

Preparation of Soluble Poly(azomethine)s Having the β -Diketonate Metal Complex in the Main Chain

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ABSTRACT: Copper complexes (**2a-Cu** and **2b-Cu**) having two amino groups were prepared from *p*-aminobenzoylacetone (**1a**) and 1-(4-aminophenyl)nonane-1,3-dione (**1b**) with copper(II) acetate, respectively. A soluble poly(azomethine) having β -diketonato copper(II) complex in the main chain was prepared by the polycondensation of **2b-Cu** with terephthalaldehyde (**3**) in dimethyl sulfoxide (DMSO) at room temperature with H₂SO₄ as catalyst. After reprecipitation into methanol, a green product was obtained in 56% yield. The complex (**5b-Cu**) was soluble in common organic solvents such as CHCl₃, tetrahydrofuran (THF), and DMSO. The number-average molecular weight (M_n) and molecular weight distribution of **5b-Cu** determined by GPC were $M_n = 3500$ (polystyrene standard) and $M_w/M_n = 1.71$, respectively. The structure of **5b-Cu** was supported by IR and elemental analysis. Thermogravimetric analysis (TGA) for **5b-Cu** showed 5% weight loss at 250°C under nitrogen. Electrochemical data as well as absorption spectra of **5b-Cu** in comparison with that of copper(II) bis[*p*-(1-aza-2-phenylethenyl)benzoylacetate] (**6**) as a model compound show that the metal centers of the multinuclear complexes may be considered nearly independent of one another.

KEY WORDS Poly(azomethine) / β -Diketonate Copper(II) Complex / Coordination Polymer / Metal-Containing Polymer / Cyclic Voltammetry /

Poly(azomethine)s are readily prepared by reactions of a diamine with a dialdehyde.^{1,2} Interest has been focused on poly(azomethine)s because of their thermal stability, electrical conduction, and photoconduction. Several conjugated poly(azomethine)s have been prepared and used to investigate the effects of molecular structure on the electronic and optical properties.^{3–8} This paper describes the synthesis of a soluble poly(azomethine) having β -diketonate copper(II) complex in the main chain. The polymerization was carried out through chemical coupling of an aromatic dialdehyde and diamine monomer of a metal complex. Our synthetic method provides a well-defined metal containing π -conjugated poly(azomethine) in which a π -conjugated spacer is directly attached to the metal coordination center. Soluble conjugated azomethine polymers having β -diketonate complex units in the main chain have been unknown prior to this study.

Metal-containing polymeric materials are interesting for their useful redox, magnetic, optical, electrical, and catalytic properties.^{10,11} In the past, several attempts have been made to prepare coordination polymers containing β -diketonate.^{12–14} However, the solubility of most products in common organic solvents was low. Examples of soluble linear coordination polymers with transition metal ions in the main chain are limited. These problems arise from the inherent skeletal rigidity of these materials, and the introduction of solubilizing or flexibilizing groups either in the polymer backbone or side group structure is necessary for useful products to be obtained. The condensation of the substitution-inert bis(β -diketone) complexes of cobalt(III) and chromium(III) with sulfur halides provides soluble metal coordination polymers.¹² Several metal ions such as nickel(II), copper(II), zinc(II) could not produce coordination poly-

mers by these methods.¹⁵

EXPERIMENTAL

Measurements

¹H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and Perkin Elmer 1600 spectrometer, respectively. TGA was made on a Shimadzu DT-30 instrument (10°C min⁻¹). UV spectra were made on a JASCO V-530 spectrophotometer. Cyclic voltammetry was carried out with a BAS CV-50W electrochemical analyzer. Gel permeation chromatography was carried out on a Tosoh G3000H_{XL} using tetrahydrofuran (THF) as eluent after calibration with standard polystyrene samples. DSC analysis was carried out on a Seiko DSC 200 instrument using 6 mg exactly weighed sample. Fast atom bombardment spectra (FAB-MS) were obtained on a JEOL JMS-SX102A using *m*-nitrobenzyl alcohol as a matrix.

Materials

Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Chloroform, toluene, and dimethyl sulfoxide (DMSO) were distilled under nitrogen over P₂O₅. *p*-Aminobenzoylacetone (**1a**) was prepared by reduction of *p*-nitrobenzoylacetone by Pd-C in methanol according to the literature.¹⁶

1-(4-Nitrophenyl)nonane-1,3-dione

To a mixture of *p*-nitroacetophenone (5.00 g, 30.3 mmol) and heptanoic anhydride (22 mL, 83.8 mmol) was added boron trifluoride-acetic acid complex (15 mL) at room temperature. The solution was stirred at room temperature for 44 h. The reaction mixture was then added to 80 mL 13% sodium acetate solution, and the resulting mixture was heated under reflux for 3 h. The

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mixture was cooled and the organic phase was separated. The aqueous phase was extracted with ethyl acetate (AcOEt), and the combined organic phase was dried over anhydrous Na_2SO_4 . Removal of the solvent under reduced pressure afforded an oily product, which was purified by column chromatography (silica ; hexane/AcOEt = 2/1, v/v, R_f =0.58) to give 5.94 g (21.4 mmol, yield 71%) of a pure product as an oil. $^1\text{H NMR}$ (CDCl_3) δ 0.88 (3H, t, J = 4.3 Hz, CH_3), 1.29 (6H, m, CH_2), 1.70 (2H, m, $\text{COCH}_2\text{-CH}_2$), 2.48 (2H, t, J = 8.1 Hz, COCH_2), 6.22 (1H, s, C(OH)=CH-CO), 8.03 (2H, d, J = 8.9 Hz, Ar-H), 8.29 (2H, d, J = 8.9 Hz, Ar-H).

1-(4-Aminophenyl)nonane-1,3-dione (**1b**)

First, 5% Pd-C (0.5 g) was put into a two-necked flask under argon and then ethanol was poured into the flask. After bubbling the solution with argon gas for 1 h, 1-(4-nitrophenyl)nonane-1,3-dione was added to the solution. Hydrogen gas was substituted for argon gas and the solution was stirred for 2 days. After the reaction was finished, Pd-C was removed by filtration. Removal of the solvent under reduced pressure afforded a red oily product (crude yield 100%). $^1\text{H NMR}$ (CDCl_3): δ 0.89 (3H, m, CH_3), 1.32 (6H, m, CH_2), 1.68 (2H, m, $\text{COCH}_2\text{-CH}_2$), 2.36 (2H, t, J = 7.6 Hz, COCH_2), 4.06 (2H, br, NH_2), 6.05 (1H, s, C(OH)=CH-CO), 6.67 (2H, d, J = 8.6 Hz, Ar-H), 7.75 (2H, d, J = 8.6 Hz, Ar-H).

β -Diketonate Complexes

A typical procedure is as follows. To a prerefluxed solution of *p*-aminobenzoyl-acetone (1.78 g, 10.0 mmol) in methanol (100 mL) were added a solution of $\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}$ (0.998 g, 5.0 mmol) and 16N NH_3aq (1 mL) in water under nitrogen. A green compound immediately precipitated. The reaction mixture was stirred under reflux condition for 3 h. The precipitate was filtered and washed with water (1 \times 20 mL) and cold methanol (2 \times 10 mL). The product was further purified by recrystallization from 2-ethoxyethanol to give 1.47 g (3.53 mmol, yield 71%) of copper(II) bis(*p*-aminobenzoylacetate) (**2a-Cu**). IR (KBr, cm^{-1}) 3368 (NH_2), 1626 (C=C), 1529 (C=O), 1496 (C=O). FAB-MS: m/z 416 (M^+), $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4\text{Cu}$ required M^+ = 416. Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4\text{Cu}$: H 4.85 ; C 57.75 ; N 6.73. Found: H 5.00 ; C 57.97 ; N 6.90.

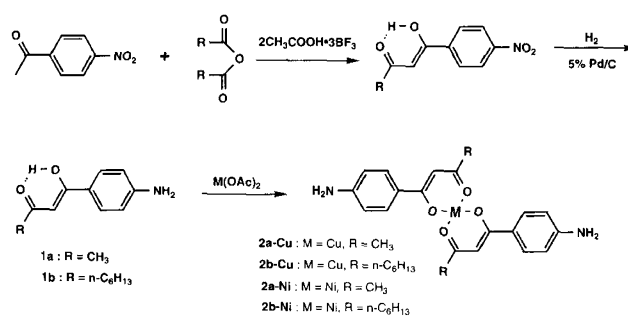
2b-Cu (yield 41%). IR (KBr, cm^{-1}), 3401 (NH_2), 1635 (C=C), 1529 (C=O), 1500 (C=O). FAB-MS: m/z 556 (M^+), $\text{C}_{30}\text{H}_{40}\text{N}_2\text{O}_4\text{Cu}$ required M^+ = 556. Anal. Calcd for $\text{C}_{30}\text{H}_{40}\text{N}_2\text{O}_4\text{Cu}$: H 7.25 ; C 64.80 ; N 5.04. Found: H 7.42 ; C 64.93 ; N 5.33.

2a-Ni (yield 74%). IR (KBr, cm^{-1}) 3316 (NH_2) 1588 (C=C), 1524 (C=O), 1501 (C=O). Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4\text{Ni} \cdot 1.0\text{H}_2\text{O}$: H 4.93 ; C 55.99 ; N 6.50. Found: H 5.11 ; C 56.39 ; N 6.58.

2b-Ni (yield 51%). IR (KBr, cm^{-1}) 3359 (NH_2), 1595 (C=C), 1525 (C=O), 1504 (C=O). FAB-MS: m/z 551 (M^+), $\text{C}_{30}\text{H}_{40}\text{N}_2\text{O}_4\text{Ni}$ required M^+ = 551. Anal. Calcd for $\text{C}_{30}\text{H}_{40}\text{N}_2\text{O}_4\text{Ni} \cdot 3.3\text{H}_2\text{O}$: H 7.68 ; C 58.89 ; N 4.23. Found: H 7.24 ; C 58.33 ; N 4.65.

Triethylene Glycol Bis(*p*-formylphenyl) Ether (**4**)

To a prerefluxed suspension of K_2CO_3 (1.87 g, 13.5 mmol) in THF (30 mL) were added a solution of *p*-



Scheme 1.

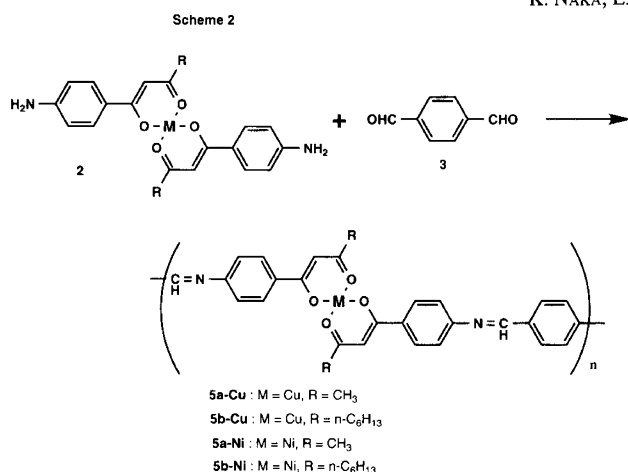
hydroxybenzaldehyde (1.84 g, 15.1 mmol) and triethylene glycol di-*p*-toluenesulfonate (2.30 g, 5.01 mmol) in THF (30 mL) under nitrogen. The mixture was stirred under reflux condition for 4 days. The product mixture was concentrated under reduced pressure, diluted with 100 mL of AcOEt, and washed with water (50 mL). The aqueous phase was extracted with AcOEt (1 \times 20 mL) and the combined organic phase was dried over anhydrous Na_2SO_4 . Removal of the solvent under reduced pressure afforded a residue, which was purified by column chromatography (silica ; hexane/AcOEt=1/1, v/v) to give 1.53 g (4.27 mmol, yield 86%) of a pure product as a white solid. $^1\text{H NMR}$ (CDCl_3): δ 3.77 (4H, s, O-CH_2), 3.90 (4H, t, J = 4.9 Hz, $\text{PhOCH}_2\text{-CH}_2$), 4.21 (4H, t, J = 4.9 Hz, PhO-CH_2), 7.01 (4H, d, J = 8.9 Hz, Ar-H), 7.82 (4H, d, J = 8.9 Hz, Ar-H), 9.88 (2H, s, CHO).

Copper(II) Bis[*p*-(1-aza-2-phenylethenyl)benzoylacetate] (**6**)

To a solution of copper(II) bis(*p*-aminobenzoylacetate) (**2a-Cu**) (0.5 g, 1.20 mmol) in DMSO (5 mL) was added one drop of conc. sulfuric acid under nitrogen. The reaction mixture was stirred at room temperature for 1 day. The product mixture was poured into methanol (100 mL) and the product precipitate was filtered and washed with water and methanol to give 0.554 g (0.936 mmol, yield 78%) of the compound **6**. IR (KBr, cm^{-1}): 1635 (C=C), 1579 (C=N), 1519 (C=O), 1490 (C=O). Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{O}_4\text{N}_2\text{Cu}$: H 4.77 ; C 68.96 ; N 4.73. Found: H 4.67 ; C 68.31 ; N 4.66.

Polymerization

A typical procedure is as follows. An example of run 1 in Table I is shown. To a solution of β -diketonate complex **2b-Cu** (0.111 g, 0.20 mmol) and terephthalaldehyde (**3**) (0.027 g, 0.20 mmol) in DMSO (5 mL) was added one drop of conc. sulfuric acid under nitrogen. The reaction mixture was stirred at room temperature for 4 days. The product mixture was poured into water (100 mL) and the product precipitate was filtered. Reprecipitation of chloroform solution of the crude product into hexane gave 73.5 mg (yield 56%) of a polymer product as a green solid. IR (KBr, cm^{-1}) 1699 (CHO), 1595 (C=N), 1519 (C=O), 1503 (C=O). Anal. Calcd for $(\text{C}_{38}\text{H}_{42}\text{O}_4\text{N}_2\text{Cu})_n$: H 6.47 ; C 69.76 ; N 4.28. Found: H 6.92 ; C 69.16 ; N 4.36.



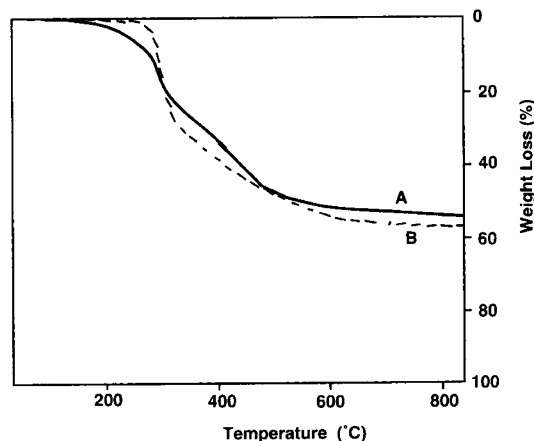
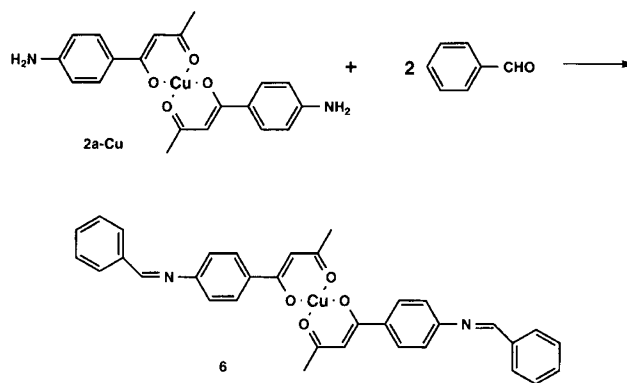
Scheme 2.

RESULTS AND DISCUSSION

Monomer Synthesis

An amine-substituted β -diketone, *i.e.*, *p*-aminobenzoylacetone (**1a**) was prepared according to the literature by the acylation of ketone with BF₃.¹⁷ To improve the solubility of the product during polymerization, 1-(4-aminophenyl)nonane-1,3-dione (**1b**) was also prepared. Copper complexes (**2a-Cu** and **2b-Cu**) having two amino groups, in which the metal replaces the enolic hydrogen and a six-membered chelate ring is produced, were easily obtained by a reaction of the β -diketone and copper (II) acetate in methanol. The metal complexes were obtained as green solids. The structures of the complexes were supported by IR, FAB-MASS, and elemental analysis. The IR spectrum of **1a** showed strong peaks at 1723 cm⁻¹ and 1637 cm⁻¹ due to a C=O stretching vibration of the keto-form and a C=O stretching vibration of the enol-form, respectively.¹⁸ The copper complex (**2a-Cu**) showed strong peaks at 1529 and 1496 cm⁻¹ which were assigned to a metal coordinated C=O vibration.^{18,19} The peaks due to the C=O stretching vibration for the keto- and the enol-forms of **1a** disappeared. The IR spectrum of **2b-Cu** also supported the complex formation. The trans isomer might be the main product estimated by thin layer chromatography.²⁰ Nickel complexes (**2a-Ni** and **2b-Ni**) having two amino groups were also prepared by the reaction of **1** with nickel(II) acetate in methanol.

The monomer **2a-Cu** was soluble in DMSO and *N,N*-dimethylformamide (DMF), whereas **2a-Ni** was only soluble in hot DMSO and hot DMF. Less solubility of the nickel complex compared with the copper complex was due to a tetrahedral configuration of nickel(II) acetylacetonato unit. On the other hand, copper(II) acetylacetonato moiety is a square-planer configuration, in which electron donating solvents can interact with the central metal ions.¹⁹ The remarkable solubility of copper(II) β -diketonates in solution is due to donor-acceptor interactions with solvent molecules. The complexes derived from the ligand having 1,3-octanedione unit (**2b-Cu** and **2b-Ni**) were soluble in common organic solvents such as CHCl₃, THF, and toluene, as well as in DMSO and DMF.

Figure 1. TGA trace of **5b-Cu** (A) and **6** (B) under nitrogen.

Scheme 3.

Polymerization

Polymerization of **2a-Cu** with terephthalaldehyde (**3**) was carried out in DMSO at room temperature with H₂SO₄ as a catalyst (Scheme 2). The product was immediately precipitated. After the precipitate was filtered and washed with methanol, a dark green product was obtained in 53% yield. The obtained product was insoluble in common organic solvents. The IR spectrum of the product shows strong peak at 1580 cm⁻¹ due to C=N vibration. A weak peak at 1698 cm⁻¹ due to the terminal aldehyde group also appeared. Reaction of **2a-Ni** with **3** in DMSO at 60°C with H₂SO₄ as a catalyst gave an insoluble product in 74% yield. The polymerization of **2a-Cu** with a flexible dialdehyde, *i.e.*, triethylene glycol bis(*p*-formylphenyl) ether (**4**), was performed in DMSO at room temperature with H₂SO₄ for 48 h. The product was precipitated during polymerization. The resulting product was partially soluble in DMSO and DMF.

The polycondensation of **2b-Cu** with **3** was carried out in DMSO at room temperature with H₂SO₄ as a catalyst (Scheme 2). Polymerization was performed in a homogeneous solution. After reprecipitation into methanol, a green product was obtained in 56% yield. The obtained complex was soluble in common organic solvents such as CHCl₃, THF, and DMSO. The number-average molecular weight (M_n) and molecular weight distribution of the complex determined by GPC were $M_n = 3500$ (polystyrene standard) and $M_w/M_n = 1.71$, respectively.

The structure of the oligomer **5b-Cu** was supported by

Table I. Polymerization of **2b-Cu** with dialdehyde

| Run | Dialdehyde | Solvent | Additive | Temp | Time/h | Yield/% ^a | M_n^b | M_w/M_n^b |
|-----|------------|-------------------|--------------------------------|--------|--------|----------------------|---------|-------------|
| 1 | 3 | DMSO | H ₂ SO ₄ | r.t. | 78 | 56 | 3500 | 1.71 |
| 2 | 3 | CHCl ₃ | LiCl | reflux | 100 | 74 | 610 | 1.89 |
| 3 | 3 | Toluene | LiCl | reflux | 96 | 86 | 2600 | 1.03 |
| 4 | 3 | Toluene | MS4Å | reflux | 48 | 21 | 1000 | 1.65 |
| 5 | 4 | DMSO | H ₂ SO ₄ | r.t. | 168 | 0 | | |
| 6 | 4 | Toluene | LiCl | reflux | 168 | 65 | 1600 | 1.18 |

^a Isolated yields after reprecipitation into *n*-hexane. ^b Determined by GPC (THF) and polystyrene standards.

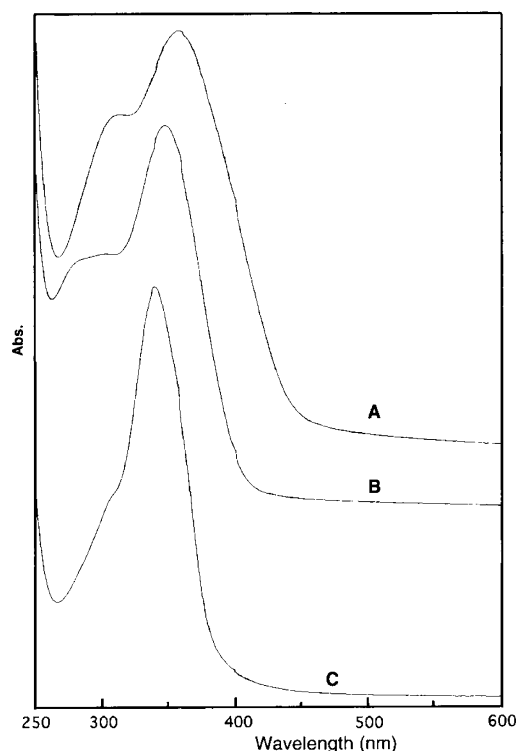


Figure 2. UV-Vis spectra of **5b-Cu** (A), **6** (B), and **2b-Cu** (C) in chloroform.

IR and elemental analysis. The IR spectrum of **5b-Cu** showed a strong peak at 1595 cm^{-1} due to a C=N vibration and strong peaks at 1519 and 1503 cm^{-1} which were assigned to metal coordinated C=O vibration. A weak peak at 1699 cm^{-1} due to the terminal aldehyde group also appeared. The IR spectrum showed no peak at 1723 cm^{-1} due to C=O stretching of free β -diketone. This indicates that the complex did not decompose during polymerization. Elemental analysis of the product was in good agreement with the calculated value (see EXPERIMENTAL). A soluble poly(azomethine) having β -diketonate copper(II) complex in the main chain was thus obtained.

Thermogravimetric analysis (TGA) for **5b-Cu** shows 5% weight loss at 250°C under nitrogen (Figure 1A). Subsequently, rapid weight loss was completed at 500°C . A model complex (**6**) quantitatively obtained by the treatment of **2a-Cu** with benzaldehyde (Scheme 3), was used as a model compound for the repeating unit of **5b-Cu**. The TG curve for **6** shows almost same profile of that of **5b-Cu** (Figure 1B). The rapid weight loss of the diamine monomer **2b-Cu** was also observed at 250°C . All β -diketonate complexes thus decompose at 250°C re-

gardless of structure. Wholly aromatic poly(azomethine)s showed relatively high thermal stability with 5% weight loss of the polymers observed at $360\text{--}390^\circ\text{C}$ under nitrogen.²¹ TG curve **5b-Cu** under air showed rapid weight loss started at 270°C and completed at 400°C . Final weight remaining was 17% corresponding to the copper oxide. The differential scanning calorimetry (DSC) thermogram of the polymer showed no melting point below 200°C .

Table I summarizes the results of the polycondensation of **2b-Cu** with **3** under various conditions. Polymerization in nonpolar solvents such as CHCl₃ and toluene with LiCl or molecular sieves as dehydrating agents gave only monomeric products. Polymerization of **2a-Cu** with the flexible dialdehyde (**4**) was performed in DMSO at room temperature with H₂SO₄. An oligomeric product was not obtained even after 1 week reaction. This can be explained by the fact that less electrophilicity of the aldehyde group of **4** compared with that of **3** due to the electron-donating alkoxy group attached at para position of the benzylaldehyde moiety. The polymerization of **2a-Cu** with **4** in toluene under reflux gave a low molecular weight product in 65% yield. When **2b-Ni** was used as monomer, the product was precipitated during polymerization. The obtained product was insoluble in common organic solvents.

Optical and Electronic Analysis

Figure 2 shows the UV-Vis absorption spectra of **5b-Cu**, **2b-Cu**, and **6**. The peak due to the $\pi\text{--}\pi^*$ transition of **6** and **5b-Cu** were observed at 351, and 358 nm, respectively.²² The slightly bathochromic shift of **5b-Cu** suggests that the metal centers may be considered almost independent.

To elucidate the redox properties of the polymer, cyclic voltammetry measurements were carried out. The electrochemical behavior of bis(β -diketonato) copper(II) chelates has been well studied.²³ The reduction potential of metal ions is sensitive to substituent groups in 1- and 3-positions of the β -diketonato ligands.²⁴ The complex **5b-Cu** gave a single-broad reduction peak at -1.77 V vs. Ag/Ag⁺. The corresponding reduction of the model compound **6** was found to occur at $E_{pc} = -1.64\text{ V}$. Although the reduction peak was located at slightly higher potential compared with that of the model compound, the electrochemical data as well as the absorption spectra showed that the metal centers of the multinuclear complexes may be considered nearly independent. This finding has also been reported for other coordination polymers.²⁵

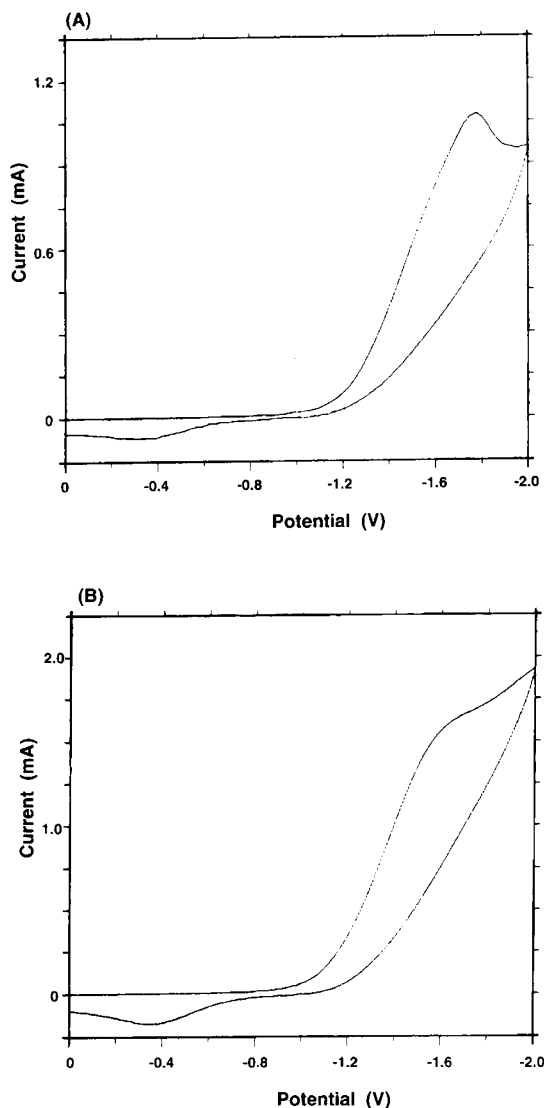


Figure 3. Cyclic voltammograms of **5b-Cu** (A) and **6** (B). Measured in CH_3CN solution of 0.1 M $[\text{NEt}_4]\text{BF}_4$ at 100 mV s^{-1} .

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