COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Photo-reversible Pb^{2+}-complexation of thermosensitive poly(*N*-isopropyl acrylamide-*co*-spiropyran acrylate) in water

Takayuki Suzuki,* Tatsuya Kato and Hiraku Shinozaki
Department of Environmental Materials of Science, Faculty of Engineering, Tokyo Denki University, 2-1200 Muzai-gakuendai, Inzai, Chiba, 270-1382, Japan. E-mail: tsuzu@chiba.dendai.ac.jp;
Fax: +81(476)46-8735; Tel: +81(476)46-8735

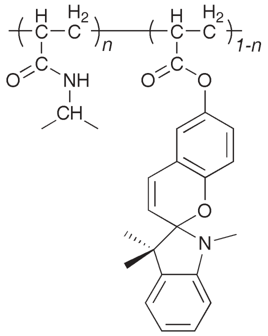
Received (in Cambridge, UK) 14th May 2004, Accepted 16th July 2004
First published as an Advance Article on the web 13th August 2004

DOI: 10.1039/b407342h

Photo-reversible Pb^{2+}-complexation in a purely aqueous environment exhibiting a thermosensitive phase transition at a lower critical solution temperature was achieved using a synthetic copolymer composed of *N*-isopropyl acrylamide and spiropyran acrylate.

The attractive features of photochromic spiropyrans have prompted a number of studies of derivatives of these compounds and their metal-binding characteristics.[1,2] Upon irradiation with UV or visible light, spiropyrans isomerize between the open and closed forms, respectively.[3] The open form is more polar. Metal ions can influence this isomerization by association with the open form through the electron-rich oxygen atom. However, visible light generates the closed form, thus hindering metal binding. Strongly polar solvents such as water and alcohols stabilize the metal-complexed open form to such an extent that in aqueous solution, visible light can no longer generate the closed form. However, Collins and coworkers[4] showed that the complexation of metal ions by quinolinospiropyran could be made photo-reversible, provided the closed form is stabilized by using acetonitrile–water mixtures. Recently, other reports have described photo-reversible metal-complexations of spiropyrans in fluoroalcohols and methanol–water mixtures.[5] Herein, we describe photo-reversible Pb^{2+}-complexation of a thermosensitive copolymer consisting of *N*-isopropyl acrylamide (NIPAAm) and a synthetic spiropyran acrylate (SPAA), **I** (Scheme 1), in water. Poly(*N*-isopropyl acrylamide), P(NIPAAm), is thermosensitive in water showing a lower critical solution temperature (LCST).[6] Above the LCST, the aqueous solution generates a solid polymer and separates into two phases. A thermosensitive copolymer that displays such phase transition behavior at the LCST is attractive for use as a metal-ion adsorbent. Above the LCST, the solid phase, containing bound metal-ions, can be easily separated from solution. However, because the solid phase forms a transparent solution below the LCST, it is easy to subsequently recover these metal-ions from the copolymer by irradiation with visible light.

Synthesis of SPAA was carried out by reaction between 1′,3′,3′-trimethyl-6-hydroxyspiro(2H-1-benzopyran-2,2′-indoline) and acryloyl chloride in toluene. Copolymerization of NIPAAm and SPAA was subsequently performed in ethanol under nitrogen at 60 °C with 2,2′-azobis(isobutyronitrile), affording **I**, ($Mw = 7.4 \times 10^4$, $Mw/Mn = 2.7$). The ratio of SPAA units in **I** was 2 mol%, as determined by ^1H NMR measurements.



Scheme 1 **I**.

An aqueous solution of **I** was prepared by adding **I** to neutralized water (pH = 7.0) at 5 °C, below the LCST (29 °C, mentioned below). The absorption spectrum of the purplish-red solution shows a strong band at 533 nm (Fig. 1(A)), attributed to the open form of the SPAA unit. This band is photobleached by irradiating with visible light (>420 nm), but reappears on standing in the dark. Solutions of **I** in non-polar THF or polar acetonitrile, kept in the dark, do not exhibit absorption bands in the visible. Clearly, the open form of the SPAA unit is stabilized in the more polar water environment. In acidic solutions of **I**, an absorption band at 422 nm (not shown), attributable to a protonated open form of the SPAA unit, was observed along with an increase in pH. The 422 nm band is absent in neutral or alkali solution, so the concentration of this species is negligible.

Absorbtion measurements after addition in the dark of a tenfold molar excess (relative to the SPAA unit) of $Pb(ClO_4)_2$ revealed a band at 433 nm (Fig. 1(B)) along with the almost complete disappearance of the 533 nm band. These changes suggest the generation of a different open form of the SPAA unit, which is thought to be the Pb^{2+}-complex. Fig. 1(C) shows the complete disappearance of the 433 nm band upon subsequent irradiation with visible light. This band reappeared after standing in the dark, attaining the same absorbance as spectrum (B) under equilibrium conditions. Thus, stabilization of the Pb^{2+}-complexed open form in an extremely polar solvent such as water did not prevent isomerization to the closed form under visible light. The complexed Pb^{2+} ions were subsequently liberated by shifting the equilibrium of the SPAA unit.

The transmittance of an aqueous solution of **I** suddenly

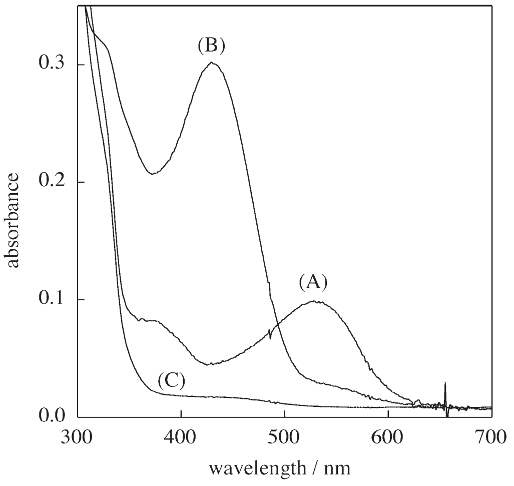


Fig. 1 Absorption spectra of aqueous solution of **I** at 5 °C. (A) 0.04 wt% of **I** ([SPAA unit] = 0.1 mM). (B) Solution after addition of $Pb(ClO_4)_2$ (1.0 mM) to solution (A). (C) The same solution as used in (B) measured under visible light irradiation.

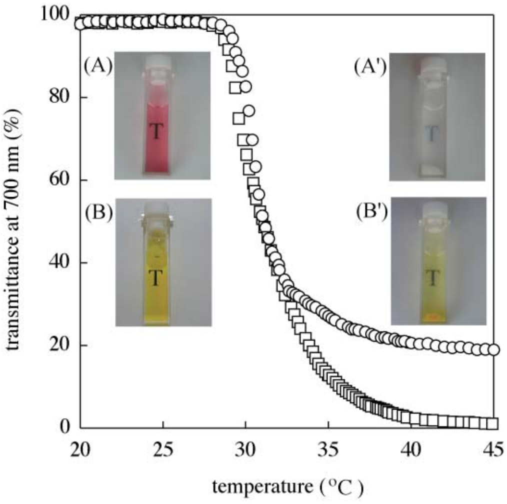


Fig. 2 Temperature dependence of optical transmittance of aqueous solution of **I**, measured in the dark at a rate of about +1 °C min^{-1}. (○) 0.04 wt% of **I** in water, (□) addition of $Pb(ClO_4)_2$ (1.0 mM, [Pb^{2+}]:[SPAA unit] = 10:1) to the solution of **I** (0.04 wt%). Inset: color changes of **I** in water.[7] 0.23 wt% of **I** at 10 °C (A) and at 40 °C (A′). 0.23 wt% of **I** and $Pb(ClO_4)_2$ (5.0 mM) at 10 °C (B) and at 40 °C (B′).

decreased as temperature increased due to the thermosensitive NIPAAm units, which exhibited an LCST at 29 °C, as shown in Fig. 2. The increase in hydrophobicity of **I** would result in a lower LCST than that of the P(NIPAAm) homopolymer (32 °C). $Pb(ClO_4)_2$ at a concentration of 1 mM did not influence the LCST of the solution. At temperatures above the LCST, **I** precipitated in water, as shown in Fig. 2(A′) and (B′). The dehydration of the copolymer chain of **I** above the LCST may result in closing of the open form of the SPAA unit, followed by the appearance of a white precipitate of (A′). This supports the suggestion that water thermodynamically stabilizes the open form of the SPAA units. In contrast, for the Pb^{2+} solution a yellow precipitate of **I** was obtained above the LCST (Fig. 2(B′)). This solid material is expected to be useful for absorbing metal ions.

To confirm the adsorption and desorption of Pb^{2+} by **I**, square-wave voltammetry of aqueous solutions of Pb^{2+} ions was performed using an amalgamated Au working electrode, as previously described.[5b] Addition of $LiClO_4$ (0.1 M) as a supporting electrolyte resulted in a shift of the LCST to lower temperature (27 °C) due to the salt effect of $LiClO_4$.[8] Voltammetry was conducted at 40 °C (>LCST) due to the difficulty in using viscous polymer-soluble solutions. The cathodic wave of free Pb^{2+} ions was observed at −0.53 V *vs.* Ag/AgCl. After addition of **I** into the solution at 40 °C, the Pb^{2+}-cathodic wave (−0.53 V) decreased in intensity, as shown in Fig. 3. The calculated Pb^{2+}-adsorption ability is 62% at [Pb^{2+}]:[SPAA unit] = 1:10 under initial concentration conditions.[9] After irradiation of the Pb^{2+}-adsorbed precipitate of **I** with visible light, 48% of the Pb^{2+} ions were desorbed from the precipitate. A decrease in current intensity at −0.53 V was again observed in the dark due to re-adsorption of Pb^{2+} ions by **I**.

In conclusion, we demonstrated photo-reversible Pb^{2+}-complexation with a thermosensitive copolymer, **I**, in water. For Zn^{2+}, Cu^{2+}, Ni^{2+} and Mn^{2+} ions, the photo-reversible metal-complexation of **I** was also examined by UV-visible spectroscopy. Modification of the system to improve photo-reversibility in water is currently under investigation. One such study involves the investigation of efficient exposure of a crosslinked hydrogel of **I** in the swollen state (<LCST) to visible light.

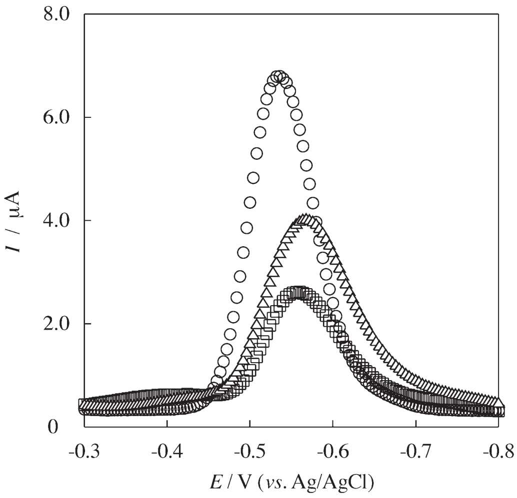


Fig. 3 Cathodic reduction of Pb^{2+} ions in aqueous solutions at 40 °C. (○) [Pb^{2+}] = 0.04 mM in water, (□) after addition of **I** (0.23 wt%) to the Pb^{2+} solution, (△) after irradiation with visible light to solution □.

This work was supported in part by the Research Institute for Technology (No. Q03M-04) at Tokyo Denki University.

Notes and references

1 (*a*) R. C. Bertelson, in *Photochromism*, ed. G. H. Brown, Wiley, New York, 1971; (*b*) R. J. Guglielmetti, in *Photochromism*, ed. H. Durr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990.

2 For recent examples, see: (*a*) J. Filley, M. A. Ibrahim, M. R. Nimlos, A. S. Watt and D. M. Blake, *J. Photochem. Photobiol. A: Chem.*, 1998, **117**, 193; (*b*) M. Inouye, K. Akamatsu and H. Nakazumi, *J. Am. Chem. Soc.*, 1997, **119**, 9160; (*c*) K. Kimura, T. Yamashita and M. Yokoyama, *J. Chem. Soc., Perkin Trans. 2*, 1992, 613; (*d*) T. Tamaki and K. Ichimura, *Chem. Commun.*, 1989, 1477.

3 R. C. Bertelson, in *Organic Photochromic and Thermochromic Compounds*, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999.

4 G. E. Collins, L-S. Choi, K. J. Ewing, V. Michelet, C. M. Bowen and J. D. Winkler, *Chem. Commun.*, 1999, 321.

5 (*a*) T. Suzuki, F.-T. Lin, S. Priyadashy and S. G. Weber, *Chem. Commun.*, 1998, 2685; (*b*) T. Suzuki, Y. Kawata, S. Kahata and T. Kato, *Chem. Commun.*, 2003, 2004.

6 (*a*) Y. Maeda, T. Higuchi and I. Ikeda, *Langmuir*, 2001, **17**, 7535; (*b*) M. Hahn, E. Görnitz and H. Dautzenberg, *Macromolecules*, 1998, **31**, 5616; (*c*) H. Feil, Y. H. Bae, J. Feijen and S. W. Kim, *Macromolecules*, 1993, **26**, 2496.

7 A letter "T" was behind the cuvette (thickness 1 cm) in order to confirm the transparency of the solution.

8 According to Maeda and co-workers, the LCST of P(NIPAAm) homopolymer (32 °C) in water decreased in proportion to the added NaCl (10 °C with 10 wt% of NaCl).[6a] Thus, the decrease in the LCST from 29 to 27 °C of **I** in water after addition of 0.1 M (∼1 wt%) of $LiClO_4$ was consistent.

9 The P(NIPAAm) homopolymer containing the equivalent mole of the NIPAAm unit in aqueous solution absorbed 15% of Pb^{2+} ions in the same initial concentration of Pb^{2+} ions at 40 °C.