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Thermo-responsive extraction of cadmium(II) ion with poly(TPEN-NIPA) gel. Effect of the chain length and branch in the spacer structure towards gel formation and the extracting behavior

ABSTRACT. *N,N,N',N'*-(tetrakis-2-pyridylmethyl)ethylenediamine (TPEN) derivatives bearing a polymerizable double bond in the substituent structure of the pyridine ring are synthesized and subjected to copolymerization with *N*-isopropylacrylamide in the presence of AIBN. The obtained poly(TPEN-NIPA) gels show thermo-responsive swelling/shrinking behaviors and are employed for the extraction of cadmium(II) ion from the aqueous solution to examine the relationship of the gel characteristics and the extraction performance. The polymer gels composed of the TPEN derivative bearing **C3**, **C4**, **C10** and branched C3 spacer chains are synthesized and temperature-dependent extraction behavior of cadmium ion is compared. These gels extract Cd^{II} ion efficiently from the aqueous solution in the swelling state at 5 °C, while little extraction is observed at 45 °C with shrinking. It is found that poly(TPEN-NIPA) gel of branched C3 spacer (**C3b**) shows the excellent thermo-responsive extraction performance.

KEYWORDS. TPEN, poly(TPEN-NIPA) gel, thermo-responsive swelling and shrinking, the number of double bond, Cd^{II} extraction

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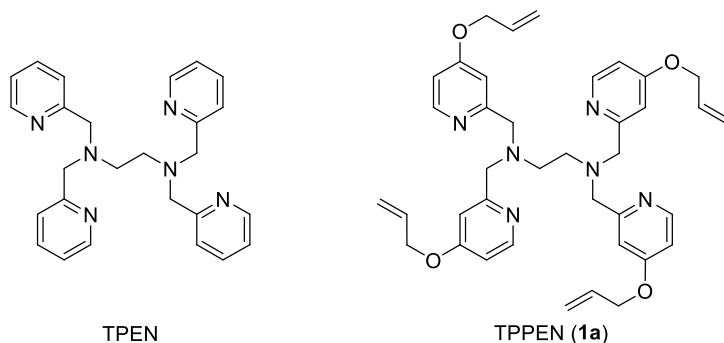
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Introduction

Functionality design based on outside stimuli attracts considerable attention in a wide range of fields. A polymer gel composed of poly(*N*-isopropyl acrylamide) (NIPA), which reversibly switch swelling and shrinking corresponding to a temperature change, is thereby intriguing as a thermo-responsive functional materials.¹⁻⁴ We have recently shown that poly(TPEN-NIPA) gel effectively extract soft metal ions such as Cd^{II} and its extraction behaviors are thermally dependent in various pH regions. It was shown to extract Cd^{II} at lower temperature, while little extraction has been observed at the elevated temperature.⁵⁻⁸ TPEN, *N,N,N',N'*-(tetrakis-2-pyridylmethyl)ethylenediamine, is recognized as a hexadentate ligand with six nitrogen donors and has been shown to chelate a variety of soft metal ions such as Hg, Cd, Au, Pd, etc.⁹⁻¹³ It was also shown to be effective for chelation of *f*-block metals and separation of minor actinides from high level radioactive waste (HLW) has been an attractive issue.¹⁴⁻²³ Thereby TPEN derivatives have been employed as an extracting agent for variety of metal ions in an organic solvent. On the other hand, it is possible to extract metal ions in aqueous solutions without organic solvent if the TPEN moiety is incorporated into a polymer gel. Since poly-NIPA (*N*-isopropyl acrylamide) gel is shown to swell at low temperature in water and shrink at the elevated temperature higher than LCST,¹ thermo-responsive swelling/shrinking can be applied for the corresponding conformational change of TPEN that induces temperature dependent change of extraction behaviors when the TPEN moiety such as **1a** is employed as a cross linker in the poly-NIPA gel.

In our recent report, we have studied the relationship of the number of polymerizable double bond on the pyridine ring and the structure of ethylenediamine moiety of TPEN derivatives with the temperature-dependent extraction behavior of a cadmium(II) ion.^{7, 8, 24-29} It was revealed that the poly(TPEN-NIPA) gel prepared from TPEN derivatives bearing at least three double bond moieties are necessary to form a stable polymer gel and to show temperature-dependent change of extraction behaviors. Accordingly, our concern is centered to the relationship of the chain length and branched structure of the spacer moiety between the polymer main chain and TPEN moiety. Herein, we report synthesis of several TPEN derivatives bearing four polymerizable double bond in the substituent on the pyridine ring with different

methylene spacer length and branched structure and studies on the temperature-dependent extraction behaviors of cadmium ion with poly(TPEN-NIPA) gels of the different spacer structure.³⁰



Experimental Section

General. NMR (500 MHz for ^1H , 125 MHz for ^{13}C) spectra were recorded on a Bruker Avance 500 spectrometer at the Center for Supports to Research and Education Activities, Kobe University. Chemical shifts are expressed in ppm using tetramethylsilane as an internal standard (0 ppm). Coupling constants (J) were shown in Hertz (Hz). IR (ATR) spectra were measured with Bruker Optics Alpha with Ge. TLC analyses were performed on analytical TLC plates coated with 60 F₂₅₄ (E. Merck) silica gel or alumina on aluminum foil. Column chromatography was performed using silica gel Wakogel C200 (Wako Chemicals Co. Ltd.) or basic alumina (Wako Chemicals Co. Ltd or Merck). High-resolution mass spectra were measured at Nara Institute of Science and Technology with JEOL JMS-700. ICP-AES analysis was carried out with SII SPS3100 at the Center for Supports to Research and Education Activities of Kobe University.

Chemicals were purchased and used without further purification.

Chloromethylpyridine derivatives were prepared in a manner described previously. These spectroscopic characteristics and physical properties are shown below:

2-Chloromethyl-4-(buta-3-en-1-yloxy)pyridine (6b): ^1H NMR (CDCl_3) δ 8.35 (d, J = 5.8, 1H), 6.98 (d, J = 2.4, 1H), 6.72 (dd, J = 5.8, 2.4, 1H), 5.81-5.91 (m, 1H), 5.10-5.19 (m, 2H), 4.60 (s, 2H), 4.07 (t, J

= 6.7, 2H), 2.52-2.57 (m, 2H); ^{13}C NMR (CDCl_3) 165.87, 158.03, 150.43, 133.54, 117.58, 109.50, 109.24, 67.25, 46.54, 33.11; IR 1595, 1568, 1308, 1295, 1034, 991, 919 cm^{-1} ; HRMS (EI+) calcd for $\text{C}_{10}\text{H}_{12}\text{ClNO}$ $[\text{M}]^+$; 197.0607; found: 197.0604.

2-Chloromethyl-4-(deca-9-en-1-yloxy)pyridine (6c): ^1H NMR (CDCl_3) δ 8.35 (d, $J = 5.8$, 1H), 6.97 (d, $J = 2.4$, 1H), 6.72 (dd, $J = 5.8$, 2.4, 1H), 5.80 (ddt, $J = 17.2$, 10.1, 6.7, 1H), 4.99 (dd, $J = 17.2$, 1.7, 1H), 4.93 (dd, $J = 10.1$, 1.0, 1H), 4.61 (s, 2H), 4.01 (t, $J = 6.6$, 2H), 2.04 (dt, $J = 6.7$, 6.6, 2H), 1.79 (quin, $J = 6.6$, 2H), 1.31-1.48 (m, 10H); ^{13}C NMR (CDCl_3) 165.93, 157.99, 150.47, 138.94, 114.07, 109.39, 109.11, 68.00, 46.64, 33.63, 29.21, 29.10, 28.88, 28.75, 28.72, 25.76; IR 2925, 2854, 1596, 1568, 1467, 1308, 1296, 1025, 992, 909 cm^{-1} ; HRMS (EI+) calcd for $\text{C}_{16}\text{H}_{24}\text{ClNO}$ $[\text{M}]^+$; 281.1546; found: 281.1541.

2-Chloromethyl-4-(2-methylprop-2-en-1-yloxy)pyridine (6d): ^1H NMR (CDCl_3) δ 8.37 (d, $J = 5.9$, 1H), 7.01 (d, $J = 2.2$, 1H), 6.75 (dd, $J = 5.9$, 2.2, 1H), 5.08 (s, 1H), 5.03 (s, 1H), 4.61 (s, 2H), 4.49 (s, 2H), 1.82 (s, 3H); ^{13}C NMR (CDCl_3) 165.71, 158.15, 150.61, 139.48, 113.70, 109.73, 109.47, 71.64, 46.68, 19.27; IR 1594, 1568, 1478, 1311, 1241, 1177, 1018, 903 cm^{-1} ; HRMS (EI+) calcd for $\text{C}_{10}\text{H}_{12}\text{ClNO}$ $[\text{M}]^+$; 197.0607; found: 197.0607.

***N,N,N',N'*-Tetrakis[4-(buta-3-en-1-yloxy)pyridin-2-ylmethyl]ethylenediamine (1b):** To a 25 mL of round-bottom flask were added compound **6b** (395.3 mg, 2.0 mmol), hexadecyltrimethylammonium chloride (3.2 mg, 0.01 mmol) and ethylenediamine (33.6 μL , 0.5 mmol) in H_2O (0.2 mL) under a nitrogen atmosphere. 5 M NaOH aq. (0.5 mL, 2.5 mmol) was added, and the resulting mixture was stirred vigorously at room temperature for 72 h. The reaction mixture was extracted with CH_2Cl_2 and the extract was washed with water, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on aluminum oxide (EtOAc:MeOH 100:0–10:1) to afford **1b** as pale brown oil in 64% yield. ^1H NMR (CDCl_3) δ 8.24 (d, $J = 5.8$, 4H), 6.98 (d, $J = 2.4$, 4H), 6.60 (dd, $J = 5.8$, 2.4, 4H), 5.76-5.89 (m, 4H), 5.07-5.16 (m, 8H), 4.60 (s, 2H), 3.94 (t, $J = 6.6$, 8H), 3.72 (s, 8H), 2.77 (s, 4H), 2.45-2.52 (m, 8H); ^{13}C NMR (CDCl_3) 165.62, 161.72, 150.19, 133.95, 117.57, 109.14, 108.61, 67.05, 60.88, 52.63, 33.39; IR 1595, 1567, 1305, 1033, 993, 918, 829 cm^{-1} ; HRMS (EI+) calcd for $\text{C}_{42}\text{H}_{52}\text{N}_6\text{O}_4$ $[\text{M}]^+$; 704.4050; found: 704.4051.

***N,N,N',N'*-Tetrakis[4-(deca-9-en-1-yloxy)pyridin-2-ylmethyl]ethylenediamine (1c):** To a solution of ethylenediamine (4.20 μ L, 0.063 mmol) in THF/toluene (1:1, 0.5 mL) were successively added **6c** (71.5 mg, 0.25 mmol), potassium carbonate (35.1 mg, 0.254 mmol) and NaI (19 mg, 0.127 mmol) under nitrogen atmosphere. The reaction mixture was stirred for 19 h at 50 °C. The suspension was filtered through a Celite pad. The filtrate was evaporated, and the resulting oil was purified by chromatography on alumina (EtOAc:MeOH 100:0–20:1) to afford **1c** (49.5 mg, 76%) as a pale yellow oil. ¹H NMR (CDCl₃) δ 8.23 (d, J = 5.8, 4H), 6.98 (d, J = 2.4, 4H), 6.59 (dd, J = 5.8, 2.4, 4H), 5.78 (ddt, J = 17.2, 10.1, 6.7, 4H), 4.96 (dd, J = 17.2, 1.7, 4H), 4.90 (dd, J = 10.1, 1.0, 4H), 3.87 (t, J = 6.6, 8H), 3.72 (s, 8H) 2.79 (s, 8H), 2.04 (dt, J = 6.7, 6.6, 8H), 1.72 (quin, J = 6.6, 8H), 1.29–1.40 (m, 40H); ¹³C NMR (CDCl₃) 165.83, 160.94, 149.74, 139.02, 114.14, 109.11, 108.69, 67.88, 60.32, 52.27, 33.71, 29.34, 29.28, 29.00, 28.91, 28.85, 25.90; IR 2925, 2853, 1594, 1567, 1467, 1305, 1024, 993, 908 cm⁻¹; HRMS (FAB⁺) calcd for C₆₆H₁₀₀N₆O₄ [M+H]⁺; 1041.7884; found: 1041.7894.

***N,N,N',N'*-Tetrakis[4-(2-methylprop-2-en-1-yloxy)pyridin-2-ylmethyl]ethylenediamine (1d):** To a solution of ethylenediamine (4.02 μ L, 0.06 mmol) in THF (0.482 mL) were successively added **6d** (47.1 mg, 0.241 mmol), potassium carbonate (33.3 mg, 0.24 mmol), *N*-hexadecyltrimethylammonium chloride (7.7 mg) and NaI (18.1 mg, 0.12 mmol) under nitrogen atmosphere. The reaction mixture was stirred for 22 h at 50 °C. The suspension was filtered through a Celite pad. The filtrate was evaporated, and the resulting oil was purified by chromatography on alumina (EtOAc) to afford **1d** (29.5 mg, 70%) as a pale yellow oil. ¹H NMR (CDCl₃) δ 8.37 (d, J = 5.9, 1H), 7.01 (d, J = 2.2, 1H), 6.75 (dd, J = 5.9, 2.2, 1H), 5.08 (s, 1H), 5.03 (s, 1H), 4.61 (s, 2H), 4.49 (s, 2H), 1.82 (s, 3H); ¹³C NMR (CDCl₃) 165.12, 161.42, 149.85, 139.54, 113.14, 108.89, 108.53, 71.06, 60.58, 52.36, 19.05; IR 1593, 1567, 1481, 1307, 1241, 1166, 1019, 903, 748 cm⁻¹; HRMS (EI⁺) calcd for C₄₂H₅₂N₆O₄ [M]⁺; 704.4050; found: 704.4044.

General Procedure for radical polymerization of NIPA with TPEN derivatives: To a 25 mL of sealed tube equipped with a magnetic stirring bar were added *N*-isopropylacrylamide (170 mg, 1.5 mmol) and TPEN derivative (0.019 mmol). The mixture was dissolved in 0.13 mL of DMF and AIBN

(1.25 mol% or 2.50 mol%) was added in one portion. The resulting mixture was heated at 60 °C for 18 h. Then, the mixture was cooled to room temperature and washed with water repeatedly. Water was removed under reduced pressure at 50 °C to leave a colorless solid. Poly(TPEN-NIPA) gels (**C3**, **C4**, **C10** and **C3b**, see scheme 2) obtained were found to swell at room temperature in water and shrinking was observed when the mixture was heated to 45 °C.

Extraction of cadmium(II) ion with poly(TPEN-NIPA) gel: A 1 mM of aqueous $\text{Cd}(\text{NO}_3)_2$ solution was prepared. The pH value of the solution was controlled to 1.9, 2.0, 5.3, 5.9 by the addition of 1 M of aq. NH_4NO_3 and 1 M of HNO_3 . Poly(TPEN-NIPA) gel (2.5 mol% of TPEN contents), whose concentration of the TPEN moiety was controlled to be 1.5 μmol , was added to 0.75 mL of the aqueous solution. Vigorous stirring of the mixture was continued for 60 min at 0 °C or 45 °C. An aliquot of the solution (0.2 mL) was taken, passed through a membrane filter (0.2 μm), and diluted with distilled water to 4 mL, which was subjected to ICP-AES analysis. Cd^{II} absorbed amount of poly(TPEN-NIPA) dry gel (mmol/g-dry gel) were summarized in Table 1.

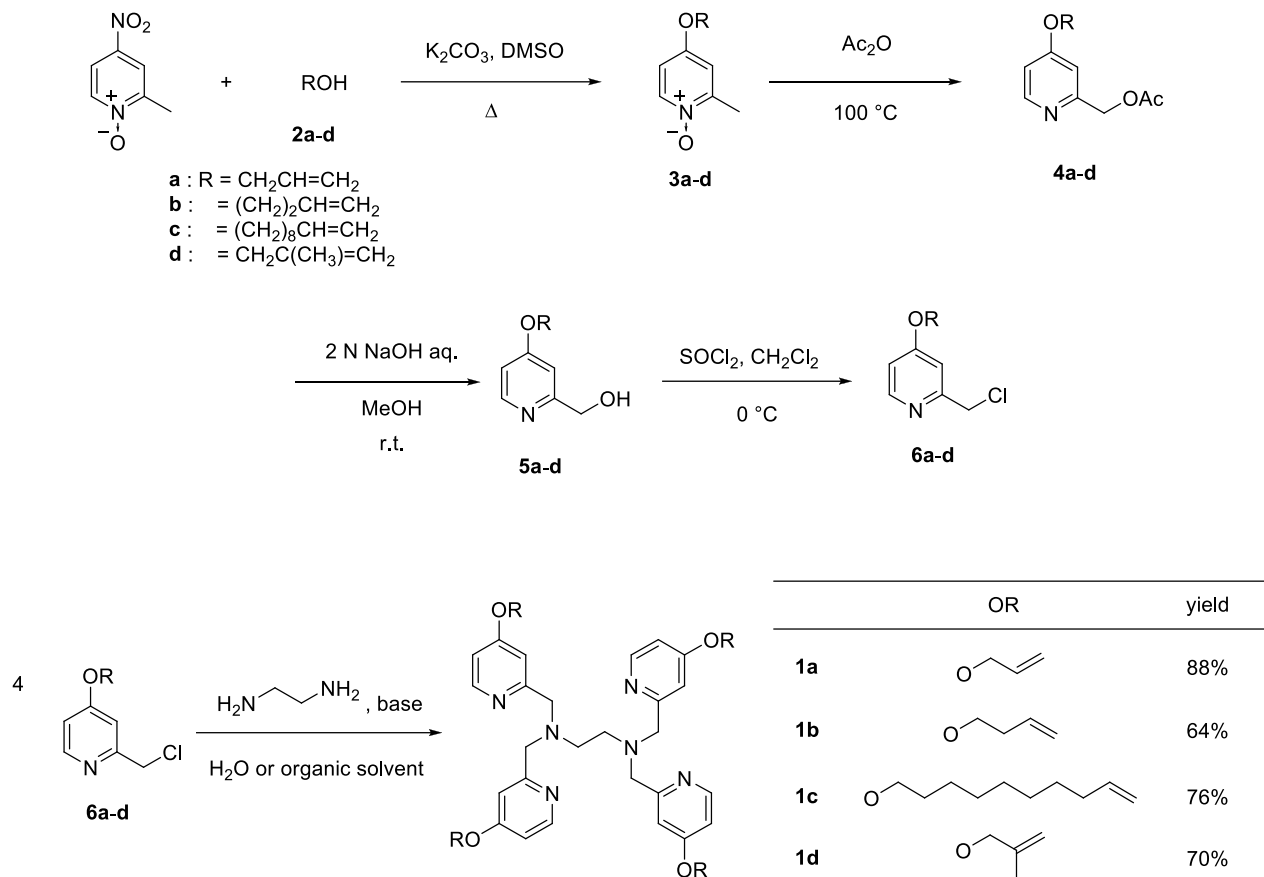
Table 1. Extraction of Cd^{II} by TPEN derivatives with chloroform.

poly(TPEN-NIPA) gel	Weight of dry-gel [mg]	Temp.	pH (before extraction)	pH (after extraction)	Cd absorbed amount [mmol/g-dry gel]
C3	7.8	5 °C	1.9	2.3	3.20×10^{-2}
			5.3	6.3	7.91×10^{-2}
		45 °C	2.0	2.5	1.07×10^{-2}
			5.9	6.7	0.08×10^{-2}
C4	7.8	5 °C	1.9	2.3	4.64×10^{-2}
			5.3	6.3	9.57×10^{-2}
		45 °C	2.0	2.4	0.48×10^{-2}
			5.9	6.5	0.04×10^{-2}
C10	8.4	5 °C	1.9	2.3	5.50×10^{-2}
			5.3	4.3	9.13×10^{-2}
		45 °C	2.0	2.4	1.64×10^{-2}
			5.9	4.9	4.62×10^{-2}
C3b	7.8	5 °C	1.9	2.5	6.40×10^{-2}
			5.3	6.5	9.60×10^{-2}
		45 °C	2.0	2.3	0.26×10^{-2}
			5.9	6.7	0.01×10^{-2}

Results and discussion

The synthetic pathway of TPEN derivatives with different side-chain length (**1a-c**) and branched structure (**1d**) was summarized in Scheme 1. Syntheses of pyridine derivatives bearing an allyloxy moiety **3a-6a** and the TPEN derivative **1a** were previously reported.⁵⁻⁷ Reactions to afford **3b-d**, **4b-d**, **5b-d**, **6b-d**, were carried out in similar manners. Although the reaction of 2-methyl-4-nitropyridine-1-oxide with allylic alcohol **2a** or **2d** proceeded smoothly, harsh conditions were found to be necessary to afford **3b** and **3c**. Other reactions concerning introduction of the OAc group, hydrolysis of the acetoxy group, and chlorination proceeded similarly. The obtained chloromethyl pyridine derivatives **6** were subjected to the reaction with 1,2-ethylenediamine to afford the corresponding TPEN derivatives with

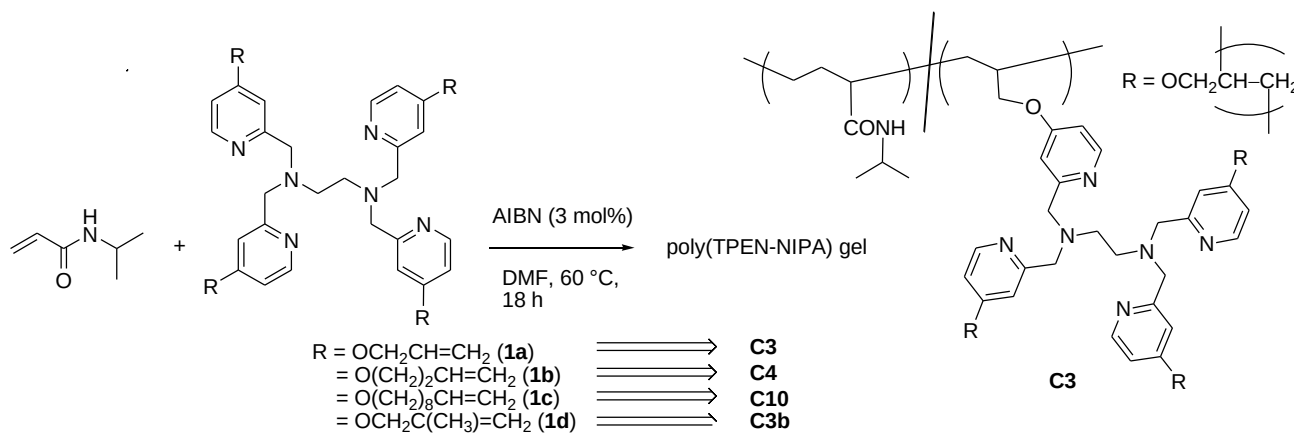
different substituents **1b-d**. The TPEN derivative **1b**, which bears 3-butenyloxy group at the 4-position of the pyridine ring, is a homologated derivative toward **1a**, while **1c** (R=9-decen-1-yl) involves longer methylene groups. On the other hand, **1d** possesses a methyl group at the C-2 carbon atom as a branched structure.



Scheme 1.

TPEN derivatives thus obtained were subjected to the radical copolymerization leading to poly(TPEN-NIPA) gel. (Scheme 2) The reaction was performed with *N*-isopropyl acrylamide (NIPA) and TPEN derivatives **1a-d** in the presence of AIBN as an radical initiator in DMF. All of the polymerization were carried out at 60 °C for 18 h. When 1.25 mol % of TPEN derivatives **1a**, **1b** and **1d** toward NIPA were employed, the corresponding polymer gels that were insoluble in water were obtained. (C3, C4, C3b, respectively) By contrast, polymerization with **1c** resulted in insufficient gel formation and the product C10 was mostly dissolved upon standing in water for 2 days. Improved gel formation was observed with

2.50 mol % of **1c**, however, slow leaching to water was found to be still inevitable. The obtained polymer gels were found to be insoluble to any organic solvents as well as water, thereby spectroscopic analyses of the gel to suggest the chemical structure were totally unsuccessful. Figure 1 shows poly(TPEN-NIPA) gels **C3**, **C4**, **C3b**, and **C10** in water as a swollen state.



Scheme 2.

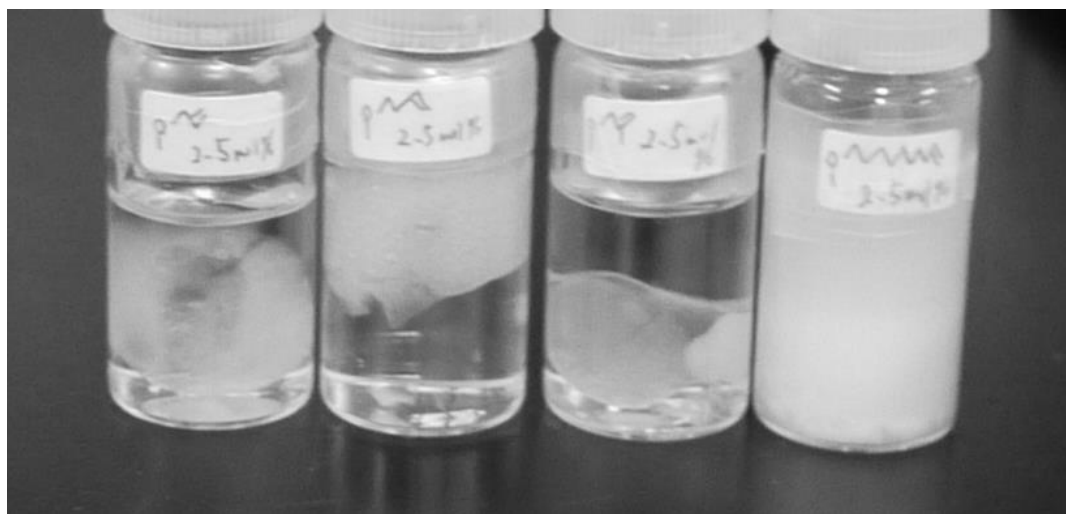


Figure 1. TPEN-NIPA gels **C3**, **C4**, **C3b**, **C10** (left to right) in water.

The obtained gels were dried with heating at 70 °C under reduced pressure to afford colorless powders, whose aqueous solutions showed repeating swelling at room temperature and shrinking by heating. The

volume change between swollen and shrinking states were found to be 25% (C3) and 18% (C10), respectively. Figure 2 shows the representative thermo-responsive change of **C4**.

Toughness of the obtained gel **C4** was mostly similar to that of **C3**. Among poly(TPEN-NIPA) gels, **C3b** was found to form the strongest gel probably due to the improved reactivity by the introduction of an electron-donating methyl substituent onto the double bond. On the other hand, the performance of poly(TPEN-NIPA) gel **C10** was inferior to other gels to result in partially dissolving in water upon standing. This would be due to the flexible longer methylene chain that inhibited stiff cross linking.

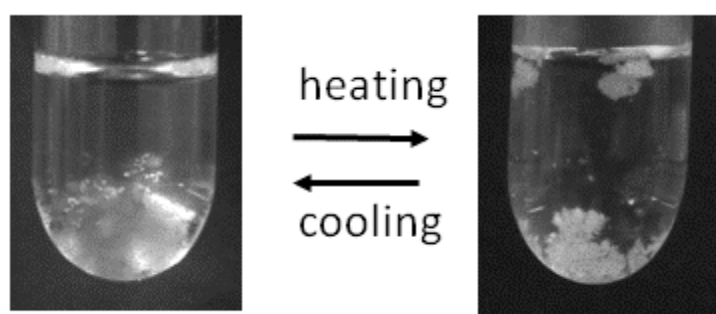


Figure 2. Thermo-responsive swelling and shrinking behaviors of **C4**.

With these poly(TPEN-NIPA) gels extraction studies were carried out using cadmium(II) ion. Temperature-dependent extraction behaviors were examined in the swollen state (5 °C) and the shrinking state (45 °C) at the pH values of ca. 2.0 and 6.5, respectively. A 1 mM solution of $\text{Cd}(\text{NO}_3)_2$ was prepared and the pH value was controlled to 1.9 and 5.3 (at 5 °C), 2.0 and 5.9 (45 °C) respectively, by the addition of NH_4NO_3 . Extraction was performed by the addition of dried poly(TPEN-NIPA) gel to 0.2 mL of 1 mM solution of $\text{Cd}(\text{NO}_3)_2$. The amount of Cd^{II} ion incorporated into the gel was estimated by ICP-AES analysis of the remaining amount of cadmium ion. Figure 3 summarizes the results.

As reported previously, **C3** extracted cadmium ion efficiently at 5 °C (7.91×10^{-2} mmol-Cd/g-dry gel) when the extraction was carried out at pH = 6.5, while at 45 °C hardly extracted Cd^{II} (0.08×10^{-2}). Such behaviors were also observed at pH = ca. 2 although the extraction performance was slightly lower (3.20

$\times 10^{-2}$ at 5 °C, 1.07×10^{-2} at 45 °C). **C4** was found to show slightly superior performance to **C3** in both the amount of extraction and the thermo-responsive difference (at pH = ca. 2, 4.64×10^{-2} at 5 °C, 0.48×10^{-2} at 45 °C). Such a better performance would be due to the homologation of the side chain, which improved hydrophobicity of the TPEN moiety.¹⁶ **C10** also showed improved performance in extraction at the pH values of both ca. 2 and 4.5 at 5 °C (5.50×10^{-2} , 9.13×10^{-2}). This would also be due to the improved hydrophobicity of long methylene chains. However, extraction in the shrinking state at 45 °C unexpectedly improved leading to the inferior thermo-responsive change at the pH of 2 and 4.5 (1.64×10^{-2} , 4.62×10^{-2}). Poly(TPEN-NIPA) gel bearing a branched structure was found to show remarkable extraction in swelling state and thermo-responsive change at pH = 6.5 to observe the highest extraction at 5 °C and little extraction at 45 °C. Worthy of note, in addition, is the remarkably high extraction at pH of 2 at 5 °C (6.40×10^{-2}) and its thermo-responsive change was also excellent (6.40×10^{-2} to 0.26×10^{-2}). This would be due to the formation of stiff gel as well as the improved hydrophobicity.

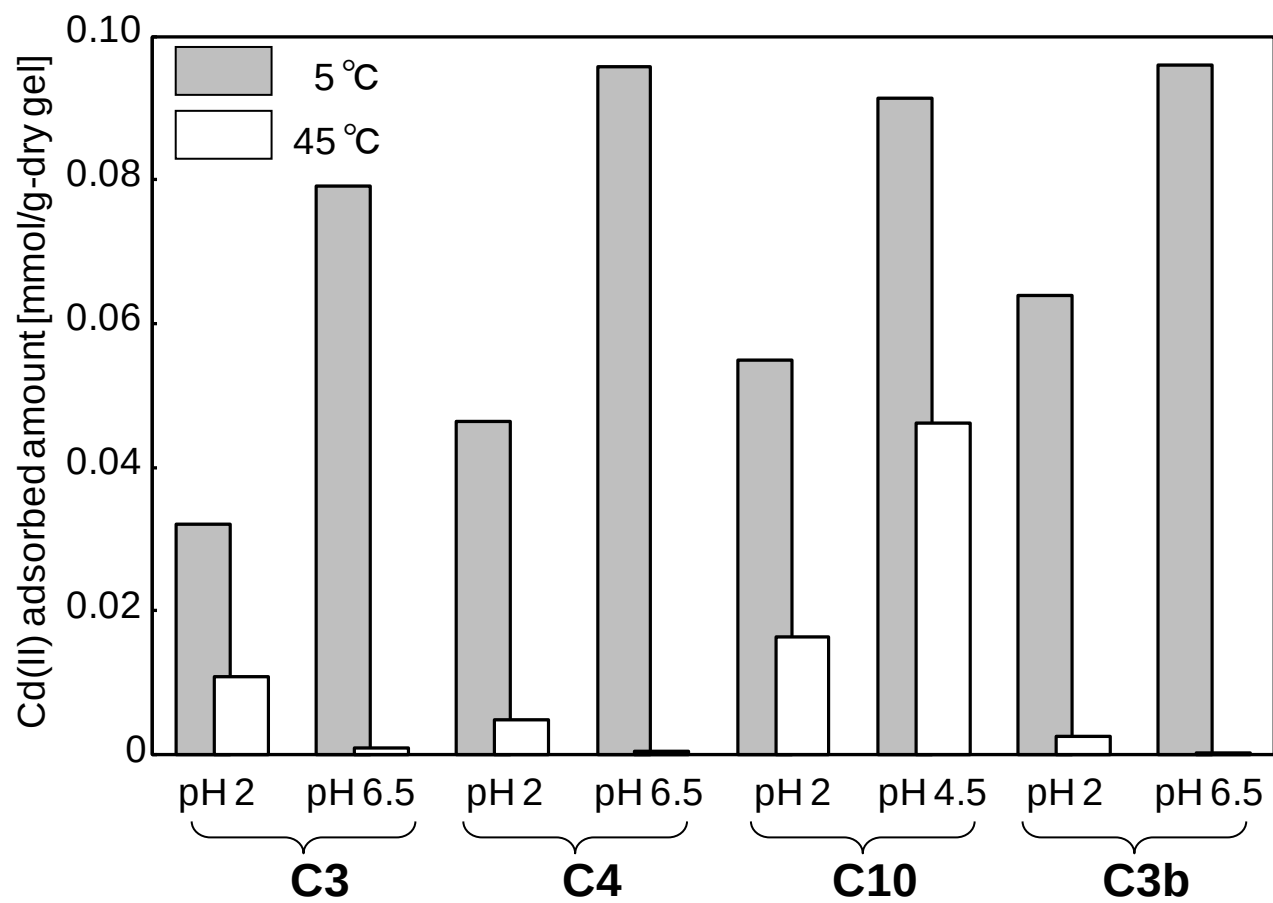


Figure 3. Thermo-responsive extraction of poly(TPEN-NIPA) gels at 5 °C and 45 °C.

Conclusion

In summary, we have synthesized TPEN derivatives bearing different side-chains involving the chain length and the branched structures and the prepared derivatives were subjected to the formation of poly(TPEN-NIPA) gels. The temperature-dependent change of extraction behaviors of cadmium(II) ion with poly(TPEN-NIPA) gels were highly influenced to the side-chain structures. The excellent thermo-responsive change particularly under highly acidic conditions such as pH=ca. 2 would be potentially practical for the chromatographic separation of metal ions, namely thermal swing chromatography, which would be applied for the separation of minor actinides from high level radioactive wastes (HLW). The high performance of TPEN-NIPA gel **C3b** is remarkably noteworthy.

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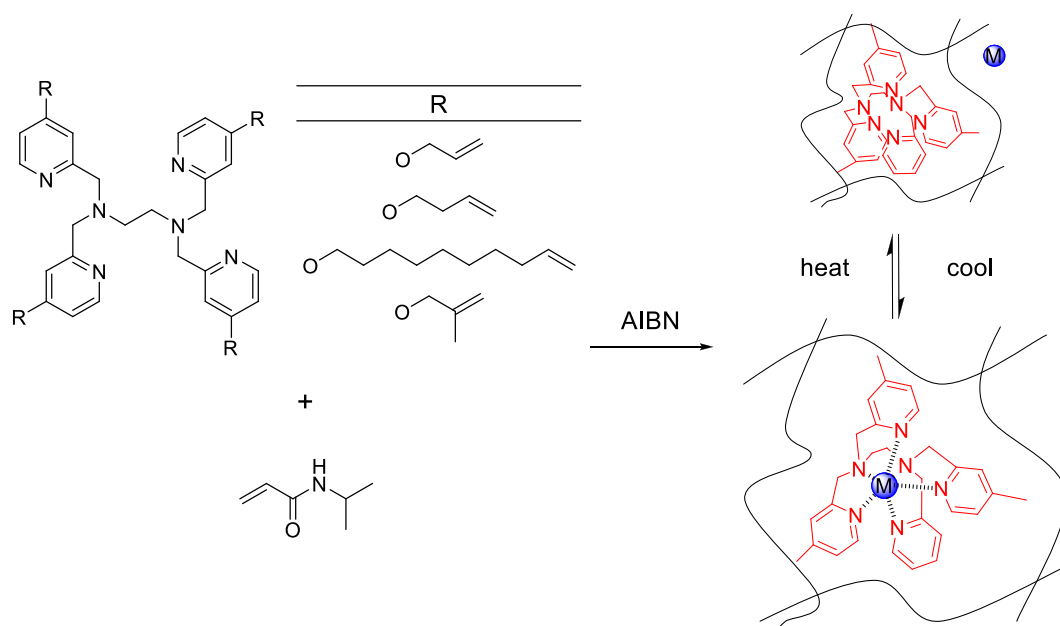
Figure legend

Figure 1. TPEN-NIPA gels **C3**, **C4**, **C3b**, **C10** (left to right) in water.

Figure 2. Thermo-responsive swelling and shrinking behaviors of **C4**.

Figure 3. Thermo-responsive extraction of poly(TPEN-NIPA) gels at 5 °C and 45 °C.

Graphical Abstract



TPEN-NIPA gels bearing polymerizable double bonds with different spacer length and branch structure are synthesized. The obtained poly(TPEN-NIPA) gels show thermo-responsive swelling/shrinking behaviors and are employed for the extraction of cadmium(II) ion. The polymer gels showed temperature-dependent change of extraction performance between swelling and shrinking. Among these TPEN gel bearing C3 spacer with branched structure showed the best performance in cadmium(II) extraction.