Macromolecules **1985**, *18*, 2357–2361

Poly(allylamine): Chelating Properties and Resins for Uranium Recovery from Seawater

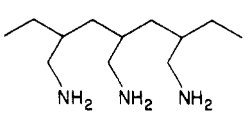
Shiro Kobayashi,*† Masazumi Tokunoh,† Takeo Saegusa,*† and Fujio Mashio‡

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan, and Research Institute for Production Development, Morimoto-cho, Shimogamo, Sakyo-ku, Kyoto 606, Japan. *Received March 4, 1985*

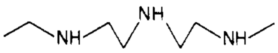
ABSTRACT: Chelating properties of poly(allylamine) (PAA) have been examined quantitatively for the heavy-metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and UO_2^{2+}. Potentiometric titrations were performed and analyzed according to the modified Bjerrum method to give successive and overall stability constants, k_n and K_n, respectively. Continuous variation analysis of PAA–Cu^{2+} and PAA–Ni^{2+} complexes examined by spectrophotometry revealed that the most stable complex is formed at the unit ratio of allylamine/Cu^{2+} = 3 (rather than 4) and allylamine/Ni^{2+} = 4, respectively. Then, three resins for recovery of uranium from seawater are derived: cross-linked PAA (CL-PAA), PAA modified by acrylic acid and cross-linked (AcCL-PAA), and CL-PAA modified by phosphorous acid/formaldehyde (PhosCL-PAA). The last resin showed the highest adsorption ability for uranium; i.e., 500 mg of the resin recovered 12.9 μg of uranium from 5 L of seawater at 25 °C for 24 h, which corresponds to 78% of uranium in the original seawater.

Introduction

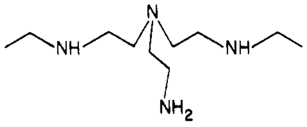
Recently, Harada and Hasegawa first succeeded in the preparation of higher molecular weight poly(allylamine) (PAA) of a clear-cut structure.[1] PAA is a polymer having pendant primary amino groups. We have undertaken quantitative investigations on the chelating properties of linear and branched poly(ethylenimines).[2] Linear poly(ethylenimine) (LPEI) contains only secondary amino groups in the main chain whereas a commercial poly(ethylenimine) (BPEI) has a branched structure consisting of primary, secondary, and tertiary amino groups in a ratio of approximately 25%, 50%, and 25%, respectively.[3]



PAA



LPEI



BPEI

It is worthwhile, therefore, to evaluate quantitatively the difference in chelating abilities of these polyamines of different structures. Poly(vinylpyridine) can also be cited as a family polymer of PAA having pendant amine groups.[4] The present paper deals with the determination of stability constants in the chelate -formation of PAA with several heavy-metal ions and with the preparation of resins from PAA for the uranium recovery from seawater.

Experimental Section

Materials. A polymer salt PAA·HCl (the weight-average molecular weight = 10 000 determined by equilibrium sedimentation method) was supplied from Nitto Boseki Co., Tokyo, Japan.[5] PAA itself was obtained by treating the salt with a strong anion-exchange resin, Amberlite IRA-402 (Rohm and Haas, Co.), as transparent caramel-like materials. Nonaethylene glycol diglycidyl ether or ethylene glycol diglycidyl ether (Nagase Chemical Co., Hyōgo, Japan) was employed as a cross-linking agent. A commercial reagent of acrylic acid was purified by vacuum distillation under nitrogen. Phosphorous acid, 35% formaldehyde aqueous solution, the heavy-metal salts, $NiCl_2$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $CdCl_2$, $UO_2(CH_3CO_2)_2 \cdot 2H_2O$ (Merck Co.), and 2,7-bis(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (Arsenazo III, Dotite reagent) were commercially available reagents, which were used as received.

Preparation of Resins. Free PAA (3.8 g, 67 unit mmol) and nonaethylene glycol diglycidyl ether (3.5 g, 7.0 mmol) were dissolved in 25 mL of water and the mixture was stirred at room temperature. The reaction mixture solidified within several minutes and was kept at 100 °C for an additional 24 h. Water was evaporated off the mixture in vacuo at 100 °C. The solid was further pulverized to give a white powder. Then, the powder was washed several times with water and dried in vacuo at 100 °C to give cross-linked PAA (CL-PAA) quantitatively.

A mixture of PAA (3.8 g, 67 unit mmol) and acrylic acid (3.0 g, 42 mmol) in 25 mL of water was refluxed for 30 min[6] and the mixture became viscous. Then, ethylene glycol diglycidyl ether (0.92 g, 5.3 mmol) was added to the mixture with stirring at room temperature. After a few minutes the mixture solidified like jelly. The mixture was heated at 120 °C for 24 h. The resulting white solid product was washed with water several times, separated by filtration, and dried in vacuo at 60 °C to give 7.6 g of resin modified with acrylic acid (AcCL-PAA). Anal. Found: C, 52.78; H, 9.73; N, 10.99. This result leads to the unit ratio of acrylic acid/allylamine = 0.66, which is close to the feed ratio of 0.63.

A mixture of resin CL-PAA (7.0 g in 70 mL of water), phosphorous acid (15 g in 20 mL of water), concentrated HCl aqueous solution (15 mL), and 35% formaldehyde aqueous solution (35 mL) was placed in a 300-mL round-bottomed flask.[7] The mixture was refluxed for 5 h. The resulting resin was separated by filtration and dried in vacuo at 60 °C to give 8.5 g of CL-PAA having (aminomethyl)phosphonic acid groups (PhosCL-PAA). Anal. Found: N, 3.47; P, 4.42. This result reveals the unit ratio of phosphonic acid/allylamine = 0.57.

Recovery and Spectroscopic Determination of Uranium. An experiment of uranium recovery from seawater using PhosCL-PAA resin is given as a typical example. Powdered PhosCL-PAA resin (500 mg) was placed in 5.0 L of seawater taken at the Straits of Kanmon in the Inland Sea of Japan. The mixture was kept at 25 °C and stirred gently for 24 h. The resin was separated by filtration. Adsorbed uranyl ions were desorbed by treating the resin with 0.7 mL of 5% $(NH_4)_2CO_3$ aqueous solution at 50 °C for 1 h. The resin was separated by filtration and washed with 10 mL of water. This desorption procedure was repeated three times. To the combined $(NH_4)_2CO_3$ solution, 1 mL of 8 N HCl solution was added. The mixture was concentrated in vacuo at 50 °C to the total volume of 1 mL. To this residual solution were added about 5 mL of water, 13.0 mL of 60% aqueous perchloric acid solution, 1.0 mL of 10% hydrazine hydrochloride, and 2.0 mL of 0.2% Arsenazo III aqueous solution. To this mixture was added water until the total volume of the mixture reached 25.0 mL. Then, the visible spectrum of the mixture was

---

† Kyoto University.

‡ Research Institute for Production Development.

0024-9297/85/2218-2357$01.50/0

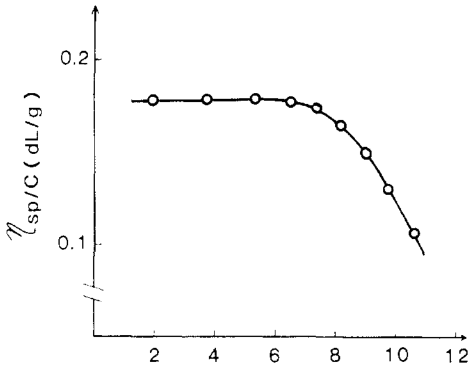


Figure 1. η_{sp}/C–pH relationship of PAA at 25 °C in water: C = 0.86 g/dL in the presence of a salt [KCl] = 1.0 mol/L.

measured. On the basis of the absorbance at 655 nm, whose caribration curve was separately obtained, the amount of uranium was determined to be 12.9 μg,[8] which corresponds to 78% of the uranium present in the original seawater.

Measurements. Potentiometric titration was carried out by employing a Horiba M-8 Type pH Meter. Visible spectra for the Arsenazo III method were recorded on a Hitachi Model 200-20 spectrophotometer. The specific viscosity was measured by using an Ubbelohde viscometer at 25 °C at the polymer concentration of C = 0.86 g/dL. The pH value was adjusted by a HCl or NaOH aqueous solution.

Results and Discussion

Stability Constants for Chelate Formation. As seen in Figure 1, the specific viscosity η_{sp}/C (dL/g) of PAA in water is not changed at the pH range $\lesssim 7$ and becomes lower with increasing pH value $\gtrsim 7$. This phenomenon suggests that at pH $\lesssim 7$ polymer chains are stretched due to the charge repulsion of ammonium groups but this kind of repulsion diminishes with an increase of pH to allow polymer chains to become less stretched. This behavior of PAA is different from that of an analogous polyamine poly(vinylamine).[9] The pH dependency of the sedimentation coefficient of poly(vinylamine) showed the poly(vinylamine) molecule to be most extended at neutral pH and partially collapsed in either acid or base. This anomalous behavior was explained by assuming a very stiff structure at the intermediate pH being stabilized by H bonding between neighbor ammonium and amine groups, probably involving a six-membered H-bonded intermediate.[9] In the PAA case, however, such an intermediate is not available.

To shed light on the chelating ability of PAA, a potentiometric titration method was used to determine stability constants in the chelation between PAA and several heavy-metal ions. The analysis was performed according to the modified Bjerrum method.[10] Figure 2 shows typical titration curves of PAA·HCl with 0.1 N NaOH in the absence and in the presence of $CuCl_2$. The ionic strength μ = 1.0 mol/L was kept constant with a neutral salt, KCl. From curve 1, it is clear that PAA·HCl behaves as a monobasic acid. The presence of $CuCl_2$ makes the system more acidic due to the chelation of Cu^{2+} to nitrogen atoms of PAA. The more the amount of $CuCl_2$, the more acidic the system becomes.

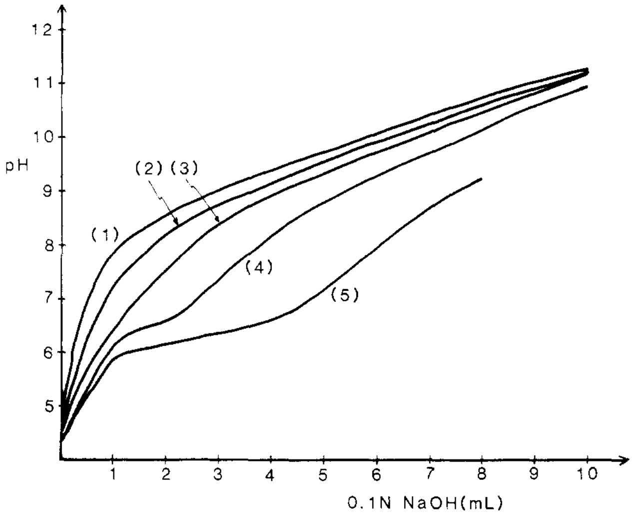


Figure 2. Titration curves of PAA·HCl ([PAA·HCl] = 2.00 × 10^{-2} mol/L; 50.0 mL of μ = 1.0 mol/L (KCl)) with 0.1 N NaOH: (1) no metal ion present; (2) Cu^{2+} = 5.00 × 10^{-4} mol/L; (3) Cu^{2+} = 1.00 × 10^{-3} mol/L; (4) Cu^{2+} = 2.00 × 10^{-3} mol/L; (5) Cu^{2+} = 4.00 × 10^{-3} mol/L.

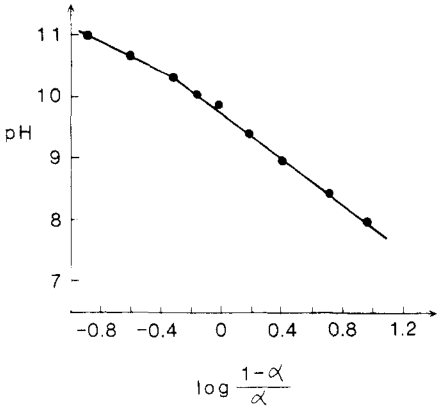


Figure 3. Plots of eq 1.

From the data of the simple neutralization curve (1) of Figure 2, plots were made according to the so-called Henderson–Hasselbalch equation

$$\mathrm{pH} = \mathrm{p}K_a - m \log \frac{1-\alpha}{\alpha} \qquad (1)$$

where α denotes the degree of neutralization and K_a is the average dissociation "constant". In Figure 3 an inflection point is observed at α = 0.7. At an α value range between 0.1 and 0.7 eq 1 is valid and a value of m = 1.85 is obtained. The m value is considered as a measure of interactions of neighboring groups. With this respect the m value of PAA is very close to that of poly(acrylic acid) (m = 1.4–2.0 under different ionic strength).[10]

The modified Bjerrum method can be analyzed as follows.[10] The average number of complexing sites toward a metal ion, $\bar{n}$ in this case, and the concentration of free ligand that is bound neither to a metal ion nor a proton, [PAA] in this case, are to be determined from measurement data. The following relationships can be given for $\bar{n}$, [PAA], [PAA·H$^+$], and K_a:

$$\bar{n} = \frac{[\mathrm{PAA_t}] - [\mathrm{PAA}] - [\mathrm{PAA{\cdot}H^+}]}{[\mathrm{metal_t}]} \qquad (2)$$

$$[\mathrm{PAA{\cdot}H^+}] = [\mathrm{PAA_t}](1-\alpha) - [\mathrm{H^+}] + [\mathrm{OH^-}] \qquad (3)$$

$$K_a = \frac{[\mathrm{PAA}][\mathrm{H^+}]}{[\mathrm{PAA{\cdot}H^+}]}\left\{\frac{[\mathrm{PAA}]}{[\mathrm{PAA_t}] - [\mathrm{PAA}]}\right\}^{m-1} \qquad (4)$$

where [metal$_t$] and [PAA$_t$] are the total metal ions and PAA unit concentrations, respectively. Equation 3 is the electroneutrality requirement. Values of K_a (2.14 × 10^{-10}) and m (1.85) from eq 1 and values of [PAA·H$^+$] from eq 3 are introduced into eq 4, giving rise to [PAA] values. From these values, $\bar{n}$ can be obtained based on eq 2. Plots

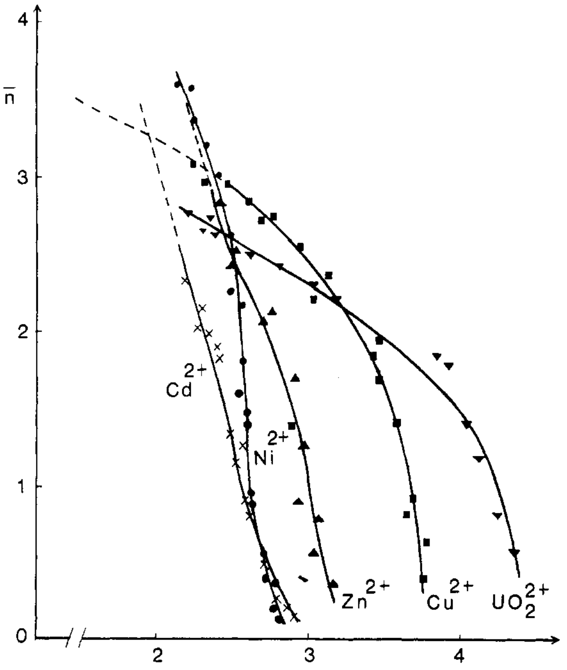


Figure 4. Formation curves for PAA complexes with five metal ions.

Table I
Stability Constants of PAA for Five Heavy-Metal Ions at 25 °C, μ = 1.0 mol/L (KCl)

metal ions	log k_1	log k_2	log k_3	log k_4	log K_3	log K_4
Ni^{2+}	2.72	2.59	2.48	2.22		10.0
Cu^{2+}	3.75	3.57	3.04	(1.5)[a]	10.4	(11.9)[a]
Zn^{2+}	3.08	2.92	2.51	(2.2)[a]	8.5	(10.7)[a]
Cd^{2+}	2.71	2.46	2.08	(1.9)[a]	7.3	(9.2)[a]
UO_2^{2+}	4.38	4.02	2.64		11.0	

[a] Values are those obtained by the extrapolation of the respective formation curve.

of p[PAA] vs $\bar{n}$ give a formation curve (Figure 4), from which a successive stability constant k_n is determined

$$\log k_n = -\log [\mathrm{PAA}]_{\bar{n}=n-1/2} = \mathrm{p}[\mathrm{PAA}]_{\bar{n}=n-1/2} \qquad (5)$$

Then, the overall stability constant K_N is given as

$$K_N = \prod_{n=1}^{N} k_n \qquad (6)$$

Table I shows values of the stability constant thus obtained. The formation curve for Ni^{2+} can be drawn in the wide range of $0.1 < \bar{n} < \sim 3.7$ and hence k_n (n = 1–4) values could definitely be determined. However, the curves for the three metal ions Cu^{2+}, Zn^{2+}, and Cd^{2+} could not be given in the range beyond $\bar{n}$ = 3. Therefore, values of k_n (n = 1–3) could be determined but those of k_4 for these metal ions were only determined for reference by extrapolating the respective curve as indicated by the broken lines (Figure 4). The ion UO_2^{2+} behaved in a different way; it forms complexes with PAA very strongly at the first and second ligand of amino groups, and from the third amino group ligand the chelation becomes much weaker.

Judging from values of the overall stability constant (K_3 or K_4), PAA is a better ligand for chelation with these metal ions than other amine type polymers such as poly(vinylpyridine).[4] But, PAA has almost the same chelating ability as linear poly(ethylenimine).[2]

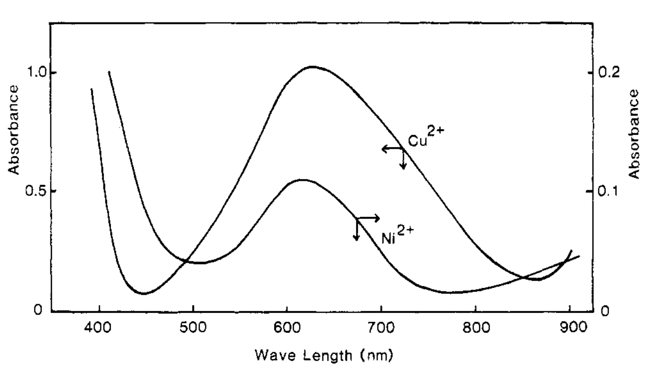


Figure 5. Visible spectra of PAA–Cu^{2+} and PAA–Ni^{2+} complex solutions. Measurement conditions: [PAA] + [Cu^{2+}] = 6.57 × 10^{-2} mol/L, [PAA]/[$CuCl_2$] = 3.0, and water as a reference sample at pH = ~8.5; [PAA] + [Ni^{2+}] = 0.10 mol/L, [PAA]/[$NiCl_2$] = 4.0, and a 0.02 mol/L of $NiCl_2$ aqueous solution as a reference sample at pH = 9.0.

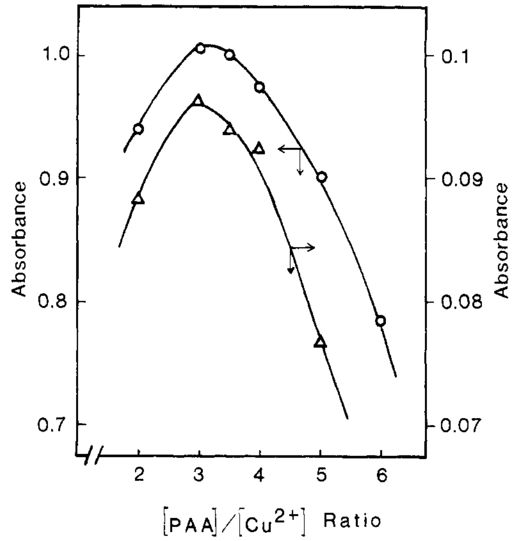


Figure 6. Continuous variation analysis of the PAA–Cu^{2+} complexes measured at 630 nm with μ = 0.1 mol/L (KCl) at 25 °C. Total concentrations; [PAA] + [Cu^{2+}] = 6.57 × 10^{-2} mol/L (○) and 6.57 × 10^{-3} mol/L (△).

Continuous Variation Analysis. Figure 5 shows visible spectra of PAA–Cu^{2+} and PAA–Ni^{2+} solutions which exhibit an absorption maximum at 630 and 620 nm, respectively, as observed for polyamine–Cu^{2+} complexes.[4] The absorption of the Cu^{2+} complexes is much stronger than that of the Ni^{2+} complexes.

Figure 6 indicates the result of continuous variation analysis of the PAA–Cu^{2+} system measured at 630 nm at the total concentration of 6.57 × 10^{-2} and 6.57 × 10^{-3} mol/L. A maximum is observed at the ratio of [PAA]/[Cu^{2+}] = 3.0 in both cases. The absorbance at the ratio [PAA]/[Cu^{2+}] = 3.5 is slightly weaker than that of 3.0 but that of 4.0 is clearly less than those at 3.0 and 3.5. These observations indicate that the predominant species under the experimental conditions is a complex having a ligand ratio amine group:Cu^{2+} = 3:1. It is known that Cu^{2+} forms the most stable complex with four ligands of amines, e.g., pyridine ligands of a partially quaternized poly(vinylpyridine).[4] However, the present result shows that PAA forms complexes with Cu^{2+} by coordinating three amino groups rather than four. These observations are in accord with the results of potentiometric titrations, in which plots of p[PAA] vs. $\bar{n}$ did not give correlations beyond $\bar{n}$ = 3.0 (Figure 4) and hence k_4 could not be determined definitely.

The PAA–Ni^{2+} solutions were similarly examined by comparing the absorption at 620 nm at the total concen-

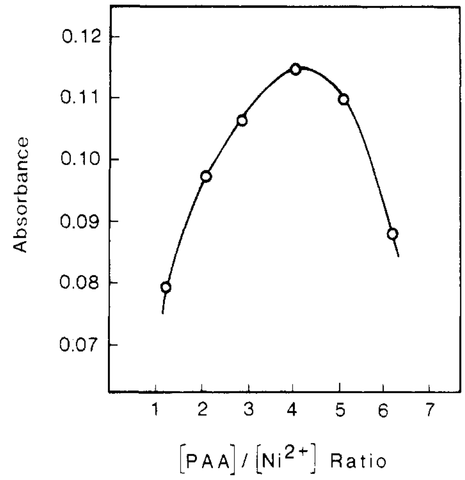


Figure 7. Continuous variation analysis of the PAA–Ni^{2+} complexes measured at 620 nm at pH = 9.0 with μ = 0.1 mol/L (KCl) at 25 °C. Total concentration [PAA] + [Ni^{2+}] = 0.10 mol/L.

tration of 0.10 mol/L (Figure 7). A maximum is clearly onserved at the ratio of [PAA]/[Ni^{2+}] = 4.0, indicating that PAA forms the most stable complexes with Ni^{2+} having four coordinating amino groups. These observations may be taken again to explain the observations of potentiometric titrations, in which plots of p[PAA] vs. $\bar{n}$ were made until $\bar{n}$ ~3.7 and hence the k_4 value was determined unambiguously.

Recovery of Uranium from Seawater. It becomes increasingly important to secure energy resources. One of possible ways is to recover uranium from seawater. A most serious problem involved here is that seawater contains only a small amount of uranyl ion (UO_2^{2+}) (~3.3 ppb)[11] as a mixture of large amounts of various ionic species such as Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^{2+}, etc. Therefore, the adsorbent for recovery of uranium from seawater is required to be rapid in rate for adsorption and to be selective for uranyl ions.[11] For this reason, various organic adsorbents have been designed[12] and inorganic adsorbents such as titanium oxide have also been employed.[13]

An attempt has been made in this study to use PAA for recovery of uranium. For the sake of convenient handling, PAA has been converted into resins by cross-linking with a bisepoxide to give CL-PAA. Further modifications were made by reacting with acrylic acid[6] and with a formaldehyde/phosphorous acid system,[7] giving rise to AcCL-PAA and PhosCL-PAA, respectively.

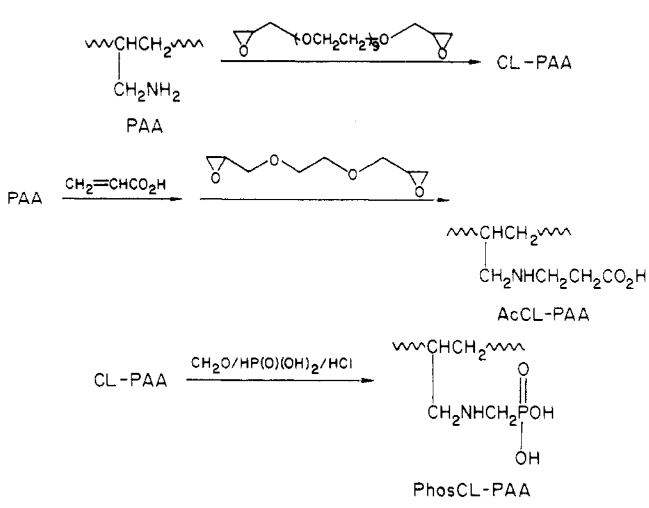


Table II
Recovery of Uranium

resins	from UO_2^{2+} solution[a] % U recvd with stirring for 2 h	 % U recvd with stirring for 4 h	from seawater[b] U recvd, µg/g·resin
CL-PAA	92.8		7.5 (23%)[c]
AcCL-PAA	93.3	95.4	11.7 (35%)[c]
PhosCL-PAA	91.4	98.2	25.6 (78%)[c]

[a] Resin = 50 mg in 1.0 mL of UO_2^{2+} (50 ppm) at pH 8.2 (H_3BO_3, KCl–NaOH, Na_2CO_3 buffer ([CO_3^{2-}] = 2 × 10^{-3} mol/L)). [b] Resin = 500 mg in 5.0 L of seawater at 25 °C with stirring for 24 h. [c] The value in parentheses corresponds to the percent of the total uranium present in the original seawater.

First, powdered resins of the above samples were employed to adsorb uranyl ions, UO_2^{2+}. A sample resin (50 mg) was suspended in 1.0 mL of water containing 50 ppm $UO_2(OAc)_2$ at pH 8.2, which is the same as that of seawater, and stirring was continued for 1 h or for 4 h at room temperature. The resins were separated by filtration and treated three times with 10% Na_2CO_3 aqueous solution. The amount of the desorbed uranium was determined by spectrophotometry based on the method using Arsenazo III[8] (Table II). It is seen that UO_2^{2+} was recovered almost quantitatively from an aqueous UO_2^{2+} (50 ppm) solution with all three resins.

Next, uranium recovery experiments from seawater were carried out for these resins by using a batch method: 500 mg of a powdered resin was placed in 5.0 L of seawater and the mixture was stirred for 24 h at 25 °C. Then the resin was separated by filtration and the uranyl ions were desorbed by treating three times with a 5% $(NH_4)_2CO_3$ aqueous solution. The amount of recovered uranium was determined similarly (Table II). It is striking that the adsorption ability of uranyl ions from seawater is very different for three resins. CL-PAA itself is a moderately effective resin for the uranium recovery from seawater. Modification of CL-PAA with acrylic acid somewhat increased the ability. CL-PAA modified with formaldehyde/phosphorous acid showed a very enhanced adsorption ability: 78% of the uranyl ions present in the original seawater was recovered by PhosCL-PAA.

The above data are enough to describe that an (aminomethyl)phosphonic acid type resin (PhosCL-PAA) is very effective for recovery of uranium from seawater, although further experiments for optimization are required. Similar types of resins from BPEI have been prepared and a study on the recovery of uranium by these resins is also in progress in our laboratories.

Acknowledgment. S.K. and F.M. acknowledge partial support of this work by Special Grant-in-Aid for Energy (No. 58040075 and 59040068) from the Ministry of Education, Science, and Culture, Japan. We are indebted to T. Tanabe for recording visible spectra in continuous variation analysis.

Registry No. U, 7440-61-1; Ni, 7440-02-0; Cu, 7440-50-8; Zn, 7440-66-6; Cd, 7440-43-9; UO_2^{2+}, 16637-16-4; PAA, 30551-89-4; nonaethylene glycol diglycidyl ether, 34206-34-3.

References and Notes

(1) Harada, S.; Hasegawa, S. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 27.
(2) Kobayashi, S.; Tokunoh, M.; Hiroishi, K.; Saegusa, T. to be reported.
(3) Dick, C. R.; Ham, G. E. *J. Macromol. Sci., Chem.* **1970**, *A4*, 1301.
(4) (a) Nishikawa, H.; Tsuchida, E. *J. Phys. Chem.* **1975**, *79*, 2072. (b) Tsuchida, E.; Nishide, H. *Adv. Polym. Sci.* **1977**, *24*, 1.
(5) Nitto Boseki Co. Ltd, Technical Catalog, "Polyallylamine", 1984.
(6) Kobayashi, S.; Gros, L.; Muacevic, G.; Ringsdorf, H. *Makromol. Chem.* **1983**, *184*, 793.

Macromolecules **1985**, *18*, 2361–2368

(7) Manecke, G.; Stockhausen, K.; Gergs, P. *Makromol. Chem.* **1969**, *128*, 229.

(8) (a) Motojima, K.; Yamamoto, T.; Kato, Y. *Japan Anal.* **1969**, *18*, 208. (b) Onishi, K.; Hori, Y.; Tomari, Y. *Bunseki Kagaku* **1977**, *26*, 74.

(9) (a) Lewis, E. A.; Barkley, J.; Pierre, T. St. *Macromolecules* **1981**, *14*, 546. (b) Rinaldi, P. L.; Yu. C.; Levy, G. C. *Ibid* **1981**, *14*, 551.

(10) (a) Gregor, H. P.; Luttinger, L. B.; Loebl, E. M. *J. Phys. Chem.* **1955**, *59*, 34. (b) Gold, D. H.; Gregor, H. P. *Ibid.* **1960**, *64*, 1461. (c) Gold, D. H.; Gregor, H. P. *Ibid.* **1960**, *64*, 1464. (d) Liu, K.-J.; Gregor, H. P. *Ibid.* **1965**, *69*, 1252.

(11) For a comprehensive reference, see: "Proceedings of an International Meeting on Recovery of Uranium from Seawater" Tokyo, Oct. 1983.

(12) (a) Tabushi, I.; Kobuke, Y.; Nishiya, T. *Tetrahedron Lett.* **1979**, 3515. (b) Tabushi, I.; Kobuke, Y.; Nishiya, T. *Nature (London)* **1979**, *280*, 665. (c) Tabushi, I.; Kobuke, Y.; Ando, K.; Kishimoto, M.; Ohara, E. *J. Am. Chem. Soc.* **1980**, *102*, 5947. (d) Egawa, H., Harada, H. *Nippon Kagaku Kaishi* **1979**, 958. (e) Egawa, H.; Harada, H.; Nonaka, T. *Ibid.* **1980**, 1767. (f) Egawa, H.; Harada, H.; Shuto, T. *Ibid.* **1980**, 1773. (g) Egawa, H.; Nonaka, T.; Ikeri, M. *J. Appl. Polym. Sci.* **1984**, *29*, 2045. (h) Schwochau, K.; Astheimer, L.; Schenk, H. J.; Witte, E. G. *Z. Naturforsch.* **1982**, *376*, 214. (i) Astheimer, L.; Schenk, H. J.; Witte, E. G.; Schwochau, K. *Sep. Sci. Technol.* **1983**, *18*, 307. (j) Best, F. R.; Driscoll, M. J. "Prospects for Uranium Recovery from Seawater" MIT-EL-80-001, Jan. 1980. (k) Manecke, G.; Danhäuser, J. *Makromol. Chem.* **1962**, *56*, 208.

(13) Kanno, M., p 12 of ref 11.

Poly(pyrrol-2-ylium tosylate): Electrochemical Synthesis and Physical and Mechanical Properties

Kenneth J. Wynne*[1] **and G. Bryan Street***

IBM Research Laboratory, San Jose, California 95193. *Received January 30, 1985*

ABSTRACT: Poly(pyrrolylium tosylate) may be prepared by the electrochemical polymerization of pyrrole in acetonitrile utilizing tetraethylammonium tosylate as a supporting electrolyte without special precautions to exclude air. Pyrolytic carbon electrodes allow the use of high currents, which shortens preparative time (e.g., 80 mA, 3 V, 4 h) and yields large samples (50 mm × 90 mm × 0.13 mm). As-prepared poly(pyrrolylium tosylate) films contain 4–6% by weight acetonitrile and 2–3% water. When an applied potential of 3 V ($\approx$80 mA) is utilized, films of composition $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ are obtained after removal of volatiles at 100 °C and 10^{-3} torr for 18 h. This is the first time that an analytically pure, anhydrous, poly(pyrrolylium anion) film has been prepared without utilizing dry-atmosphere techniques. The analytical data show that neither irreversible oxidation nor hydrogenation of the pyrrole moiety occurs, even in the presence of water. The anion/polycation segmer ratio found for these films (0.43) is higher than that observed previously (0.28–0.32) and may be due to the higher applied potential utilized. Films of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ are hygroscopic, taking up $\approx$3% water to form $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n \cdot {}^1/_4H_2O$ within 12 h. Slower water uptake continues, reaching $\approx$5% over the course of 3 months. This water absorption is reversible, the original composition being obtained after removal of water at 100 °C for 24 h. $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ exhibits a tensile strength of 69 MPa (1×10^4 psi), a Young's modulus of 2 GPa (3×10^5 psi), and an elongation-to-break of 8–18%. Acetonitrile/water, present in freshly prepared films, plasticizes poly(pyrrolylium tosylate) and reduces the modulus and tensile strength by ${}^1/_3$, while increasing the elongation-to-break to 50%. Poly(pyrrolylium tosylate) has been characterized by conductivity, X-ray, and SEM studies, as well as infrared, ESR, core-level X-ray photoelectron, and ^{13}C NMR spectroscopy. The conductivity of the amorphous films (105 S cm^{-1}) is only slightly affected on exposure to air over long periods of time (months). A variable-temperature study from 273 to 4.4 K showed that the conductivity of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ follows that predicted for a variable-range hopping mechanism and that the conductivity remains high (4.9 S cm^{-1}) even at 4.4 K. The narrow ESR line (0.38 G) due to free spins present in $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ is rapidly broadened on exposure to air but is narrowed back (0.5 G) almost to its original value after heating in vacuo overnight. The picture of poly(pyrrolylium tosylate) that emerges from the above studies is that of an easily prepared polymer film whose composition depends on the applied potential used for electropolymerization and the presence of adsorbed solvent/water. The mechanical properties are strongly dependent on the presence of solvent. While the conductivity of poly(pyrrolylium tosylate) is remarkably unaffected by exposure to air for long periods of time, physical and chemical changes that occur quickly (broadening of the ESR line, water uptake) and on a slower time scale (continued weight gain due to water absorption, attenuated spin density) are easily detected.

Introduction

Conducting polymeric materials containing the polypyrrolylium microstructure (Figure 1) have been the object of a number of investigations since the discovery of the electrochemical synthesis of films by Dall'Olio.[2] Thus, the preparation and characterization of poly(pyrrolylium tetrafluoroborate),[3,4] poly(pyrrolylium perchlorate),[5] and a variety of other poly(pyrrolylium anion) compositions[6,7] have been described. The relative ease of preparation of these films has resulted in numerous efforts directed at elucidating the details of the polymer chain structure as well as the spectroscopic, electronic, and optical properties.[8–11] An interesting conclusion derived from ESR studies is that the charge carriers in poly(pyrrolylium anion) films are spinless.[8] The existence of dications or "bipolarons" (Figure 1) that would allow spinless conductivity has been shown to be favorable energetically.[12–14] Evidence for the existence of these bipolarons has been obtained from optical as well as ESR data. Electrooptical studies have revealed optical absorptions in the band gap consistent with the presence of bipolarons.[14,15]

Poly(pyrrolylium anion) films are coherent and adhere well to the electrode. These properties, the robust nature of the films, and their redox behavior have led to utilization of poly(pyrrolylium anion) films as electrode materials.[16,17] Potential applications as a free-standing film place additional materials requirements, including good mechanical properties, and raise questions concerning the invariance

0024-9297/85/2218-2361$01.50/0