

NOTES

**Functional Metallomacrocycles and Their Polymers XXXIII.
Autoxidation of Thiol Catalyzed by Thermoelastic
Polyurethane Resin Containing a Cobalt(II)phthalocyanine**

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Metallophthalocyanine has attracted considerable interest because of its structural similarity to the active center of naturally occurring haemoenzymes. We studied a series of functional metallophthalocyanines and their polymers as models for *catalase*, *peroxidase*, and *oxidase*.^{1–5}

Foul odor is emitted from the spoiled garbage and sewage. Such foul odor results from mercaptan, hydrogen sulfide, and ammonia. Recently, we found that mercaptan and hydrogen sulfide decomposes through the catalytic reaction of Fe(III)- and Co(II)-phthalocyanine supported on rayon staple fiber. Using this fact, we developed a new type of biomimetic odor-removing fiber.^{6,7}

Quite recently, we synthesized thermoelastic polyurethane (TPU) resins containing metallophthalocyanine ring (M-pc, M = Fe(III), and Co(II)) in the chain.⁸ The introduction of metallophthalocyanine units in a polyurethane had no negative influence upon the principal properties of the practical polyurethane such as melting behavior, dynamic viscoelasticity, tensile properties and thermal properties. These resins may be useful as odor-removing films and fibers.

The autoxidation of thiols was investigated to develop catalysts which could be used for disulfurization of natural odor gas and oil, as well as to clarify the enzymatic removal of thiols.

Numerous attempts have been made in recent years to determine the mechanism of aerobic oxidation of thiols catalyzed by cobaltophthalocyanine polymeric systems. However, no evidence for the reaction catalyzed by polymers containing Co(II)-pc in the main chain has been presented. To evaluate the catalytic ability of this Co(II)-pc containing polyurethane, we examined the aerobic oxidation of 2-mercaptoethanol catalyzed by Co(II)-pc containing polyurethane in aqueous solution. Metallophthalocyanine immobilized into the polymer matrix becomes stable and can be repeatedly utilized. Therefore, the stability of the polymer catalyst for the thiol autoxidation reaction was also studied.

EXPERIMENTAL

Materials

A thermoelastic polyurethane resin containing a cobalt(II) phthalocyanine ring in the

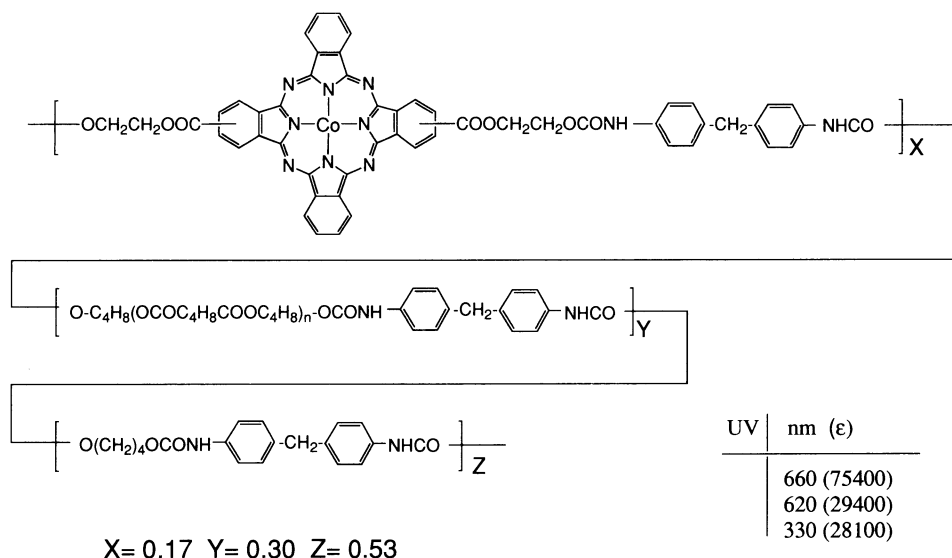


Figure 1. Structure of thermoeleastic polyurethane resin containing a cobalt(II) phthalocyanine ring in the chain.

chain (Figure 1) was prepared by the copolyaddition of 4,4'-diphenylmethane diisocyanate (MDI) with a mixture of poly(butyleneadipate)glycol (PBA), 1,4-butanediol and cobalt(II)-phthalocyanine bis(2-hydroxyethyl carboxylate) (Co(II)-dapc) as described previously.⁸ The copolymer was purified by reprecipitation from *N,N'*-dimethylformamide solution with water and ground to a powder (50–70 μm diameter). The copolymer contained 0.5 mol% Co(II)-pc ring. 2-Mercaptoethanol (RSH) and other reagents were of analytical grade. Deoxygenated doubly distilled water was used to prepare all solutions. Co(II)-dapc, a low molecular weight compound of Co(II)-pc-TPU was also prepared and purified as described in a previous paper.⁹

Measurement of Catalytic Activity

The reaction rates of autoxidation of thiol in the presence of the catalysts were measured based on the oxygen consumption in the reaction mixture with a micro oxygen electrode. All the experiments were conducted at 20–30°C at a shaking speed of 150 rpm. Various pH solutions of RSH were prepared by mix-

ing 0.2 M- Na_2CO_3 and 0.2 M- NaHCO_3 aqueous solution. The exact concentration of RSH stock solution was determined by reaction with a I_2 solution, followed by titrating excess I_2 with a $\text{Na}_2\text{S}_2\text{O}_3$ solution. The initial reaction rate, $V_0 = -d[\text{O}_2]/dt$ (in $\text{mol}^{-1} \text{s}^{-1}$) was taken from the slope of the oxygen consumption. Actually, the amount of RSH oxidized by that of oxygen was calculated from the amount of oxygen consumed.

RESULTS AND DISCUSSION

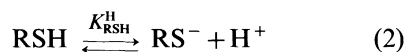
Figure 2 shows the amount of oxygen consumed in the autoxidation of RSH catalyzed by Co(II)-pc-TPU in aqueous solution at pH 10.3 and 30°C. Oxygen consumption was observed using Co(II)-pc-TPU as a catalyst. Oxygen consumption was little using the copolyurethane without Co(II)-pc. The autoxidation of thiols obeys eq 1, in which the consumption of 4 molecules of RSH in accompanied by that of 1 molecule of O_2 . From Figure 2, the polymer catalyst containing Co(II)-pc catalyzed the autoxidation of RSH in the presence of oxygen.



From the rate of oxygen consumption given Figure 3, catalytic activity (mol thiol/mol M_{pc} unit min^{-1}) was obtained (Table I). The catalytic activity of dicarboxyphthalocyaninatocobalt(II) (Co(II)-dapc) was also obtained from the rate of oxygen consumption.

The oxidation reaction of RSH in the presence of Co(II)-pc-TPU was carried out at various pH. Figure 3 shows the dependence of initial reaction rate (V_0) on pH. V_0 increased with pH from 8 to 10 and decreased after passing a maximum at pH 10.5. This is con-

sidered due to the dissociation of RSH, as shown in eq 2, where RS^- donates $^-\text{SCH}_2\text{-CH}_2\text{OH}$ species and $K_{\text{RSH}}^{\text{H}}$ is the dissociation constant of thiol group.



The reactive species for the autoxidation of RSH is RS^- formed by the dissociation of RSH at high pH condition ($\text{p}K_{\text{a}} = 9.60$). The change of V_0 brought about increased of RS^- concentration at high pH. It is thought that the decrease in V_0 above pH 10.5 caused competitive inhibition by increasing the concentration of hydroxide ion. Figure 4 shows

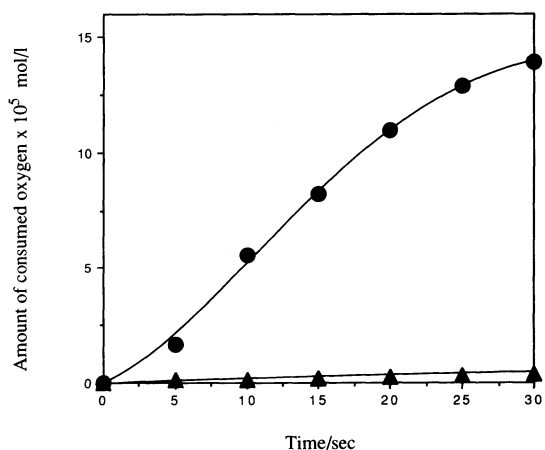


Figure 2. Autoxidation of 2-mercaptoethanol catalyzed by Co(II)-pc-TPU (●) and TPU (▲) in aqueous solution. $[\text{Co(II)-pc-TPU}]$, $[\text{TPU}] = 1 \times 10^{-3} \text{ g l}^{-1}$ ($1.1 \times 10^{-5} \text{ mol l}^{-1}$); $[\text{RSH}]_0 = 2.5 \times 10^{-2} \text{ mol l}^{-1}$; $[\text{O}_2]_0 = 2.4 \times 10^{-4} \text{ mol l}^{-1}$; pH = 10.3 at 30°C.

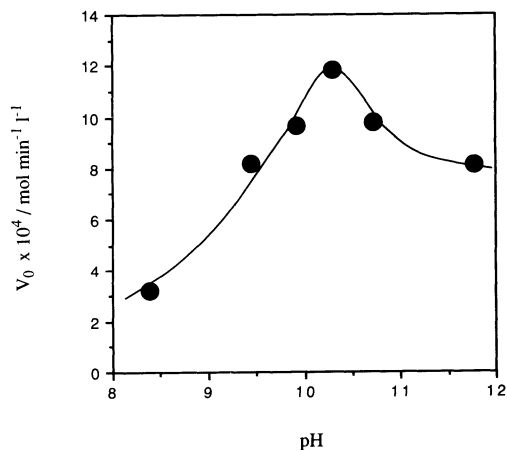


Figure 3. pH dependence on initial autoxidation rate (V_0) of 2-mercaptoethanol catalyzed by Co(II)-pc-TPU in aqueous solution. $[\text{Co(II)-pc-TPU}] = 1 \times 10^{-3} \text{ g l}^{-1}$ ($1.1 \times 10^{-5} \text{ mol l}^{-1}$); $[\text{RSH}]_0 = 2 \times 10^{-2} \text{ mol l}^{-1}$; $[\text{O}_2]_0 = 2.4 \times 10^{-4} \text{ mol l}^{-1}$ at 25°C.

Table I. Kinetic parameters for the autoxidation of 2-mercaptoethanol catalyzed by Co(II)-pc-TPU and Co(II)-dapc at 30°C in aqueous solution at pH 10.3

	O_2 Consumption	$[\text{RSH}]$	$[\text{Catalyst}]$	Turnover number ^a
	$\text{mol l}^{-1} \text{ min}^{-1}$	mol l^{-1}	mol l^{-1}	
Co(II)-pc-TPU	1.12×10^{-3}	3.75×10^{-2}	1.10×10^{-5}	101
Co(II)-dapc	2.26×10^{-4}	3.75×10^{-3}	9.12×10^{-8}	2480

^a Turnover number = $\frac{\text{O}_2 \text{ consumption}}{[\text{catalyst}]} (\text{min}^{-1})$.

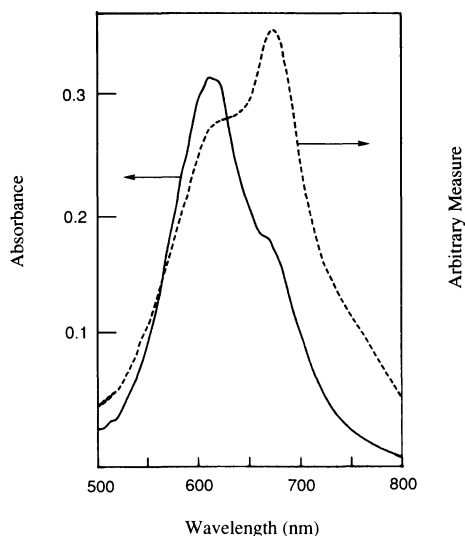


Figure 4. Electronic spectra of Co(II)-pc-TPU(---) in film and Co(II)-dapc(—) in aqueous solution at pH 10.3.

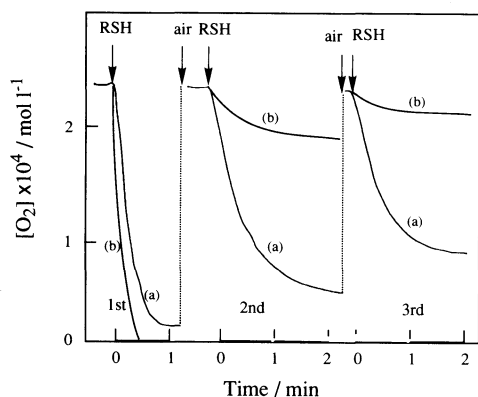


Figure 5. Change in dioxygen concentration with oxidation of 2-mercaptoethanol: $[\text{Co(II)-pc-TPU}] = 5 \times 10^{-3} \text{ g l}^{-1}$ ($5.5 \times 10^{-5} \text{ mol l}^{-1}$); $[\text{RSH}]_0 = 6.25 \times 10^{-4} \text{ mol l}^{-1}$; $[\text{O}_2]_0 = 2.4 \times 10^{-4} \text{ mol l}^{-1}$; pH = 10.3 at 30°C . (a) Co(II)-pc-TPU; (b) Co(II)-dapc.

the visible spectra of the film of copolyurethane containing Co(II)-pc and aqueous solution of Co(II)-dapc.

The visible spectrum of Co(II)-dapc exhibited absorption with a peak around 620 nm and a shoulder around 680 nm. The absorption band at 680 nm is a monomeric species of Co(II)-pc, and that at 620 nm is a dimeric

species.¹ From the spectra, it can be seen that the absorption coefficient at 620 nm of Co(II)-pc bound to the copolyurethane is lower than that of Co(II)-dapc. This suggests that the aggregation of Co(II)-pc is restricted in copolyurethane by the steric hindrance of the polymer chain. Catalytic activity for autoxidation of RSH by aggregated Co(II)-pc is slightly lower than that of monomeric species.⁴ For the copolyurethane, catalytic activity is nevertheless about one-twenty fifth smaller than that for Co(II)-dapc. This may be attributed to the fact that the oxidation may mainly proceed on the surface of the polymer. No reaction may occur at the inner part of copolyurethane. The color of Co(II)-dapc used for the autoxidation of RSH varied from initially green to yellow at the end during the reaction. This means the decomposition of Co(II)-dapc in the process of catalytic reaction. Immobilized natural enzymes on the polymer matrix become stable. Therefore, repeated runs of the autoxidation of thiol catalyzed by Co(II)-pc-TPU were examined. As shown in Figure 5, the Co(II)-pc-TPU is very stable compared with Co(II)-dapc, a low molecular weight catalyst, and can be repeatedly utilized as catalyst for autoxidation of RSH. Co(II)-pc becomes a very stable catalyst for the autoxidation of RSH in the main chain of copolyurethane. Co(II)-pc-TPU can be molded into fibers, film, etc.

Therefore, Co(II)-pc-TPU resins are useful as a new disulfurization material of natural odor gases and oil.

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