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Synthesis of polymer having *β,β*-triketone unit in the main chain and its copper (II) complex

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Summary

A novel polymer having β,β-triketone unit in the main chain was prepared by polycondensation of triethylene glycol bis(*p*-butoxycarbonylphenyl) ether (**1**) with triethylene glycol bis(*p*-acetylacetophenyl) ether (**4**). The obtained polymer was soluble in $CHCl_3$, DMF, and DMSO. The structure of the polymer was confirmed by ^{1}H-NMR. Insoluble brownish yellow copper (II) chelate was obtained by adding a methanol solution of copper (II) acetate to a chloroform solution of the polymer. The IR analysis and the measurement of copper content by iodometric titration showed the quantitative formation of binuclear copper (II) complex.

Introduction

β,β-Triketones are potentially dinegative, tridentate ligands, and their metal complexes have been prepared with transition-metal and lanthanide and actinide ions [1]. One of the interesting properties of β,β-triketones is their ability to chelate two metal ions relatively close together [2]. They also have unique photochemical properties such as photoaddition of styrene to β,β-triketones [3].

The polymers having β,β-triketone units in the main chain may have unique properties not only for polymer chelating agents but also photoreactive polymers. However, very few examples were made in synthesis of β,β-triketones containing polymers. To our knowledge, homo- and copolymerizations of styrenic β,β-triketones were the only reported examples [4]. In that case, homopolymers were obtained as insoluble resins. Although the main chain type polymeric ligands having β-diketone unit were already synthesized by the reaction of dimethyl terephthalate with bisacetyl derivatives in the presence of sodium dispersion [5], there is no documented example for polymers having β,β-triketone units in the main chain.

Synthesis of the polymer containing bimetallic complexes is an important step to the development of material chemistry because these polymers can exhibit ferromagnetism and unique catalytic properties. Here, we wish to report synthesis of the polymer having β,β-triketone unit in the main chain via acylation of ester. A binuclear copper (II) complex of this polymer was also prepared in this study.

Results and Discussion

Monomer Synthesis. β,β-Triketones are usually prepared by acylation of β-diketones with esters [6]. Polymers having β,β-triketone unit could be prepared by polycondensation of bis(β-diketone) monomers with diester monomers. To improve the solubility of the product during polymerization, triethylene glycol was used as a spacer for both monomers. A diester monomer (1) was prepared from triethylene glycol di-*p*-toluenesulfonate (2) and butyl *p*-hydroxybenzoate (3) (Scheme I). Although methyl esters were usually used for preparation of β,β-triketones, butyl ester was chosen for its ease of purification by silica column. A bis(β-diketone) monomer (4) was prepared from triethylene glycol di-*p*-acetophenyl ether (5) and ethyl acetate according to Scheme II.

Polymerization. Polymerization of **1** with **4** was carried out using freshly prepared lithium diisopropylamine (LDA) in ethylene glycol dimethyl ether (DME) solution

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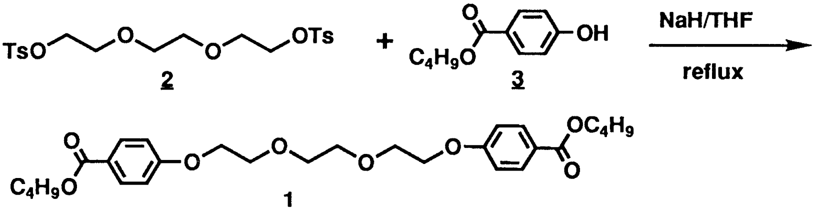
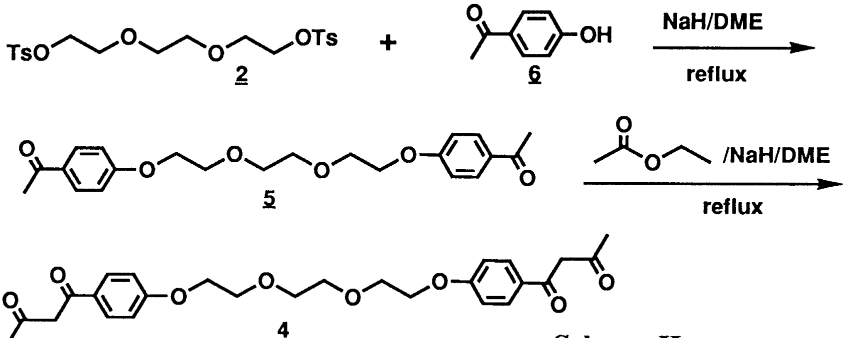
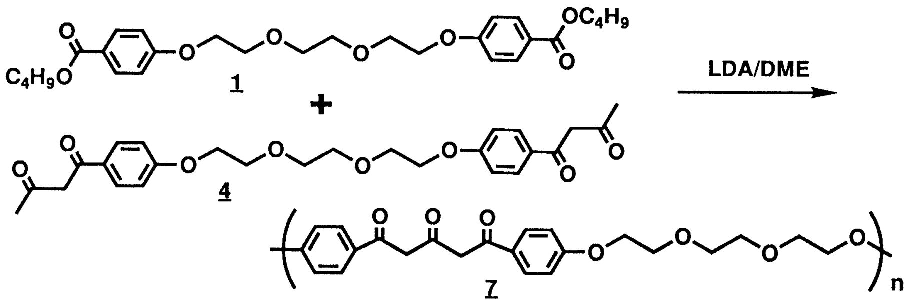
under reflux condition for 10 days (Scheme III). After acidification and reprecipitation for several times, a yellow solid was obtained (11% yield). The obtained polymer (7) was soluble in $CHCl_3$, DMF, and DMSO. The number-average molecular weight (M_n) and the molecular weight distribution (MWD) of 7 by GPC were $M_n = 4670$ (polystyrene standard) and $M_w/M_n = 1.32$, respectively.



Scheme I



Scheme II



Scheme III

The structure of 7 was supported by ^{1}H-NMR (Figure 1). Useful information is afforded by the methine resonances for the formation of β,β-triketones moieties [7]. The two methine resonances at 5.88 and 6.21 ppm were assigned to the dienol and the monoenol protons of β,β-triketone moiety, respectively. The methylene resonance at 4.33 ppm assigned to the triketone tautomer was hardly recognized in Figure 1. Comparison of peak areas of β,β-triketones moiety shows a $CDCl_3$ solution at 25°C to be a mixture of monoenol (70%) -dienol tautomers (30%). The methine resonance of terminal β-diketone also appeared at 6.11 ppm. The two methyl signals at 2.18 and 2.28 ppm can be also assigned to enolic and diketone tautomers of terminal β-diketone, respectively. The methylene signal at 4.25 ppm due to the terminal butoxycarbonyl moiety was observed in a shoulder of the resonances at 4.16 ppm assigned to the methylene protons of triethylene glycol unit. From the integral ratio of the terminal signal of β-diketone moiety, the degree of polymerization was estimated to be 11. This is in good agreement with that from GPC analysis.

A hydrolysis of the ester group was not observed in ^{1}H NMR and IR spectra. Therefore, low yield of the polymer was due to low solubility of lithium salts of the adduct during polymerization. Enhancement of the yield and the degree of polymerization can be achieved by introduction of more soluble spacer than triethylene glycol.

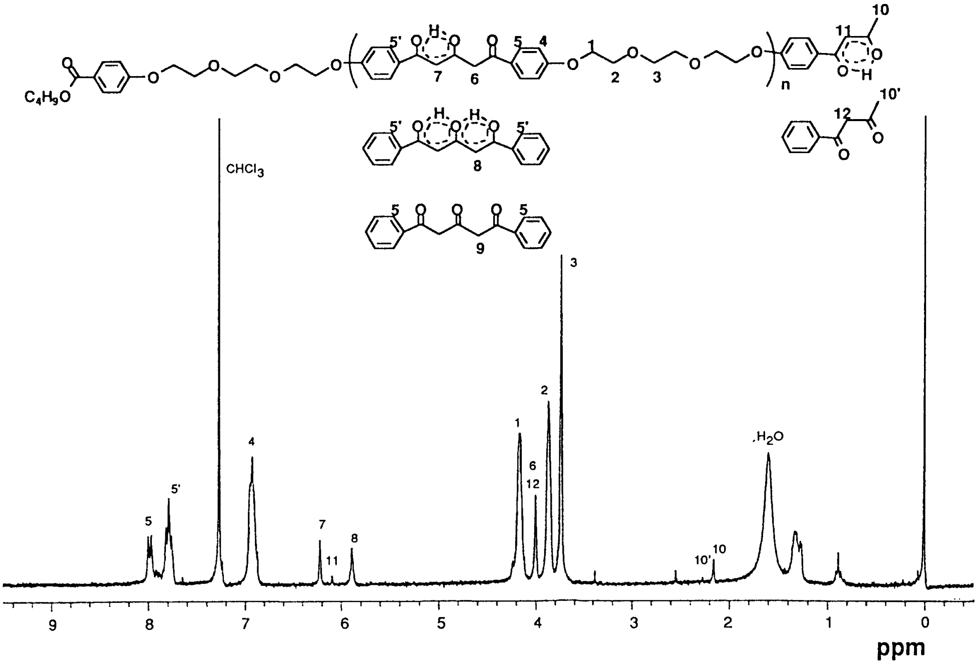


Figure 1. ^{1}H-NMR Spectrum of 7

Complexation of 7 with Cu (II). A polymer metal complex was prepared by adding a methanol solution of copper (II) acetate to a chloroform solution of 7. The product was immediately precipitated under reflux condition. After the precipitate was filtrated and washed with water and $CHCl_3$, 7-Cu complex was obtained quantitatively as a brownish yellow solid.

Figure 2 shows IR spectra of 7 and 7-Cu complex. The IR spectrum of 7 shows strong absorption at 1601 cm^{-1} due to a mixture of C=C and C=O vibrations. The polymer metal complex shows strong absorption at 1526 cm^{-1} which is assigned to a metal coordinated C=O vibration. This observation indicated a formation of metal complex in the β,β-triketone unit.

To estimate the metal ion content in 7-Cu complex, the amount of uncoordinated copper (II) ion was determined by a standard iodometric analysis. We found that equimolar amount of Cu per repeating unit was incorporated into the polymer matrix. This result supported that all carbonyl groups of 7 were coordinated with copper ion.

Copper (II) acetate and β,β-triketones react in 1 : 1 molar ratio to give binuclear chelates, while a 1 : 2 ratio to give mononuclear chelates (Scheme IV). Both types of complexes show several strong absorption bands in the region 1600-1500 cm^{-1} which are a mixture of C=C and C=O vibrations [8, 9]. In addition, the mononuclear chelates show strong absorptions between 1710 and 1680 cm^{-1} which are assigned to a presence of non-coordinated and free-hydrogen bonded carbonyl group. Binuclear chelates appear to contain only coordinated carbonyl groups while mononuclear chelates contain both chelated and free carbonyl groups. The IR spectrum of 7-Cu complex shows 1600 and 1582 cm^{-1}, and no absorption bands corresponded to free carbonyl groups. Mononuclear chelates are usually prepared at low temperature (ca. 0°C), and are rapidly converted into corresponding binuclear chelates in solution at room temperature [9]. These results indicated that the β,β-triketone unit of 7 gave binuclear chelates.

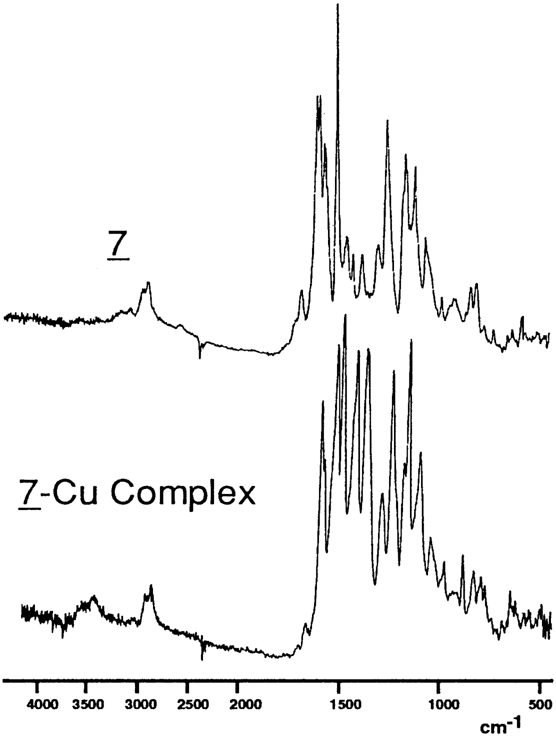
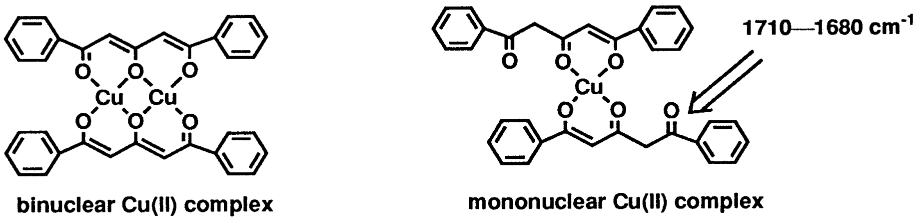


Figure 2. IR Spectra of 7 and 7-Cu Complex



Scheme IV

Experimental Section

General. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. DME was distilled under nitrogen from $LiAlH_4$. ^1H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin Elmer 1600 spectrometer, respectively. Gel permeation chromatography was carried out on a Shodex K-803L by using chloroform as an eluent after calibration with standard polystyrene samples.

Triethylene glycol bis(*p*-butoxycarbonylphenyl) ether (1). To a suspension of NaH (328 mg, 8.2 mmol) in DME (15 ml) was added a solution of triethylene glycol di-*p*-toluenesulfonate (2) (1.52 g, 3.3 mmol) and *p*-hydroxybutylbenzoate (3) (1.81 g, 9.3 mmol) in DME (20 ml). The mixture was stirred under reflux condition for 3 days. The product mixture was then concentrated under reduced pressure, diluted with 100 ml of

AcOEt, and washed with water (10 ml). The aqueous phase was extracted with AcOEt (2 X 10 ml), and the combined organic phase was dried over anhydrous Na_2SO_4. Removal of solvent under reduced pressure afforded a residue, which was purified by chromatography (silica; hexane / AcOEt = 2 / 1, v/v) to give 1.22 g (74%) of triethylene glycol bis(*p*-butoxycarbonylphenyl) ether as a white solid; ^{1}H-NMR ($CDCl_3$, 270 MHz) (δ, ppm) 0.97 (CH_3-, t, J = 7.2 Hz, 6H), 1.47 (-CH_2-, m, 4H), 1.73 (-CH_2-, m, 4H), 3.75 (-CH_2-O, s, 4H), 3.87 ($PhOCH_2$-CH_2-, m, 4H), 4.17 (PhO-CH_2-, t, J = 4.8 Hz, 4H), 4.28 (-CH_2-OCO, t, J = 6.6 Hz, 4H), 6.91 (C_6H_4, d, J = 8.4 Hz, 4H), 7.97 (C_6H_4, d, J = 8.4 Hz, 4H). Anal. Calcd for $C_{28}H_{38}O_8$: C, 66.91; H, 7.62; O, 25.47. Found: C, 66.72; H, 7.70; O, 25.27.

Triethylene glycol di-*p*-acetophenyl ether (5). To a suspension of NaH (605 g, 15.1 mmol) in DME (30 ml) was added a solution of triethylene glycol di-*p*-toluenesulfonate (**2**) (2.57 g, 5.6 mmol) and *p*-hydroxyacetophenone (**6**) (2.31 g, 17.0 mmol) in DME (30 ml). The mixture was stirred under reflux condition for 3 days. The product mixture was then concentrated under reduced pressure, diluted with 100 ml of AcOEt, and washed with water (50 ml). The aqueous phase was extracted with AcOEt (2 X 20 ml), and the combined organic phase was dried over anhydrous Na_2SO_4. Removal of solvent under reduced pressure afforded a residue, which was purified by chromatography (silica; hexane / AcOEt = 2 / 1, v/v) to give 2.07 g (96%) of triethylene glycol di-*p*-acetophenyl ether as a white solid; ^{1}H-NMR ($CDCl_3$, 270 MHz) (δ, ppm) 2.55 (CH_3CO, s, 6H), 3.76 (-CH_2-O, s, 4H), 3.89 ($PhOCH_2$-CH_2-, m, 4H), 4.19 (PhO-CH_2-, t, J = 4.8 Hz, 4H), 6.94 (C_6H_4, m, 4H), 7.92 (C_6H_4, m, 4H).

Triethylene glycol bis(*p*-acetylacetophenyl) ether (4). To a suspension of NaH (258 mg, 6.45 mmol) in DME (15 ml) was added a solution of **5** (501 mg, 1.30 mmol) and ethyl acetate (239 mg, 2.71 mmol) in DME (15 ml). The mixture was stirred under reflux condition for 3 days. The product mixture was then concentrated under reduced pressure, diluted with 20 ml of Et_2O, and washed with water (30 ml). The organic phase was washed with water (2 X 10 ml). The combined aqueous phase was acidified with conc. HCl, and extracted with CH_2Cl_2 (3 X 20 ml). The combined organic phase was dried over anhydrous Na_2SO_4. Removal of solvent under reduced pressure afforded a residue, which was purified by chromatography (silica; hexane / AcOEt =2 / 1, v/v) to give 345 mg (56%) of triethlene glycol bis(*p*-acetylacetophenyl) ether as a pale yellow solid; ^{1}H-NMR ($CDCl_3$, 270 MHz) (δ, ppm) 2.16 (CH_3CO, s), 2.28 (CH_3CO, s), 3.75 (-CH_2-O, s, 4H), 3.88 ($PhOCH_2$-CH_2-, m, 4H), 4.03 ($COCH_2CO$, s), 4.19 (PhO-CH_2-, t, J = 4.5 Hz, 4H), 6.09 (CH=CO, s), 6.93 (C_6H_4, d, J = 9.0 Hz, 4H), 7.83 -7.89 (C_6H_4, m, 4H). Anal. Calcd for $C_{26}H_{30}O_8$: C, 66.37; H, 6.43; O, 27.20. Found: C, 66.27; H, 6.47; O, 26.90.

Polymerization of 1 with 4. A typical procedure is as follows. To a mixture of *s*-BuLi (4.1 mmol) and diisopropylamine (0.6 ml, 4.3 mmol) in DME (3 ml) was added a solution of **4** (0.32 g, 0.68 mmol) in DME (5 ml) at -78°C under nitrogen. The reaction mixture was stirred at -78°C for 0.5 h. To the reaction mixture was added a solution of **1** (0.32 g, 0.65 mmol) in DME (5 ml) at -78°C. After stirring at -78°C for 1 h, the mixture was warmed to room temperature. The mixture was then stirred under reflux condition for 10 days. The product mixture was then concentrated under reduced pressure, diluted with 10 ml of $CHCl_3$, and washed with water (10 ml). The combined aqueous phase was acidified with conc. HCl, and extracted with $CHCl_3$ (3 X 10 ml). The combined organic phase was dried over anhydrous Na_2SO_4 and evaporated to give the crude product. The product was further purified by reprecipitation from $CHCl_3$ solution into Et_2O. Isolated yield was 60 mg (11%). ^{1}H-NMR ($CDCl_3$, 270 MHz) (δ, ppm) 2.16 (s, CH_3), 2.28 (s, CH_3), 3.75 (-CH_2-O, s, 4H), 3.88 ($PhOCH_2$-CH_2-, m, 4H), 4.03 (s, CH_2), 4.19 (PhO-CH_2-, t, J = 4.5 Hz, 4H), 5.88 (CH of dienol, s) 6.09 (s, CH), 6.22 (CH of monoenol, s) 6.93 (C_6H_4, d, J = 9.0 Hz, 4H), 7.83 - 7.89 (C_6H_4, m, 4H).

Complexation of the polymer (7) with Cu (II). A $CHCl_3$ (2 ml) solution of the polymer (7) (41.7 mg, 0.10 mmol) was added to a methanol solution (2 ml) of $Cu(OAc)_2$ monohydrate (41.4 mg, 0.21 mmol). The brownish yellow compound was immediately precipitated. The reaction mixture was stirred under reflux condition for 3 h. The resulting green precipitates were collected and washed with water (3 X 10 ml) and $CHCl_3$ (3 X 10 ml), and dried under reduced pressure to give 68 mg of polymer complex. The all filtrate was combined and the organic phase was washed with water (2 X 10 ml). The combined aqueous phase was concentrated under reduced pressure, and diluted with 10 ml of water. Analysis of the solution was carried out by adding KI and titrating the I_3^- released with 0.01N Na_2SO_3.

References and Notes

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