

Reactivity of Poly(vinyl Chloride) Containing N-Methyl-N-Carboxymethyl 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-N-carboxymethyl dithiocarbamate (PSDC) with metal ions in a heterogeneous system and the effect of γ -irradiation on the reactivity were studied. Slurried PSDC has an affinity for a number of metal ions in aqueous solutions. On the basis of analyses for nitrogen and sulfur and on infrared spectra, a possible chelating structure for PSDC was deduced. The gaseous products evolved during the gamma radiolysis of PSDC under vacuum were measured. Although the dithiocarbamate group bonded to the main chain gave some protection against the dehydrochlorination of poly(vinyl chloride) component, a small amount of the carboxymethyl group was decomposed. It was found that with γ -irradiation doses up to 30 Mrad, only about 1 mole-% out of 17.6 mole-% of N-methyl-N-carboxymethyl dithiocarbamate in the polymer was decomposed. It was shown that the reactivity of the irradiated PSDC in water toward metal ions was almost the same as that before irradiation.

INTRODUCTION

Previous work by the authors on the reaction between powdered poly(vinyl chloride) containing N-methyl dithiocarbamate (PMD) and metal ion showed that the reactivity in methyl alcohol was not affected by γ -irradiation from cobalt 60 in the dose range of 10-30 Mrad.¹ However, the PMD powder did not show any reactivity toward metal ion in aqueous solution because of the hydrophobic property of the polymer. Also, in methyl alcohol solutions, the rates of the reaction were rather low. Antiradiation polymers which react with metal ions in aqueous solutions have more practical uses than antiradiation polymers which do not react with metal ions in aqueous solutions. Amberlite-50, a well-known ion exchange resin having a carboxylate group (COO⁻), was found by us to have a remarkable radiolysis in aqueous media.

Our studies of antiradiation polymers have now been extended to examine the reactivity of poly(vinyl chloride) containing N-methyl-N-carboxymethyl dithiocarbamate (PSDC) with metal ions in aqueous solutions and the effect of γ -irradiation on this reactivity. The syntheses and the properties of this polymer, e.g., the reactivity with Cu, Ni, and Ag in homogeneous dimethylformamide solution were already reported by one of the authors.²

EXPERIMENTAL

Synthesis of PSDC Slurry

A detailed discussion of the synthesis of PSDC has been published by the authors elsewhere.² Poly(vinyl chloride) (D.P. = 800) manufactured by Sumitomo Chemical Co., Ltd., and sodium N-methyl-N-carboxymethyl dithiocarbamate, which was prepared from sarcosin, carbon disulfide, and sodium hydroxide, were dissolved in dimethylformamide separately, and both solutions were mixed in an amber-colored flask equipped with a mechanical stirrer. During the reaction, the flask was immersed in a constant-temperature bath kept at 50°C. The reaction mixture was then poured into a 10% aqueous solution of sodium chloride. A cotton-like swollen polymer was precipitated. The polymer was separated by filtration and immediately dispersed in distilled water and stirred vigorously. This slurry was centrifuged, and then the supernatant was decanted. These operations were repeated several times until chlorine ion was not detected in the supernatant. The purified PSDC was preserved in a small quantity of water. The swollen polymer thus obtained is hereafter called PSDC slurry. The degree of substitution of N-methyl-N-carboxymethyl dithiocarbamate group was determined by an analysis for sulfur and nitrogen of a perfectly dried sample of PSDC.

Reaction with Metal Ions

Metal acetates, 25 mmoles, were dissolved separately in 1 liter water; 20 ml of this solution was placed in a 100-ml glass-stoppered Erlenmeyer flask. To this solution was added 5 ml of a slurry containing about 0.1 g PSDC. The slurry was shaken on a mechanical shaker at given temperature. This made the initial concentration of metal ion 20 mmole/l. After a given time, the polymer was collected by filtration, washed repeatedly with water, and dried under vacuum. The dried polymer was analyzed for metal and the infrared spectra were taken. The filtrate was diluted and the concentration of metal ion was determined with atomic absorption analysis using a Perkin-Elmer 107 analyzer.

The metal contained in the reacted PSDC was determined as follows. The polymer was oxidized with plasma oxygen using an International Plasma Corporation Model 1003B and the metal oxide was dissolved in a small quantity of hydrochloric acid and diluted. The concentration of the solution was determined by the method mentioned above.

γ -Irradiation of PSDC

The PSDC slurry was sealed in an ampoule tube with air. The dried PSDC was sealed under vacuum. Both samples were irradiated with γ -rays from cobalt 60 with a dose rate of 1.0 Mrad/hr. The dried PSDC was irradiated to determine the radiolysis of the N-methyl-N-carboxymethyl dithiocarbamate group. The method of measuring the gaseous products has been reported elsewhere.³

Measurement of Infrared Spectra and ESR

The measurements of the infrared spectra and ESR were made with a Perkin-Elmer 180 high-resolution infrared spectrometer and a Varian E-9 electron spin resonance spectrometer, respectively. For the ESR measurements, films of PSDC were prepared from a solution of dimethylformamide by evaporation of the solvent.

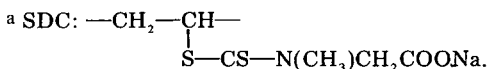
RESULTS AND DISCUSSION

Preparation of PSDC Slurry

The synthesis of PSDC was reported in detail by one of the authors elsewhere.² In this paper, PSDC was synthesized at 50°C. After a given time, the reaction mixture of PSDC and dimethylformamide was poured into water

TABLE I
Poly(vinyl Chloride) Containing N-Methyl-N-carboxymethyl Dithiocarbamate (PSDC)

Polymer	Reaction time, hr ^b	Nitrogen, wt-%	Sulfur, wt-%	SDC ^a in polymer, mole-%
PSDC-1	1	0.8	4.8	4.7
PSDC-2	2	1.3	5.9	6.7
PSDC-3	3	1.6	7.2	8.5
PSDC-4	4	1.8	7.9	9.7
PSDC-5	5	2.2	9.3	12.2
PSDC-6	6	2.3	10.3	13.4
PSDC-17	7	2.8	12.7	17.6
PSDC-27	7	2.5	11.7	15.5



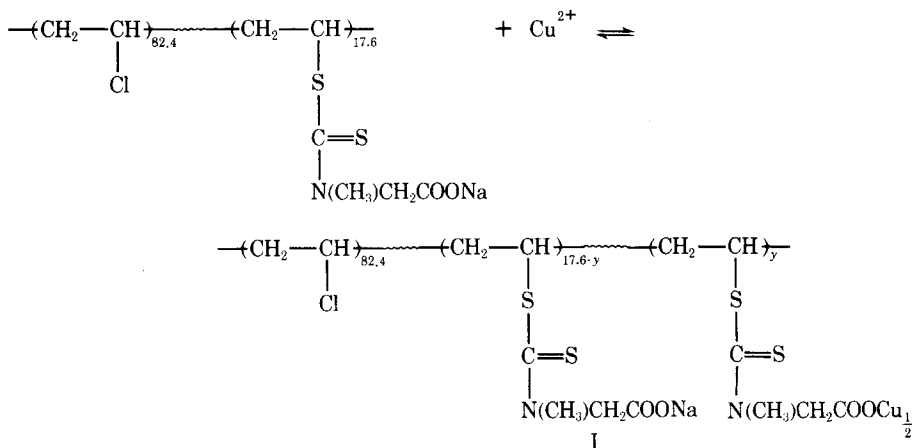
^b Reaction condition: poly(vinyl chloride), 20 g; sodium N-methyl-N-carboxymethyl dithiocarbamate, 20 g; dimethylformamide, 600 ml; H₂O, 12 ml; 50°C.

or methyl alcohol. However, no slurry-like precipitate of the polymer appeared and no turbidity was even observed. A PSDC slurry could be obtained by dropping the reaction mixture into 10% sodium chloride aqueous solution. The aqueous solution included in the PSDC slurry was repeatedly replaced by pure water until chloride ion was not detected. This purified PSDC slurry was stored in distilled water; 5 ml of the PSDC slurry contained about 0.1 g polymer. This suggests that PSDC is quite different from poly(vinyl chloride) and is hydrophilic after substituting chlorine with a N-methyl-N-carboxymethyl dithiocarbamate group. However, the precipitated PSDC did not dissolve in water and methyl alcohol. PSDC of varying degrees of substitution was obtained by controlling the reaction time, and the degree of substitution was calculated from an analysis for sulfur or nitrogen. The results are summarized in Table I. Unless stated otherwise, all future references in this work will be to PSDC-17 or PSDC-27. The degree of substitution for PSDC-17 and PSDC-27 was higher than any other PSDC preparation.

Reaction of PSDC Slurry with Metal Ions

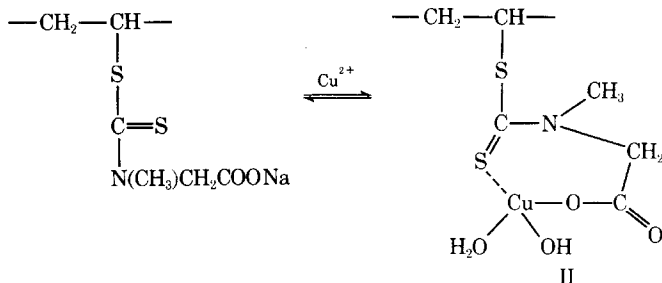
PSDC slurry, 5 ml, was added to 20 ml of an aqueous solution including 25 moles/l. copper ion. This means that PSDC was treated with 20 mmoles/l. copper ion as the initial concentration. This mixture was shaken for about 30 hr at 50°C. Analysis showed the copper content of the treated PSDC to be 8.57 wt-%. PSDC-17 treated with copper ion is hereafter abbreviated as Cu-PSDC-17.

McLaren et al.⁴ studied the interaction of copper ion and nickel ion with the carboxylate group of poly(acrylic acid). They reported that these metals formed complexes in which two or more carboxylate groups were involved, depending upon the polymer concentrations. In the case of PSDC-17, on the assumption that every carboxylate group is bound with copper as shown in compound I, the theoretical value of carboxylate reacted is 17.6 mole-%. However, the copper analysis suggests a value of 24.6 mole-% was obtained. In the present investigation, y in I should be less than 17.6 if physical adsorption could be neglected:



The copper content in PVC or PVC containing N,N-dimethyl dithiocarbamate group which was treated with the same experimental condition as mentioned above was less than 0.05 meq/g. Therefore, it is reasonable to neglect the physical adsorption.

A hypothetical chelation complex of Cu-PSDC-17 is shown in II:



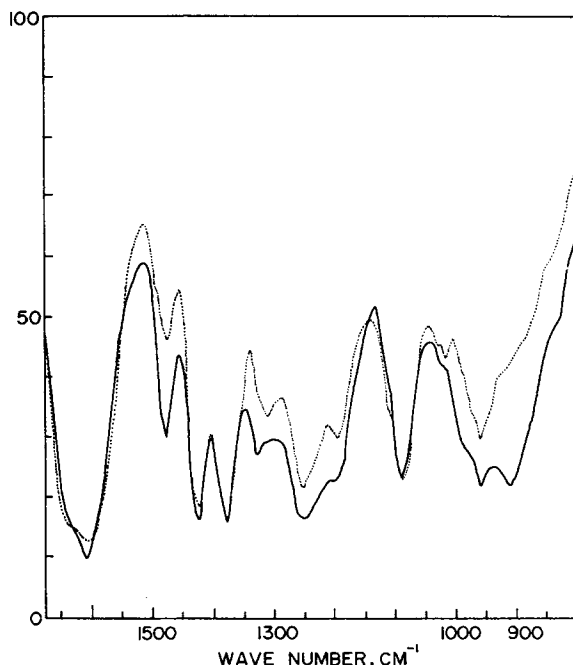


Fig. 1. Change in infrared spectra in the range of 800–1600 cm^{-1} for PSDC-17 and Cu-PSDC-17: (—) PSDC-17; (---) Cu-PSDC-17.

According to formula II, y in I was calculated to be 13.4. This value suggests that about 76% N-methyl-N-carboxymethyl dithiocarbamate group was reacted with copper ion. The reaction of one mole dithiocarbamate group with one mole copper ion took place in the aqueous heterogeneous system. Formula II has already been discussed in a previous paper.² The reaction between PSDC and copper acetate in dimethylformamide was confirmed from an elemental analysis of the precipitate. The infrared spectra of Cu-PSDC-17 and Cu-PSDC obtained in the homogeneous dimethylformamide solution were virtually identical. As shown in Figure 1, the absorptions of 1480 cm^{-1} and 910 cm^{-1} which are attributed to $\nu_{\text{N}=\text{C}}$ ($\text{N}=\text{C}=\text{S}$) and $\nu_{\text{N}-\text{C}}$ ($-\text{S}-\text{CS}-\text{N}$), respectively, decrease remarkably in Cu-PSDC-17. This difference in absorption behavior is considered to be one evidence in favor of the suggested chelation.

Effect of Reaction Conditions on Reaction of PSDC with Copper Ion

Effect of Reaction Time. The relation between the reaction time and the amount of copper ion reacted with the polymer is shown in Figure 2. The temperature ranged from 10° to 50°C , the initial copper ion concentration was 20 mmol/L, and the pH was 5.8. It can be seen from Figure 2 that the PSDC slurry reacted more rapidly with copper ion than did PMD. For the PSDC slurry, the equilibrium was obtained within 30 min.

For comparison, the reacted value of copper obtained for the dried PSDC powder is also shown in Figure 2. The dried PSDC was less reactive and the amount of reacted copper decreased. Decreased wettability of the dried

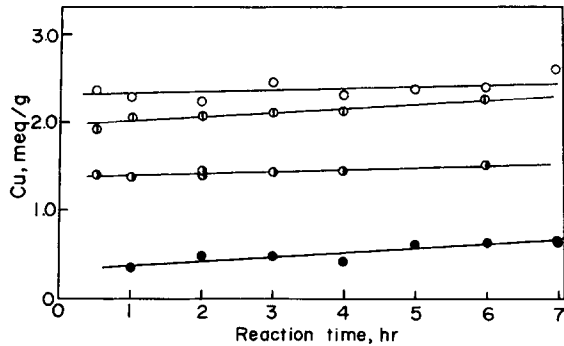


Fig. 2. Amount of copper reacted as a function of time: (○) PSDC-17, 50°C; (○) PSDC-27, 50°C; (○) PSDC-27, 30°C; (●) PSDC-5, dry powder, 50°C.

PSDC may account for this behavior. The hydrophilic groups of PSDC may have combined firmly with each other through hydrogen bonding to form a weakly crosslinked structure in the dried PSDC powder. For this structure, the hydrophobic poly(vinyl chloride) component may have covered the hydrophilic groups and produced a powder which was difficult to wet. The dry powder, when added to an aqueous solution of copper, did not sink but floated on the surface of the aqueous solution.

Effect of pH. It was thought that the formation of carboxylate anion would be favored in a high pH environment. As a result, the amount of copper reacted with the polymer would increase in the same region. The amount of copper reacted with PSDC is given as a function of pH in Figure 3. Measurement in the region above pH 6 was impossible because copper hydroxide was precipitated. The equilibrium between PSDC and Cu^{2+} should favor the chelate as pH increases. As can be seen in Figure 3, the amount of copper increased with high pH value. In addition to the increasing carboxylate anion, the high pH region might favor the formation of a copper complex such as compound II.

Effect of Temperature. In Figure 4, the amount of copper reacted with PSDC is plotted versus temperature of the solution. The discernible differ-

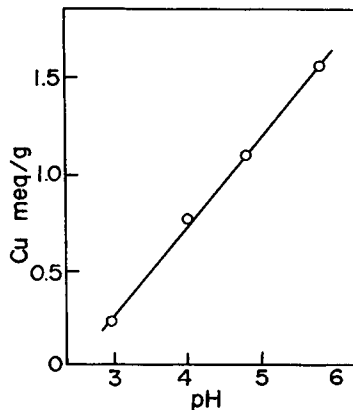


Fig. 3. Amount of copper reacted as a function of pH. PSDC-5, 30°C, 1 hr.

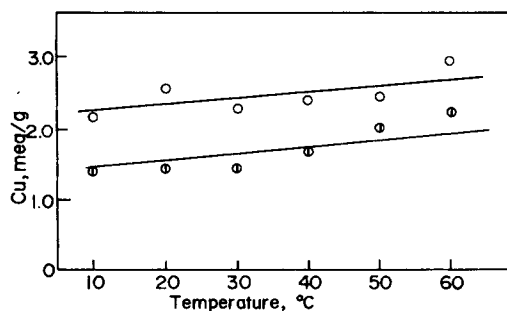


Fig. 4. Amount of copper reacted as a function of temperature: (O) PSDC-17, 1 hr; (□) PSDC-5, 1 hr.

ence of the amount of the copper reacted appears to be rather small in the temperature range of 10–60°C. This suggests that the reaction took place mainly through ionic mechanism and did not depend on the diffusion of copper ion into the polymer slurry.

Effect of Initial Concentration of Metal Ion. The relation between the initial concentration of copper ion and the amount of copper reacted at 50°C is shown in Figure 5. The amount of copper on the ordinate axis was obtained by an elemental analysis of the chelate after 0.1 g PSDC was reacted to equilibrium with 25 ml copper solution of the given initial concentration shown along the abscissa. The concentration shown on the right-side ordinate was the final concentration of the solution. From these results, the amount of PSDC required to treat a certain given volume of copper solution can be estimated. For example, the copper contained in a 25-ml copper solution whose initial concentration is 3 mmoles/l. will be removed by 0.1 g PSDC-17.

Selectivity of PSDC Slurry Toward Other Ions

The PSDC slurry was estimated to have a reactivity toward a number of other metals, and a study of some of these complexes was undertaken. In some cases, the selectivity of chelating polymers was determined simply by batch equilibration according to the same method as used in the case of cop-

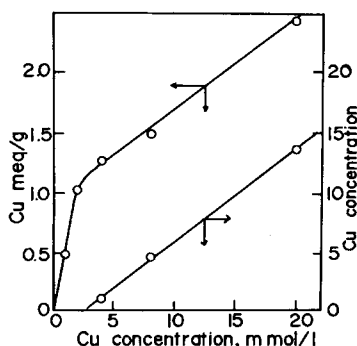


Fig. 5. Amount of copper reacted as a function of initial concentration of copper and final concentration of copper in 25 ml after treatment with 0.1 g PSDC-17. 50°C, 3 hr.

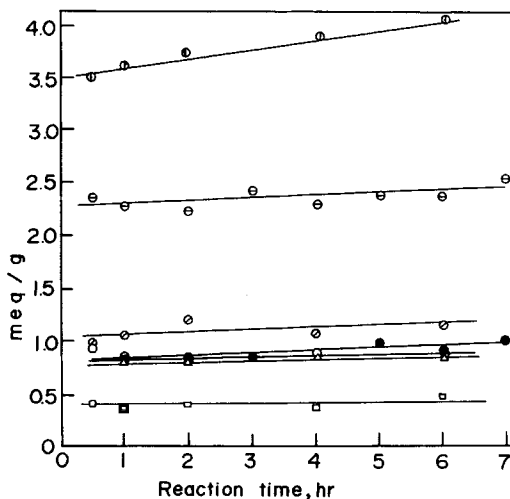


Fig. 6. Amount of metal reacted with PSDC-17 as a function of time: (O) Ag; (⊖) Cu; (○) Cd; (●) Co; (○) Zn; (Δ) Sr; (□) Ni. 50°C.

per. The results are shown in Figure 6. Each metal ion reacted to equilibrium within 30 min. Aqueous acetate solutions of each metal were used. The pH of the solutions were between 6.7 and 7.7, except copper acetate and chromic acetate.

The observed pH values were as follows: Cu^{2+} (5.8), Cr^{3+} (4.78), Cd^{2+} (6.91), Co^{2+} (7.59), Zn^{2+} (6.77), Sr^{2+} (7.71), Ni^{2+} (7.56), and Ag^{+} (6.90). The order of the reactivity obtained was $\text{Ag}^{+} > \text{Cu}^{2+} > \text{Cr}^{3+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Sr}^{2+} > \text{Ni}^{2+}$. From Figure 6, it is clear that the PSDC slurry is selective as a chelating polymer and has a large affinity for Ag. The reaction of PSDC with univalent silver ion was investigated in a homogeneous dimethylformamide solution.² The adsorption of Ag with the N-methyl-N-carboxymethyl dithiocarbamate group was estimated in addition to the reaction of this group with Ag. The same type of binding of Ag was considered to occur even in the case of the heterogeneous system. If Ag were bound only to the carboxylate group for PSDC-25 with 15.7 mole-% substitution, then 1.82 meq/g polymer of Ag would theoretically be reacted. However, the observed amount was two times this calculated value.

Radiolysis of PSDC and Effect of γ -Irradiation on Reactivity of PSDC Toward Copper Ion

Radiolysis of PSDC Under Vacuum. It was stated in previous papers that the N-methyl dithiocarbamate group³ and the N,N-dialkyl dithiocarbamate group⁵ bonded to the main chain of poly(vinyl chloride) provide protection against radiolysis of the neighboring poly(vinyl chloride) component. Also, radiolysis of the dithiocarbamate group produced very little evolved gaseous products. Therefore, it is possible to assume that N-methyl-N-carboxymethyl dithiocarbamate having the $-\text{CH}-\text{S}-\text{CS}-\text{N}$ moiety would show protection against the radiolysis of the polymer.

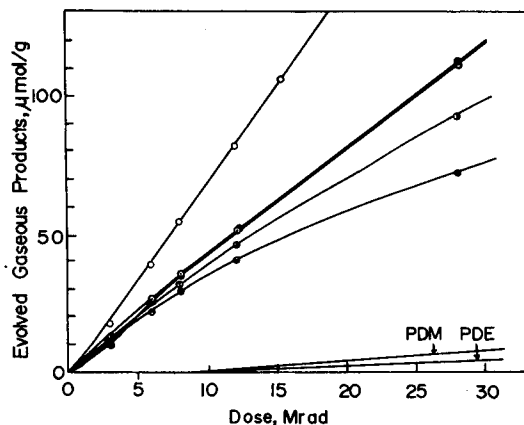


Fig. 7. Evolved gaseous products as a function of dose: (○) PVC; (●) PSDC-17; (⊙) PSDC-5; (○) PSDC-3; (⊖) PSDC-1.

The total gaseous products produced with doses up to 30 Mrad at 25°C were examined by the variable pressure method and mass spectroscopy and found to comprise mostly carbon dioxide. These results are shown in Figures 7 and 8. For comparison, Figure 9 also shows data of the radiolysis of poly(vinyl chloride) containing *N,N*-dialkyl dithiocarbamate (PDM, PDE). In the case of PDM and PDE, the amounts of the evolved gaseous products had already been shown to decrease with the degree of substitution of dithiocarbamate derivatives.^{3,5} As can be seen from Figure 7, however, the opposite results were obtained in the radiolysis of PSDC. The results of Figures 7 and 8 suggest that radiolysis of *N*-methyl-*N*-carboxymethyl dithiocarbamate group did occur. No hydrogen chloride was detected by mass spectroscopy of the evolved gases. This suggests that *N*-methyl-*N*-carboxymethyl dithiocarbamate protected the poly(vinyl chloride) component from degradation by γ -irradiation.

Support for this explanation can also be found in the ESR spectrum at -196°C shown in Figure 9. The ESR spectrum of the γ -irradiated PSDC membrane showed absorption at the high *g*-values of 2.069, 2.054, 2.036, and 2.030. These are strongly anisotropic and are virtually identical with those of the irradiated poly(vinyl chloride) containing *N,N*-dimethyl dithiocarba-

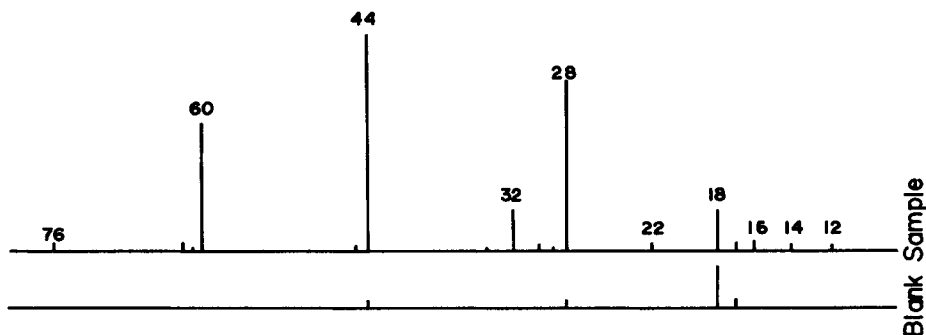


Fig. 8. Mass spectrum of gaseous products evolved from PSDC-17 with irradiation of 30 Mrad.

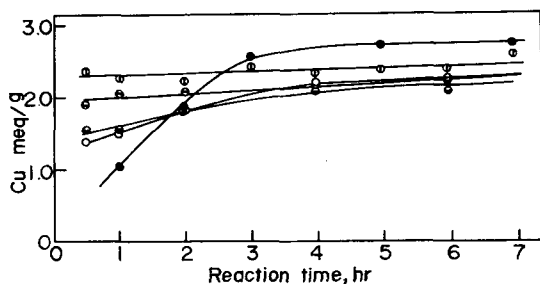


Fig. 10. Amount of copper reacted with γ -irradiated PSDC as a function of time: (●) PSDC-17, 30 Mrad; (○) PSDC-17, no irradiation; (⊖) PSDC-27, no irradiation; (◐) PSDC-27, 10 Mrad; (◑) PSDC-27, 30 Mrad.

product would imply the degradation of only 1.07 mole-% of the dithiocarbamate group. However, gases other than carbon dioxide were obtained, and therefore the mole-% of the degraded dithiocarbamate is less than 1.07.

If the PSDC slurry shows the antiradiation properties in an aqueous system, the application of the treatment to a radioactive waste solution might be possible. For the so-called "cold run" experiments, the PSDC slurry was irradiated and then treated with copper ion. A commercial cation exchange resin having sodium carboxylate group was irradiated with 30 Mrad under the same conditions as the irradiation for the PSDC slurry. An increase in the viscosity of the water solution was observed. This implies that degradation of the main chain took place, and the moiety containing carboxylate was dissolved in the water solution. Such a phenomenon was not observed in the case of PSDC. The effect of γ -irradiation for the dose range of 10–30 Mrad on the amount of copper ion reacted with the PSDC slurry is shown in Figure 10. It might be said on the basis of the results of Figure 10 that γ -irradiation of these doses cannot produce the significant changes in the reactivity of the PSDC slurry toward copper ion. The rate of the reaction was rather slow in the first stage, as shown in Figure 10, and this is probably due to slow diffusion of the ion into the polymer, because of the formation of crosslinked structure by γ -irradiation.

Studies are in progress to determine the reactivity of the PSDC slurry toward radioactive metal ions in an aqueous system.

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Received February 20, 1975

Revised June 16, 1975