

# Preparation of Modified Poly(vinyl Chloride) Containing N,N-Di( $\beta$ -hydroxyethyl)dithiocarbamate and Its Reaction with Metal Ions

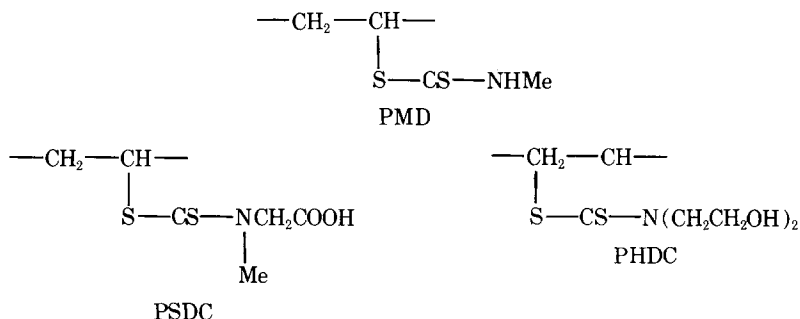
KAZUHISA HIRATANI, YOKO MATSUMOTO, and TSUTOMU  
NAKAGAWA, *Industrial Products Research Institute, Shimomaruko,  
Ota-ku, Tokyo, Japan*

## Synopsis

Reaction of N,N-di( $\beta$ -hydroxyethyl)dithiocarbamate ion with poly(vinyl chloride) (PVC) was undertaken, and the reaction with metal ions of the polymer obtained was investigated. The effect of  $\gamma$ -irradiation on the reaction with metal ion was also studied. The modified PVC (PHDC) obtained from the reaction with N,N-di( $\beta$ -hydroxyethyl)dithiocarbamate ion is pale yellow even after reaction at 100°C for 5 hr in dimethylformamide (DMF); it is soluble in dipolar solvents and its chlorine content is decreased considerably. This polymer reacted well with acetate salts of copper(II), nickel(II), zinc(II), and silver(I) heterogeneously in aqueous solution because of the introduction of hydrophilic groups (two hydroxy groups). The reactivity of the metal ions toward the polymer was of the order  $\text{Ag(I)} \gg \text{Cu(II)} > \text{Ni(II)} > \text{Zn(II)}$ . From the result of the reaction of  $\gamma$ -irradiated polymer with cupric ion, the polymer was judged to have fairly good antiradiation property.

## INTRODUCTION

One of the authors has previously reported<sup>1</sup> that PVC modified by dithiocarbamate has antiradiation property. Polymers containing N-methyldithiocarbamate (PMD) and N-methyl-N-carboxymethyldithiocarbamate (PSDC) were allowed to react with various metal ions and the amount of metal adsorbed was not decreased after  $\gamma$ -ray ( $\text{Co}^{60}$ ) irradiation (maximum 30 Mrad).<sup>2,3</sup> However, in the case of PMD, the polymer reacted only in organic dipolar solvents but never in aqueous solution. On the other hand, PSDC reacted with metal ions heterogeneously even in aqueous solution, but once the polymer was dried completely, the amount adsorbed decreased extremely.<sup>3</sup> Additionally, both polymers were prepared only at a low substitution ratio of dithiocarbamate because the reaction of PVC with the dithiocarbamate ions occurred easily because of crosslinking, and the modified PVC became insoluble in DMF.

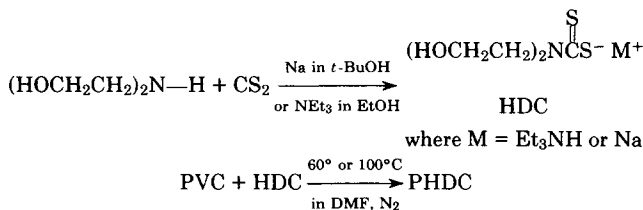


In this paper, the reaction of the polymer, prepared by reaction of N,N-di( $\beta$ -hydroxyethyl)dithiocarbamate ion with PVC, with acetate salts of Cu(II), Ni(II), Zn(II), and Ag(I) in aqueous solution has been investigated. This modified PVC (PHDC), which has a dithiocarbamate group containing two hydrophilic hydroxyethyl groups on the nitrogen atom, is expected to react with metal ions heterogeneously in aqueous solution and may be of great practical value as a chelating polymer. Besides, the hydroxyethyl group itself is not only hydrophilic but also may contribute to the stabilization of the chelate as ligand.

## RESULTS AND DISCUSSION

### Reaction of N,N-Di( $\beta$ -hydroxyethyl)dithiocarbamate Ion (HDC) with PVC

Two kinds of salts of HDC were prepared quantitatively by the reaction of diethanolamine with a little excess of carbon disulfide in alkaline alcohol solution. Upon reaction of sodium or triethylammonium salt of HDC with PVC in DMF at 60° or 100°C under nitrogen atmosphere, pale-yellow polymer was obtained:



The polymer (PHDC) was dissolved in THF and reprecipitated into water. PHDC is soluble in dioxane, THF, DMF, and HMPA, and swelled in alcohols and ethyl ether.

The relation between chlorine and nitrogen contents from elemental analysis and reaction time at 60°C (PHDC II) and 100°C (PHDC I and III) is shown in Table I and Figure 1. PHDC I, II, and III were prepared by the reaction of PVC with sodium HDC at 100°C, with sodium HDC at 60°C, and with triethylammonium HDC at 100°C, respectively. The change in chlorine and nitrogen contents with reaction time cannot be explained only by the substitution reaction

TABLE I  
Reaction of PVC with N,N-Di( $\beta$ -hydroxyethyl)dithiocarbamate Ion

	Reaction conditions		Elemental analysis	
	Temp., °C	Time, hr	N, %	Cl, %
PVC	—	—	0	56.71
PHDC I	100	5	5.14	0.59
PHDC II	60	1	2.04	37.37
		3	3.07	26.96
		5	3.42	22.49
		24	4.59	8.79
PHDC III	100	1	3.46	17.0
		3	4.82	6.35
		5	5.07	4.48

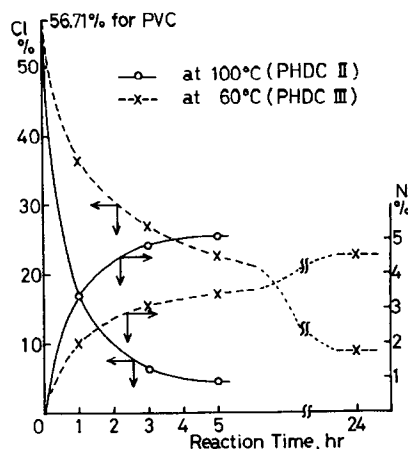


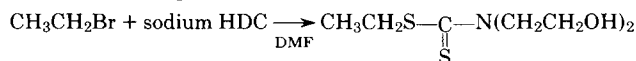
Fig. 1. Relation between chlorine and nitrogen contents and reaction time.

of the dithiocarbamate ion (HDC) for chlorine because the degree of decrease in chlorine content is very large in comparison with the degree of increase in nitrogen content. It is remarkable that in spite of the large decrease in chlorine content the polymer is still soluble in dipolar aprotic solvents and, furthermore, that the color of the polymer stays pale yellow. It is suggested that the hydroxyethyl group on the dithiocarbamate may contribute to these phenomena because in the reaction of PVC with alkyl or dialkyldithiocarbamate ion without hydroxy group at 100°C in DMF, the polymer dissolved becomes gelatinous within 1 hr.<sup>4</sup>

In the reaction of sodium HDC with PVC for 5 hr at 100°C in DMF under nitrogen atmosphere, the polymer in the reaction mixture is not crosslinked and the color of the polymer changes only from white to pale yellow although the chlorine content of the polymer decreases from as much as 56.71% (chlorine content of PVC) down to only 0.59%. It is known that during the thermal dehydrochlorination (less than about 55% chlorine content) of PVC in DMF the color changes to brown or dark brown.<sup>5</sup> Therefore, it must be assumed that the dithiocarbamate group inhibits deep discoloration of the polymer in spite of the remarkable decrease in chlorine content. It has been reported that in the reaction of PVC with lithium thiophenoxide at 100°C for 25 hr, discoloration of the polymer does not occur and the dehydrochlorination is considered to be depressed for the reason that thiophenoxide ion reacts with PVC to be introduced in PVC and successive E2 elimination is depressed.<sup>6</sup>

From Table I, the reactivity of sodium HDC with PVC seems to be larger than that of triethylammonium HDC because the increase in nitrogen content of PHDC I with reaction time is more than that of PHDC III at 100°C under the same conditions. Thus, a kind of salt effect was observed in this reaction. It is expected that PHDC I is more reactive toward metal ions than PHDC III. In fact, the reactivity of PHDC I toward metal ion has been observed to be larger than that of PHDC III (see Table II).

The IR spectra of PHDC III-5, which was obtained by the reaction at 100°C for 5 hr, and of S-ethyl-N,N-di( $\beta$ -hydroxyethyl)dithiocarbamate as a model compound are shown in Figure 2.



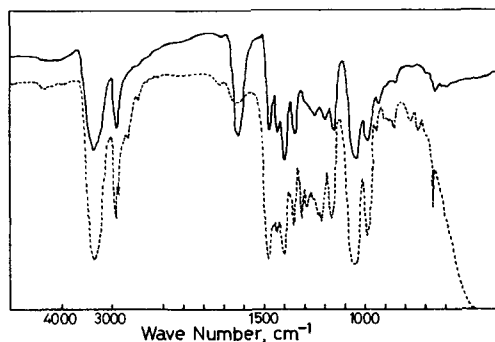


Fig. 2. Infrared spectra: (—) PHDC III-5; (---) S-ethyl-N,N-di( $\beta$ -hydroxyethyl)dithiocarbamate.

The IR spectra indicate the absorption bands at 3400, 1480, 1160, and 990  $\text{cm}^{-1}$  assigned to the dithiocarbamate group and a strong absorption band at 1640  $\text{cm}^{-1}$ . The introduction of the dithiocarbamate group into PVC could be confirmed by comparison with the IR of the model compound.

In Figure 2, a strong absorption band appears at 1640  $\text{cm}^{-1}$ ; and if the band could be assigned to a carbon-carbon double bond, this polymer should have a long conjugated system of carbon-carbon double bonds judging from the elemental analysis data which show that the chlorine content decreases considerably with reaction time. This possibility, however, can be ruled out by the discoloration of the polymer (pale yellow). Therefore, this absorption band might be attributed to the further reaction of N,N-di( $\beta$ -hydroxyethyl)dithiocarbamate with PVC and/or a lone carbon-carbon double bond formed by the dehydrochlorination. As shown later, the strong absorption band at 1640  $\text{cm}^{-1}$  does not participate at all in the reaction with metal ions.

At the present time it is assumed that amide carbonyl or thiolcarbamate, to which the absorption band at 1640  $\text{cm}^{-1}$  could be assigned, is formed in the further reaction involving the participation of neighboring dithiocarbamate<sup>7</sup> from the following experimental results: (1) A strong absorption band appears at 1640  $\text{cm}^{-1}$  in the IR spectrum of the product obtained by the reaction of 1,3-dibromopropane or 1,2-dichloroethane with salt of HDC. (2) On the other hand, the band does not appear at all in the reaction of monohalogenated reactants such as bromoethane and benzyl chloride with salt of HDC (see Fig. 2). (3) In addition, the band does not appear at all in the reaction of PVC with sodium N,N-diethyl- or N,N-dimethyldithiocarbamate.<sup>7</sup> (4) Also with use of poly(chloromethylstyrene), which is not susceptible to the participation of neighboring dithiocarbamate because of the long distance between neighboring chlorine atoms, unlike PVC, the absorption band does not appear.

On the basis of these experimental data, it is assumed that in the reaction of PVC with salt of HDC, a six-membered heterocyclic intermediate may partially be formed by the neighboring-group participation of the dithiocarbamate group and then further react with the hydroxy group\* on the dithiocarbamate itself, finally to change into a substituent containing amide or thiolcarbamate group.

\* It has been reported that such a heterocyclic compound in a low molecular model can undergo reaction with hydroxide and ethoxide ions.<sup>8</sup>

## Reaction of PHDC with Metal Ions

### *Reaction of PHDC With cupric ion*

In this study, three kinds of polymers, prepared (i) by the reaction with sodium HDC at 100°C for 5 hr in DMF under nitrogen atmosphere (abbr. PHDC I-5); (ii) with sodium HDC at 60°C for 24 hr (PHDC II-24), and (iii) with triethylammonium HDC at 100°C for 5 hr (PHDC III-5), were ground to a fine powder below 0.5 mesh in liquid nitrogen and used in the reaction with metal ions.

First, the reaction of PHDC I-5, II-24, and III-5 with 20 mmole/l. aqueous cupric acetate at 50°C was undertaken; and the amount (meq/g) of cupric ion reacted as a function of time is shown in Table II. In this reaction the pH in the aqueous solution was not adjusted. Change of pH as a function of time for PHDC III-5 is also shown in Table II. It was found that these polymers could react moderately with cupric ion. Although the reactivity of the three polymers could not be compared quantitatively with each other, the degree of cupric ion reactivity seems to be inclined to increase with increase in nitrogen content (Table I). It is also evident that the larger the reaction amount of cupric ion, the less the pH in aqueous solution. Acetic acid was probably generated during the reaction of the polymer with cupric acetate, making the solution acidic.

The IR spectrum of the PHDC-cupric ion complex changes remarkably in comparison with that of the original polymer. The IR spectra of PHDC I-5 reacted with cupric ion at 50°C for 5 and 24 hr and that of the original polymer are shown in Figure 3. The absorption band at 1480  $\text{cm}^{-1}$  assigned to the thione amide group decreased upon reaction with metal ion. The absorption bands at 1160  $\text{cm}^{-1}$  and 990  $\text{cm}^{-1}$  also decreased considerably. Presumably nitrogen and/or sulfur atoms participate significantly in the reaction. However, the intensity of the band at 1640  $\text{cm}^{-1}$  does not change at all.

Next, the effect of the concentration of cupric ion on the reaction was investigated. The result for PHDC III-5 is shown in Figure 4; the higher the concentration, the larger the reaction amount of cupric ion.

Dependence of pH on the reaction of PHDC I-5 with cupric ion was also investigated. Each buffered solution was adjusted by a mixture of 1 *M* sodium acetate and 1 *N* HCl. The relation between reaction amount and pH is shown in Table III. The pH decreases as the reaction of polymer with metal ion proceeds. It was also found that increasing pH tends to increase the amount of cupric ion that reacts with the polymer. Apparently the basicity of the hy-

TABLE II  
Reaction Amount of Cupric Ion<sup>a</sup>

	Reaction amount, meq/g				
	0 hr	1 hr	3 hr	5 hr	24 hr
PHDC I-5	0	—	—	2.79	4.56
PHDC II-24	0	1.20	1.47	1.87	2.27
PHDC III-5	0	1.32	1.80	2.28	3.15
pH	5.8	5.2	5.0	4.8	4.4

<sup>a</sup> Reaction conditions: polymer 0.300 g, at 50°C; unbuffered aqueous  $\text{Cu}(\text{OAc})_2$ , 20 mmole/l., 50 ml.

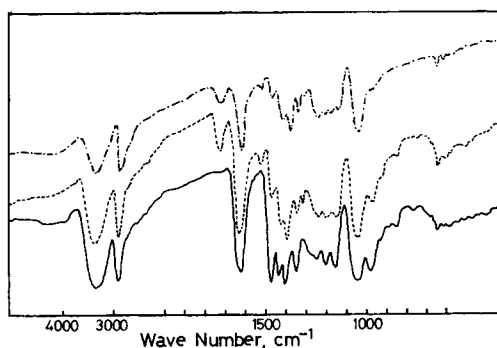


Fig. 3. Change in infrared spectra: (—) PHDC I-5; (---) Cu-PHDC I-5 treated for 5 hr at 50°C in aqueous 20 mmole/l. cupric ion; (- · - ·) Cu-PHDC I-5 treated for 24 hr at 50°C.

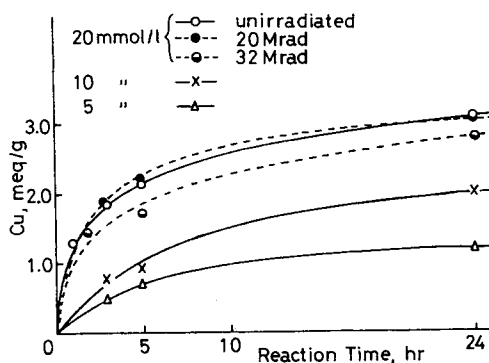


Fig. 4. Effect of concentration of cupric ion and irradiation of PHDC III-5 on reaction amount at 50°C in unbuffered solution.

TABLE III  
Dependence of pH on the Reaction Amount of Cupric Ion<sup>a</sup>

pH before reaction	Reaction amount, meq/g	pH after reaction
1.1	1.58	1.0
2.5	2.20	2.3
3.5	2.50	3.4
3.8	2.96	3.7
4.8	3.27	4.7
5.3	4.80	—
5.9	5.73	5.0

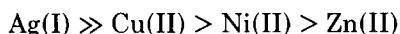
<sup>a</sup> Reaction conditions: PHDC I-5, 0.150 g, at 50°C for 24 hr; buffered aqueous  $\text{Cu}(\text{OAc})_2$ , 20 mmole/l., 25 ml.

droxyethyl group on the dithiocarbamate group as ligand increases with increasing pH, that is, the coordination ability of the dithiocarbamate group increases. The pH after reaction for 24 hr decreases, as shown in Table III. But the pH in the case of buffered solution decreases less than with use of unbuffered solution (Table II). Also in the case of PHDC III-5, the reaction amount of cupric ion reached 3.55 meq/g at 50°C for 24 hr in the buffered solution at an initial pH of 5.9. Accordingly, it is apparent that the reaction amount of metal ion depends largely on pH; as a result, the reaction amount rises to above the amount that

reacts even with use of buffered solution the pH of which is a little less than the initial pH of the unbuffered solution.

*Heterogeneous Reaction with Other Metal Ions in Water*

It is of interest how the prepared polymer reacts with other metal ions in comparison with the reactivity of cupric ion. The metal salts used were acetates of zinc(II), nickel(II), and silver(I). The reaction of PHDC III-5 with 20 mmole/l. acetate salts was carried out in the same manner as the reaction with cupric acetate. The results are shown in Table IV. A buffered solution was used; and the pH before and after the reaction is also shown in Table IV. From this result, the reactivity of metal ions toward the polymer has the following tendency:



The pH after the reaction indicates a moderate change in comparison with before the reaction. In the case of silver ion the difference between the pH after and before the reaction is most remarkable. This is compatible with the fact that silver ion had the highest reaction amount in this reaction. The excellent reactivity of silver ion can be attributed to the fact that silver ion is bidentate and has a strong affinity for sulfur atom. The reaction amount of silver ion reached a maximum of 13.3 meq/g.

Next, it was investigated whether the polymer containing dithiocarbamate (HDC) had a selectivity toward metal ions in aqueous solution containing two metal ions. A competitive reaction between cupric ion and another ion of the three toward the polymer was attempted. In Table IV the result with unbuffered solution is shown. Cupric ion reacted with PHDC III-5 much more than zinc and nickel ions and less than silver ion. In the case of Ag(I)-Cu(II) mixed solution, though the concentration of each metal ion was 10 mmole/l., the reaction amount of silver ion agrees well with that in the case of the solution containing only 20 mmole/l. silver ion. Thus, it is apparent that the polymer has excellent selectivity toward silver ion compared with cupric ion, and toward cupric ion compared with zinc and nickel ions.

It can be expected from these results that cupric ion fixed on the polymer will be exchanged for free silver ion in aqueous solution. The exchange reaction between cupric and silver ions was attempted. After the polymer, which had been allowed to react with cupric ion at 50°C for 24 hr in aqueous solution, was washed well with water followed by methanol, it was allowed to react with silver

TABLE IV  
Reaction of PHDC III-5 with Metal Ions [Zn(II), Ni(II), Cu(II), and Ag(I)]

	Metal ion <sup>a</sup>				Mixed metal ions, <sup>b</sup>					
	Zn	Ni	Cu	Ag	Zn-Cu	Ni-Cu	Ag-Cu			
pH before reaction	5.4	5.4	5.3	5.4	5.4	5.5	5.3			
Amount of metal ion reacted, meq/g	0.98	1.43	2.00	13.3	0	1.35	0.4	1.32	13.0	0
pH after reaction	5.3	4.7	4.8	—	5.2	5.1	—			

<sup>a</sup> Reaction conditions: polymer 0.150 g (0.050 g for the reaction with silver ion); metal ion 20 mmole/l., 25 ml (50 ml for the reaction with silver ion); at 50°C for 5 hr.

<sup>b</sup> Reaction conditions: polymer 0.150 g (0.030 g for the reaction with Ag-Cu mixed ions); mixed metal ions 10 mmole/l. (for each metal ion), 50 ml; at 50°C for 5 hr.

ion at 50°C for 1, 3, and 5 hr. The result is shown in Table V. Free silver ion exchanged obviously for cupric ion fixed on polymer. Very little free silver ion remained in aqueous solution after the reaction in all cases for 1, 3, and 5 hr under these conditions. Therefore, it can be anticipated that the exchange reaction will proceed further when the free silver ion concentration remains high because silver ion is much more reactive than cupric ion toward the polymer (Table IV).

*Effect of  $\gamma$ -Ray Irradiation (Co<sup>60</sup>) on the Reaction of Polymer  
with Cupric Ion*

As previously reported,<sup>1</sup> the reactivity of the polymer containing the dithiocarbamate (HDC) group toward metal ion can also be expected to remain stable because dithiocarbamate has antiradiation property. The reaction of polymer with cupric ion was examined. After PHDC III-5 was irradiated from a cobalt 60 source with 20 and 32 Mrad  $\gamma$ -rays as total dose. The relation between reaction amount and reaction time is shown in Figure 4. The reaction amount of the 20 Mrad-irradiated polymer did not change in comparison with unirradiated polymer. With the 32 Mrad-irradiated polymer also little decrease in reaction amount was observed. From this result the polymer is judged to have fairly good antiradiation property.

## EXPERIMENTAL

### Materials

Poly(vinyl chloride) (D.P. 800) employed was purified by dioxane-methanol reprecipitation and dried at 50°C for one day under vacuum.

All reagents and solvents employed were commercially available materials and purified by standard methods.

### Preparation of Sodium HDC

In a dried 1-l. Erlenmeyer flask equipped with reflux condenser was placed 9.2 g (0.4 mole) sodium metal in 400 ml *t*-butanol and stirred at 60°C to complete reaction. To the mixture was added 45.6 g (0.6 mole) carbon disulfide with stirring at room temperature. Then to the stirred solution at room temperature was added dropwise 42.0 g (0.4 mole) diethanolamine over a period of 1 hr, and

TABLE V  
Reaction of Silver Ion with Cupric Ion-Polymer Complex<sup>a</sup>

Reaction time, hr	meq/g of Ag(I) <sup>b</sup>	meq/g of Cu(II) <sup>c</sup>
1	9.3	2.5
3	9.5	2.4
5	9.6	2.4

<sup>a</sup> Reaction conditions: PHDC I-5, 0.150 g; aqueous Cu(II), 20 mmole/l., 25 ml (initial pH 5.3), at 50°C for 24 hr; actual Cu(II) ion adsorbed by PHDC I-5, 4.8 meq/g polymer.

<sup>b</sup> Ag(I) amount remaining in the polymer.

<sup>c</sup> Cu(II) amount reacted with the Cu(II)-polymer complex.



the mixture was stirred at room temperature for two days. The solvent was removed under reduced pressure giving a pale-yellow solid. After the product was washed with tetrahydrofuran followed by ethyl ether, it was dried under vacuum and obtained quantitatively.

The product was confirmed to be sodium HDC by the reaction with ethyl bromide in DMF to give S-ethyl-N,N-di( $\beta$ -hydroxyethyl)dithiocarbamate; IR, see Figure 2; NMR ( $\text{CDCl}_3$ ) (ppm): 1.35 (3H, *t*,  $J = 7.8$  Hz), 3.26 (2H, *q*,  $J = 7.8$  Hz), 4.02 (2H, *s*) and 3.66–4.70 (8H, broad); mass:  $m/e$  209( $\text{M}^+$ ).

### Preparation of Triethylammonium HDC

To a mixture of 45.5 g carbon disulfide and 43.0 g triethylamine in 20 ml ethanol, which was cooled below 5°C, was added dropwise 42.2 g diethanolamine over a period of 1 hr. After the mixture was stirred for 18 hr, the solvent and excess carbon disulfide were evaporated to give a yellowish-orange sticky liquid quantitatively.

### Reaction of Sodium HDC with PVC

In a 500-ml three-necked flask equipped with a stirrer, thermometer, gas inlet tube, and condenser was placed a solution of 22.8 g (0.365 mole) PVC in 300 ml DMF, which was then raised up to 100°C under nitrogen atmosphere. To the stirred solution was added 74.1 g (0.365 mole) sodium HDC in 100 ml DMF. The mixture was stirred at 100°C for 5 hr under nitrogen atmosphere. The reaction mixture was then poured into water. A pale-yellow polymer was precipitated. The polymer was separated by filtration and again dispersed in water for one day. After the polymer was separated by filtration, it was dissolved in THF and reprecipitated in a large amount of water. This precipitated polymer was filtered and washed several times with water and then dried under vacuum. Yield, 41 g.

By the same procedure the reaction at 60°C gave also a pale-yellow polymer, and the reaction of triethylammonium HDC with PVC at 100°C gave also a pale-yellow polymer.

The polymer obtained in the final course of the preparation was put into a vessel, then liquid nitrogen was added, and the polymer was ground to a fine powder below 0.5 mesh. Powdered polymer was employed in the reaction with metal ions.

### Measurement of Amount of Metal Ion Reacted with PHDC

General method: A 0.300-g sample of the powdered polymer was placed in a 100-ml glass-stoppered Erlenmeyer flask, and into it was poured 50 ml aqueous solution containing 20 mmole/l. metal ion. Then the flask was partially immersed in a thermostat bath held to  $\pm 0.5^\circ\text{C}$ . During the experiment the flask was agitated by shaking at 50°C. After a given time, the powder 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 polymer was calculated from the difference between the concentration of 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.

### $\gamma$ -Irradiation of PHDC

The polymer (PHDC III-5) was irradiated with cobalt 60  $\gamma$ -rays. The total doses were 20 and 32 Mrad, and the dose rate was 1.0 Mrad/hr. About 3 g of the polymer powder was sealed with 50 ml distilled water in a glass tube and irradiated at 23°C. The irradiated polymer sample was used for the reaction with metal ions.

### References

1. T. Nakagawa and Y. Fujiwara, *J. Appl. Polym. Sci.*, **15**, 753 (1976).
2. T. Nakagawa, J. Taniguchi, and Y. Fujiwara, *J. Appl. Polym. Sci.*, **15**, 733 (1976).
3. T. Nakagawa, N. Oishi, and Y. Fujiwara, *J. Appl. Polym. Sci.*, **15**, 745 (1976).
4. Unpublished result.
5. Y. Iwami, H. Ishikawa, and Y. Minoura, *Kogyo Kagaku Zasshi*, **72**, 2478 (1969).
6. Y. Iwami and Y. Minoura, *Kogyo Kagaku Zasshi*, **72**, 2475 (1969).
7. T. Nakai, Y. Ueno, and M. Okawara, *Tetrahedron Lett.*, 3831 (1967); *Bull. Chem. Soc. Jpn.*, **43**, 156 (1970); T. Nakai, H. Kawaoka, and M. Okawara, *ibid.*, **42**, 508 (1969).
8. T. Nakai and M. Okawara, *Bull. Chem. Soc.*, **43**, 1864 (1970).

Received March 11, 1977