Reaction with Metal Ions of Chloromethylated Polystyrene Resin Containing Dithiocarbamate Group*

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Synopsis

The derivatives of poly(chloromethylstyrene) resin (PCMS) with N-methyl-N-carboxylmethyldithiocarbamate (1), N,N-di(β-hydroxyethyl)dithiocarbamate (2), N-methyl-N-carboxylmethylamino (3), and di(β-hydroxyethyl)amino (4) groups were prepared, and the metal ion reactivity of the polymer resins with these functional groups were investigated. Additionally, the effect of γ irradiation on the reaction with metal ion was also investigated. In the reaction of PCMS under the same conditions, the substitution ratio order is as follows: (2) > (1) > (4) > (3). In the reaction of the resins with cupric ion, the reaction amount reached a maximum of 4.17 mequiv/g for resin (1) and 4.75 mequiv/g for (2). The polymers containing sulfur atom have a large reactivity toward metal ion in comparison to the polymers without sulfur atom. The reactivity of polymer (1) toward metal ions decreased in the following order: Ag(I) $\gg$ Cu(II) > Zn(II) $\gtrsim$ Ni(II) $\gtrsim$ Co(II). The other metal ions, except Ag(I) and Cu(II), hardly reacted with polymer (2). Thus, polymer (2) has a remarkable selectivity. It was also found that the reaction amount of polymers containing sulfur after γ irradiation is almost the same as that before γ irradiation.

INTRODUCTION

The authors, in previous attempts to prepare metal ion reactive polymers having antiradiation properties, found that the dithiocarbamate group on poly(vinyl chloride) (PVC) can protect the destruction of the polymer by γ irradiation.[1-4] Though there are many reports on the preparation and reactivity of ion exchange resin which used PCMS as support of stational phases, there are few reports concerning to the preparation of PCMS containing dithiocarbamate[5] and no report about its reactivity with metal ions.

In this article, the role of the dithiocarbamate group on the modified PCMS was investigated in comparison with the corresponding polymers without sulfur atom. The preparation of four kinds of polymers, containing N-methyl-N-carboxylmethyldithiocarbamate (1), N,N-di(β-hydroxyethyl)dithiocarbamate (2), N-methyl-N-carboxylmethylamino (3), and di(β-hydroxyethyl)amino (4) groups, was attempted. Next, the reaction of these polymers with metal ions was investigated in the heterogeneous system. The effect of γ irradiation on the reaction amount of metal ions was also investigated.

* Dedicated to Prof. Georg Manecke on his 65th birthday.

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EXPERIMENTAL

Materials

Chloromethylated polystyrene, 100%, crosslinked by 2 mole % divinylbenzene was used in this study (resin diam ~0.5 mm). All reagents and solvents employed were commercially available materials and purified by standard methods.

Preparation of Sodium *N*-Methyl-*N*-carboxylmethyldithiocarbamate

In a 1-liter four-necked round flask equipped with a reflux condenser, a thermometer, a drop funnel, and a mechanical stirrer were placed 46 g (0.6 mole) CS_2 and 24 g sodium hydroxide in 60 ml water. The solution was then cooled at 5°C. To the stirred solution were added 54 g (0.6 mole) salcosine and 24 g NaOH in 120 ml aqueous solution dropwise over a period of 2 hr. The temperature was kept below 7°C during the addition. Then, the mixture was stirred for 1 hr at room temperature and thereafter for 3 hr at 50°C.

The mixture was evaporated under reduced pressure to remove water and dried under vacuum. The hygroscopic solid was obtained quantitatively. The product was confirmed to be the disodium salt of *N*-methyl-*N*-carboxylmethyldithiocarbamic acid by the reaction with benzyl chloride in DMF as described below.

Preparation of *S*-Benzyl-*N*-methyl-*N*-carboxylmethyldithiocarbamate

In a 200-ml Erlenmeyer flask were placed 6.84 g of the dithiocarbamate salt prepared as discussed above in 50 ml DMF. To the stirred solution were added 3.16 g benzyl chloride in 20 ml DMF over a period of 2.5 hr at room temperature. The solution was stirred overnight at room temperature. To the solution was added 400 ml water, and then the aqueous solution was acidified by addition of 15 ml acetic acid to precipitate a white solid. The white solid was extracted with 300 ml ether. The ethereal solution was washed three times with water and dried over magnesium sulfate. After the ether was evaporated, the residue was recrystallized in methanol and water.

The product was obtained in 84% yield: IR, see Figure 1; NMR($CDCl_3$), δ(ppm): 3.38(3H, s), 4.50(2H, s), 4.81(2H, s), 7.31(5H, s), 10.68(1H, broad); mass: m/e 255(M^+).

ANALYSIS: Calcd H 5.10, C 51.76, N 5.49 for $C_{11}H_{13}O_2NS_2$. Found: H 5.64, C 51.60, N 5.50.

Preparation of Sodium *N,N*-Di(β-hydroxyethyl)dithiocarbamate

The preparation was undertaken in the similar manner as reported previously.[4]

S-Benzyl-*N,N*-di(β-hydroxyethyl)dithiocarbamate was prepared by the reaction of the dithiocarbamate salt with benzyl chloride in methanol at 60°C to be obtained in 92% yield: IR, see Figure 2; NMR(DMSO-d_6), δ(ppm): 3.5 ~ 4.3(8H, m), 4.4(2H, s), 4.5 ~ 5.1(2H, broad), 7.2(5H, s); mass: m/e 271(M^+).
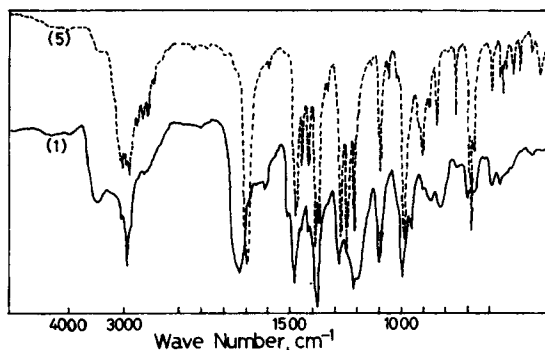
Fig. 1. Infrared spectra: (—) resin (1); (- - -) S-benzyl-N-methyl-N-carboxylmethyldithiocar-bamate (5).

Reaction of Disodium Salt of N-Methyl-N-carboxylmethyldithiocarbamic Acid with PCMS Resin

To PCMS resin (31 g, 0.2 mole) swelled in 100 ml DMF were added 45 g salt in 150 ml DMF. Then the solution was stirred at 60°C for 5 hr. Then, the resin was poured into water and separated by filtration. The resin was washed well with water, THF, and methanol, in succession, and then dried under vacuum. The resin was neutralized with acetic acid in THF to yield resin with free carboxyl group.[1]

By the same procedure the resins (2) and (4) were obtained.

Preparation of Resin (3)

To the stirred mixture of salcosine (8.9 g) and sodium hydroxide (4.0 g) in 100 ml of DMF, were added 30 ml of water, yielding the homogeneous solution. To this solution were added 15.3 g PCMS resin swelled in 50 ml of DMF. The solution was then stirred at 60°C, for 5 hr, and then post-treated as in the case of resin (1).
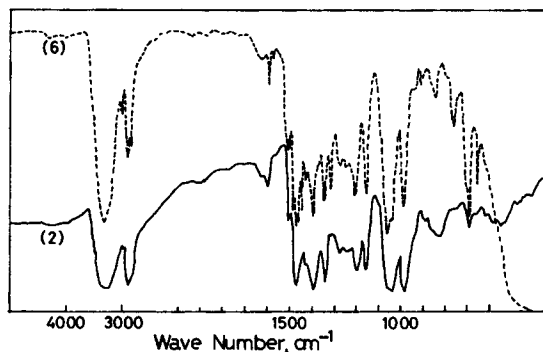

Fig. 2. Infrared spectra: (—) resin (2); (- - -) S-benzyl-N,N-di(β-hydroxyethyl)dithiocarbamate (6).

Measurement of Amount of Metal Ion Reacted with Resins (1)–(4)

General method: A 0.300-g sample of the resin was placed in a 100-ml glass-stoppered Erlenmeyer flask and into it was poured 25 ml aqueous solution containing 20 mmole/l. metal ion.   Then, the flask was partially immersed an a thermostatted bath held to ±0.5°C.   During the experiment the flask was agitated by shaking at 30°C.   After a given time, the resin was filtered off and the concentration of the residual metal ion in the filtrates was measured with a Perkin–Elmer model 107 atomic absorption spectrometer.   The amount of the metal ion reacted with the resin was calculated from the difference between the concentration of the metal ion in solution before and after the reaction.

The reaction under the different reaction conditions was also carried out by the same procedure.

The pH values of the solution were measured at room temperature with a Mitamura Riken MRK pH-mV meter after calibration with a combination of appropriate standard buffers.

γ-Irradiation of Resins (1)–(4)

The resins prepared were irradiated with ^{60}Cobalt γ rays.   The doses were 10, 22, and 32 Mrad, and the dose rate was 1.0 Mrad/hr.   The resins (2–10 g) were sealed with 50 ml distilled water in a glass tube and irradiated at 23°C.   The irradiated resin samples were used for the reaction with metal ions.
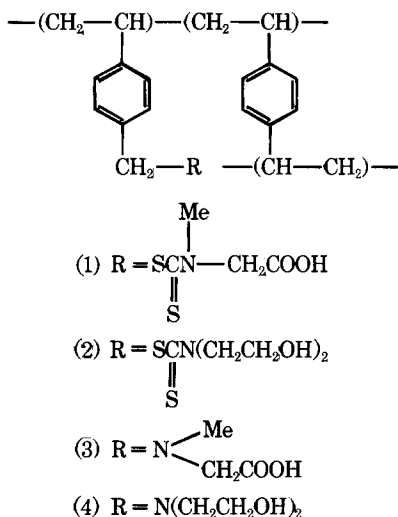
RESULTS AND DISCUSSION

Preparation of Polystyrene Derivatives Containing N,N-Substituted Dithiocarbamate and Amino Groups

Two kinds of sodium dithiocarbamate were prepared by previously reported methods.[4,6]   The salts in both cases were obtained quantitatively from the reaction of the corresponding amine with carbon disulfide.   The PCMS used was a bead (diam ~0.5 mm) which was composed 100% chloromethylated styrene and 2 mole % divinylbenzene.

Pale yellow polymer was obtained from the reaction of PCMS (crosslinked by 2 mole % divinylbenzene) with salts of dithiocarbamate ion in DMF at 60°C for 5 hr.   From the reaction of PCMS with salcosine and diethanolamine polymers containing N-methyl-N-carboxylmethylamino and N,N-di(β-hydroxyethyl)amino groups, respectively, were obtained.   In the case of the reaction with salcosine in DMF/H$_2$O mixed solvent, a white polymer with moderate substitution ratio could be obtained.   These polymers without sulfur atom were prepared in order to compare the metal ion reactivity and the antiradiation property

with (1) and (2) containing sulfur atoms:

$$-(CH_2-CH)-(CH_2-CH)-$$

(structure with two para-substituted benzene rings)

$$CH_2-R \quad -(CH-CH_2)-$$

(1) $R = SCN\underset{\|}{}\overset{Me}{}-CH_2COOH$, with $\|$ S below the C

(2) $R = SCN(CH_2CH_2OH)_2$, with $\|$ S

(3) $R = N\diagup^{Me}_{\diagdown CH_2COOH}$

(4) $R = N(CH_2CH_2OH)_2$

As corresponding model compounds, the S-benzyldithiocarbamates, (5) and (6), were obtained in excellent yields from the reaction of benzyl chloride with sodium dithiocarbamate in DMF at 60°C. They were confirmed by IR, NMR, and mass-spectroscopic methods and elemental analysis:

$$CH_2SCN\diagup^{Me}_{\diagdown CH_2COOH} \quad \text{with } S \text{ double bond}$$

(5)

$$CH_2SCN(CH_2CH\ OH)_2 \quad \text{with } S \text{ double bond}$$

(6)

The IR spectra of the polymers, (1) and (2), and benzyl dithiocarbamates, (5) and (6), are shown in Figures 1 and 2. The spectra of the polymers are almost in accord with those of the model compounds. Before treatment of (1) with acetic acid, the carboxyl absorption band appears at 1615 cm^{-1} and the IR is almost in accord with that of the sodium salt of (5) [the absorption band of carboxylate ion of (5) appears at 1620 cm^{-1}]. By treatment of (1) with acetic acid, the peaks of the stretching absorption band of carboxyl of (1) and (5) appear at 1720 and 1700 cm^{-1}, respectively. The difference of 20 cm^{-1} between (1) and (5) is due to the difference in the association state of the molecules. That is, (5) can associate to form hydrogen bonding between two molecules, while the carboxyl group of the crosslinked polymer (1) can hardly associate intermolecularly.

In resin (2), the band at 1640 cm^{-1}, which appeared in the reaction of PVC with sodium N,N-di(β-hydroxyethyl)dithiocarbamate,[4] does not appear at all (Fig. 2). It is considered that this resin cannot be subject to neighboring group participation. As previously reported, the substitution ratio of N-methyl-N-carboxylmethyldithiocarbamate group for PVC was at most only 17.6% after the reaction in DMF at 50°C for 7 hr,[1] and the substitution ratio of N,N-di(β-hydroxyethyl)dithiocarbamate group for PVC could not be calculated on account of its side reaction.[4] On the other hand, PCMS resin can easily react with di-

thiocarbamate ion without side reaction, and the substitution ratio reached a maximum of 83% in the case of N,N-di(β-hydroxyethyl)dithiocarbamate and 67% in the case of N-methyl-N-carboxylmethyldithiocarbamate in the reaction in DMF at 60°C for 5 hr.

The degree of substitution was calculated from an analysis for nitrogen. The polymer beads were ground to a fine powder in liquid nitrogen. The polymer powder to be analyzed was washed well with water, THF, and then methanol and dried thoroughly under reduced pressure. Additionally, (1) and (3) were treated with acetic acid to form completely free carboxylic acid. The results are summarized in Table I.

From these results, the degree of substitution of (1) and (2) is apparently larger than that of (3) and (4). The resin (2) has about a twofold larger degree of substitution than (4) under the same reaction conditions. Thus, polymers (1) and (2) with a high degree of substitution of the dithiocarbamate group could be obtained because of the large nucleophilicity of sulfur anion.

Reaction of Polymers with Metal Ions

Reaction with Cupric Ion

In this study four kinds of poly(chloromethylstyrene) resin (PCMS) derivatives, (1), (2), (3), and (4), were used. First, the reaction of these polymers with 25 ml 20 mmole/l. aqueous cupric acetate buffered solution (pH 5.85) at 30°C was undertaken, and the amount (mequiv/g) of cupric ion reacted and change in pH as a function of time are shown in Table II. The value of reacted amount of cupric ion was estimated from the amount of the residue of cupric ion in the solution.[7]

The color of the PCMS resins was changed as follows: (1) pale yellow → yellowish green → green; (2) pale yellow → yellow → yellowish brown; (3) and (4) white → pale blue → blue. The blue color of the solution became gradually thinner in every case.

In Table II the amount of cupric ion absorbed increases with the reaction time, and the pH of the solution decreases gradually because acetic acid generated during the reaction of the polymer with cupric acetate makes the solution acidic.

TABLE I
Preparation of PCMS Derivatives Containing Dithiocarbamate Group

Resin	Elemental Analysis, %[a]			Substitution ratio,[b] %	Mole of substituent in 1 g resin,[b] mmole/g
	H	C	N		
(1)	5.39 (5.47)	59.65 (58.72)	3.97	67	2.85
(2)	6.49 (6.37)	62.09 (61.67)	4.33	83	3.09
(3)	6.90 (6.71)	70.80 (71.10)	3.70	46	2.66
(4)	7.44 (7.64)	71.85 (72.19)	3.72	48	2.68

[a] Values in parentheses were calculated from substitution ratio. These are in fair agreement with the analytic ones.

[b] These values were calculated from the observed ones of N%.

TABLE II
Reaction of the Resins with Cupric Ion

Resin		Reaction time, hr					
		0	1	2	3	5	24
(1)	mequiv/g	0	1.53	1.98	2.08	2.15	2.92
	pH	5.85	5.83	5.78	5.70	5.68	5.45
(2)	mequiv/g	0	0.40	0.66	0.66	0.83	2.12
	pH	5.85	5.65	5.65	5.54	5.53	5.19
(3)	mequiv/g	0	1.12	—	1.35	1.37	1.45
	pH	5.85	5.68	—	5.58	5.58	5.48
(4)	mequiv/g	0	0.87	—	1.20	1.30	1.34
	pH	5.85	5.60	—	5.47	5.47	5.42

Although resin (2) reacts apparently more slowly with cupric ion than the other resins, the reaction amount after 24 hr is larger than that of (3) and (4). The apparent reaction amount per 1 g of each polymer decreases in the following order: (1) > (2) > (3) ∼ (4). The reaction ratio per two substituents on the polymers, which was calculated from the substitution ratio of each polymer in Table I and the reaction amounts (mequiv/g) after 24 hr in Table II, is shown in Table III. The reactivity of the polymers toward cupric ion decreases in the same order as the apparent reactivity.

Thus, resins (1) and (2) containing dithiocarbamate have a remarkable increase in their reactivity in comparison with resins (3) and (4) without sulfur atom. Apparently, sulfur atom or dithiocarbamate participates largely in the formation of chelate with metal ion. In the IR spectrum of (1) and (2) after a reaction time of 24 hr, the absorption band at 1480 cm^{-1} assigned to the thioneamide group decreased upon reaction with metal ion. The band at 990 cm^{-1} assigned to the thiocarbonyl group also decreased considerably. From the result, it appears that nitrogen and/or sulfur atoms participate significantly in the reaction.

Effect of Concentration of Cupric Ion and Volume of Solution on Reactivity

A similar reaction was undertaken in the buffered solution of cupric acetate (pH 5.9), 10 and 40 mmole/l. The effect of volume of solution on the reactivity was also investigated. The results after the reaction at 30°C, 24 hr, are shown with the results in 20 mmole/l. of cupric ion solution in Table III.

TABLE III
Effect of Concentration of Cupric Ion and Volume of Solution on Reactivity

Resin[a]		10 mmole/l. Cu^{2+}	20 mmole/l. Cu^{2+}				40 mmole/l. Cu^{2+}
		50 ml	25 ml	50 ml	75 ml	100 ml	50 ml
(1)	mequiv/g[b]	3.06	2.92	3.26	3.56	4.17	4.17
	Reaction ratio[c]	1.07	1.02	1.14	1.25	1.46	1.46
(2)	mequiv/g[b]	2.46	2.12	3.03	2.90	3.06	4.75
	Reaction ratio[c]	0.80	0.69	0.98	0.94	0.99	1.50
(3)	mequiv/g[b]	—	1.45	—	—	1.74	1.83
	Reaction ratio[c]	—	0.55	—	—	0.65	0.69
(4)	mequiv/g[b]	—	1.34	—	—	2.11	2.87
	Reaction ratio[c]	—	0.50	—	—	0.79	1.07

[a] A 0.300-g sample of the resin was used in all cases.
[b] Reaction amount after 24 hr at 30°C.
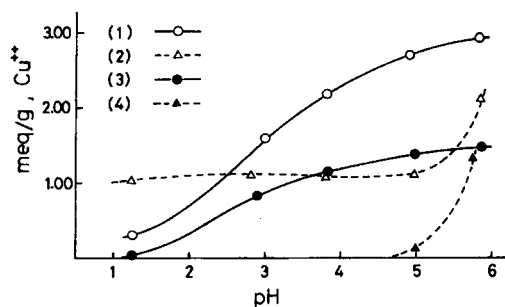[c] Reaction ratio per two substituents on the resin.

Fig. 3. Dependence of pH on reaction amount of cupric ion.

In all polymers, the higher the concentration of the cupric ion, the more the reaction amount. The reaction amounts of both (1) and (2) are more than 4 mequiv/g in the 40 mmole/l. solution. Also, the larger the volume of the 20 mmole/l. solution for the polymer, the larger amount of the reaction. In the case of (1), the mequiv/g in 100 ml of a 20 mmole/l. solution reached almost the same reaction amount as in 50 ml of a 40 mmole/l. solution under the same conditions. On the other hand, the reaction amounts in (2) are constant in the 20 ml of solution containing more than 50 mmole/l. cupric ion. From these results, it can be said that the decrease in concentration of cupric ion is not so significant in a large volume of solution, and the decrease in pH with the reaction is small when the amount of solution is sufficiently large.

TABLE IV
Reaction Amount of Metal Ions [Zn(II), Ni(II), Co(II), Cu(II), and Ag(I)][a]

| Resin | Reaction amount, mequiv/g | | | | |
	Cu pH 5.85	Zn pH 6.00	Ni pH 6.00	Co pH 6.00	Ag pH 4.68
(1)	2.92	2.09	1.85	1.70	6.76
(2)	2.12	0.0	0.0	0.2	5.84
(3)	1.45	0.34	0.45	0.42	—
(4)	1.34	0.0	0.0	0.2	—

[a] Reaction conditions: resin 0.30 g (0.10 g for the reaction with silver ion); metal ion 20 mmole/l., 25 ml (50 ml for the reaction with silver ion); at 30°C, 24 hr.

TABLE V
Effect of Irradiation of the Resins on Reaction Amount of Cupric Ion

| Resin | Reaction amount, mequiv/g | | | |
	0 Mrad	10 Mrad	22 Mrad	32 Mrad
(1)	2.89	2.93	2.98	2.84
(2)	2.08	2.22	2.18	2.13
(3)	1.53	—	—	1.29
(4)	1.31	—	—	1.09

[a] Reaction conditions: resin 0.30 g, at 30°C, 24 hr; buffered aqueous cupric acetate, 20 mmole/l., 25 ml (pH 5.9).

Effect of pH on Reactivity

The dependence of pH on the reactivity toward cupric ion was also investigated. The pH was adjusted by Michaelis' buffer ($0.1N$ CH_3COOH and $0.1M$ CH_3COONa) and Walpole's buffer ($1.0N$ HCl and $1.0M$ CH_3COONa). The results after a reaction time 24 hr are shown in Figure 3. The slope of the pH–mequiv/g curve of (1) is similar to that of (3). On the other hand, the slope of (2) is similar to that of (4). In the cases of (1) and (3), the mequiv/g increases gradually with increasing pH; in the cases of (2) and (4), the mequiv/g does not change in the region of pH less than 5; and in the region above pH 5 the mequiv/g increases rapidly. Polymer (4) reacts hardly below pH 5. Such a slope with polymer (2), which contains N,N-di(β-hydroxyethyl)dithiocarbamate group, was also observed in the case of the PVC derivatives.[4]

Reaction with Other Metal Ions

Metal salts used were acetates in zinc(II), nickel(II), and cobalt(II) and silver nitrate. Reactions of the polymer (0.30 g) with zinc, nickel, and cobalt ions were undertaken in 25 ml buffered solution (pH 5.9) containing 20 mmole/l. metal ion at 30°C, 24 hr, while reaction of the polymer (0.10 g) with silver nitrate was undertaken in 50 ml unbuffered solution (initial pH 4.68) containing 20 mmole/l. silver ion. The reaction amounts after 24 hr are shown in Table IV.

The reaction amounts of metal ions toward polymers (1) and (3) decrease as follows: Ag $\gg$ Cu > Zn > Ni > Co for (1) and Cu > Ni > Co > Zn for (3). The results are not inconsistent with the Irving–Williams order.[8] The reactivity of their polymers toward divalent metal ions is fairly good and has not so a good selectivity for them. The superior reactivity of (1) toward silver ion is attributed to the fact that silver ion is bidentate and has a strong affinity for sulfur atom. On the other hand, polymers (2) and (4) have good reactivity toward silver and cupric ions as shown in Table IV. However, they react slightly with cobalt ion and do not react with zinc and nickel ions at all. Apparently, these polymers have excellent selectivity toward divalent metal ions, that is, they react satisfactorily only with cupric ion among these divalent metal ions.

Effect of ^{60}Co γ Irradiation on Reaction of Polymer with Metal Ions

The polymers containing dithiocarbamate groups are expected to have antiradiation property, as previously reported. The reactivity of the polymers irradiated from a ^{60}Co source with 10, 22, and 32 Mrad γ rays total dose with cupric ion was investigated, and the results were compared with those of unirradiated polymers. Polymer in water in a sealed glass tube was irradiated. The reaction with cupric ion was undertaken in a similar way. The results are shown in Table V.

In the polymers containing dithiocarbamate groups, (1) and (2), the reaction amount of cupric ion almost did not change even after 32-Mrad irradiation. A difference in the IR spectra of these polymers before and after irradiation could not be observed. On the contrary, the amounts of cupric ion were lower obviously in the polymers without dithiocarbamate groups (3) and (4).

Thus, polymers containing dithiocarbamate groups evidently antiradiation properties in their reactivity with cupric ion does not change upon γ-ray irradiation.

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