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Synthesis and chelating properties of poly[(*N*,*N*-dicarboxymethyl)allylamine] derived from poly(allylamine)

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SUMMARY

Poly[(N,N-dicarboxymethyl)allylamine] as a water-soluble polymeric chelating agent was prepared by carboxymethylation of poly(allylamine) (PAA) with chloroacetic acid or bromoacetic acid. The ^{1}H-NMR, IR, and elementary analyses showed that the iminodiacetic group was introduced quantitatively into the amino group of PAA. Chelating properties of this polymeric chelating agent toward Cu^{2+}, Ni^{2+}, Zn^{2+}, and Ba^{2+} were examined by potentiometric titration.

INTRODUCTION

Poly(allylamine) (PAA) is a water-soluble polymer having pendant primary amino groups and its chelating properties for metal ions have been studied(1). In addition, the chemical reactivity of the primary amino group allows introduction into the polymer of various functional groups such as biguanide residue for a novel polycationic polymer (2), long chain perfluoroalkyl groups for polymer Langmuir-Blodgett films (3), or cyclodexitrin moiety for polymeric catalysts (4). PAA was also reported to react with chloroacetic acid to partially introduce an iminodiacetic acid group for developing setting retardants (5) or anticorrosive and scale-inhibiting agents for water (6). Poly(vinylamine) (PVA) is known as a typical water-soluble polymer having primary amino groups and its amino groups have been converted to various functional groups such as iminodiacetic acid or thiourea (2). However, the degree of functionalization for PVA was generally low due to the steric hindrance of primary amino groups compared with PAA.

We described here the synthesis and characterization of poly[(N,N-dicarboxymethyl)allylamine] as a water-soluble polymeric chelating agent from PAA with chloroacetic acid or bromoacetic acid and its chelating properties toward metal ions was examined by potentiometric titration and continuous variation analysis.

EXPERIMENTAL

General

Unless stated otherwise, all reagents and chemicals were obtained from Wako Pure Chemical Co. and used without further purification. Poly(allylamine) (PAA-L, $Mw=1X10^4$, PAA-H, $Mw=1X10^5$) were obtained from Nittobo Co. ^{1}H NMR, IR, and UV spectra were recorded on a JNM-GSX 400, a Shimadzu FT-IR-4200, and a Hitachi U-2000 instruments, respectively. Potentiometric titration was carried out by using a Toko TR-100 pH Meter.

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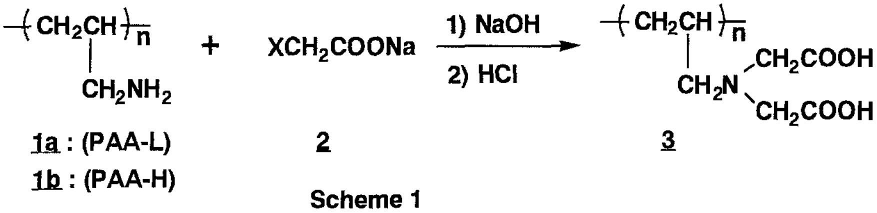
Poly[(N,N-dicarboxymethyl)allylamine] (3).

General procedure is as follows. To an aqueous solution containing chloroacetic acid (6.69 g, 0.07 mol) was added dropwise a solution made from NaOH (2.80 g, 0.07 mol) plus 25 ml of water with stirring at 30 °C. Then, the solution was added dropwise to an aqueous solution of poly(allylamine) (PAA-L) (**1**) (5.06 g, 0.018 mol) with stirring at 50 °C. The reaction mixture was kept for 1 hr at 50 °C, and heated at 90-95 °C for 2 hrs with adding 30 % NaOH solution to maintain at pH 10. After the reaction mixture was kept at room temperature for one over night, pH was adjusted to 1 by conc. HCl. The remaining precipitate was dissolved in 50 mL of NaOH water and adjusted the pH to 1 by conc. HCl. This reprecipitation process was repeated 2 times. After the resulting precipitate was separated and dried in vacuo, colorless solid polymer was obtained. The polymer yield was 70 %. Anal. Calcd for $(C_7H_{11}NO_4)_n$: C, 48.55 %; H, 6.40 %; N, 8.09 %; O, 39.96 %. Found: C, 48.87 %; H, 6.53 %; N, 8.49 %; O, 36.11 %. ^1H-NMR (D_2O) d (ppm): 1.0-2.2 (br, 3H, $-CH_2CH-$), 2.7-3.3 (br s, 2H, $-CH_2N$), 3.4-3.8 (br s, 4H, NCH_2COO). IR (KBr): 1630, 1730 cm^{-1} (νC=O) and 1400 cm^{-1} (νC-O).

RESULTS AND DISCUSSION

Synthesis of Poly[(N,N-dicarboxymethyl)allylamine] (3)

Poly(allylamine) (PAA) of which average molecular weight were 1 X 10^4 (PAA-L) and 1 X 10^5 (PAA-H) were used for the introduction of iminodiacetic group into amino group. Sodium chloroacetic acid or bromoacetic acid were added to PAA solution and heated with adding 30 % NaOH solution to maintain at pH 10. After the reaction mixture was acidified with conc.HCl, a polymer product was precipitated. The reaction condition and the results were summarized in Table 1.



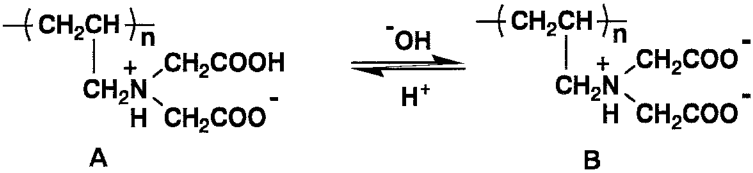
Scheme 1

Table 1 Preparation of Poly[(N,N-dicarboxymethyl)allylamine] (3)

	carboxymethylation				product		
run no.	M_n of **1**	X of **2**	temp., °C	time, h	yield, %	**3**	F_n[a]
1	$1X10^4$	Cl	90	2^b	70	**3a-1**	0.95
2	$1X10^4$	Br	90	2^b	54	**3a-2**	0.87
3	$1X10^4$	Br	50	16	90	**3a-3**	0.88
4	$1X10^5$	Cl	90	2^b	89	**3b-1**	1.00

a Degree of functionalization per repeating unit of **1**. Determined by ^1H-NMR.
b Reaction mixture was stirred at 50°C for 1h before heating.

The reaction of PAA-L with chloroacetic acid gave a moderate yield of the polymer product (run no. 1). The IR spectrum of the acidified 3a-1 showed disappearance of the bands at 1510 cm^{-1} and 1599 cm^{-1} which are correspond to N-H deformation vibration and appearance of two varieties of carboxyl group, the 1730 cm^{-1} band is due to C=O stretching in $>HN^+-CH_2COOH$ group and the 1630 cm^{-1} band is due to C=O stretching in $>HN^+-CH_2COO^-$ group. This result indicates that the ionic structure of the iminodiacetic group is A state as shown in Scheme 2. A similar result is known for the acid EDTA. The spectrum of 3a-1 isolated from pH 8.0 solution showed that only 1630 cm^{-1} band was observed, which means that the ionic structure of the iminodiacetic group is B state. The IR spectrum of 3a-1 isolated from pH 10 solution also showed 1630 cm^{-1} band due to C=O stretching in $>HN^+-CH_2COO^-$ group.



Scheme 2

The ^1H-NMR of 3a-1 shows a signal at δ 3.6 corresponding to the NCH_2COO proton. The comparing the relative peak intensity between $-CH_2N$ proton at δ 3.0 and carboxymethyl proton at δ 3.6 suggests that the iminodiacetic moiety is introduced quantitatively into the amino groups of PAA-L. The elementary analysis also indicates the reaction is completely for run no. 1.

The reaction of PAA-L with bromoacetic acid under the same condition as that for run no. 1 showed low yield (run no. 2). We assume that the most amino group of PAA can not react with bromoacetic acid, because the conversion of bromoacetic acid to hydroxyacetic acid under the basic condition is faster than that of chloroacetic acid. Therefore, the most reaction products were remained in acidic solution due to their polycationic nature. The product yield reached 90 % when the reaction was carried out at 50 °C for 16 h (run no. 3). However, the introduction of iminodiacetic group was not quantitative according to the ^1H-NMR and elementary analyses. The reaction of PAA-H with chloroacetic acid under the same condition as that for run no. 1 also showed a good yield (run no. 4). The ^1H-NMR of 3b-1 shows that the amino groups of PAA-L is completely converted to the iminodiacetic groups.

Chelating Property of Poly[(N,N-dicarboxymethyl)allylamine] (3)

To evaluate the chelating abilities of the obtained polymer, a potentiometric titration method has been employed. Figure 1 shows the titration curves of 3a-1 in 2.0 M KCl solution with a 0.1 N NaOH aqueous solution in the absence and presence of several metal ions. From the curve (no metal), one equivalent point that corresponded to the neutralization of COOH was obtained at pH 7.0. Second equivalent point corresponded to the neutralization NH^+ was not observed clearly. The titration curve of iminodiacetic acid also shows a property which is similar to that for 3a-1 (7). In the presence of Cu^{2+}, Ni^{2+}, or Zn^{2+}, the titration curves shifted downward, suggesting the chelate formation of metal ion. Although the titration curve did not so shifted in the case of Ba system, curve Ba also shows the chelate formation at pH > 8. An extent of a lowering pH in the presence of metal ion qualitatively indicates an strength of stability constant of chelate formation. The pH titration curves of each metal ion suggested that the relative stability constants were in the order $Cu^{2+} > Ni^{2+} > Zn^{2+} > Ba^{2+}$. This order is same as that for iminodiacetic acid resin (8). Poly[(N,N-dicarboxymethyl)allylamine] (**3b-1**) prepared from PAA-H was also showed the same titration curve as that in Figure 1.

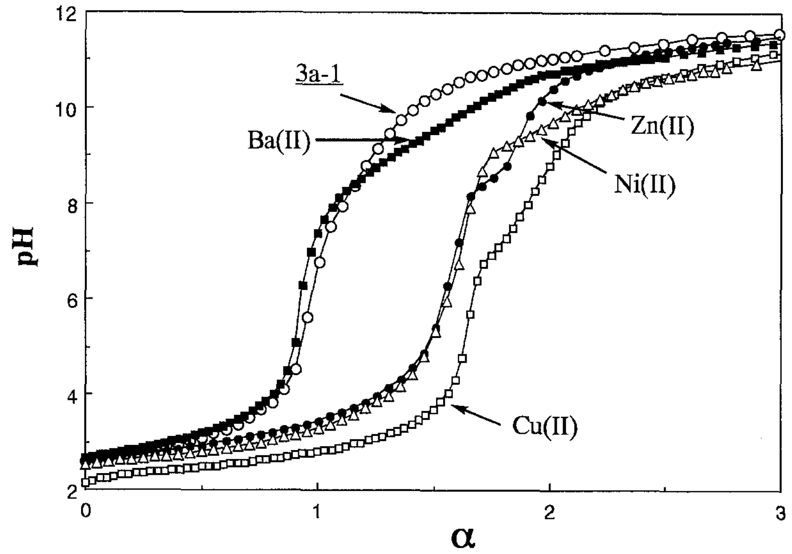


Figure 1. Titration of 4.4 mM (repeating unit) **3a-1** and **3a-1** in the presence of 2.2 mM Cu^{2+}, Ni^{2+}, Zn^{2+}, and Ba^{2+} in 2.0 M KCl solution with 0.1 N NaOH solution.

Coordination numbers of the metal ion complexes on the resulting polymeric chelating agents prepared from PAA-L (**3a-1**) and PAA-H (**3b-1**) were confirmed by the continuous variation method. It is known that the iminodiacetic acid- Cu^{2+} complex shows an absorption maximum at 265 nm (9). Figure 2 indicates the results of continuous variation analysis for the both polymer- Cu^{2+} system measured at 265 nm at the total concentration of $2X10^{-3}$ mol/L at pH 5-6. A maximum for **3a-1** and **3b-1** are observed at ratio of $[Cu^{2+}]/([Cu^{2+}] + [\mathbf{3}]) = 0.4$ and 0.3, respectively. This indicates that Cu^{2+} bonds to 1.5 of repeating unit for **3a-1** and 2.5 of repeating unit for **3b-1**. It is known that Cu^{2+} forms 1 : 1 complex with iminodiacetic acid group in neutral region and forms 1 : 2 complex in strong basic media (7). However, the present results show that PAA forms a complex with more than one iminodiacetic group although the analysis is carried out at pH 5-6 . In the case of general polymeric ligands, the situations are complicated because of their steric hindrance. In our poly[(N,N-dicarboxymethyl)allylamine]-Cu^{2+} system, these observations indicates that the predominant species under the experimental conditions is a complex having a ligand ratio iminodiacetic acid : Cu^{2+} = 1 : 1 and some extent of free ligand can exist due to their steric hindrance.

In this paper we have shown that the iminodiacetic moiety was introduced quantitatively into the amino groups of poly(allylamine) which is a water-soluble linear polymer having pendant primary amino groups. Chelating properties of Poly[(N,N-dicarboxymethyl)allylamine] can be easily studied by various analytical techniques due to its homogeneous character in water. This homogeneous character in water is also advantageous for preparing a polymer-metal chelate precursor for high T_C superconducting ceramics (10).

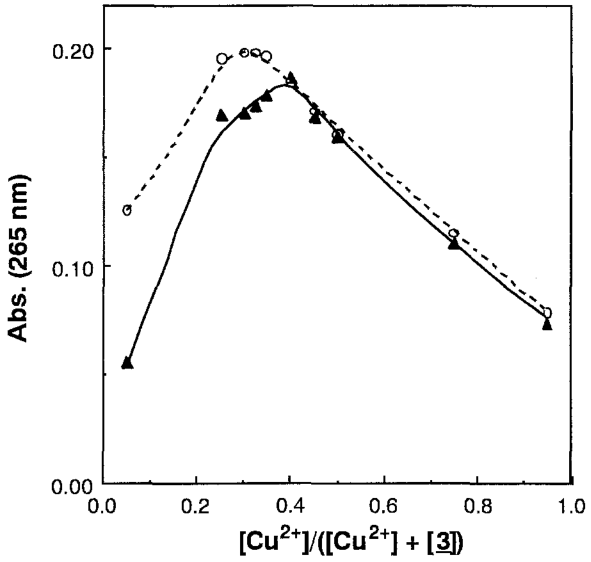


Figure 2. Continuous variation analysis of 3a-1 (▲) and 3b-1 (○)-Cu^{2+} complexes measured at 265 nm at pH 5-6. Total concentrations; [repeating unit of 3] + [Cu^{2+}] = 2X10^{-3}mol/L.

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