

Reactivity of Poly(vinyl Chloride) Containing N-Methyl Dithiocarbamate Toward Metal Ions in Heterogeneous System and Effect of γ -Irradiation on the Reactivity

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Synopsis

The reaction of poly(vinyl chloride) containing N-methyl dithiocarbamate (PMD) with metal ions in a heterogeneous system and the effect of γ -irradiation on the reactivity were studied. PMD powder suspended in aqueous solutions did not show any reactivity toward metal ions. However, the PMD powder suspended in a methyl alcohol solution formed a chelate with various metal ions. The effects of the reaction time, pH, and the initial concentration of the metal ion were examined. PMD irradiated in methyl alcohol with γ -irradiation doses up to 28 Mrad was compared with the original PMD. The reactivity of the irradiated PMD toward the metal ions did not show any apparent decrease.

INTRODUCTION

One of the processes for the treatment of radioactive waste solutions containing radioactive metal ions is the use of ion exchange resins. However, the radiolysis of sulfonic acid-type cationic exchange resins in water leads to the decomposition of the acid groups.¹ One of the present authors reported that poly(vinyl chloride) containing about 11 mole-% N-methyl dithiocarbamate showed antiradiation property from the viewpoint of the evolution of gaseous products² and that the polymer reacted with metal ions in dimethylformamide solutions to form the insolubilized gels by chelate formation.³ Therefore, poly(vinyl chloride) containing N-methyl dithiocarbamate (PMD) might be expected to be a useful polymer for the treatment of radioactive waste solutions, provided that PMD powder were to show a reactivity toward metal ions in a heterogeneous system.

The purpose of the present investigation was to study the reactivity toward metal ions of a suspension of finely powdered PMD, and the effect of γ -irradiation on the reactivity. In this experiment, nonradioactive metal ions were used for reasons of convenience.

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EXPERIMENTAL

Synthesis of Poly(vinyl Chloride) Containing N-Methyl Dithiocarbamate

Poly(vinyl chloride) containing N-methyl dithiocarbamate was prepared according to the previously reported procedure from the reaction of poly(vinyl chloride) ($P = 800$) and sodium N-methyl dithiocarbamate.³ The degree of substitution of dithiocarbamate group to the polymer was controlled by the reaction time. The dry cotton-like polymer obtained in the final course of the synthesis was put into a vessel, then liquid nitrogen was added, and the polymer was ground to a fine powder below 0.5 mesh. Using this method, troubles due to static electricity were diminished.

Measurement of Amount of Metal Ion Reacted with the PMD Powder

A 0.3-g sample of the PMD powder was placed into a 100-ml glass-stoppered Erlenmeyer flask containing 20 ml of a solution containing 20 mmoles/l. metal ion. Then the vessel was partially immersed in a thermostat bath held to $\pm 0.5^\circ\text{C}$. The reaction temperatures ranged from 30° to 50°C . During the experiment, the vessel was agitated by shaking. After a given time, the powder was filtered and washed with distilled water. The concentrations of the metal ion in the filtrates were measured with a Perkin-Elmer Model 107 atomic absorption spectrometer. The amounts of the metal reacted with the PMD powder were calculated from the difference between the concentration of metal ion in the solution before and after the addition of the polymer. The following method was also sometimes used: about 100 mg PMD which had been reacted with metal ion was sealed in a thick glass tube with 1–2 ml fuming nitric acid, then heated at 250°C for about 5 hr. The tube was then cooled to room temperature, opened, and distilled water added. The concentration of metal ion in the solution was measured with an atomic absorption spectrometer.

γ -Irradiation of PMD

PMD was irradiated with cobalt 60 gamma-radiation. The total dose was about 30 Mrad, and the dose rate was 1.0 Mrad/hr.

Irradiation in Methyl Alcohol. About 6 g of the PMD powder was sealed with 60 ml methyl alcohol in a glass tube and irradiated at 23°C .

Irradiation in Air. About 8 g of the PMD powder was sealed in a glass tube under air and irradiated at 23°C .

These irradiated PMD samples were used for the reaction with the metal ions.

Measurements of Infrared Absorption Spectra and ESR Spectra

A Perkin-Elmer 180 high-resolution spectrometer with a dry nitrogen purge was used to study the $1500\text{--}3400\text{ cm}^{-1}$ region. For measurement of ESR spectra, samples of PMD film were put in a quartz tube and irradiated

with 10 Mrad at 23°C. The irradiated tube was stored in liquid nitrogen, and ESR spectra were measured at -196°C with a Varian E-9 ESR spectrometer.

RESULTS AND DISCUSSION

Fine PMD Powder

To remove metal ions efficiently from waste solutions, polymers with large surface areas are required. A few techniques such as a combination of dissolution of a polymer in a good solvent and reprecipitation with a poor solvent or mechanical grinding the cotton-like PMD in a vessel were carried out. However, in the former, the filtration was rather difficult because of the formation of a colloidal state of the PMD, and in the latter the static charge formed by grinding of hydrophobic polymer in a dry condition prevented continued grinding. Therefore, the method described in the experimental section was used to obtain a fine powder of PMD.

Heterogeneous Reaction of PMD with Metal Ions

Reaction in Aqueous Solution. It was considered that the reaction of PMD with metal ions in an aqueous solution was rather difficult because of the hydrophobic property of the polymer, i.e., the poor wettability of PMD powder to water. Therefore, the following two methods were tried. In the first method, the polymer was immersed in methyl alcohol and then a copper solution was added. In the second method, the polymer was pretreated with water containing about 20–25% dimethylformamide, dioxane, and hexamethyl phosphotriamide, respectively, as a swelling agent, and the copper solution was then added. As a result, in both cases, the amount of copper reacted or adsorbed with the PMD powder was only 0.03 meq/g polymer, and this value was equal to that for PVC. This means that only physical adsorption took place on the surface of the polymer and PMD did not show any reactivity toward copper ion in the aqueous system.

Reaction in Methyl Alcohol Solution. Methyl alcohol is a perfect nonsolvent but had wettability with PMD. Therefore, the reaction of PMD powder with copper ion was carried out in methyl alcohol solution. Solutions containing 2–20 mmoles copper acetate in 1 liter were used. The amounts of the copper ion reacted were calculated from the difference of the concentration of the copper ion. Unless stated otherwise, PMD-48 or PMD-68 whose degree of substitution was 14.0 mole-% was used. The effects of the reaction time, temperature, pH, and the initial concentration of copper acetate on the amount of the copper included in the PMD powder are shown in Figures 1a to 1c. As can be seen in Figure 1a, under the reaction condition of 50°C, 20 mmoles/l. copper acetate and 3 hr of reaction time, PMD powder contained 1.53 meq/g polymer of copper. However, PVC powder and PVC containing N,N-dimethyl dithiocarbamate group of 11 mole-% contained 0.02 meq/g polymer of copper under the same reaction condition. It is evident from these results that the amount of the copper included in the PMD powder was not due to the adsorption but was due to the reaction with the N-methyl dithiocarbamate groups in the heterogeneous system.

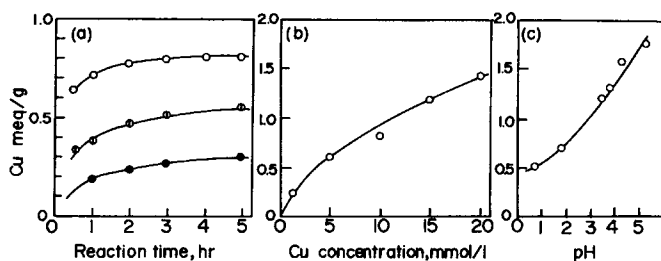
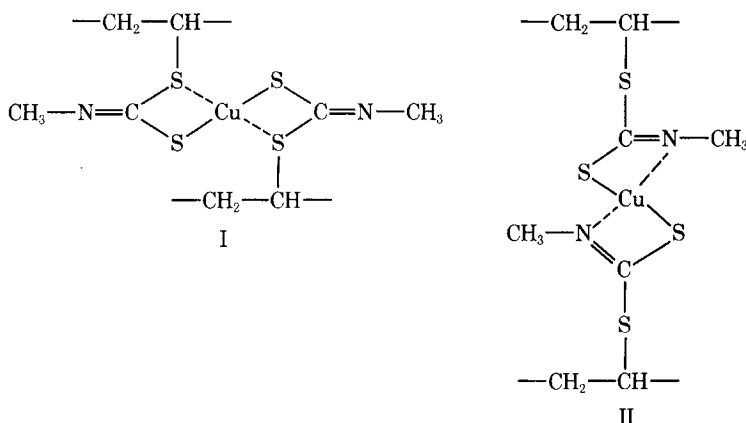


Fig. 1. Amount of copper reacted as a function of time (a), pH (b), and initial concentration (c). (a): (○) 50°C; (○) 35°C; (●) 20°C.

The following two forms were considered as the structure PMD reacted with copper ion:



The infrared spectra of PMD and Cu-PMD are shown in Figure 2. The typical changes of the high-resolution infrared spectra are summarized in Table I. In Table I and Figure 2, Cu-PMD means PMD reacted with copper. When the infrared spectra of PMD are compared with those of Cu-PMD, the most pronounced difference is the shift and decrease in $\nu_{\text{C-N}}$ absorption in the region of 1500 cm^{-1} . If Cu-PMD had the chelated structure as shown in I, the absorption of $\nu_{\text{C-N}}$ might not be changed remarkably. Therefore, it should be noted that the shift and decrease in $\nu_{\text{C-N}}$ in Cu-PMD are probably due to the coordination of copper, thus being decidedly in favor of structure II. From Figure 1a, it is seen that the rate of the reaction decreases with time and the amount of the reacted copper approached gradually a constant value. When the concentration was increased, the reacted amount also increased. These results showed the chemical equilibrium between the Cu-PMD and copper ion as follows:

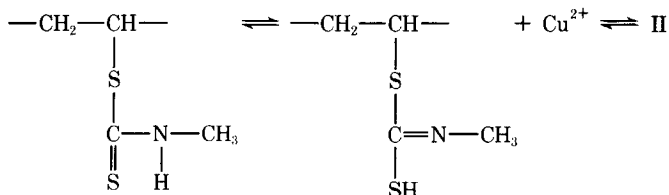
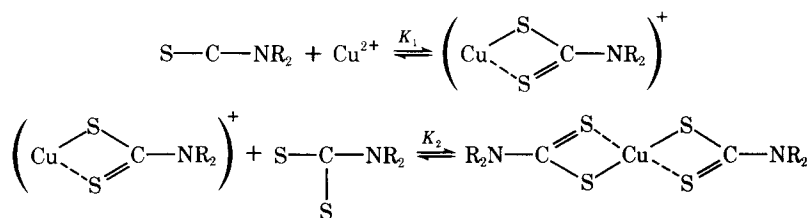


TABLE I
Change in Infrared Absorption for PMD and Cu-PMD

Assignment	Wave number, cm^{-1}	
	PMD	Cu-PMD
$\nu_{\text{N-H}}$	3360	decrease
$\nu_{\text{C-N}}(\text{—N—C=S})$	1502	1513, decrease
$\nu_{\text{C-N}}(\text{—C—N(—C=S)})$	1338	1333, decrease
$\nu_{\text{C=S}}$	1163	1167, decrease
$\nu_{\text{C=S}}$	1032	decrease
—S—C—N— $\quad \quad \quad \parallel$ $\quad \quad \quad \text{S}$	933	decrease

In order to confirm this, 103.5 mg Cu-PMD containing 1.53 mg/g polymer of copper was sealed with 50 ml water-methyl alcohol (20/80 vol-%) in a glass tube and shaken for about 20 hr at 50°C; 1.7 mg copper was detected in this solution. This means that 0.54 mg/g polymer was resolved out. These results suggested that the reaction between PMD and copper ion was at equilibrium. In the case of a low molecular weight model compound, it was reported that the following equilibrium was seen in the reaction between sodium N,N-dialkyl dithiocarbamate and copper ion or zinc ion⁴:



It was shown from the formula of Cu-PMD that 2 moles N-methyl dithiocarbamate reacted with 1 mole Cu^{2+} . Therefore, the content of 1.4 meq/g polymer means that about 73% dithiocarbamate group reacted with the copper. It was also shown that the color of PMD powder changed from pale yellow to amber or brown gradually as the reaction proceeded.

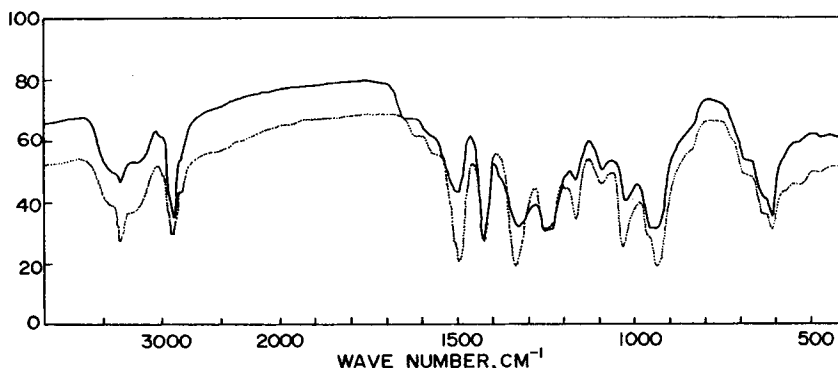
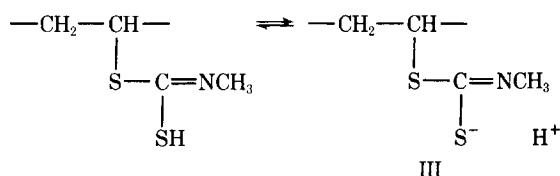


Fig. 2. Change in infrared spectra for PMD and Cu-PMD: (---) PMD; (—) Cu-PMD-treated for 3 hr at 50°C in CH_3OH containing 20 mmoles/l. copper ion.

Tetrahydrofuran is a good solvent for PMD. However, Cu-PMD was not soluble in this solvent, and 90% of the insolubilized part was observed even when the content of copper was only 0.6 meq/g polymer. This suggests that the chelation was formed between dithiocarbamate groups of the two PMD molecules and the copper as shown in II.

In order to study the effect of pH, it was impossible to use buffer solutions because of the hydrophobic property of PMD. Therefore, the weighed samples of PMD powder were equilibrated at 50°C for 4 hr in 20 ml of 20 mmoles/l. copper acetate in methyl alcohol at different pH's prepared by the addition of sodium hydroxide or nitric acid. The results are shown in Figure 1c. When the pH of the solution was raised, the amount of copper reacted was increased considerably, although the swelling of the powder was not observed. These phenomena were easily understood by taking into account that the sulfhydryl form of N-methyl dithiocarbamate dissociates like ethyl mercaptan whose pK_a is 10.5 at 20°C:



The reaction between III and copper ion was more favorable in the higher concentration of III produced at the higher pH values. Near the upper pH limit at which the hydrolysis of the copper ion would occur, the amount of 1.92 meq/g polymer was obtained. This means that about 90% N-methyl dithiocarbamate group reacted with copper ion.

The reactivity toward other metal ions was also examined. Sodium N,N-dialkyl dithiocarbamate forms a chelate compound by reaction with various metal ions, and the order of the stability constants of the complexes has been confirmed⁴: $\text{Hg} > \text{Cu} > \text{Ni} > \text{Co} > \text{Bi} > \text{Pb} > \text{Cd} > \text{Fe} > \text{Sn} > \text{Zn} > \text{Mn}$. In our case, the reaction of the PMD powder with 20 mmoles/l. of various acetates of metals in methyl alcohol was carried out, and the results are summarized in Table II. It can be seen that the selective reaction of metal ions is present in this system.

TABLE II
Amount of Metal Reacted with PMD and γ -Irradiated PMD^a

Polymer	Amount of metal reacted, meq/g polymer							
	Ag	Cu	Cd	Zn	Cr	Ni	Sr	Co
PMD	2.18	1.43	1.44	1.10	1.06	0.51	0.17	0.05
γ -Irradiated PMD, 19 Mrad	2.00	1.60	1.44	1.00	1.08	0.50	0.14	0.05

^a Initial concentration of metal ion, 20 mmoles/l.; temperature, 50°C; reaction time, 3 hr

Effect of γ -Irradiation on Reactivity of PMD with Metal Ions

The radiolysis of PMD under vacuum has been investigated in detail.² PMD containing about 11 mole-% N-methyl dithiocarbamate was irradiated

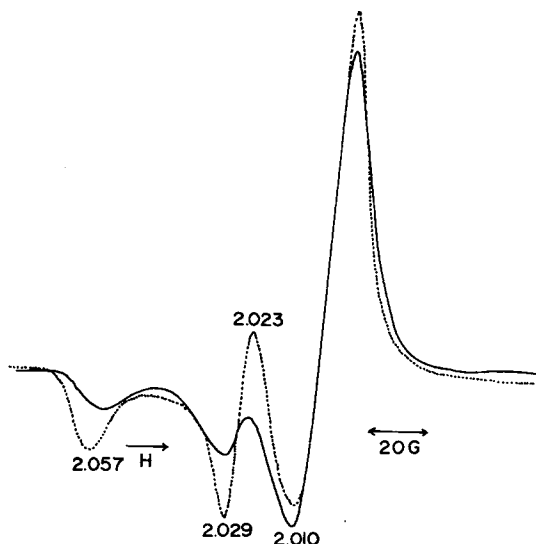


Fig. 3. ESR spectra of γ -irradiated PMD under vacuum and in air: (---) under vacuum; (—) in air. Dosage, 10 Mrad.

at a total dose of 20 Mrad. It was shown that the gaseous products were less than 1×10^{-5} mole/g polymer. The number of the sulfur radicals formed was about 7.2×10^{16} /g polymer.² These results suggested that the reactivity of PMD toward metal ions was not decreased remarkably within the same total dose. No differences in the infrared absorption peaks were observed in the original PMD and the irradiated PMD in air, under vacuum, and in methyl alcohol.

The ESR of the irradiated PMD under vacuum was compared with that of the irradiated PMD in air. As shown in Figure 3, no significant distinctions are discernible in the spectra. It should be noted from these results that the sulfur radicals were extremely stable and did not show any changes with oxy-

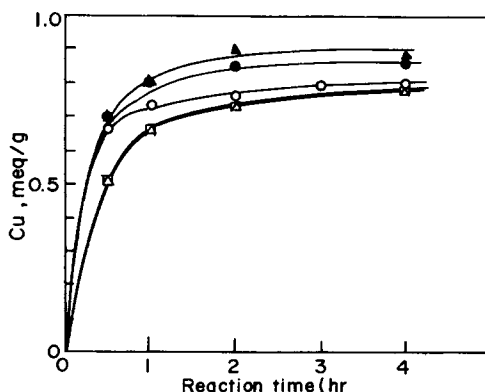


Fig. 4. Amount of copper reacted with γ -irradiated PMD as a function of time: (●) irradiated in CH_3OH , 3 Mrad; (▲) irradiated in CH_3OH , 19 Mrad; (○) no irradiation; (□) irradiated in air, 3 Mrad; (Δ) irradiated in air, 19 Mrad. Initial concentration of copper, 10 mmoles/l.; temperature 50°C .

gen. The radiolysis of PMD in the presence of oxygen was quite small and resembled that of PMD irradiated under vacuum.

In order to correlate the evidence relating to the antiradiation property of PMD to the reactivity toward metal ions, the following experiments were carried out. The PMD powder was irradiated in sealed glass tubes by γ -ray in the presence of air and methyl alcohol, respectively. The reaction of the irradiated PMD was then examined according to the same procedure as described above. The results are shown in Figure 4. In the case of the PMD irradiated in air, no differences are discernible in the reaction rate for the different total doses. Slightly less copper was reacted than with no irradiation. In the early stage, the rate of the reaction was rather slow. One possible reason for that might be a crosslinking of PMD. PMD is known to be quite easily crosslinked by γ -irradiation with 3 Mrads,² and this leads to the slower diffusion of the copper ion into the polymer. On the contrary, the amounts of copper reacted with PMD irradiated in methyl alcohol were somewhat increased as a whole. It is difficult to explain conclusively the reason of this phenomenon because of the complexity of radiolysis of methyl alcohol and the polymer system. One possible mechanism, however, might be illustrated as follows. Methyl alcohol has been reported to form $\cdot\text{CH}_2\text{OH}$ radicals by radiolysis,⁵ which might combine with the polymer chain. Thus, the hydroxymethyl group in the polymer chain might have reacted with copper ion. However, hydroxyl group was not clearly detected by the infrared spectrum.

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