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Thermo-responsive extraction of cadmium(II) ion with TPEN-NIPA gel. Effect of the number of polymerizable double bond toward gel formation and the extracting behavior

Sachio Fukuoka [a], Tatsuya Kida [a], Yasutaka Nakajima [a], Takayuki Tsumagari [a], Wataru Watanabe [a], Yusuke Inaba [a], Atsunori Mori [a,*], Tatsuro Matsumura [b], Yoshio Nakano [c], Kenji Takeshita [c,*]

[a] Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe, Hyogo 657-8501, Japan
[b] Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, 2-4 Shirakatashirane, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan
[c] Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan; Integrated Research Institute, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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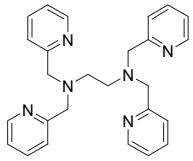
ABSTRACT

N,*N*,*N*′,*N*′-(Tetrakis-2-pyridylmethyl)ethylenediamine (TPEN) derivatives bearing the different number (1–4) of a double bond moiety on 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 three or four double bonds exhibit temperature-dependent change of swelling and shrinking in water. These gels extract Cd^{II} ion efficiently from the aqueous solution in the swelling state at 5 °C, while little extraction was observed at 45 °C with shrinking.

1. Introduction

Solvent extraction technique has been of considerable interest and extensively applied for separation of metal ions with a chelating agent. Organic molecules composed of multiple nitrogen atoms are particularly important for the extraction of soft metals,[1] such as Hg, Cd, Au and Pd, and development of separation for *d*- or *f*-block metals has been an attractive issue. A wide range of chelating agent has been developed so far for the purpose of separation of, for example, minor actinides (MA) from high level radioactive wastes (HLW).[2] TPEN, which is *N*,*N*,*N*′,*N*′-(tetrakis-2-pyridylmethyl)ethylenediamine **1** suggested to be a hexadentate ligand with six nitrogen atoms to chelate a metal ion,[3] is a potential candidate for the practical and selective extracting agent for MAs from HLW.[4] Much effort has been paid to the use of TPEN for the extraction, however, difficulties on the practical use of TPEN is its highly water soluble and ease of protonation characteristics under acidic conditions.[3b] Accordingly, incorporation of the TPEN structure into a side chain of polymers is a method to avoid leaching into water phases during extraction.

On the other hand, the polymer of *N*-isopropylacrylamide (NIPA) has attracted interesting characteristics, that is, water soluble at low temperature and becomes hydrophobic by raising the temperature to higher than ca. 35 °C.[5] Thereby, the corresponding poly-NIPA gels show thermo-responsive swelling/shrinking behaviors on that temperature and have applied for metal extraction using temperature-dependent change of chelation ability.[6] Accordingly, change of extraction characteristics of TPEN derivatives induced by the thermo-responsive behaviors of such gel is intriguing if poly-NIPA gel is prepared with a cross-linker, in which TPEN moiety is incorporated.



TPEN (**1**)

* Corresponding authors. Tel./fax: +81 788036181.
E-mail address: amori@kobe-u.ac.jp (A. Mori).

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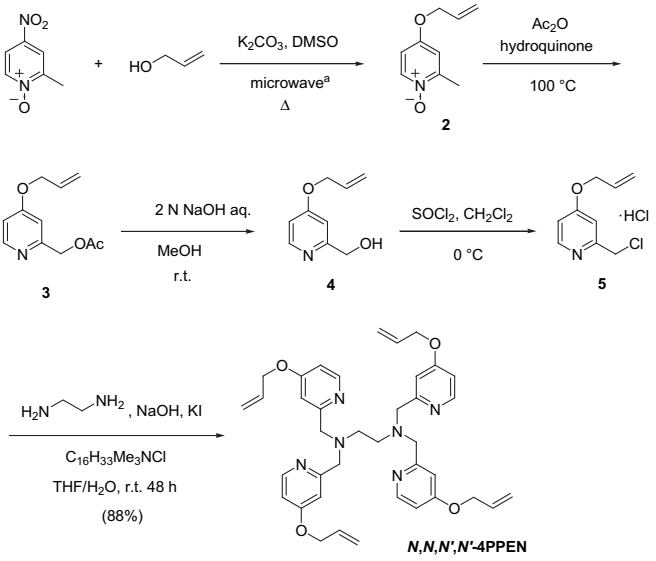
In our previous works, we have shown that a TPEN-NIPA gel was synthesized by radical polymerization of NIPA in the presence of a TPEN derivative bearing four polymerizable double bonds on the pyridine ring and showed temperature-dependent change of extraction behavior of Am^{III} and Cd^{II}, which was recognized as a model metallic species of MAs.[7] The TPEN-NIPA gel effectively extracted Cd^{II} ion at swelling state (5 °C), while little extraction of Cd^{II} ion was confirmed at the elevated temperature (45 °C) where shrinking of the gel was observed.[7] Our further concern has focused on the relationship of the formation of polymer gel with the number of the terminal polymerizable double bond, which would be highly important toward improved molecular design of the polymer gel. We herein report syntheses of TPEN derivatives bearing the different number of the terminal double bond, formation of polymer gels with such TPENs, and studies on temperature-dependent extraction behaviors of a Cd^{II} ion[8] with the obtained TPEN-NIPA gel.

2. Results and discussion

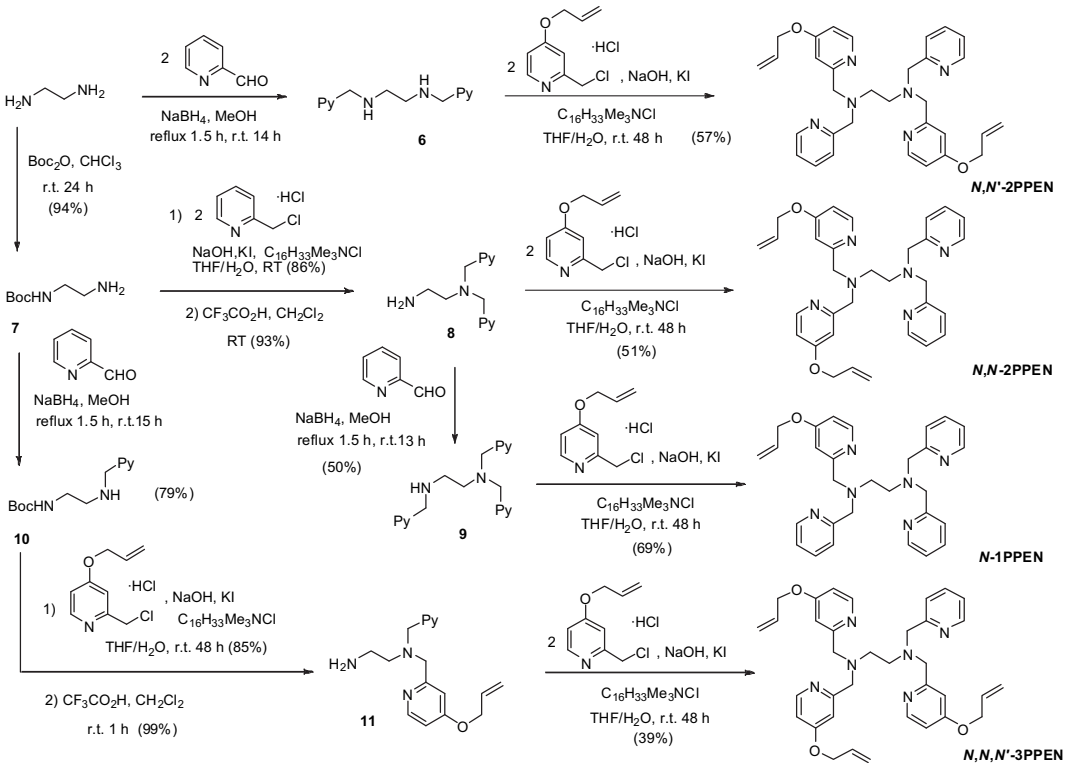
Synthesis of TPEN derivatives bearing the different number of the polymerizable functional group was carried out as outlined in Schemes 1 and 2. The synthetic strategy was based on the controlled introduction of functionalized and unsubstituted chloromethylpyridine derivatives into ethylenediamine. Chloromethylpyridine bearing an allyloxy group at the 4-position of the pyridine ring **5** was prepared in a manner as described previously with a slight modification from commercially available 2-methyl-4-nitro-pyridine 1-oxide and allyl alcohol and used as hydrochloride, which was isolated directly from the mixture of the reaction of hydroxymethylpyridine **4** with thionyl chloride (Scheme 1).

Reductive amination of 2-pyridinecarbaldehyde with ethylenediamine lead to (*N*,*N*′-pyridylmethyl)ethylenediamine **6**, which was employed for the following reaction without further purification. The following reaction of **5** and **6** in a biphasic THF/water system in the presence of NaOH, KI, and a catalytic amount of $C_{16}H_{33}Me_3NCl$ (2 mol %) at room temperature afforded symmetric *N*,*N*′-bifunctionalized TPEN derivative ***N*,*N*′-2PPEN** in 57% overall yield.

Other TPEN derivatives were synthesized with *N*-Boc-ethylenediamine **7**, which was prepared by the reaction of ethylenediamine with $(Boc)_2O$.[10] The reaction of **7** with chloromethylpyridine hydrochloride in the manner for the reaction of **6** and **5** and following removal of the Boc group afforded *N*,*N*-difunctionalized compound **8** in an excellent yield. On the other hand, reductive amination of 2-pyridinecarbaldehyde with **8** lead to **9**, which was further treated with **5** in a similar manner to the reaction of **5**



Scheme 1.



Scheme 2.