CHEMISTRY LETTERS, pp. 657 - 660, 1984.

SYNTHESIS OF MACROCYCLIC SCHIFF BASE POLYMER LIGAND AS A HIGHLY SELECTIVE EXTRACTANT FOR COPPER(II)

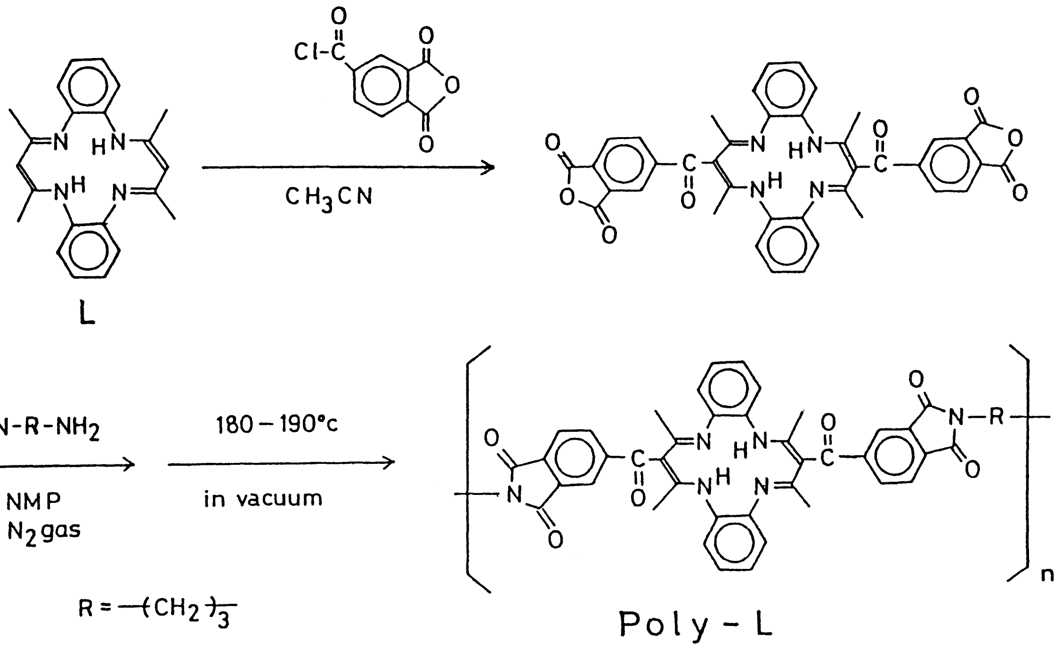
Takayuki MATSUSHITA,* Noboru KUBOTA, Manabu FUJIWARA,
and Toshiyuki SHONO
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadaoka, Suita, Osaka 565

A novel polymer ligand (Poly-L) in which 6,8,15,17-tetramethyldibenzo-5,9,14,18-tetraazacyclotetradecene (L) is present as an integral part of the polymer backbone was synthesized and its solvent extraction of copper(II) and nickel(II) was investigated in comparison with L. The complexation reactions of Poly-L with the above metal ions were found to be much faster than those of L, with a high selectivity for copper(II).

Although crown ethers have been extensively investigated as highly selective extractants for alkali and alkaline earth metal ions,1) the extraction properties of nitrogen-containing macrocyclic compounds have been little studied. Recently, Zolotov et al. reported a series of N-containing macrocycles as extractants for heavy metal ions.2,3) Of them L was found to possess a high selectivity for copper(II). However, its extraction rate is slower than those observed for the lipophilic derivatives of cyclam.4) This may be ascribed to that the rate of chelate formation of L is slow in the extraction process. On the other hand, L was studied as a reagent for colorimetric determination of copper(II), because the copper(II) complex of L has a high molar extinction coefficient.5) Such selectivity for copper(II) appears to result from a rigid structure of L itself.

Here we wish to report the synthesis of a novel polymer ligand in which L is present as an integral part of the polymer backbone and application as an extractant selective for copper(II).

Poly-L was synthesized according to the following scheme. L was prepared by the method described in the literature.6) A dianhydride derivative of L was obtained by reacting 4-chloroformylphthalic anhydride with L in acetonitrile, by



Scheme for synthesis of Poly-L.

a slight modification of the method described in the literature.[7,8)] Poly(amic acid) was prepared by reacting the above dianhydride with 1,3-propanediamine in N-methyl-2-pyrrolidone (NMP) under a nitrogen atmosphere. Upon heating at 180–190 °C in vacuo for one hour, it yielded Poly-L. The conversion of poly(amic acid) into poly(imide) was confirmed by the infrared spectra; appearance of the absorption bands characteristic of the phthalimide ring at 1770 and 1710 cm^{-1} and disappearance of the absorption band of the amide around 1630 cm^{-1}. Poly-L is soluble in benzene, chloroform, and N,N-dimethylformamide (DMF), but is insoluble in ethanol and water. The inherent viscosity of Poly-L determined in NMP at 25 °C was 0.12. The low viscosity and analytical data[8)] suggest that Poly-L is an oligomer whose degree of polymerization (n) is about four.

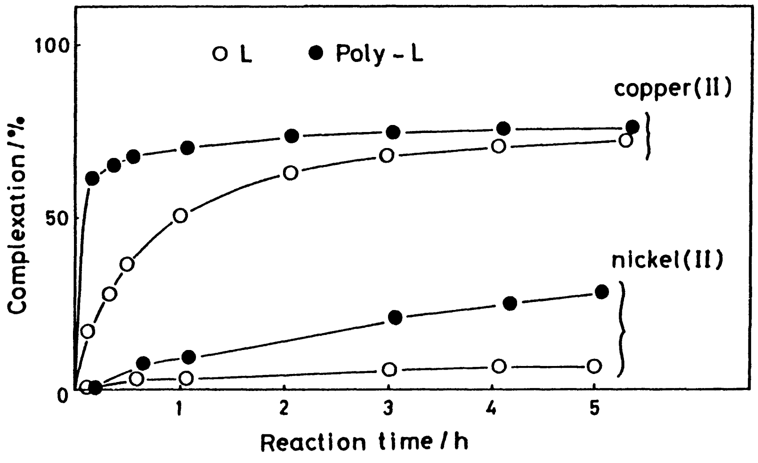


Fig. 1. Time courses of complexation of Poly-L (5×10^{-5} unit M) and L (5×10^{-5} M) with copper(II) and nickel(II) (5×10^{-5} M) in DMF at 25 °C.

Solvent extractions were carried out by shaking a 10-cm^3 test tube with a stopper at room temperature in which contains a chloroform solution (5 cm^3) of the ligands as an organic phase and an equivolume of acetate buffer solution (0.2 M; 1 M = 1 mol dm^{-3}) of the metal ions as an aqueous phase. The content of the residual metal ions in aqueous phase was determined by atomic absorption spectrometry. In the case of L, the content of the copper(II) transferred into the chloroform phase was determined by measuring its absorbance at 382 nm, which is the absorption maximum of the copper(II) complex of L.

The complexation reactions of Poly-L with copper(II) and nickel(II) were studied in a homogeneous DMF solution compared with L. Figure 1 shows the plots of the extent of complexation of Poly-L and L with the above metal ions at 25 °C. These were determined by the absorption spectral changes of the DMF solutions containing each of the ligands and the equimolar metal ions. The absorption maximum of free L at 344 nm was shifted to 382 and 392 nm by the complex formation with copper(II) and nickel(II), respectively, and that of free Poly-L at 323 nm was shifted to 383 and 387 nm for copper(II) and nickel(II), respectively. The complexation rates of Poly-L and L with copper(II) were found to be much faster than those for nickel(II). Moreover, the complexation rates of Poly-L with both metal ions were found to be much faster than those for L. Thus we have applied this Poly-L to an extractant for copper(II) and nickel(II).

Figure 2 shows the pH dependence of extraction of copper(II) by Poly-L and L. The concentration of the ligands was 10 times as much as that of copper(II) and the

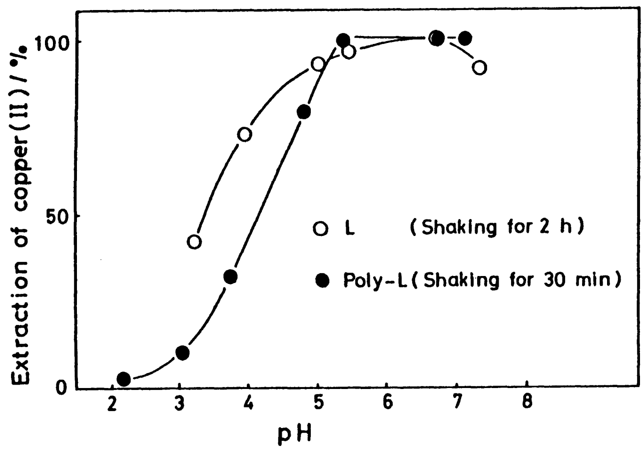


Fig. 2. The pH dependence of extraction of copper(II) (1x10^{-4} M) by Poly-L (1x10^{-3} unit M) and L (1x10^{-3} M).

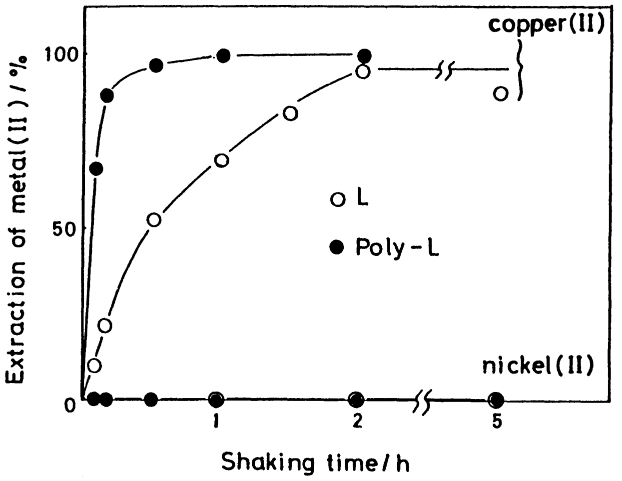


Fig. 3. Extraction of copper(II) and nickel(II) (1x10^{-4} M) by Poly-L (1x10^{-3} unit M) and L (1x10^{-3} M) at pH 5.4.

shaking time was 30 min and 2 h for Poly-L and L, respectively. The efficiency of extraction by both ligands decreases with a decrease in pH of the aqueous phase. With Poly-L the maximal extraction (100%) was observed in the pH range 5 to 7, whereas with L it was observed in the narrow pH range (at pH 6.75).

Figure 3 shows the plots of extraction of copper(II) and nickel(II) by Poly-L and L as a function of shaking time at pH 5.4. It is noteworthy that no extraction of nickel(II) by them occurs after shaking for 5 h under the same conditions as those for copper(II). Moreover, the extraction rate of copper(II) by Poly-L was found to be much faster than that by L: With the former nearly 100% copper(II) in the aqueous phase was transferred into the chloroform phase after shaking for 30 min, whereas with the latter nearly 95% copper(II) transferred even after 2 h.

In conclusion, the present Poly-L has a marked advantage over L in the extraction rate, with a high selectivity for copper(II) as well as L. This can be ascribed to its fast complexation rate as shown in Fig. 1. This may be caused by "polymer effects", that is, a local increase in concentration of the chelating group (L) is established in Poly-L.

The studies on the recovery of the copper(II) extracted by Poly-L and its extractability for heavy metal ions other than copper(II) and nickel(II) are now in progress.

References

1) I. M. Kolthoff, Anal. Chem., 51, 1R (1979).
2) Yu. A. Zolotov, V. F. Ionov, V. A. Bodnja, G. A. Larikova, N. V. Niz'eva, G. E. Vlasova, and E. V. Rybakova, Zh. Anal. Khim., 37, 1543 (1982).
3) E. A. Krasnushkina and Yu. A. Zolotov, Trends Anal. Chem., 2, 158 (1983).
4) I. Tabushi and M. Fujiyoshi, Heterocycles, 7, 851 (1977).
5) T. Toda, H. Miyata, and K. Toei, Bunseki Kagaku, 28, 440 (1979). (in Japanese)
6) V. L. Goedken, M. C. Weiss, D. Place, and J. C. Dabrowiak, Inorg. Synth., 20, 115 (1980).
7) J. C. Dabrowiak, D. P. Fisher, F. C. McElrory, and D. J. Macero, Inorg. Chem., 18, 2304 (1979).
8) Analytical data for dianhydride derivative of L, Found: C, 68.84; H, 4.27; N, 8.04%. Calcd for $C_{40}H_{28}N_4O_8$: C, 69.36; H, 4.07; N, 8.09%. For Poly-L, Found: C, 69.90; H, 5.11; N, 11.51%. Calcd for $H_2N-(CH_2)_3-(C_{43}H_{34}N_6O_6)_4-NH_2$: C, 70.13; H, 4.91; N, 12.15%.

(Received January 23, 1984)