CHEMISTRY LETTERS, pp. 615-618, 1994.

Preparation of Water Soluble Polymer with 8-Quinolinol Group and Its Specific Reactivity with Cd(II)

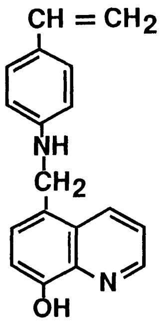
Takeo HAMAYA,* Kazuhisa HIRATANI, and Kosaburo OHASHI†
National Institute for Materials and Chemical Research, Higashi, Tsukuba, Ibaraki 305
†Department of Chemistry, Faculty of Science, Ibaraki University, Mito, Ibaraki 310

Water soluble polymer with 8-quinolinol group (**3**) was prepared and its fluorescent feature was studied. Polymer ligand **3** was found to form water soluble fluorescent chelate complexes with some metal ions in aq. solution without precipitating. Among them, Cd complex was shown especially to emitt fluorescence intensively.

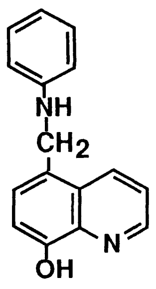
8-Quinolinol and its derivatives have found extensive application as analytical reagents, for example, in solvent extraction, absorption spectrophotometry and fluorometry because of their ability to form complexes with many metal ions.1)

For the analytical use of 8-quinolinol, however, the process is somewhat troublesome because it is insoluble in water. Then several ways of water-solubilizing of 8-quinolinol have been so far searched like the preparation of its derivative, 5-sulfonic acid,2) and coexistive use of surfactant.3,4) As one of attempts of water-solubilizing of 8-quinolinol, we prepared water soluble polymer **3** having 8-quinolinol group within its own molecule.

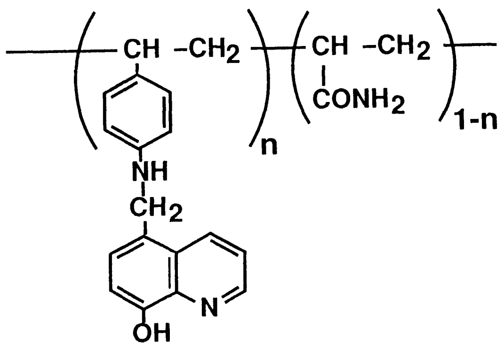
It is very interesting to elucidate the following questions about **3**, which will serve to develop new functional polymeric materials. Dose **3** form the complex with a variety of metal ion in aq. solution ? If it dose, whether or not the complex precipitates from the aq. solution ? The precipitation might be caused by complex formation between polymer chains via. metal. How is the spectrophotometric behavior (UV or fluorescence) of complex formation in aq. solution ? 8-Quinolinol chelate complex with Zn(II) is said to be nonfluorescent in the DMF-water mixed solvent (50:50) in spite of being fluorescent in pure DMF.8) So polymer **3** chelate complex might be nonfluorescent in the pure water. Can be seen any special reactivity or selectivity of **3** toward metal ions ?



1



2



3

In this paper, we report the fluorescence spectra of chelate complexes of **3** with several metal ions in aq. solution in order to answer above questions.

A monomer having 8-quinolinol group, 5-(4-vinyl anilinomethyl)-8-hydroxyquinoline (**1**), was synthesized from the reaction of 5-chloromethyl-8-hydroxyquinoline hydrochloride with equimolar 4-vinylaniline under the excess of triethylamine in DMF.5) Model compound, 5-(4-anilinomethyl)-8-hydroxyquinoline (**2**) was synthesized in the same way by using aniline in stead of 4-vinylaniline.6) Water soluble polymer **3** was obtained by copolymerization of acrylamide (water soluble monomer) and **1** with catalytic amount of N,N'-azobisisobutyronitrile in DMF at 70 °C for 24 h. Polymer was purified by repeated reprecipitation method; pouring the aq. solution into large amount of acetone. The value of n was determined to be 0.0025 from the comparison of UV spectrum of model compound **2**.

Figure 1 shows the UV spectra of **2** and **3**, compared with that of acrylamide homopolymer. The polymer **3** has the intense absorption at 245 nm, while acrylamide homopolymer has no absorption near here. This intense absorption at 245 nm was attributed to be 8-quinolinol group because model compound has also intense absorption near here (λ_{max}: 244 nm, ε: 4.4x10^4).

Fluorescence spectra of chelate complex of **3** and a variety of metal ion were shown in Fig. 2 and further the pH dependence on the fluorescence intensities of some fluorescent chelate complex was shown in Fig. 3.
The following facts can be observed from Fig. 2.
The polymer **3** itself and its chelate complexes with transition metal ions such as Cu(II), Ni(II), Co(II) and Fe(III) are nonfluorescent. (Polymer ligand **3** itself emitt a little fluorescence, but its intensity is so weak as unobservable.)
Chelate complexes with some metal ions such as Zn(II), Mg(II), Al(III) and Cd(II), which are known to form fluorescent chelate complex with 8-quinolinol or 5-sulfo-8quinolinol derivative,7-16) were found to emitt fluorescence as same as low molecular weight compound. Interestingly, Cd chelate complex showed the most intense fluorescence among all other fluorescent chelates.

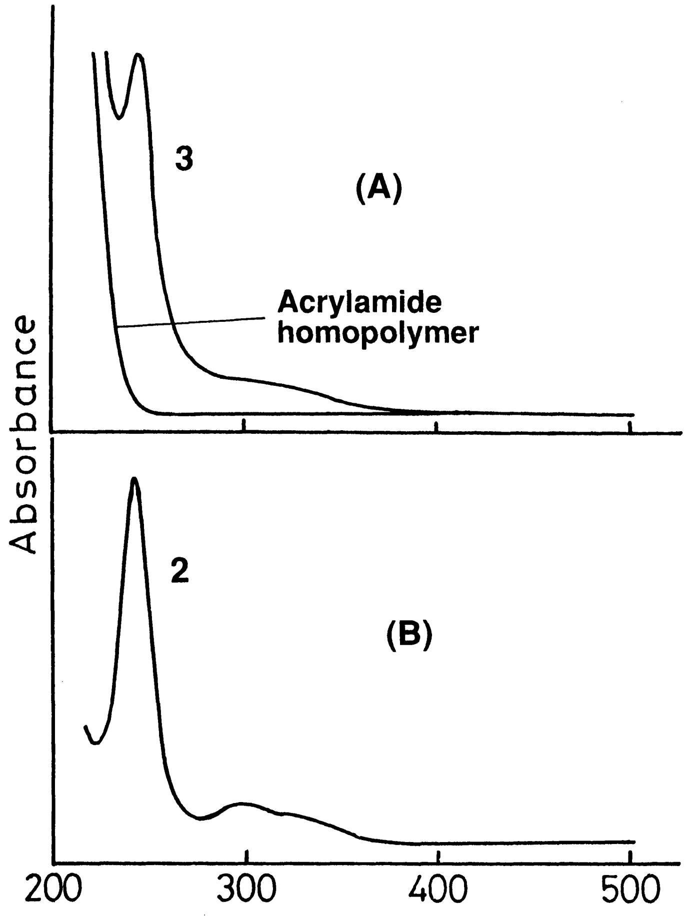


Fig. 1. UV spectra of polymer and model compound.
(A) Polymer **3** and polyacrylamide in aq. solution ([Polymer]:1x10^{-2} M; [Quinolinol unit]:5x10^{-5} M)
(B) Model compound **2** in acetonitrile([**2**]:5x10^{-5} M).

In Fig. 3, fluorescence intensities at λ_{max} of four kind of chelate complexes were plotted to pH of the solution. It can be seen that there exists optimal pH for the formation of each fluorescent chelate complex. Here we examined about some characters of the Cd chelate complex because we observed special reactivity of the polymer **3** with Cd(II) in Fig. 2 and Fig. 3. At first, fluorescent chelate complex was found to be composed of

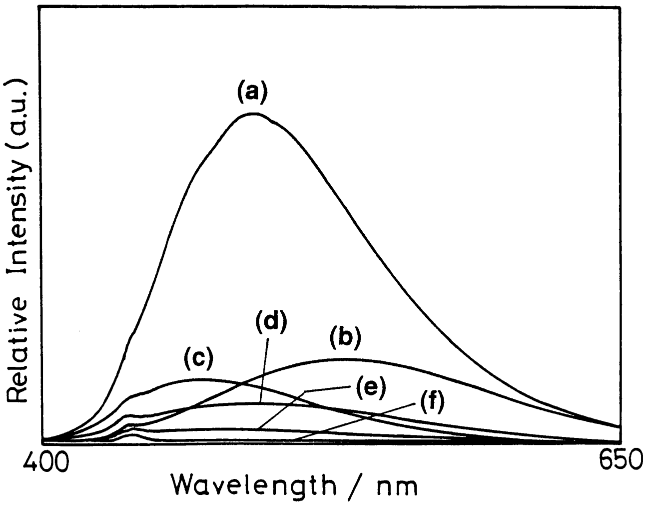


Fig. 2. Fluorescence spectra of the complex of polymer ligand **3** with a variety of metal ion in phosphate buffer solution (pH=7.0). [**3**]: 5x10^{-5} M(oxine unit), [M^{n+}]: 1x10^{-4} M, E$_x$:380 nm, (a) Cd(II),(b) Zn(II), (c) Mg(II), (d) Al(III), (e) Ca(II), (f) Cu(II), Ni(II), Co(II), Fe(III), Hg(II), Ag(I), Li(I),and Na(I).

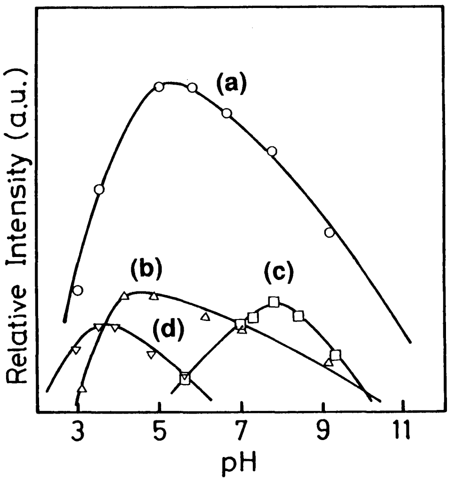


Fig. 3. pH dependence on the fluorescence intensities of chelate complexes of polymer **3** with several metal ion in water. [**3**]: 5x10^{-5} M, [M^{n+}]: 1x10^{-4} M; E$_x$:380 nm, (a) Cd(II), (b) Zn(II) (c) Mg(II) and (d) Al(III). pH were controlled by adding HCl or NaOH aq. solution.

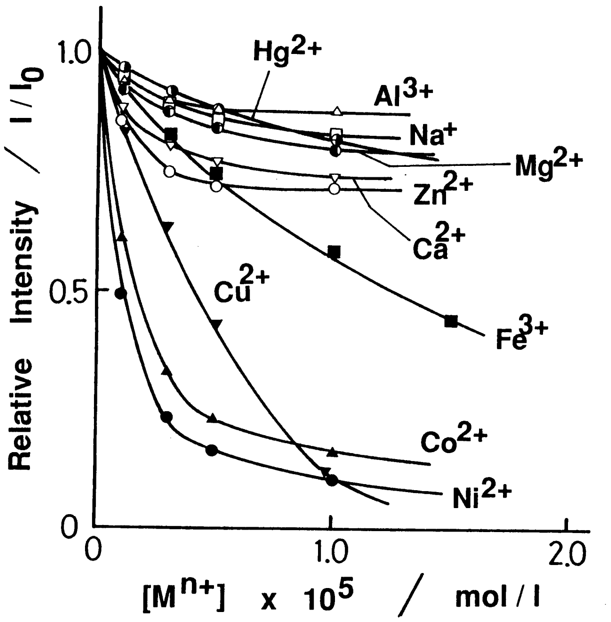


Fig. 4. Influence of the foreign metal ion on the fluorescence intensities of chelate complex of polymer **3** and Cd^{2+} in phosphate buffer solution (pH = 7.0). [**3**]: 5x10^{-5} M, [Cd^{2+}]: 2x10^{-5} M, E$_x$:380 nm, E$_m$:491 nm.
I$_0$: Fluorescence intensity when without foreign metal ion.
I:Fluorescence intensity when foreign metal ion was added.

2:1 for ligand (8-quinolinol unit): Cd(II) from the continuous variation method (not shown in the paper). Secondly, in Fig. 4 the influence of foreign metal ion to the fluorescence intensity of Cd chelate complex of **3** was examined.[17] It can be seen that the transition metal ions such as Cu(II), Ni(II), Co(II), and Fe(III) quench strongly the fluorescence. So when we try to this polymer ligand to the fluorometric determination of Cd^{2+}, it is neccessary to eliminate a slight amount of transition metal ion existing in a solution.

Conclusively, polymer **3** ligand was found to form water soluble fluorescent chelate complexes with some metal ions in aq. solution without precipitating. Among them, Cd complex was shown especially to emitt fluorescence strongly. It has been also cleared that the transition metal ions quench the fluorescence strongly. These results are very important when we use this polymer ligand fluorometrically. By cross-linking of this polymer, chromatographic or sensoring application will be developed in a future.

References

1) R. G. W. Hollingshead, " Oxine and Its Derivatives," Butterworths, London (1954–56), Vols, I - IV.

2) J. C. Liu and J. C. Bailar, *J. Am. Chem. Soc.*, **73**, 5432 (1951).

3) M. Kodama, H. Matsushita, and T. Tominaga, *Nihon Kagaku Kaishi*, **1976**, 614.

4) H. Nishida, *Bunseki Kagaku*, **34**, 564 (1985).

5) mp 179 – 180 °C. ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.85 (br s, 1H, – NH), 4.55 (s, 2H, – CH_2), 4.98 (dd, J=1.5 Hz, J'=10.5 Hz, 1H, Φ–CH=CH, syn), 5.47 (dd, J=1.5 Hz, J'=17.5 Hz, 1H, Φ–CH=CH, anti), 6.37–7.48 (m, 9H, 1 quinolyl 3-H, 6 aromatic H, –OH and Φ–CH=C), 8.30 (dd, J=1.8 Hz, J'=9.0 Hz, 1H, quinolyl 4-H), 8.72 (dd, J=1.8 Hz, J'=4.0 Hz, quinolyl 2-H). Anal. Found:C, 77.9; H, 5.7; N, 10.0%. Calcd for $C_{18}H_{16}N_2O$: C, 78.3; H, 5.8; N, 10.1%.

6) mp 136 – 137 °C. ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.87 (br s, 1H, –NH), 4.55 (s, 2H, –CH_2), 6.53–7.52 (m, 9H, 1 quinolyl 3-H, 7 aromatic H and –OH), 8.33 (dd, J=1.8 Hz, J'=9.0 Hz, 1H, quinolyl 4-H), 8.72 (dd, J=1.8 Hz, J'=4.0 Hz, quinolyl 2-H). Anal. Found: C, 75.4; H, 5.5; N, 10.7%. Calcd for $C_{16}H_{14}N_2O$: C, 76.8; H, 5.6; N, 11.2%.

7) H. M. Stevens, *Anal. Chim. Acta*, **20**, 390 (1959).

8) O. Popovych and L. B. Rogers, *Spectrochim. Acta*, **16**, 49 (1960).

9) J. A. Bishop, *Anal. Chim. Acta*, **29**, 172 (1963).

10) D. A. Carter and W. E. Ohnesorge, *Anal. Chem.*, **36**, 327 (1964).

11) D. E. Ryan, A. E. Pitts, and R. M. Cassidy, *Anal. Chim. Acta*, **34**, 491 (1966).

12) V. Patrovsky, *Collect. Czechoslov. Chem. Comm.*, **32**, 2656 (1967).

13) M. P. Bratzel, J. J. Aaron, J. D. Winefordner, S. G. Schulman, and H. Gershon, *Anal. Chem.*, **44**, 1240 (1972).

14) Z. Zhujun and W. R. Seitz, *Anal. Chim. Acta*, **171**, 251 (1985).

15) D. A. Phillips, K. Soroka, R. S. Vithanage, and P. K. Dasgupta, *Mikrochim. Acta*, **1**, 207 (1986).

16) K. Soroka, R. S. Vithanage, D. A. Phillips, B. Walker, and P. K. Dasgupta, *Anal. Chem.*, **59**, 629 (1987).

17) In the case of Mg^{2+} and Zn^{2+}, the increases of fluorescence intensities were observed with increasing concentrations of those ions added above $2x10^{-5}$ mol/l after the slight decreases in the low concentrations. The phenomena of the increasing fluorescence intensities might be explained by the additive property. For the quenching behaviors, we can not explain quite well at the present time. Further studies will be needed.

(Received December 2, 1993)