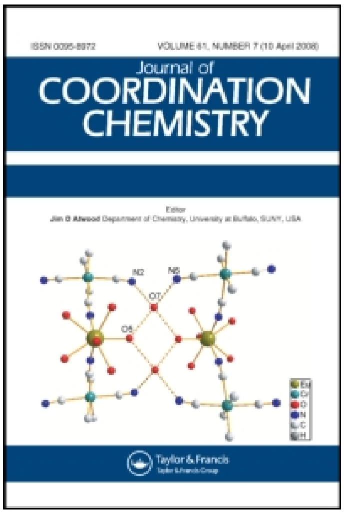

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Mitsuo Yamada[a][b]; Makoto Takagi[a]; Keihei Ueno[a]
[a] Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka, Japan [b] Central Research Laboratories, Toyo Soda Manufacturing Co. Ltd., Tonda, Shin-Nanyo-shi, Japan

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SYNTHESIS AND CHELATING BEHAVIOR OF BIS(CARBOXYMETHYL)IMINOMETHYLENE DERIVATIVE OF OLIGOMERIC STYRENE†

MITSUO YAMADA‡, MAKOTO TAKAGI and KEIHEI UENO

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

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A new macromolecular water soluble ligand, bis(carboxymethyl)iminomethylene derivative of oligostyrene ($\bar{P}n$ = 6 ~ 8), was synthesized through the reaction between chloromethylated oligostyrene and dimethyl iminodiacetate in DMF.

Acid dissociation constants and chelate stability constants were obtained from the results of titrations of the ligand in the absence and the presence of metal ions in aqueous solution; pKa_1 2.8($n = 1.08$), pKa_2 9.56($n' = 1.24$); $\log K_{MA}$ 4.56(Ca^{II}), 4.19(Mg^{II}), 7.45(Co^{II}), 8.17(Ni^{II}), 7.56(Zn^{II}), $\log K_{MA_2}$, 6.05(Co^{II}), 6.43(Ni^{II}), 6.28(Zn^{II}) at 25°C, $\mu = 0.1(KNO_3)$.

INTRODUCTION

During the course of our investigation on the selective membrane dialysis of metal ion with the combined use of the perme-resistant water soluble high molecular-weight chelating agent,[1] the synthesis and the investigation on the chelating behavior of such ligands have been undertaken in our laboratory. The oligomer of styrene having methyleneiminodiacetic acid groups on the aromatic rings as chelating sites seemed to be a successful ligand for our purpose. The skeletal structure of the ligand is similar to that of the chelating resin such as Dowex A 1, the only difference from the water soluble ligand being that the main chain in Dowex A 1 forms three dimensional network to give a water insoluble polymer.

Many synthetic routes have been reported to introduce methylene iminodiacetic acid group to the aromatic rings of polystyrene as shown in scheme 1,[2–7] but we found none of them could be applied to the preparation of water soluble polystyrene derivatives. Finally, it was found that the reaction of chloromethylated oligostyrene with dimethylester of iminodiacetic acid in DMF followed by alkaline hydrolysis yielded a water soluble derivative.

A potentiometric investigation of this ligand in the absence and presence of metal ions revealed that the chelating behavior of this polymeric ligand is similar to that of N-benzyliminodiacetic acid which is the monomeric unit of the polymer ligand. However, some metals caused extensive precipitation of the polymer–metal complex under the conditions where N-benzyliminodiacetic acid does not form precipitates.

EXPERIMENTAL

The ligands were synthesized according to scheme 2.

Synthesis of (3)

Polystyrene($\bar{P}n$ = 1600 ~ 1800) and oligostyrene($\bar{P}n$ = 6 ~ 8) were chloromethylated with chloromethylmethyl ether in the presence of zinc chloride at 25 ~ 40°C, to obtain chloromethyl polystyrenes (2) of 30 ~ 55% chloromethylation degree for the polymer of $\bar{P}n$ = 1600 ~ 1800, and 90.9% for the oligomer, both of which were easily soluble in organic solvents.

A solution of 2.05 g (17.0 m mol chloromethyl unit) of (2)($\bar{P}n$ = 6 ~ 8; degree of chloromethylation, 91%) in 50 ml of DMF was placed in a reaction flask, to which 9.80 g (60 m mol) of dimethyl iminodiacetate was added and the mixture was stirred at 70°C under nitrogen for 8 hr. After the reaction, precipitate of dimethyliminodiacetate hydrochloride was filtered off, and the filtrate was poured into aqueous methanol to precipitate the crude product. It was finally purified by repeated

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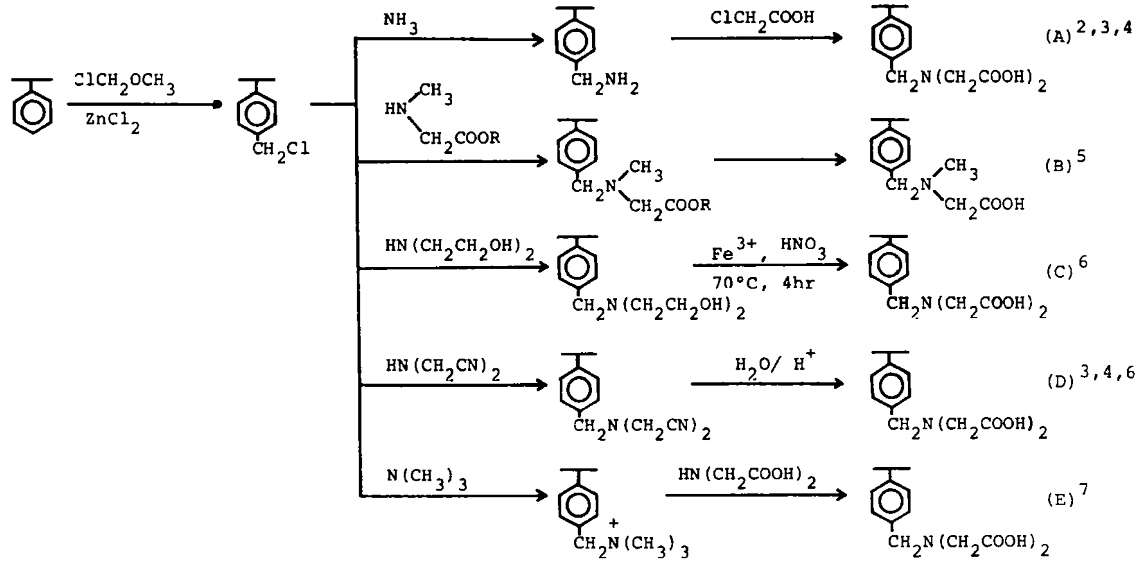
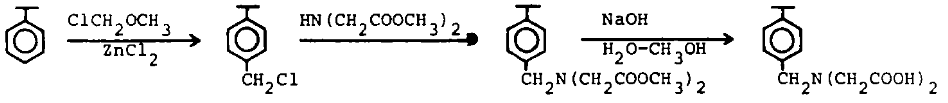
†Contribution No. 524 from the Department of Organic Synthesis, Kyushu University.

‡Present address: Central Research Laboratories, Toyo Soda Manufacturing Co. Ltd., Tonda, Shin-Nanyo-shi, 746 Japan.



SCHEME 1



(1) (2) (3) (4)

SCHEME 2

precipitation from DMF solution with aqueous methanol (70 ~ 90% yield). The pure polymer ester was negative to Beilstein's test, and was soluble in various organic solvents, such as benzene, chloroform or dioxane.

Infrared spectra: $\nu_{C=O}$ 1750 cm^{-1}. ^{1}H NMR spectra (Bruker WH-90, $CDCl_3$, δ ppm from TMS): 6.89, 7.15 (s, broad, aryl H), 3.77 (s, broad, Aryl-CH_2-), 3.47 (s, O-CH_3), 3.37 (s, N-CH_2-) and 1.1 ~ 2 (m, broad, polymer chain -CH_2-CH-). *Anal.* Calcd for $(C_8H_8)_{0.091}$ $(C_{15}H_{19}NO_4)_{0.909}$: C, 65.96; H, 6.94; N, 4.87. Found: C, 65.78; H, 7.18; N, 4.74.

Synthesis of (4)

A mixture of 1.5 g of (3) ($\bar{Pn}$ = 1600 ~ 1800), 1.6 g (0.04 mol) of NaOH and 30 ml of water was heated at 60°C under stirring. During the reaction, polymer seemed to swell, but did not dissolve into aqueous alkali even heated at 90°C.

A similar treatment of 3.2 g of (3) ($\bar{Pn}$ = 6 ~ 8) with a solution of 3.2 g (0.08 mol) of NaOH in water–methanol (50 : 70) at 60°C for 95 hr yielded a transparent solution. The solution, after removing methanol by evaporation, was passed through a column of Amberlite IR 120 (H^+ form). A milky white effluent was collected and centrifuged to collect the precipitated free acid. The product was washed and centrifuged several times in water. Yield 2.34 g (81%).

The free acid (4) is not soluble in organic solvents but soluble in aqueous mineral acid and aqueous alkali. Infrared spectra: $\nu_{C=O}$ 1735 and 1630 cm^{-1}. *Anal.* Calcd for $(C_8H_8)_{0.091}$ $(C_{13}H_{15}NO_4)_{0.909}$: C, 63.75; H, 6.12; N, 5.39. Found: C, 63.55; H, 6.45; N, 5.19.

Potentiometric Titration

Acid dissociation constants and chelate stability constants were determined by the potentiometric titration of ligand in the absence and in the presence of metal ion as in a conventional manner.[8]

For the determination of dissociation constants,

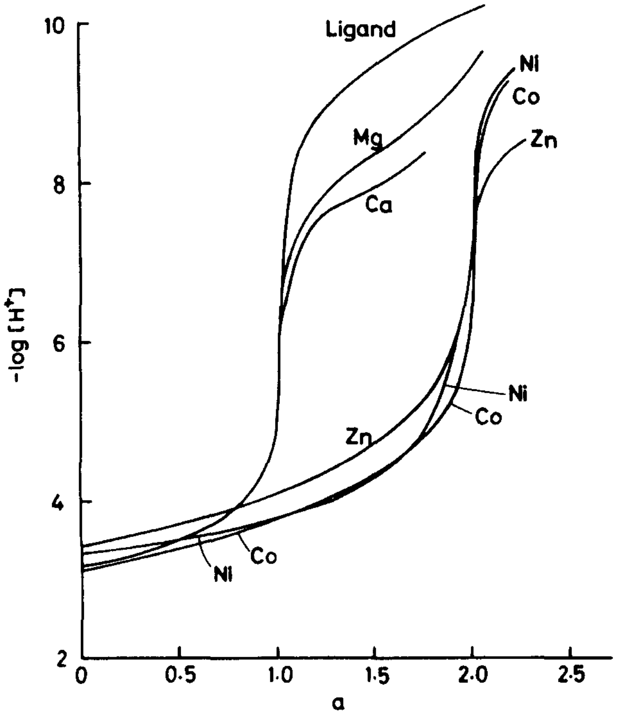


FIGURE 1. Titration curves of polymer ligand and 1 : 1 metal–ligand mixture. Ca, Mg, Co: $[H_2L] = 1 \times 10^{-3}$ M. Zn, Ni: $[H_2L] = 5 \times 10^{-4}$ M, a: moles of standard alkali added per mole of monomer unit of the polymer ligand.

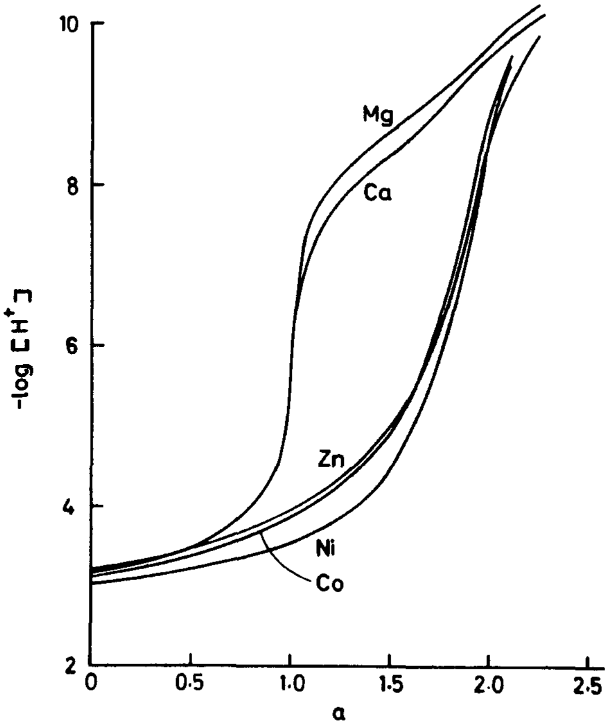


FIGURE 2. Titration curves of 1 : 2 metal–ligand mixtures. $[H_2L] = 1 \times 10^{-3}$ M; a, moles of standard alkali added per mole of monomer unit of the polymer ligand.

1×10^{-3} M (mol/dm^3 ; The concentration of benzyliminodiacetic acid unit is referred.) solution of the ligand was titrated with 0.1 M KOH solution in a thermostatted cell (25° ± 0.1°C) under nitrogen stream. Ionic strength of the solution was adjusted to 0.1 with KNO_3. For the determination of chelate stability constant, similar solutions containing 1 : 1 or 1 : 2 molar ratio of metal ion to monomeric ligand unit were titrated in the same fashion. The pH of the solution was observed with a Toa Dempa hybrid electrode (GST-155 C) and Orion Ion-meter (801 A). The titration curves of ligand only and 1 : 1 metal–ligand mixtures, and of 1 : 2 metal–ligand mixtures are shown in Figures 1 and 2, respectively.

CALCULATION OF EQUILIBRIUM CONSTANTS

Acid Dissociation Constants

If one expresses the acid dissociation scheme of polymeric ligand as shown below,

$$H_2L \rightleftharpoons HL^- + H^+ \qquad (1)$$

$$HL^- \rightleftharpoons L^{2-} + H^+ \qquad (2)$$

the corresponding dissociation constants can be given as follows, as have been discussed by Katchalsky,[9]

$$Ka_1 = \frac{[HL^-][H^+]}{[H_2L]}\left(\frac{[HL^-]}{[L]_T - [HL^-]}\right)^{n-1} \qquad (3)$$

$$Ka_2 = \frac{[L^{2-}][H^+]}{[HL^-]}\left(\frac{[L^{2-}]}{[L]_T - [L^{2-}]}\right)^{n'-1} \qquad (4)$$

where $(L)_T$ stands for the total concentration of the ligand, and n and n' stand for the correction factor for polymer, the values of which depend on the extent of interaction among the neighbouring functional groups in the polymeric ligand. In the case of monomeric ligand, n or n' becomes unity, so that Ka can be simply expressed as $[Base^-][H^+]/[Acid]$.

As is clear from Figure 1, the proton dissociation of the first and the second steps can be treated separately, and the final equations for evaluating Ka and n can be given as:

$$Ka_1 = \frac{[H^+][HL^-]^n}{[H_2L]^n} = \frac{[H^+]\{a[L]_T + [H^+]\}^n}{\{[L]_T - (a[L]_T + [H^+])\}^n} \qquad (5)$$

$$\mathrm{Ka}_2 = \frac{[\mathrm{H}^+]\,[\mathrm{L}^{2-}]^{n'}}{[\mathrm{HL}^-]^{n'}} = \frac{[\mathrm{H}^+]\{(a-1)[\mathrm{L}]_\mathrm{T} - \mathrm{Kw}/[\mathrm{H}^+]\}^{n'}}{\{[\mathrm{L}]_\mathrm{T} - \{(a-1)[\mathrm{L}]_\mathrm{T} - \mathrm{Kw}/[\mathrm{H}^+]\}\}^{n'}} \quad (6)$$

where a stands for the moles of alkali added per monomer unit mole of the polymer ligand. The values of Ka and n can be evaluated from the linear plots of log $[\mathrm{H}^+]$ vs. log $[\mathrm{HL}^-]/[\mathrm{H_2L}]$ or log $[\mathrm{L}^{2-}]/[\mathrm{HL}^-]$. The mean values of pKa and n on several titrations are summarised in Table I.

TABLE I

Proton dissociation constants of oligo {bis(carboxymethyl)-iminomethylene}styrene and related ligands. $\mu = 0.1$ ($\mathrm{KNO_3}$), 25°C

	pKa_1	n	pKa_2	n'
oligostyrene deriv.	2.8[a)]	1.08	9.56[b)]	1.24
benzyliminodiacetic acid[8]	4.53		8.90	

[a]variation, ± 0.2 [b]variation, ± 0.04

Chelate Stability Constants

Chelate stability constants were evaluated according to Gregor,[10] who modified the Bjerrum's method[11] to apply it to polymeric ligands. The chelate formation equilibrium can be expressed as

$$\mathrm{M}^{2+} + \mathrm{L}^{2-} \rightleftharpoons \mathrm{ML} \quad (7)$$

$$\mathrm{ML} + \mathrm{L}^{2-} \rightleftharpoons \mathrm{ML}_2^{2-} \quad (8)$$

from which, the following definitions can be given.

$$\mathrm{K_{ML}} = \frac{[\mathrm{ML}]}{[\mathrm{M}^{2+}]\,[\mathrm{L}^{2-}]} \quad (9)$$

$$\mathrm{K_{ML_2}} = \frac{[\mathrm{ML}_2^{2-}]}{[\mathrm{ML}]\,[\mathrm{L}^{2-}]} \quad (10)$$

These values were evaluated from the formation curves according to the standard Bjerrum's procedure. However, a modification was made on the estimation of $[\mathrm{HL}^-]$ and $[\mathrm{L}^{2-}]$ values which can be obtained from the following equations, by solving for $[\mathrm{HL}^-]$ and $[\mathrm{L}^{2-}]$, respectively.

$$\mathrm{Ka}_1 = \frac{[\mathrm{HL}^-]\,[\mathrm{H}^+]}{\{\frac{1}{2}(2-a)[\mathrm{L}]_\mathrm{T} - [\mathrm{HL}^-] - [\mathrm{H}^+] + [\mathrm{OH}^-]\}} \left(\frac{[\mathrm{HL}^-]}{[\mathrm{L}]_\mathrm{T} - [\mathrm{HL}^-]}\right)^{n-1} \quad (11)$$

$$\mathrm{Ka}_2 = \frac{[\mathrm{L}^{2-}]\,[\mathrm{H}^+]}{[\mathrm{HL}^-]} \left(\frac{[\mathrm{L}^{2-}]}{[\mathrm{L}]_\mathrm{T} - [\mathrm{L}^{2-}]}\right)^{n'-1} \quad (12)$$

Since n and n' are not integers, the values of $[\mathrm{HL}^-]$ and $[\mathrm{L}^{2-}]$ were computed by the successive approximation method. The formation curves thus obtained are illustrated in Figure 3.

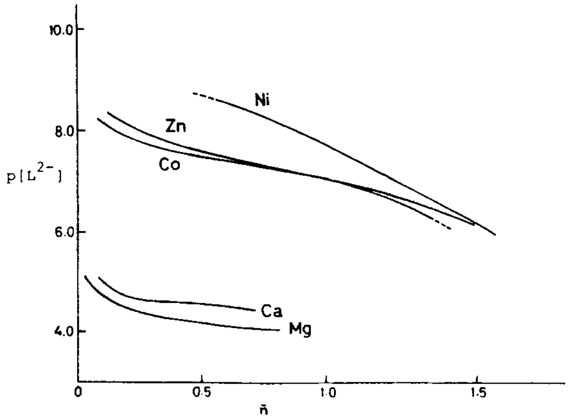


FIGURE 3. Formation curves of polymer–metal complexes. M: $\mathrm{H_2L}$ = 1 : 2

Although it is necessary to consider the intramolecular electrostatic interaction upon complexation by the polymeric ligand as was done on the analysis of proton dissociation equilibrium, the approximate stability constants thus obtained by the modified Bjerrum's procedure may still be useful for the meaningful discussion for the present purpose. The chelate stability constants are summarized in Table II along with those of the related monomeric ligands.

RESULTS AND DISCUSSIONS

Synthesis of Ligand

Although various synthetic routes have been reported on the introduction of methyleneiminodiacetic acid group to the aromatic ring of styrene polymer as shown in Scheme 1, the products were usually the crosslinked insoluble polymer.

The only exception was the method D, which have been reported to give a water soluble polymer.[4] However, we were unable to reproduce their result, but found that the product obtained under their reaction conditions was a pyridinium derivative.

TABLE II

Chelate stability constants. 25°C, μ = 0.1 (KNO_3)

ligand	Ca		Mg		Co(II)		Ni		Zn	
	$\log K_{ML}$	$\log K_{ML_2}$	$\log K_{ML}$	$\log K_{ML_2}$	$\log K_{ML}$	$\log K_{ML_2}$	$\log K_{ML}$	$\log K_{ML_2}$	$\log K_{ML}$	$\log K_{ML_2}$
oligostyrene^a) ligand	4.56	—	4.19	—	7.45	6.0	8.17	6.43	7.56	6.28
Benzylimino-diacetic acid[8]	3.13	—	2.63	—	6.88	—	7.98	—	6.97	—
Iminodiacetic acid[1,2]	2.6^b)	—	2.9^b)	—	6.95^c)	5.34^c)	8.21^c)	6.35^c)	7.03^c)	5.14^c)

a) Constants for Cu(II) and Fe(III) could not be obtained due to precipitation. The variation of the constants were within ± 0.04 in log unit. Log K_{ML_2} value for Co(II) was obtained by extrapolation.

b) 20°C, μ = 0.10

c) 30°C, μ = 0.10

Thus, chloromethylated polystyrene was reacted with iminodiacetonitrile in pyridine, but the infrared and Raman spectra of the reaction product did not show a band due to $\nu_{C \equiv N}$. Moreover, the result of elemental analysis was far from the calculated value for the expected structure, and the observed C/N weight ratio of 17.75 was exactly the same as that calculated (17.75) for the polymer pyridinium chloride.

A detailed investigation under similar conditions using benzylchloride as a model compound also proved that the reaction does not give benzyliminodiacetonitrile but N-benzylpyridinium salt in quantitative yield. Accordingly, it is very likely that the reported product obtained by the method D is not an iminodiacetic acid derivative but a pyridinium derivative which is, of course, water soluble, and is capable of showing poly-electrolyte properties.

Thus, we finally took an alternative route which was described in the experimental part. The reaction of chloromethylated polystyrene with dimethyliminodiacetate in DMF was carried out at 70 ~ 90 °C for 8 hr to give the expected polymer ester in 70 ~ 90% yield. The ester was hydrolyzed by heating in a methanolic sodium hydroxide solution. In the case of high-molecular polystyrene ($\bar{Pn}$ = 1600 ~ 1800), the hydrolyzed product was not soluble in the reaction medium, but the product from oligostyrene ($\bar{Pn}$ = 6 ~ 8), gave a transparent solution, from which free acid was precipitated by acidification. The product was characterized as bis(carboxymethyl)iminomethylene derivative of oligostyrene (degree of substitution 90.9%) by infrared spectra, elemental analysis, neutralization equivalence and solubility behavior in acid and in alkali. However, we are unable to prepare the water soluble ligand from the polystyrenes of higher molecular weight.

Behavior as a Chelating Ligand

As expected, pKa values of the ligand is very much similar to that of benzyliminodiacetic acid, which is a monomeric unit of the ligand under investigation. The fact that *n* value equals nearly unity indicates that the very slight intramolecular interaction is operative among the neighbouring functional groups during the course of the first proton dissociation step. On the contrary, a higher *n*′ value indicates the existence of weak interaction among the neighbouring functional groups during the second proton dissociation. However, the *n* and *n*′ values of this ligand is much less than those observed on polymethacrylic acid (pKa 7.3, $n = 2.3$) or polyacrylic acid (pKa 6.3, $n = 2.2$).[8,13]

The order of chelate stability constants were found to be Ni > Zn > Co ≫ Ca > Mg, and is similar to those of benzyliminodiacetic acid[9] or iminodiacetic acid.[12] A slightly higher chelate stability and a relative ease of 1 : 2 chelate formation in comparison with the corresponding benzyliminodiacetic acid, may be ascribed to the polymer effect.

In the cases of iron(III) and copper(II), precipitation or turbidity was observed when 1×10^{-3} M ligand solution was mixed with metal ion solution in 1 : 1 or 1 : 2 ratio, and for nickel and zinc in 1 : 1 ratio, so that the titration could not be carried out to determine the stability constant.

The relative ease of precipitation of the ligand when mixed with metal ion even before the titration with alkali, may be due to the cross-linking of the polyelectrolyte by metal ion and not due to the hydrolysis of metal ion. However, the methyleneiminodiacetic acid derivative of oligostyrene was found to be a successful macromolecular chelating ligand which stays in solution even after chelate formation with certain metal ions.

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