal complex while plasma polymerization takes place and eventually a greater portion of the fragments is removed from the gas phase resulting in decrease in pressure.

As the concentration of metal complex in the plasma is increased with increasing percent loading, a greater portion of the fragments is removed from the gas phase due to the interactions between the *trans*-2-butene fragments and metal complex in the plasma, eventually transforming gas-phase fragments to solid-phase matrix, and the pressure in the glow discharge begins to decrease. It should be noticed that even without these interactions, a significant pressure reduction could be expected because the partial pressure of *trans*-2-butene would be lowered with increasing metal complex content. The thickness of polymer films depended on the deposition time period but was adjusted to be 100 nano meters in this work. The deposition rate was approximately 30 Å/min measured by a deposition monitor. The metal sublimation rate and the monomer supply rate were controlled by adjusting the heating current and monomer flow rate, respectively. To obtain the polymer matrix with uniform surface, the film deposition rate was strictly controlled within 30 Å/min. Over 25% loading of metal complex the plasma polymer deposition rate maintains constant and up to 48% loading of metal complex has been achieved.

**Oxygen Binding to Metal Center.** CoTPP has been chosen as a metal complex in this work since it is capable of binding oxygen reversibly and in a special case binding oxygen irreversibly. An oxygen molecule binds to the metal center by donating an electron pair ( $\sigma$ -bond).<sup>8,9</sup> This is accompanied by  $\pi$ -back donation of electron density to the oxygen molecule. The exchange of electron density must be balanced

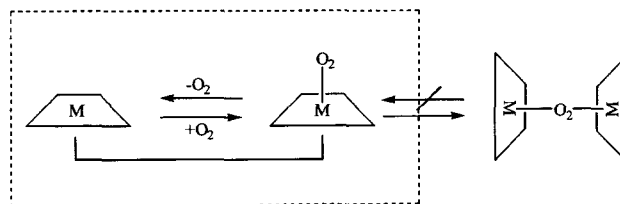


Figure 5. Schematic illustration of reversible and irreversible O<sub>2</sub> binding with metal complex.

properly to allow for reversible oxygen binding. In case of adjacent CoTPP molecules in the aggregated metal phase, irreversible oxygen binding occurs as schematically shown in Figure 5.

The reaction of the metal complex with oxygen can be represented:



where  $M$  is the metal complex and  $MO_2$  is the complex with bound  $O_2$ . The equilibrium constant for the above reversible reaction is

$$K_{eq} = \frac{[MO_2]}{[M][O_2]} \quad (2)$$

and

$$K_{eq} = \frac{k_{on}}{k_{off}} = \frac{k_f}{k_r} \quad (3)$$

where  $[MO_2]$  is the concentration of  $MO_2$ ,  $[M]$  is the concentration of the complex alone,  $k_{on} = k_f$  is the forward reaction constant,  $k_{off} = k_r$  is the reverse reaction constant.  $K_{eq}$  is obtained from the sorption measurement.

**Oxygen Uptake Kinetics.** The oxygen uptake or sorption datum has been fitted into the dual mode sorption model, which is expressed by the equation:

$$C = K_D P + \frac{C_H' b p}{1 + b p} \quad (4)$$

where  $C$  is the concentration of sorbed gas in  $\text{cm}^3(\text{STP})/\text{cm}^3$  polymer,  $K_D$  is the so-called Henry's law constant in  $\text{cm}^3(\text{STP})/\text{cm}^3$  polymer-cmHg,  $C_H'$  is the Langmuir mode capacity constant,  $b$  is the Langmuir affinity constant, and  $p$  is pressure. The first term in the above equation refers to Henry's law sorption and the second one describes the filling of microvoids or lower density regions which may partially immobilized as the Langmuir mode.

A typical oxygen binding curve is shown in Figure 6. Due to the pressure effect, the initial reading value of deposition monitor jumped up to a certain point. The actual oxygen binding curve is obtained by subtracting this blank curve. The capability of uptaking oxygen is remarkable compared to that in the conventional glassy polymer films due to the presence of reactive sites in the polymer films. The uptaking

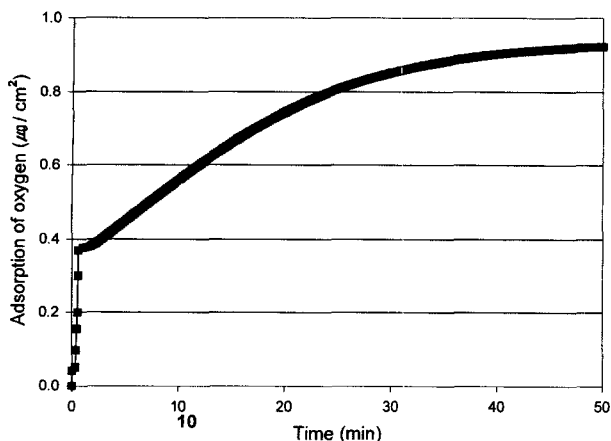


Figure 6. Typical oxygen binding curve for 5% loading of CoTPP.

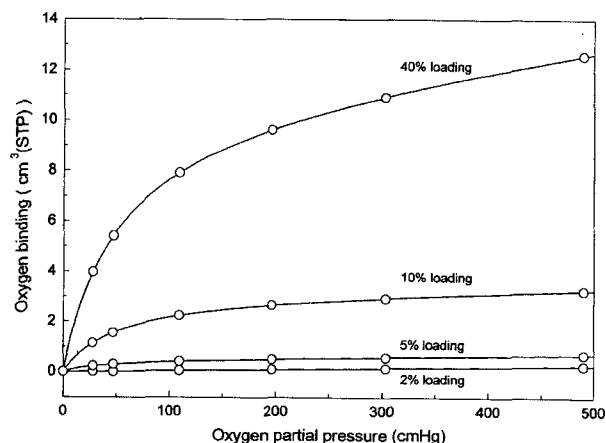


Figure 8. Dual mode sorption isotherms for various loading of CoTPP.

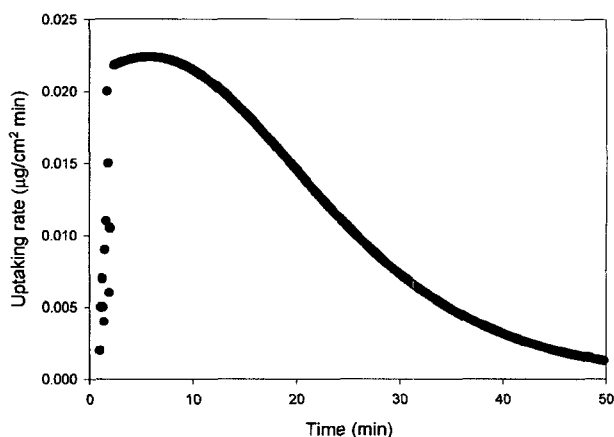


Figure 7. Oxygen uptaking rate for 5% loading of CoTPP.

rate, as shown in Figure 7, reaches its maximum value at the early stage of oxygen binding and then gradually decreases until the adsorptive reaction reaches equilibrium. During the adsorptive reaction autoacceleration behavior was not observed.

Dual mode sorption parameters are obtained from the Eq. (4) by iteration using the nonlinear regression program and shown in Table I. Dual mode sorption isotherms are plotted with perfectly matching with experimental data in Figure 8,

in which solid lines indicate that the theoretical isotherms calculated by substituting dual sorption mode parameters to the model equation provide well defined oxygen binding behavior. The model equation to analyze the sorption behavior shows a good agreement with the experimental data. Langmuir capacity constant increases linearly with increasing % loading of CoTPP and Langmuir mode solubility is extremely high while the Henry's law solubility constants maintain almost same at lower values. The results of sorption measurements showed that metal complex molecules in the polymer film are considered to have chances to reversibly share the oxygen molecules. In the repeated sorption measurements, it has been observed that the oxygen binding capability of metal complex molecules gradually decreases possibly due to the irreversible oxygen binding with adjacent metal complex molecules.

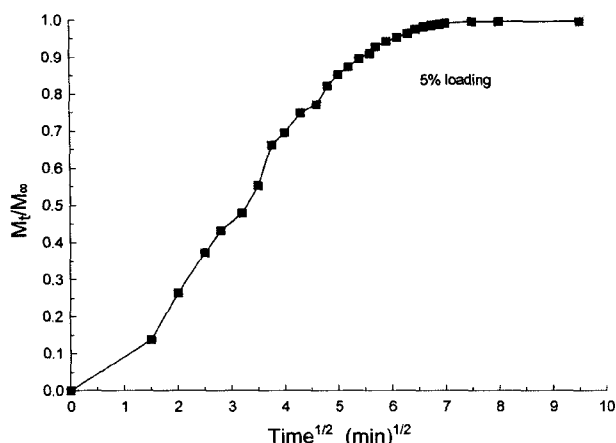
The overall diffusion coefficient ( $D$ ) was obtainable by plotting the amount of binding oxygen versus the square root of time using the Eq. (5), which is widely used to estimate the diffusion coefficient for the mass transport through the polymer film:

$$\frac{M_t}{M_\infty} = \frac{4D}{l\pi} t^{\frac{1}{2}} \quad (5)$$

where  $M_\infty$  is the amount of binding oxygen at the equilib-

Table I. Parameters of Dual Mode Sorption Model

Loading	$K_D$ ( $\text{cm}^3(\text{STP})/(\text{gm cmHg})$ )	$C_H'$ ( $\text{cm}^3(\text{STP})/\text{gm}$ )	$K_{eq}$ ( $1/\text{cmHg}$ )	Diffusion Coefficient ( $\text{cm}^2/\text{sec}$ )
2%	0.0005	0.47	0.03	$7.0 \times 10^{-13}$
5%	0.0010	0.91	0.03	$9.20 \times 10^{-13}$
10%	0.0008	3.13	0.02	$8.1 \times 10^{-13}$
40%	0.0061	10.57	0.02	$8.4 \times 10^{-13}$



**Figure 9.** Typical kinetic run for  $O_2$  sorption for 5% loading of CoTPP.

rium state,  $M_t$  is the amount of binding oxygen at a certain time,  $l$  is the thickness of the plasma polymer film, and  $t$  is time. The overall diffusion coefficient can be calculated from the slope of the sorption data plotted in Figure 9 using the Eq. (5). The sorption or mass transport behavior seems very similar to that shown in the conventional glassy polymer films.

The overall diffusion coefficients are very small due to the highly crosslinked polymer matrices, as shown in Table I. For better mass transport, the crosslinking density should be considered and controlled during the polymerization process. A lower crosslinking density would be preferred in the future work.

## Conclusions

The incorporation of a metal complex, CoTPP into *trans*-2-butene plasma polymer films has been achieved with up to 48% loading of metal complex. The thickness of the polymer films was about 100 nanometers and was controlled successfully. According to the results of sorption measurements, metal complex molecules in the polymer films are capable of binding oxygen reversibly, which indicates that the metal complex structure is conserved during plasma polymerization in the glow discharge phase because relatively low power has been employed (7–9 Watts). The results of sorption measurements showed that metal complex molecules in the polymer film have chances to reversibly share the oxygen molecules. Repeated sorption measurements

have shown that the oxygen binding capability of metal complex molecules gradually decreases possibly due to the irreversible oxygen binding with adjacent metal complex molecules. This metal/polymer composite film can be used as bio-compatible materials, particularly tissues where facilitated oxygen transport is strongly required.

Reversible binding of oxygen, with extremely high solubility, in the plasma polymer films containing metal complex has been successfully analyzed by the dual mode sorption theory, which fits experimental data within tolerance. Dual mode sorption parameters were determined by iterative calculation using a nonlinear regression program. Due to the high crosslinking density of polymer matrices, the overall diffusion coefficients were relatively small. Another attempt will be made to control the crosslinking density via photopolymerization in the undergoing work.

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