Synthesis and Selective Au(III) Adsorption of Ureido Polymers Containing Large Repeating Rings

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ABSTRACT: Two polymers (polyBAUEE and polyBAUP) containing 25- and 20-membered rings are synthesized by the cyclopolymerization of bifunctional monomers 1,2-bis(acryloyloxyethyl-ureidoethoxy)-ethane (BAUEE) and 1,3-bis(acryloyloxyethylureido)propane (BAUP) and studied for the adsorption of precious metal ions. PolyBAUEE and polyBAUP selectively adsorb Au(III) with the adsorption efficiencies above 99.0% after adsorption equilibrium. PolyBAUEE adsorbed faster than polyBAUP, and the Au(III) adsorption is selective in the presence of nine interfering metal ions with similar concentrations (ca. 1 mg/L) in an aqueous solution including Pd(II) and Pt(II). The maximum Au(III) adsorption capacities of polyBAUEE and polyBAUP are 37.6 and 31.8 mg/g, respectively. Au(III) is reduced to Au(0) nanoparticles during the adsorption process. The selective adsorption behavior depends on the controlling regioselective recognition of the ring structure and the ureido groups.

1. INTRODUCTION

Heavy metal ion pollution in water has caused serious ecological problems, and how to deal with water pollution is a hot issue.1,2 A lot of methods are studied to remove heavy metal ions from the wastewater. Among the techniques, various functional polymers are used as adsorbents for heavy metal ions, which are to be scavenged due to the preciousness or toxicity.3−13 Polymers containing macrocyclic rings have attracted significant attention because of their unique properties to capture specific heavy metal ions,1−5 such as cadmium, lead, mercury, copper, silver metal ions, and so forth. To tune the ability of binding metal ions, proper designs of the functional groups and the ring’s size are necessary, as for crown ethers,14,15 porphyrin,16,17 and cyclodextrins.18,19 Polymers containing large rings can be synthesized by (1) cyclopolymerization,20−24 (2) polymerization of monomers with macrocyclic structures,25 and (3) modification of polymers using large-ring molecules.26,27 In all cases, the simple and efficient introduction of macrocyclic structures remains a challenge. Cyclopolymerization offers polymers with cyclic repeating units via an alternating intramolecular−intermolecular chain propagation.20−24 Despite the advantage in facile-ness, typical cyclopolymerization requires highly diluted concentrations to avoid cross-linking, which tend to limit the yield of the product.

In order to solve the limitation of macrocyclic polymer synthesis, our group22−24 developed polymers containing 19-membered ring units through efficient cyclopolymerization of bis(meth)acrylates with constrained conformation by the cyclic structures and hydrogen bonds giving the polymers in excellent yields. Specifically, polyTBAUCH, the recently developed polymers containing ureido groups prepared by the polymerization of trans-1,2-bis(acryloyloxyethylureido)cyclohexane (TBAUCH), can selectively capture Ag+ with an excellent efficiency even in the presence of interfering 19 metal ions.25 The excellent Ag+ selectivity of polyTBAUCH relies on the unique character of the ureido ligands having tuneable selectivity only with lighter elements. Additionally, polymers bearing 18-crown-6 groups can selectively capture K+, 15-crown-5 groups can selectively capture Na+, which depend on the O atoms and ring size.14,15 Therefore, cyclic molecules consisting of ureido groups attained selective adsorption of heavy metal ions28,29 and nitro-substituted compounds.30,31 The selectivity depends on the size and functional groups, and different designs of the cyclic structures will enable selective capture of other industrially important precious metals.

2. EXPERIMENTAL SECTION

Materials. Dichloromethane was dried over anhydrous magnesium sulphate and filtrated. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were dried over CaH2 and...
distilled under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Water was deionized on a Nomura Micro Science MINIPURE TW-300R instrument. Other reagents were used as received.

Preparation of Monomers and Polymers. Monomers were synthesized easily by a one-step reaction of acryloyloxyethylisocyanate (AOI) and 1,2-diaminoethylethane in a similar manner with other bis(ureido) derivatives prepared from 2-methacryloyloxyethyl isocyanate (MOI).

Synthesis of 1,2-Bis(acryloyloxyethyl ureido ethoxyl)ethane (BAUEE). A solution of 1,2-diaminoethylethane (1.480 g, 10.0 mmol) in anhydrous dichloromethane (20.0 mL) was added dropwise to a stirred solution of AOI (2.820 g, 20.0 mmol) in anhydrous dichloromethane (30 mL) under a nitrogen atmosphere. The solution was stirred at ambient temperature for 2 h under a stream of nitrogen. Then, the solution was concentrated by reducing pressure, and a white solid appeared overnight. The solid was washed with n-hexane (3 × 10 mL). The white solid was dried under high vacuum.

Yield: 93.5\% (3.64 g). Anal. Calcd. for C_{18}H_{30}N_{4}O_{8}: C, 50.55; H, 6.79; N, 15.72; O, 20.93; Found: C, 50.82; H, 6.31; N, 15.67; O, 20.8\%.

Synthesis of 1,3-Bis(acryloyloxyethyl ureido)propane (BAUP). A solution of 1,3-diaminopropane (28005 μmol, 0.10 M) in anhydrous dichloromethane (20.0 mL) was added dropwise to a stirred solution of AOI (2.820 g, 20.0 mmol) in anhydrous dichloromethane (30 mL) under a nitrogen atmosphere. The solution was stirred at ambient temperature for 2 h under a stream of nitrogen, and a white solid appeared. Then, the solid was collected by suction filtration and washed with dichloromethane (3 × 10 mL). The white solid was dried under high vacuum.

Yield: 96.3\% (3.44 g). Anal. Calcd. for C_{13}H_{30}N_{4}O_{8}: C, 52.39; H, 8.35; N, 18.33; O, 20.93; Found: C, 52.35; H, 8.37; N, 18.37; O, 20.91. 1H NMR (400 MHz, CDCl_{3}, δ in ppm): 2.22 (6H, s, −CH_{3}), 3.40 [2H, t, J = 6.5 Hz, (CH_{2})_{2}NCH_{2}−], 3.21–3.25 (2H, m, −NHCHCH_{2}O−), 3.47–3.51 [2H, m, (CH_{2})_{2}NCH_{2}−], 4.22–4.25 (2H, m, −COOCH−), 5.18 (H, br, −NHCONH−), 5.57 (1H, br, −NHCONH−), 5.85 (1H, dd, J = 10.4, 1.2 Hz, CHH=CH−),

3.14 (1H, dd, J = 17.4 and 10.2 Hz, CH_{2}═CH−), 6.42 (1H, dd, J = 1.2, 17.2 Hz, CHF=CH−). 13C NMR (100 MHz, CDCl_{3}, δ in ppm): 38.3 (−COOCHCH_{2}−), 40.5 (−CONHCH_{2}−), 64.2 (−COOCHCH_{2}−), 70.3 (−CH_{2}OCH_{2}CH_{2}−), 70.7 (−OCH_{2}CH_{2}O−), 128.2 (CH_{2}═CH−), 131.4 (CH_{2}═CH−), 158.7 (−NH(═O)−), 166.4 (CH_{2}═CH(═O)−).

Free Radical Polymerization of the Monomer (Typical Procedure). A monomer (500 μmol), AIBN (10 μmol), and DMF (5.0 mL) were placed in a glass tube. The polymerization was conducted at 75 °C for 20 h under N_{2} atmosphere. After the reaction, the mixture was poured into an excess amount of tetrahydrofuran. The precipitate was collected by filtration and dried in vacuo at 80 °C overnight.

3. RESULTS AND DISCUSSION

Two polymers consisting of larger 25- and 20-membered repeating units with two ureido groups (Scheme 1) were developed, which efficiently adsorb Au(III) from aqueous solutions. These polymers were synthesized by the cyclo-polymerization of bifunctional monomers, 1,2-bis(acryloyloxyureidoethoxyl)ethane (BAUEE) and 1,3-bis(acryloyloxyureido)propane (BAUP), respectively. In order to compare, an acrylic polymer, polyDMUEA, was also synthesized by the similar method.

The polymerization of BAUEE (0.10 M) was conducted in the presence of AIBN (Table 1). The low concentration of 0.10 M was chosen to limit the rate of intermolecular propagation and to avoid cross-linking before cyclization. The polymerization proceeded homogeneously regardless of the [M]_{0}/[AIBN] ratios during the polymerization periods (runs

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applying a \([M]/[AIBN]\) ratio of 50/1 and a concentration of temperature was investigated in the range of 65−85°. The probability of the intermolecular propagation. The effect of temperature was investigated in the range of 65−85 °C, applying a \([M]/[AIBN]\) ratio of 50/1 and a concentration of 0.10 M (runs 2 and 7). With the increase of concentration, \(M_w\) became larger. The polymerization at 0.25 M afforded an insoluble product (run 8), whose infrared (IR) spectrum is identical to that of the soluble polymer, suggesting that the cross-linking reaction occurred by the increased probability of the intermolecular propagation. The effect of temperature was investigated in the range of 65−85 °C, applying a \([M]/[AIBN]\) ratio of 50/1 and a concentration of 0.10 M (runs 2, 4, and 5). The polymerization at 75 °C resulted in the highest \(M_w\) and narrowest \(M_w/M_n\) and was found to be a suitable temperature for this cyclopolymerization. PolyBAUP (content of ureido = 32.6%) was also synthesized by a similar method using BAUP (Scheme 1a; run 9). The polymerization behavior of BAUP was almost identical to that of BAUEE. The polymerization of 2-(3-[2-(dimethylamino)ethyl]ureido)ethyl acrylate (DMUEA), a mono-acrylate analogue of BAUEE and BAUP, was also carried out, and the corresponding polymer with acyclic units (polyDMUEA, content of ureido = 25.3%) was obtained in an excellent yield (92.6%) (Scheme 1b; run 10).

Table 1. Cyclopolymerization of BAUEE and BAUPa

| run | monomer   | \([M]/[AIBN]\) | temp. (°C) | sol. (M) | yield (%)b | \(M_w\) (10^3) | \(M_w/M_n\) |
|-----|-----------|----------------|------------|---------|------------|---------------|-------------|
| 1   | BAUEE     | 30/1           | 75         | 0.10    | 75         | 6.7           | 2.4         |
| 2   | BAUEE     | 50/1           | 75         | 0.10    | 80         | 7.1           | 2.0         |
| 3   | BAUEE     | 100/1          | 75         | 0.10    | 83         | 7.2           | 1.9         |
| 4   | BAUEE     | 50/1           | 65         | 0.10    | 78         | 5.6           | 1.9         |
| 5   | BAUEE     | 50/1           | 85         | 0.10    | 80         | 6.4           | 2.1         |
| 6   | BAUEE     | 50/1           | 75         | 0.05    | 66         | 5.5           | 1.6         |
| 7   | BAUEE     | 75             | 0.15        | 90      | 8.6         | 1.8           |
| 8   | BAUEE     | 50/1           | 75         | 0.25    | 96         | crosslinked polymer |
| 9   | BAUP      | 50/1           | 75         | 0.10    | 81         | 7.1           | 1.5         |
| 10  | DMUEA     | 50/1           | 75         | 0.15    | 93         | 8.3           | 1.2         |

aConditions: 20 h, DMF, and N₂ protection. bIsolated yield after precipitation with tetrahydrofuran. cEstimated by SEC (DMF containing 10 mM LiBr, polystyrene standard). \(M_w\), number-average molecular weight; \(M_n\), weight-average molecular weight; and \(M_w/M_n\), polydispersity index.

1H NMR Characterization. Figure 1 shows the 1H NMR spectra of BAUEE, polyBAUEE, and deuterium-exchanged polyBAUEE. The spectrum of polyBAUEE (Figure 1b) indicates the signals agreeable to the expected structure, namely, signals of the methylene protons in the side chains, a broad signal of the ureido protons, and a broad signal at 1.50 ppm assignable to the methyne and methylene groups of the main chain formed by cyclopolymerization. Very small signals assignable to the residual vinyl groups were also observed at 5.84−5.87, 6.10−6.17, and 6.41−6.45 ppm, as observed in the spectrum of BAUEE. The residual content of the vinyl group is below 0.8% according to the deuteration-exchanged spectrum of polyBAUEE (Figure 1c). The 13C NMR and IR spectra (Figures S4 and S18 in the Supporting Information) also agree well with the expected structure. This observation supports that the free radical polymerization of BAUEE proceeds in an excellent cyclization efficiency. PolyBAUP could also be characterized in a similar manner (Figure S1), and the content of the residual vinyl group is below 0.7% (Figure S16).

Adsorption of Single Metal Ions. PolyBAUEE, polyBAUP, and polyDMUEA (500 mg/L) were examined for the adsorption of Au(III), Pd(II), and Pt(II) in their aqueous single metal ion solution (pH = 2, ca. 1100 μg/L) (Figure 2a−c). The concentration of Au(III) was decreased below 5 μg/L in the presence of polyBAUEE and polyBAUP, respectively, while the concentrations of Pd(II) and Pt(II) were decreased less than that of Au(III). The adsorption efficiencies of Au(III) on both polyBAUEE and polyBAUP exceeded 99.5% after adsorption equilibrium (8 h and 28 h for polyBAUEE and polyBAUP, respectively, as described later), while the adsorption efficiencies of Pd(II) and Pt(II) stayed 30−40%. The maximum Au(III) adsorption capacities of polyBAUEE and polyBAUP were 37.6 and 31.8 mg/g, respectively (Supporting Information, eq S2). PolyBAUEE and polyBAUP can be reused three times with adsorption efficiency >75%. By contrast, polyDMUEA did not adsorb Au(III), Pd(II), and Pt(II), as can be confirmed by the ignorable decrease in the concentrations. The adsorption with contact time is shown in Figure 2d. The interactions result in an increase in the uptake of Au(III) ions onto polyBAUEE until the adsorption equilibrium is reached at 8 h. However, the adsorption equilibrium of Au(III) ions onto polyBAUP is 28 h. The faster adsorption by polyBAUEE originates from the larger ring structure and hydrophilic linker structure (more oxygen atoms and ureido groups) (Figures 2d, 1, and S1).

Effect of pH. Effect of pH on adsorption of Au(III) onto polyBAUEE and polyBAUP was studied by preparing 20 mg/L...
HAuCl₄ with different pH values at 25 °C (Figure 3a). pH has a similar effect on Au(III) adsorbing onto PolyBAUEE and polyBAUP. When pH is increased from 1 to 2, the concentration of H⁺ decreases in the solution, which results in increased adsorption capacity of Au(III) ions onto the adsorption sites, attaining maximum adsorption at pH = 2. When pH > 2, adsorption capacity decreases with the increase of pH.

**Effect of the Initial Concentration of Au(III) Ions.** The initial concentration of Au(III) ions plays an important role in studying the kinetics of adsorption. In order to study the effect of initial concentration of the adsorbate, different concen-

Figure 2. Adsorption of single metal ions by (a) polyBAUEE, (b) polyBAUP, and (c) polyDMUEA; (d) time course of adsorption of Au(III) on polyBAUEE and polyBAUP in HAuCl₄ aqueous; conditions: [M³⁺]₀ = 1.1 mg/L, Cₚolymer = 500 mg/L, pH = 2, 25 °C, and 28 h.

Figure 3. Effect of (a) pH [conditions: C₀ = 20 mg/L, Cₚolymer = 200 mg/L, 25 °C, 8 h (polyBAUEE), and 28 h (polyBAUP)] and (b) initial concentration on the adsorption of Au(III) ions on polymers [conditions: Cₚolymer = 200 mg/L, pH = 2, 25 °C, 8 h (polyBAUEE), and 28 h (polyBAUP)].

Figure 4. Plots of (a) pseudo-first-order kinetics and (b) pseudo-second-order kinetics.
trations of the Au(III) ion, 1, 5, 10, 15, and 20 mg/L, were taken at 25 °C (Figure 3b). It is shown that, with higher initial concentration, the higher quantity of Au(III) ion was adsorbed by polyBAUEE and polyBAUP at equilibria. This can be attributed to the probability of the adsorbent−adsorbate interaction increasing rapidly with higher Au(III) ion concentration, which results in the increase of adsorption.

Adsorption Kinetics. Two kinetic models,1,2 pseudo first order (eq 1) and pseudo second order (eq 2), were used to determine the rate of adsorption of Au(III) onto polyBAUEE. The results are shown in Figure 4 and Table 2. The linear forms of the two models are given below

\[
\ln(q - q_t) = \ln Q_e - k_1t
\]  

(1)

\[
t = \frac{1}{k_2Q_e^2} + \frac{t}{Q_e}
\]  

(2)

where \( q_e \) is the actual equilibrium adsorption capacity, \( q_t \) is the adsorption capacity at time \( t \), \( Q_e \) is the theoretical equilibrium adsorption capacity, and \( k_1 \) and \( k_2 \) are first order and second order rate constants, respectively.

On comparing the \( R^2 \) values (Table 2 and Figure 4a,b), pseudo-first-order plot with \( R^2 = 0.999 \) and pseudo-second-order plot with \( R^2 = 0.976 \) were observed. \( Q_e \) obtained by the pseudo-first-order dynamic model is close to \( Q_{eexp} \). Therefore, the kinetic process of the adsorption of Au(III) ions by polyBAUEE is closer to the pseudo-first-order kinetic model.

Adsorption Isotherm. Langmuir adsorption isotherm (eq 3) and Freundlich adsorption isotherm (eq 4) were used to process the experimental data. The results are shown in Figure 5 and Table 3. The Langmuir adsorption isotherm equation and Freundlich adsorption isotherm equation, respectively, and the specific parameter results are shown in Table 3. The Langmuir adsorption

![Figure 5](https://example.com/figure5.png)

Table 3. Coefficient of the Langmuir and Freundlich Isotherm Adsorptions of Au(III) Ions on PolyBAUEE at 298 K

| T (K) | \( Q_m/(mg/g) \) | \( k_L/(L/mol) \) | \( R^2 \) | \( K_F/(mg/g)/(mg/L)^{1/n} \) | \( n \) | \( R^2 \) |
|------|-----------------|-----------------|-------|-----------------|-----|-------|
| 298  | 38.42 ± 0.99    | 2.658 ± 0.444   | 0.999 | 15 ± 0.54       | 1.257 ± 0.123 | 0.684 |

As the \( T \) increases, the \( Q_m \) decreases, the \( k_L \) increases, and the \( K_F \) decreases. These results indicate that the adsorption of Au(III) ions by polyBAUEE is endothermic.
isotherm equation was used to fit the experimental data, and the correlation coefficient ($R^2 > 0.999$) showed a good fit. However, when the Freundlich adsorption isotherm equation was used to fit the experimental data, the correlation coefficient ($R^2 = 0.684$) was very low. Therefore, the adsorption isotherm of polyBAUEE for Au(III) ion conforms to the Langmuir isotherm model, showing a single layer adsorption.

As shown in Figure 6a,b, the color of the polymers changed from white to purple (Figure S6), which is characteristic of gold nanoparticles (AuNPs), after adsorption of Au(III) from HAuCl$_4$ solution. The formation of AuNPs during the adsorption process probably originated from the spontaneous reduction of Au(III) as reported in various systems$^{33-35}$ due to the high susceptibility of reduction of Au(III). The TEM images of the polymers after adsorption of Au(III) show evenly distributed and nanosized black spots assignable to AuNPs with the diameters of 2–5 nm (Figure 6c,d). High-resolution transmission electron microscopy (HRTEM) and diffuse reflectance (DR) spectroscopy revealed the formation of AuNPs. The HRTEM image shows a characteristic spacing of 0.235 nm for the (111) lattice fringe of face-to-face cubic gold (Figure 6e). The DR spectra show broad peaks with peak tops at 550–570 nm, agreeing well with the surface plasmon resonance of AuNPs$^{33,35}$ (Figure 6f).

Selective Adsorption of Au(III). The selectivity of adsorption of Au(III) by faster polyBAUEE was examined in the presence of multiple ions (Figure 7a). The aqueous solution of the multiple metal ions used for this adsorption study was prepared by diluting a multielement calibration standard solution containing Au(III), and the concentrations of the metal ions were adjusted to approximately 1 mg/L. The
10 ions included were Au(III), Hf(IV), Ir(III), Pd(II), Pt(II), Rh(III), Ru(III), Sb(III), Sn(IV), and Te(II). Disposable plastic bottles were used as containers to avoid contamination with trace elements possibly drained out from glassware. PolyBAUEE (500 mg/L) was placed in the multi-ion solution (pH = 2) at 25 °C. The color of the polymer was changed to purple during the adsorption. The adsorption efficiency of Au on polyBAUEE reached 99.6% after shaking for 8 h. The adsorption efficiencies of the other nine metal ions were significantly low, while the adsorptions of softer Pd(II) and Pt(II) are slightly higher than those of the others. By contrast, polyDMUEA, an acyclic analogue consisting of identical structures, negligibly adsorbed the examined ions (Figure 7b), which indicates that the adsorption of gold ions on the acyclic polymer with ureido and ester groups is weak. The selective affinity of polyBAUEE to Au(III) is attributed to the cooperative coordination of the four carbonyl groups in the ureido and ester groups aligned in the rings suitable for the specific recognition of Au(III). Calculation by the density functional theory (B3LYP/6-31G(d) + SDD) supports the acceptable structure of the complex including Au(III) in the ring of a model compound (Figures S9 and S11; Tables S3 and S6).

4. CONCLUSIONS

In summary, we have described the design and synthesis of polymers, polyBAUEE and polyBAUP, containing 25- and 20-membered rings as repeating ring units by the cyclopolymerization of BAUEE and BAUP derived from an isocyanate and 1,2-bis(2-aminoethoxy)ethane and 1,3-diaminopropane, respectively. These polymers showed excellently selective adsorption for Au(III), and more hydrophobic polyBAUEE adsorbed faster than polyBAUP. The adsorption of Au(III) was followed by the spontaneous reduction to Au(0) nanoparticles. The selectivity was not deteriorated in the presence of nine other interfering metal ions. The selective adsorption for Au(III), and more hydrophilic nopropane, respectively. These polymers showed excellently selective adsorption of noble metal ions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03869.

Experimental details; results of ICP−MS and SEC analyses; H and 13C NMR spectra of monomers and polymers; Optical microscopy and SEM images of polymers and polymer-Au; IR spectra of monomers, polymers, and polymer-Au; and optimized calculation of polymer units and polymer-Au(III) by the density functional theory (PDF)

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Notes

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