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Dioxouranium(VI) Dicarboxylate Polymers: Synthesis and Characterization of Tractable Coordination Polymers and Evidence for Rigid Rod Confirmation

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# Dioxouranium(VI) Carboxylate Polymers: Synthesis and Characterization of Tractable Coordination Polymers and Evidence for Rigid Rod Conformation

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## ABSTRACT

A series of polymeric dicarboxylato dioxouranium(VI) species have been synthesized via an equilibrium controlled solution reaction where bis-(acetato)dioxouranium(VI) dihydrate undergoes an acid interchange with a dicarboxylic acid. The solution synthesized species have number average molecular weights of up to  $1.8 \times 10^4$  based on end group analysis, gel permeation chromatography, inherent viscosity and elemental analysis. The empirical Mark-Houwink relation of viscosity to molecular weight has been demonstrated for poly[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)] where  $a = 0.91$  and  $K = 3.19 \times 10^{-5}$ , which is indicative of rigid rod conformation. This series has also been prepared interfacially where the disodium salt of a dicarboxylic acid in an aqueous phase reacted with bis(nitrato)dioxouranium(VI) hexahydrate in diethyl ether.

## INTRODUCTION

In an effort to elucidate the effect of heavy metals on the radiation chemistry of macromolecules we have synthesized a series of polymers based on dioxouranium(VI) and simple dicarboxylic acids. The dioxouranium(VI) ion is

the most stable oxo-metal cation known.<sup>1</sup> The stereochemistry of dioxouranium(VI) compounds are derived from a basis of apical oxo ligands and an equatorial plane available to interact with 4 to 6 additional ligand donor atoms (L). This results in 6, 7, and 8 coordinate complexes of octahedral (1), pentagonal bipyramidal (2), and hexagonal bipyramidal (3) geometries, respectively.<sup>2-4</sup>

Insert Structures 1,2,and 3 here.

Most linear metal chelate polymers have been found to be intractable and, consequently, fundamental polymer properties, such as molecular weight, have been difficult to evaluate.<sup>5-7</sup> Coordination metal polymers containing dioxouranium(VI) centers generally appear to be more tractable materials.<sup>8-15</sup> Presumably this results from the disruption of interunit interactions by the apical oxo ligands. In addition, the tendency of uranium to extra-coordination of neutral donors also appears to promote tractability. The coordination of a solvent molecule of sufficient bulk will disrupt uranium-oxygen-uranium interactions. Simple dioxouranium(VI) salts have been shown to be polymeric in the solid state; drastic changes in the solid state structure have been observed by varying the number and identity of neutral extra-coordinated species.<sup>16-18</sup> Despite the observation that certain dioxouranium(VI) coordination polymers are soluble in various aprotic donor solvents,<sup>8-15</sup> fundamental polymer properties such viscosity-molecular weight relationships and molecular weight distributions had not been previously elucidated.

We have prepared a series of dioxouranium(VI) carboxylate polymers via two different methods. Method one is an equilibrium controlled condensation polymerization based on an acid interchange reaction between bis(acetato)dioxouranium(VI) dihydrate and simple nonchelating dicarboxylic acids. The reaction is conducted in a good aprotic donor solvent such as dimethyl sulfide and is driven to high conversion by removing acetic acid via vacuum dis-

tillation under mild conditions. The acetate ligands which are retained as end groups are detectable with high resolution Fourier transform NMR. The concentration of acetate relative to bridging ligand provides a good estimation of the number average molecular weight of the polymer. The previously reported solution syntheses of dioxouranium(VI) polymers were either conducted in poor polymer solvents or lacked any means of shifting the reaction equilibrium to favor polymer formation.<sup>8-15,19-21</sup> Method two is an interfacial reaction between bis(nitrato)dioxouranium(VI) hexahydrate in diethyl ether and the disodium salt of a simple nonchelating dicarboxylic acid in an aqueous solution. Polymerization under nonequilibrium conditions has been shown to allow the preparation of unusually high molecular weight condensation polymers,<sup>22</sup> but most of the materials we have prepared via this route are intractable and not subject to extensive characterization.

Insert Method 1 and Method 2 schemes close to the above paragraph.

## EXPERIMENTAL

### Reagents

The following chemicals were used without further purification: 2,2-dimethylsuccinic acid, Aldrich; 2,2-dimethylglutaric acid, Aldrich; 3,3-dimethylglutaric acid, Aldrich; 2,2,6,6-tetranethylpimelic acid, Chem Service; maleic acid, Mallinckrodt; fumaric acid, Eastman; phthalic acid, Aldrich; isophthalic acid, Aldrich; terephthalic acid, Aldrich; uranyl acetate dihydrate, Fisher; uranyl nitrate hexahydrate, Alfa; diethyl ether, laboratory grade, Fisher; dimethyl sulfoxide, Aldrich. Thiodiglycolic acid, Aldrich, was recrystallized from benzene/ethanol. Acetylenedicarboxylic acid was prepared from the monopotassium salt, Aldrich, by diethyl ether extraction of the free acid from a solution of the salt in 2.0 M HCl. N-Methyl-2-pyrrolidone, Burdick and Jackson, was dried

over calcium hydride under reflux conditions and distilled under vacuum.

**Poly[(2,2-dimethylbutanedioato)(dimethyl sulfoxide)dioxouranium(VI)]**

Two (2.0000) g of 2,2-dimethylsuccinic acid (13.685 mmole) and 5.8053 g of uranyl acetate (13.687 mmole) were dissolved in 100 mL of dimethyl sulfoxide (DMSO). The solution was heated with a 45°C oil bath and the DMSO was distilled under reduced pressure until no solvent remained. The product remained in solution as the total volume was reduced until only a clear yellow viscous solid remained. As the last traces of solvent were removed the residue bubbled and expanded into a brittle self-supporting foam. The foam was broken up and dried under vacuum, protected from light, at 100°C for 16 h. The final product was a bright yellow powder. The yields of this and the following solution polymerizations are essentially quantitative.

Anal. Calcd. for  $[C_8H_{14}O_7SU]_n$ : C, 19.5; H, 2.9; S, 6.5; U, 48.4.  
Found: C, 19.6; H, 2.9; S, 6.7; U, 48.3.

**Poly[(2,2-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)]**

One (1.0000) g of 2,2-dimethylglutaric acid (6.243 mmole) and 2.6484 g of uranyl acetate (6.244 mmole) were dissolved in 75 mL of DMSO. The solution was heated to 45°C and DMSO distilled under reduced pressure until only a clear yellow glass remained. This material was broken up and dried at 100°C under reduced pressure, protected from light, for 8 h. After this period of time the sample was found to have reformed a yellow glass similar to the initial product. Elemental analysis of this material indicated that approximately 1.5 moles of DMSO were present for every mole of uranium. The product was dried at 100°C under reduced pressure, protected from light, and repeatedly broken up into a powder over a 60 h period. The final form of the product was a fine bright yellow powder.



Anal. Calcd. for  $[C_9H_{16}O_7SU]_n$ : C, 21.4; H, 3.2; S, 6.3; U, 47.0.

Found: C, 21.4; H, 3.3; S, 6.9; U, 46.1.

Poly[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)]

One (1.0000) g of 3,3-dimethylglutaric acid (6.243 mmole) and 2.6484 g of uranyl acetate (6.244 mmole) were dissolved in 100 mL of DMSO. The solution was heated to 45°C and DMSO distilled under reduced pressure until no further solvent remained. The product stayed in solution as the total volume was reduced until only a clear yellow viscous solid remained. As the last traces of solvent were removed this residue expanded into a yellow brittle self-supporting foam. The product was broken up and dried at 100°C under reduced pressure, protected from light, for 16 h.

Anal. Calcd. for  $[C_9H_{16}O_7SU]_n$ : C, 21.4; H, 3.2; S, 6.3; U, 47.0.

Found: C, 21.1; H, 3.2; S, 6.7; U, 47.1.

A series of poly[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)] of varying molecular weight were synthesized by changing the stoichiometry of reactants. All the reactions were conducted in 75 mL of DMSO in a manner identical to the above preparation.

One half (0.5000) g of 3,3-dimethylglutaric acid (3.122 mmole) and 1.3904 g of uranyl acetate (3.278 mmole) were reacted as per the above procedure.

Anal. Calcd. for  $[C_9H_{16}O_7SU]_n$ : C, 21.4; H, 3.2; S, 6.3; U, 47.0.

Found: C, 21.1; H, 3.3; S, 6.5; U, 46.8.

The above reaction was repeated using 0.5000 g of 3,3-dimethylglutaric acid (3.122 mmole) and 1.4566 g (3.434 mmole) of uranyl acetate.

Anal. Calcd. for  $[C_9H_{16}O_7SU]_n$ : C, 21.4; H, 3.2; S, 6.3; U, 47.0.

Found: C, 20.9; H, 3.2; S, 6.3; U, 47.2.

The above reaction was repeated using 0.5000 g of 3,3-dimethylglutaric acid (3.122 mmole) and 1.5890 g of uranyl acetate (3.746 mmole).

Anal. Calcd. for  $[C_9H_{16}O_7SU]_n$ : C, 21.4; H, 3.2; S, 6.3; U, 47.0.

Found: C, 20.8; H, 3.3; S, 6.4; U, 47.7.

The above reaction was repeated using 0.5000 g of 3,3-dimethylglutaric acid (3.122 mmole) and 1.8539 g of uranyl acetate (4.371 mmole).

Anal. Calcd. for  $[C_9H_{16}O_7SU]$ : C, 21.4; H, 3.2; S, 6.3; U, 47.0.

Found: C, 19.7; H, 3.1; S, 6.4; U, 48.0.

The above reaction was repeated using 0.5000 g of 3,3-dimethylglutaric acid (3.122 mmole) and 2.6484 g (6.244 mmole) of uranyl acetate.

Anal. Calcd. for  $[C_9H_{16}O_7SU]$ : C, 21.4; H, 3.2; S, 6.3; U, 47.0.

Found: C, 18.6; H, 3.0; S, 6.8; U, 48.7.

Poly[(2,2,6,6-tetramethylheptanedioato)(dimethyl sulfoxide)dioxouranium(VI)]

One-half (0.5000) g of 2,2,6,6-tetramethylpimelic acid (2.312 mmole) and 0.9807 g uranyl acetate (2.312 mmole) were dissolved in 100 mL of DMSO. Gentle heat was required to completely dissolve the diacid. The solution was heated to 45°C and DMSO distilled under reduced pressure. The distillation was continued until only a pale yellow opaque mass remained. The product was broken up into a powder and dried at 100°C under reduced pressure, protected from light, for 40 h.

Anal. Calcd. for  $[C_{13}H_{24}O_7SU]_n$ : C, 27.8; H, 4.3; S, 5.7; U, 42.3.

Found: C, 27.8; H, 4.3; S, 5.6; U, 42.5.

Poly[(thio $\bar{\alpha}$ 2,2'-bis(acetato))bis(dimethyl sulfoxide)dioxouranium(VI)]

One (1.0000) g of thiodiglycolic acid (6.660 mmole) and 2.8251 g of uranyl acetate (6.661 mmole) were dissolved in 100 mL of DMSO. The solution was heated to 45°C and DMSO was distilled under reduced pressure until no fur-

ther solvent remained. The product residue was a clear pale yellow glassy film deposited on the walls of reaction vessel. The product was broken up into a powder and dried under reduced pressure, protected from light, at 100°C for 15 hours. The elemental analysis is consistent with 2 moles of DMSO being present for every mole of uranium and the NMR spectra show that 2 moles of DMSO were present for mole of bridging ligand.

Anal. Calcd. for  $[C_8H_{16}O_8S_3U]_n$ : C, 16.7; H, 2.8; S, 16.7; U, 41.4.  
Found: C, 17.0; H, 2.7; S, 16.8; U, 41.7.

Poly[(((Z)2-butenedioato)bis(dimethyl sulfoxide)dioxouranium(VI))]

Two (2.0000) g of maleic acid (17.231 mmole) and 7.3092 g of uranyl acetate (17.233 mmole) were dissolved in 150 mL of DMSO. The mixture was stirred and, with gentle heating, formed a bright clear yellow solution. The solution was heated to 45°C and DMSO distilled under reduced pressure to dryness. The product stayed in solution until the original solution had been reduced by approximately 95%. At that point dense spherical particles began to form. The product was pulverized into a bright yellow powder and dried at 100°C under reduced pressure, protected from light, for 16 hours. The elemental analysis is consistent with 1.75 moles of DMSO per mole of uranium and the NMR spectra show there are 1.75 moles of DMSO per mole of bridging ligand.

Anal. Calcd. for  $[C_{7.5}H_{12.5}O_{7.75}S_{1.75}U]_n$ : C, 17.3; H, 2.4; S, 10.8; U, 45.7. Found: C, 17.5; H, 2.5; S, 10.5; U, 45.4.

Poly[(((E)2-butenedioato)bis(dimethyl sulfoxide)dioxouranium(VI))]

Two (2.0000) g fumaric acid (17.231 mmole) and 7.3092 g of uranyl acetate (17.233 mmole) were added to 150 mL of DMSO. The mixture was stirred, and gentle heat applied, until both reagents were completely dissolved. The solution was heated to 45°C and DMSO distilled under reduced pressure until no

further solvent remained. When the solution volume had been reduced by approximately 80% the product began to precipitate as a finely divided yellow powder. The product was dried at 100°C, protected from light, for 16 h. The elemental analysis is consistent with 2 moles of DMSO per mole of uranium and the NMR spectra show an identical ratio of DMSO to fumaric acid.

Anal. Calcd. for  $[C_8H_{14}O_8S_2U]_n$ : C, 17.8; H, 2.6; S, 11.9; U, 44.1.  
Found: C, 17.8; H, 2.6; S, 11.5; U, 43.8.

Poly[(1,2-benzenedicarboxylato)bis(dimethyl sulfoxide)dioxouranium(VI)]

One (1.0000) g of phthalic acid (6.019 mmole) and 2.5534 g of uranyl acetate (6.020 mmole) were dissolved in 100 mL of DMSO. The solution was heated to 45°C and DMSO distilled under reduced pressure to dryness. The product stayed in solution until nearly all the solvent had been removed. As the last bit of DMSO volatilized the product formed a hard opaque yellow mass. The product was pulverized to a powder and dried at 100°C under reduced pressure, protected from light, for 18 h. The elemental analysis is consistent with two moles of DMSO per mole of uranium and the NMR spectra show there are two moles of DMSO per mole of bridging ligand.

Anal. Calcd. for  $[C_{12}H_{16}O_8S_2U]_n$ : C, 24.4; H, 2.7; S, 10.9; U, 40.3.  
Found: C, 24.3; H, 2.8; S, 10.6; U, 40.5.

Poly[(1,3-benzenedicarboxylato)(dimethyl sulfoxide)dioxouranium(VI)]

One (1.0000) g of isophthalic acid (6.019 mmole) and 2.5534 g uranyl acetate (6.020 mmole) were added to 150 mL of DMSO. The mixture was stirred and gentle heat was applied until both reagents were completely dissolved. The solution was heated to 45°C and DMSO distilled under reduced pressure until no further solvent remained. When approximately 75% of the solvent had been removed the product began to precipitate as a finely divided yellow pow-

der. The product was dried at 100°C under reduced pressure, protected from light, for 18 h. The elemental analysis is consistent with 1.25 moles of DMSO per mole of uranium and the NMR spectra show that there are 1.25 moles of DMSO per mole of bridging ligand.

Anal. Calcd. for  $[C_{10.5}H_{11.5}O_{7.25}S_{1.25}U]_n$ : C, 23.7; H, 2.2; S, 7.5; U, 44.8. Found: C, 23.8; H, 2.0; S, 7.6; U, 44.9.

**Poly[(1,4-benzenedicarboxylato)bis(dimethyl sulfoxide)dioxouranium(VI)]**

One (1.0000) g of terephthalic acid (6.019 mmole) and 2.5534 g of uranyl acetate (6.020 mmole) were added to 150 mL of DMSO. The mixture was stirred and gentle heat applied until both reactants completely dissolved. The solution was heated to 45°C and DMSO distilled under reduced pressure to dryness. When the solution volume had been reduced by approximately one half the product began to precipitate as a finely divided yellow powder. The product was dried at 100°C under reduced pressure, protected from light, for 18 h. The elemental analysis is consistent with two moles of DMSO per mole of uranium and the NMR spectra show that there are two moles of DMSO per mole of terephthalic acid.

Anal. Calcd. for  $[C_{12}H_{16}O_8S_2U]_n$ : C, 24.4; H, 2.7; S, 10.9; U, 40.3. Found: C, 24.2; H, 2.7; S, 10.9; U, 40.2.

**Poly[(2-butyndioato)bis(dimethyl sulfoxide)dioxouranium(VI)]**

Initially 0.5892 g of acetylenedicarboxylic acid (5.166 mmole) and 2.0818 g of uranyl acetate (4.908 mmole) were added to 50 mL of DMSO. Both reactants readily dissolved to form a clear orange solution. The solution was heated to 45°C and DMSO distilled under reduced pressure until all that remained was a very dark orange oil. The product was dried at room temperature under reduced pressure, protected from light, for 16 h. Despite this treatment the product

remained in the form of a dark orange oil. The best fit of the elemental analysis data were achieved when one assumed that two moles of DMSO were present per mole of uranium.

Anal. Calcd. for  $[\text{C}_8\text{H}_{12}\text{S}_2\text{O}_8\text{U}]_n$ : C, 17.9; H, 2.3; S, 11.9; U, 44.2.  
Found: C, 19.9; H, 2.9; S, 11.9; U, 41.5.

CAUTION: All of the following interfacial polymerizations were conducted behind an explosion shield. Diethyl ether solutions of uranyl nitrate are shock sensitive, especially on standing or when exposed to light. All the diethyl ether solutions of uranyl nitrate were freshly prepared and quickly used. Such solutions should be handled with extreme caution at all times.

#### Poly[(2,2-dimethylbutanedioato)(aquo)dioxouranium(VI)]

Five mmole of 2,2-dimethylsuccinic acid (0.7307 g) was neutralized with 2.0 M NaOH and diluted with water to a total solution volume of 10 mL. Five mmole of uranyl nitrate (2.5107 g) was dissolved in 25 mL of diethyl ether. The aqueous phase was added in a running stream to the ether phase with high speed stirring. The stirring was continued for 30 s following the complete addition of the aqueous phase. The rapid stirring resulted in a frothy yellow emulsion which quickly reformed two phases. A yellow precipitate was present at the interface and on the walls of the blender-reactor. The reaction solution was filtered and the gummy yellow precipitate was washed with cold water. On standing for several minutes the aqueous phase yielded a second precipitate, presumably due to the cooling effect of the evaporating ether. This precipitate was filtered from the solution and both product fractions were dried at 100°C under reduced pressure, protected from light, for 16 h. The material isolated from the interface totalled 0.146 g, 6%. A substantial amount of material was unrecovered from the reactor surfaces.

Anal. Calcd. for  $[\text{C}_6\text{H}_{10}\text{O}_7\text{U}]_n$ : C, 16.7; H, 2.3; U, 55.1.

Found: C, 15.8; H, 2.1; U, 57.7.

The product isolated from the aqueous phase totalled 1.210 g, 51%.

Anal. Calcd. for  $[\text{C}_6\text{H}_{10}\text{O}_7\text{U}]_n$ : C, 16.7; H, 2.3. Found: C, 13.5; H, 1.8.

Poly[(3,3-dimethylpentanedioato)(aquo)dioxouranium(VI)]

Two mmole of 3,3-dimethylglutaric acid (0.3203 g) was dissolved in 50 ml of water along with 0.16 g of NaOH (4.0 mmole); 2.0 M NaOH was added dropwise until a neutral pH was achieved. Two mmole of uranyl nitrate (1.0043 g) was dissolved in 50 mL of diethyl ether. Both phases were placed in the blender and stirred at high speed for 30 s. A generous amount of yellow material precipitated at the interface immediately. The precipitate was filtered, washed with cold water, and then dried at 100°C under vacuum, protected from light, for 16 h; yield 0.511 g, 57%.

Anal. Calcd. for  $[\text{C}_7\text{H}_{12}\text{O}_7\text{U}]_n$ : C, 18.8; H, 2.7; U, 53.4.

Found: C, 20.0; H, 2.9; U, 54.2.

Poly[(2,2,6,6-tetramethylheptanedioato)(aquo)dioxouranium(VI)]

Two mmole of 2,2,6,6-tetramethylpimelic acid (0.4326 g) was added to 100 mL of deionized distilled water along with 0.16 g of NaOH (4.0 mmole). The mixture was stirred and gently heated until complete dissolution had occurred. Two (2.0) M NaOH was added dropwise until a neutral pH was achieved. Two mmole of uranyl nitrate (1.0043 g) was dissolved in 50 mL of diethyl ether. Both solutions were placed in the blender-reactor and stirred at high speed for 30 s. A generous amount of material precipitated at the interface immediately. The yellow product was filtered, washed with cold water, and dried at 100°C in vacuo, protected from light, for 16 h; yield 0.689 g, 69%.

Anal. Calcd. for  $[C_{11}H_{20}O_7U]_n$ : C, 26.3; H, 4.0; U, 47.4.

Found: C, 25.8; H, 3.9; U, 50.7.

Poly[(2,2-thiobis(acetato))(aquo)dioxouranium(VI)]

Initially 3.7538 g of thiodiglycolic acid (25.000 mmole) was dissolved in 25.0 mL of 2.0 M NaOH. Additional NaOH solution was added dropwise to neutrality. 12.5533 g of uranyl nitrate (25.000 mmole) was very carefully dissolved in 100 mL of diethyl ether. The ether solution was placed in the blender-reactor and subjected to high speed stirring while the aqueous phase was added in a flowing stream. The stirring was continued for 30 s following the complete addition of the aqueous solution. A large amount of yellow material immediately precipitated at the interface. The product was filtered, washed with cold water (which resulted in a considerable loss of material), and dried at 100°C under vacuum, protected from light, for 16 h; yield 1.316 g, 12%.

Anal. Calcd. for  $[C_4H_6SO_7U]_n$ : C, 11.0; H, 1.4; S, 7.4; U, 54.6.

Found: C, 11.8; H, 1.4; S, 7.7; U, 58.8.

Poly[((Z)-2-butenedioato)(aquo)dioxouranium(VI)]

Initially 2.9018 g of maleic acid (25.000 mmole) was added to 25.0 mL of 2.0 M NaOH. Additional NaOH solution was added dropwise to neutrality. 12.5533 g of uranyl nitrate (25.000 mmole) was dissolved in 100 mL of diethyl ether with caution. Both phases were placed in the blender-reactor and stirred at high speed for 30 s. A large amount of yellow material precipitated immediately at the interface. This material was recovered via filtration, washed with cold water and dried under vacuum at 100°C, protected from light, for 16 h; yield 5.256 g, 52%.



Anal. Calcd. for  $[C_4H_4O_7U]_n$ : C, 12.0; H, 1.0.

Found: C, 12.1; H, 1.0.

Poly[(((E)2-butenedioato)(aquo)dioxouranium(VI))]

Initially 2.9018 g of fumaric acid (25.000 mmole) was dissolved in 25.0 mL of 2.0 M NaOH. Additional base was added dropwise to neutrality. 12.5533 g of uranyl nitrate (25.000 mmole) was cautiously dissolved in 100 mL of diethyl ether. Both solutions were placed in the blender-reactor and subjected to high speed stirring for 30 s. A large amount of yellow material precipitated immediately at the interface. This material was filtered, washed with cold water, and dried at 100°C under reduced pressure, protected from light, for 16 h; yield 4.315 g, 43%.

Anal. Calcd. for  $[C_4H_4O_7U]_n$ : C, 12.0; H, 1.0. Found: C, 14.3; H, 1.2.

Poly[[(2-butynedioato)(aquo)dioxouranium(VI)]]

Initially 3.0148 g of the monopotassium salt of acetylenedicarboxylic acid (19.815 mmole) was dissolved in 15 mL of deionized distilled water. 2.0 M NaOH was added until neutrality was achieved. 9.9507 g of uranyl nitrate (19.817 mmole) was dissolved in 100 mL of diethyl ether. The ether phase was stirred at high speed while the aqueous phase was added in flowing stream. The stirring was continued for 30 s following the complete addition of the aqueous solution. An oily yellowish orange material appeared at the interface. The product was filtered with a fine porosity frit and dried under vacuum at room temperature, protected from light, for 16 h. The final form of the product was an orange granular powder; yield 0.577 g, 7%.

Anal. Calcd. for  $[C_4H_4O_8U]_n$ : C, 11.5; H, 1.0; U, 57.0.

Found: C, 14.8; H, 0.9; U, 52.9.

## Physical Properties

Infrared spectra were recorded on a Perkin-Elmer model 283 spectrometer over the range 200 to 4000  $\text{cm}^{-1}$ . The samples were analyzed in a KBr glass.

Gel permeation chromatography was conducted on a  $10^3$  Angstrom Ultrastyrage column (Waters) with N-methyl-2-pyrrolidone (NMP) as the solvent. Sample solutions were prepared by completely dissolving 5 mg of polymer in 1.0 mL of NMP. All solutions were filtered with a 0.45 micron PTFE membrane prior to use.

Nuclear magnetic resonance studies were conducted in  $\text{DMSO-d}^6$  using a Varian model XL-300 spectrometer. Sample solutions were prepared by dissolving approximately 75 mg of polymer in 0.7 g of  $\text{DMSO-d}^6$  with the aid of one drop of concentrated HCl. The large proton peak resulting from the HCl was eliminated from the spectrum by irradiation with instrument's decoupling feature. The final spectra were the result of at least 128 separate spectral acquisitions, which were subjected to Fourier transform analysis.

Viscosity data in triplicate were collected in a Cannon W-118 viscometer, with a #75 capillary bore, equilibrated at  $30.00 \pm 0.02^\circ$ . The solvent was NMP.

Thermal gravimetric analyses were conducted using a Perkin-Elmer model TGS-2 thermal analyzer. The studies were run using at least 6 mg of sample with a temperature increase rate of  $20^\circ$  per minute.

## RESULTS

The formation of polymeric dioxouranium(VI) chelates via distillation ligand exchange yields remarkably characterizable materials. The removal of

acetate ligand, as acetic acid, when codistilled with an aprotic donor solvent of high boiling point (in the presence of a suitable replacement ligand) occurs readily under reduced pressure at reasonably mild temperatures.

The lack of any side reaction leads to classic stoichiometry and solubility limited step growth polymerization. The strong solubilizing properties of many aprotic donor solvents allows dioxouranium(VI) polymeric chelates to remain in solution until relatively high degrees of polymerization are achieved.

The tendency of dioxouranium(VI) to extra-coordination invariably leads to strong retention of at least one solvent molecule per uranium in polymeric chelates where metal bridging is accomplished with dicarboxylates. By using reaction solvents which contain a heteroatom, degrees of solvation can be easily estimated with elemental analysis. The degrees of DMSO solvation of the solution synthesized polymers are listed in Table I.

The elemental analyses indicate, after the degree of DMSO solvation is accounted for, a ratio of one dicarboxylate bridging ligand to one uranium within experimental error. No influence of end group on elemental ratios is discernable indicating a reasonably high degree of polymerization. Elemental analyses of the acetylenedicarboxylate based material and all of the interfacially synthesized species are generally poor.

Nuclear magnetic resonance confirms the degree of DMSO solvation indicated by elemental analysis and also allows one to detect acetate end groups. The concentration of end group relative to bridging ligand can be directly related to number average molecular weight. Table I lists the ratio of acetate end group to bridging ligand and the corresponding degree of polymerization and number average molecular weight for the solution synthesized

species. The interfacially prepared materials do not have a unique NMR active end group.

Inherent viscosities for the completely soluble polymeric chelates were determined using Kraemer's approximation<sup>23</sup>:

$$[\eta]_{inh} = (1/c) \ln (t_{solution}/t_{solvent})$$

where  $[\eta]_{inh}$  = inherent viscosity

c = concentration in g/dL

t = time in seconds

Table II lists the inherent viscosities as determined in NMP; a negligible concentration dependence for a series of dilute solutions was observed.

Combining the NMR end group analysis technique and measurement of inherent viscosity allow the demonstration of the Mark-Houwink<sup>24</sup> relation of viscosity and molecular weight for poly[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)] where  $a = 0.91$  and  $K = 3.19 \times 10^{-5}$  and

$$[\eta] = KM^a.$$

Table III contains the results of a viscosity study, NMR end group analysis and GPC calibration for a series of poly[(3,3-dimethylpentanedioato)-(dimethyl sulfoxide)dioxouranium(VI)] of varying molecular weight. This series was synthesized by varying the stoichiometric balance of uranyl acetate and the 3,3-dimethylglutaric acid bridging ligand. Figure 1 illustrates the plot of viscosity versus molecular weight.

The relation of relative acetate end group concentration to molecular weight was derived from the classic relation of degree of polymerization to reactant ratio and extent of reaction for step growth polymerization<sup>25</sup>

$$X_n = \frac{Na(1 + 1/r)/2}{Na[1-p + (1-rp)/r]/2}$$

where  $r = Na/Nb =$  reactant mole ratio ( $Na < Nb$ )

$p =$  extent of reaction

Given the purity of the polymerization reagents, iteration gave a likely extent of reaction of 0.98. Combining the extent of reaction with the reactant ratio allows the calculation of the probability of end groups being acetate versus monocomplexed bridging ligand, where

$$[Na(1-p) + Nb(1-rp)] = \text{total number of end groups.}$$

Infrared analyses show shifts in the carbonyl asymmetric stretching frequency assigned to the bridging ligand to lower energies. Such shifts are characteristic of carboxylate-metal coordination.<sup>26</sup> Table IV lists the spectral values of this absorption for the parent acids and the corresponding polymers.

Thermal analysis of the uranyl polymers generally showed stepwise weight loss corresponding to loss of coordinated solvent and then decomposition of bridging ligand. In some species the loss of solvent and general decomposition occur at similar temperatures. Table V contains the TGA data.

Gel permeation chromatography (GPC) studies of the polymers completely soluble in NMP generally show molecular weight distributions typical of simple step growth polymers. The exceptions include the few soluble interfacially

synthesized materials where shifts to high molecular weight are seen. The high apparent molecular weight of the interfacially synthesized species is not consistent with the nonideal conditions inherently present in the synthetic method. However independent confirmation of the apparent molecular weight with a reliable method has not been attempted. Several of the solution synthesized species also have nonideal molecular weight distributions and anomalously high number average molecular weights relative to the end group analysis data. Table VI gives the retention volumes and polystyrene equivalent molecular weight for the species studied.

For the series of poly[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)] of varied molecular weight a straight line relation was observed when the log molecular weight was plotted versus retention volume as shown in Figure 2. Similarly a plot of the product of the viscosities and the respective log molecular weight versus retention volume gives a reasonably good correlation with the polystyrene universal calibration curve (see Figure 3).

## DISCUSSION

A simple synthetic route leading to a soluble characterizable coordination metal polymer has long been sought.<sup>7,27</sup> The area of metal chelate polymers has been plagued with polymer intractability and low molecular weight. The problem of polymer intractability generally acts as a powerful barrier to complete characterization as well as the development of any significant commercial uses.

The high affinity of the dioxouranium(VI) ion for small chelate rings

such as carboxylates is well known.<sup>28</sup> This characteristic, along with the reasonably high vapor pressure of acetic acid, allows a simple distillation driven acid interchange polymerization to occur smoothly and to a high degree of conversion. Premature precipitation of the polymer product is prevented by the use of an aprotic solvent, such as DMSO, which is known to be a good polymer solvent and to readily solvate dioxouranium(VI).<sup>29</sup> The steric bulk of DMSO appears to affect polymer tractability via the extra-coordination of solvent by dioxouranium(VI). In fact we have found that all the aquo solvated dioxouranium polymers are significantly less tractable than the corresponding DMSO solvates.<sup>30</sup>

The presence of a heteroatom in DMSO allows an assessment of the degree of solvation via elemental analysis. The amount of solvation is usually exactly one or two moles, or occasionally one and a fraction, of DMSO per uranium. The ratio of DMSO to the bridging ligand, which can be determined with NMR, is in agreement with the elemental analyses.<sup>30</sup> The TGA analyses reflect the high affinity of DMSO for uranium. Loss of one equivalent of DMSO occurs at temperatures as high as 300°C. Any solvation above one mole of DMSO per uranium is lost at or near the boiling point of DMSO.

The elemental analyses are also consistent with a ratio of one uranium to one bridging ligand within experimental error. In these materials the sensitivity of elemental ratios to degree of polymerization is diluted by the high relative weight of uranium. However the lack of an effect of end group on the observed elemental ratios is still indicative of a reasonable degree of polymerization. The interfacially synthesized species generally have poor elemental analyses. Presumably this is due to reaction byproducts which are occluded in the product during the rapid precipitation at the interface.

The infrared spectra provide evidence for the interaction of the carboxylate moieties and the dioxouranium(VI) centers. The species based on the four simple aliphatic diacids exhibit energies of the carbonyl asymmetric stretch which are indicative of symmetrical carboxylate chelation.<sup>26</sup> The higher energy asymmetric carbonyl stretches observed in the species based on the thio bridged diacid and the unsaturated diacids are consistent with either unsymmetrical carboxylate chelation or unsymmetrical carboxylate bridging of uranium centers.<sup>26</sup> The fact that most of these species are soluble and are clearly polymeric (based on the viscosity, SEC, and end group analysis data) suggests that unsymmetrical chelation is a much more likely possibility.<sup>31</sup>

End group analysis via NMR detection of residual acetate ligand provides a very accurate means of determining the degree of polymerization. The polymers synthesized with a reactant ratio of exactly one to one should have, overall, an equal number of acetate and monocomplexed bridging ligand end groups. For the purpose of calculating degrees of polymerization and number average molecular weight we have made this assumption. When analogous syntheses are conducted with imbalances in reactant ratios, an unequal probability of acetate versus bridging ligand end group exists. In these instances incorporation of the end group probability into the calculations results in good agreement between experimental and theoretical degrees of polymerization.

The inherent viscosity values, which range from about 0.07 to 0.14 dL/g in NMP, are consistent with low to medium molecular weight condensation polymers. The second-order viscosity term in Kraemer's equation is not necessary for these species. The viscosity results, coupled with the NMR end group analysis and SEC data, clearly show a dependence of solution viscosity on molecular weight for the 3,3-dimethylglutaric acid based material (vide



infra). This combination of analytical techniques provides an excellent means of characterizing these species.

A systematic variation of reactant ratio for the polymer based on 3,3-dimethylglutaric acid allows the synthesis of species with varying molecular weight. When the log of the NMR derived number average molecular weight are plotted versus the log of the respective inherent viscosities, a straight line is obtained. This finding is consistent with the Mark-Houwink relation<sup>24</sup>  $[\eta] = K M^a$  where  $K = 3.19 \times 10^{-5}$  and  $a = 0.91$ . The assignment of  $K$  and  $a$  values for similar coordination polymers has, to our knowledge, never appeared previously. These values are within the realm known for organic polymers; specifically being most similar to rigid rod systems.<sup>32-34</sup> This raises the intriguing possibility of new materials with unusual properties given the well known photochemical and photocatalytic properties of dioxouranium(VI)<sup>35-39</sup>.

Evaluation of the molecular weight distribution is possible with size exclusion chromatography (SEC) when NMP is the solvent. Most of the solution synthesized, and several of the interfacially synthesized, polymers are completely soluble in NMP. The majority of the solution synthesized materials give molecular weight distributions which are typical of species prepared via equilibrium-controlled step-growth polymerization.<sup>25</sup> The evaluation of coordination polymers with SEC has seldom been accomplished.<sup>40-41</sup> Inorganic materials tend to suffer from secondary phenomena which exaggerate molecular size.<sup>42</sup> The SEC evaluation of bis(acetato)dioxouranium(VI) in a NMP medium reproducibly gives a sharp, symmetrical peak at an elution volume consistent with a monomeric species<sup>30</sup> (see figure 4). This behavior suggests that large secondary effects are not inherent to the SEC of dioxouranium(VI) species.<sup>42</sup> However secondary effects have been observed in several of the species

reported here.

A plot of SEC retention volume versus log molecular weight for the series of poly[(3,3-dimethylpentanedionato)(dimethyl sulfoxide)dioxouranium(VI)] of varying molecular weight gives a straight line. In addition, inclusion of the viscosity data into the calibration results gives a reasonable correlation with the universal calibration curve (UCC) based on polystyrene standards. However the basis for comparison is limited to a small section of the low molecular weight region of the UCC.

The species which give anomalous molecular weight distributions (as determined by SEC) fall into two categories. First are the interfacially synthesized species where the deviation from ideality typically occurs in the form of a bimodal distribution. The major peak is consistent with the expected relatively low molecular weight. The second peak occurs at high molecular weight; if a tail extends into the zone of nonfractionated molecular size a third peak will appear at the exclusion limit of chromatography column. A nonideal molecular weight distribution is expected for polymers prepared under non-equilibrium controlled conditions. All the soluble interfacially synthesized dioxouranium(VI) polymers we have studied with SEC possess such distributions.

The second category consists of three solution synthesized species. These are the dioxouranium(VI) polymers where the bridging ligand is 2,2-dimethylglutaric acid, fumaric acid and isophthalic acid. The molecular weight distribution consists of a bimodal distribution. However, in contrast to the interfacially synthesized species, the major peak occurs at high molecular weight. The fumaric acid and isophthalic acid based materials might reasonably be expected to have an unusual distribution given the con-

formational limitations of both bridging ligands and the presumably rigid rod character of the macromolecules. In addition, the facility of addition reactions at the trans substituted carbon-carbon double bond of fumaric acid may cause a small amount of secondary polymerization. However, the non-ideal molecular weight distribution of the 2,2-dimethylglutaric acid containing polymer is not so readily rationalized.

In summary, we believe we have demonstrated a superior solution polymerization technique for coordination polymers. The species we have prepared exhibit a reasonably high degree of polymerization and are amenable to a relatively complete level of characterization. Greater tractibility might result from the use of a bulkier reaction solvent or mixtures of bridging ligands. We have also evaluated the radiation sensitivity of these materials. Several of the species described herein are show unusually high sensitivity to gamma radiation. We expect to report those results in the near future.

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Table I. NMR of Solution Synthesized Polymeric  
Dioxouranium(VI) Carboxylates

Bridging ligand (DMSO solvation) <sup>a</sup>	Ratio acetate to bridging ligand <sup>b</sup>	dP <sup>c</sup>	M <sub>n</sub> <sup>d</sup>
2,2-Dimethylsuccinate(DMSO)	1 to 18	36	8900
2,2-Dimethylglutarate(DMSO)	1 to 18	36	9300
3,3-Dimethylglutarate(DMSO)	1 to 24	48	12200
2,2,6,6-Tetramethylpimelate(DMSO)	1 to 21	42	12400
Thiodiglycolate(2 DMSO)	1 to 28	56	16200
Maleate(1.75 DMSO)	1 to 8	16	4200
Fumarate(2 DMSO)	1 to 24	48	13000
Phthalate(2 DMSO)	1 to 30	60	17800
Isophthalate(1.25 DMSO)	1 to 32	64	17100
Terephthalate(2 DMSO)	1 to 26	52	15400

<sup>a</sup>Amount of DMSO solvation per bridging ligand determined by integration of respective NMR absorptions. <sup>b</sup>Determined by ratio of respective integrated NMR absorptions. <sup>c</sup>Degree of polymerization calculated assuming equal probability of acetate and bridging ligand end group. <sup>d</sup>Number average molecular weight based on one acetate and one bridging ligand end group.

Table II. Dilute Viscosities<sup>a</sup> of Solution Synthesized  
Polymeric Dioxouranium Carboxylates

Bridging Ligand	Relative viscosity	Intrinsic viscosity (g/dL)
2,2-Dimethylsuccinate	1.015	0.10
2,2-Dimethylglutarate	1.018	0.12
3,3-Dimethylglutarate	1.019	0.13
2,2,6,6-Tetramethylpimelate	1.014	0.09
Thiodiglycolate	1.011	0.07
Maleate	1.016	0.11
Fumarate	1.022	0.14
Phthalate	1.020	0.13
Isophthalate	1.022	0.14
Acetylenedicarboxylate	1.011	0.07

<sup>a</sup>Viscosity data in NMP at 30.0 °C.



Table III. Calibration of GPC with Dioxouranium(VI)

3,3-dimethylglutarate Polymer

Ratio <sup>a</sup> uranyl acetate to bridging unit	$[\eta]_{in}^b$ (dL/g)	Acetate <sup>c</sup> to bridge unit	End <sup>d</sup> group	$\overline{dP}^e$	$\overline{dP}^f$	$M_n^g$	GPC <sup>h</sup> ; mL
1 to 1	0.13	1 to 24.0	0.50	48	50	12200	8.09(7.97)
1.05 to 1	0.10	1 to 14.7	0.75	22	23	5700	8.24(8.13)
1.1 to 1	0.06	1 to 7.5	0.85	13	15	3400	8.77(8.63)
1.2 to 1	0.04	1 to 3.9	0.91	7	9	1900	8.94(8.79)
1.4 to 1	0.02	1 to 1.5	0.95	5	5	1500	9.05(8.84)
2 to 1	0.013	1 to 1.0	0.98	3	3	860	9.14(9.00)

<sup>a</sup>Mole ratio of uranyl acetate to bridging ligand reactant used in a DMSO solution synthesis. <sup>b</sup>Intrinsic viscosity in NMP at 30.0 °C. <sup>c</sup>Ratio of acetate to bridging ligand in polymer as determined by NMR. <sup>d</sup>Probability of acetate end group based on the reactant ratio and an extent of reaction of 0.98. <sup>e</sup>Mean degree of polymerization based on the end group analysis. <sup>f</sup>Theoretical mean degree of polymerization based on the reactant ratio and an extent of reaction of 0.98. <sup>g</sup>Number average molecular weight based on the end group analysis. <sup>h</sup>Retention volume for the number average molecular weight; retention volume for the weight average molecular weight in parentheses.

Table IV. Energies of Infrared Asymmetric Carbonyl Absorption for Polymeric Dioxouranium(VI) Carboxylate Chelates and the Free Acids.

Bridging ligand	Coord. ( $\text{cm}^{-1}$ )	Free acid ( $\text{cm}^{-1}$ )
2,2-Dimethylsuccinate	1570	1700
2,2-Dimethylglutarate	1560	1720
3,3-Dimethylglutarate	1580	1700
2,2,6,6-Tetramethylpimelate	1575	1695
Thiodiglycolate	1630	1700
Maleate	1640	1705
Fumarate	1635	1690
Phthalate	1620	1700
Isophthalate	1620	1700
Terephthalate	1620	1680
Acetylenedicarboxylate	1620	1700

Table V. Thermal Gravimetric Analysis of Polymeric  
Dioxouranium(VI) Carboxylates

Bridging ligand (Solvation) <sup>a</sup>	Thermal behavior <sup>b</sup> , (°C)
2,2-Dimethylsuccinate(DMSO)	loss of DMSO: 270; decomp: 360
2,2-Dimethylglutarate(DMSO)	loss of DMSO and decomp: 240
3,3-Dimethylglutarate(DMSO)	loss of DMSO: 185, 260; decomp: 360
2,2,6,6-Tetramethylpimelate(DMSO)	loss of DMSO: 245; decomp: 430
Thiodiglycolate(2 DMSO)	loss of DMSO and decomp: 225
Thiodiglycolate(H <sub>2</sub> O)	loss of water: 100; decomp: 270
Maleate(1.75 DMSO)	loss of DMSO and decomp: 170
Fumarate(2 DMSO)	loss of DMSO: 165, 240; decomp: 370
Phthalate(2 DMSO)	loss of DMSO: 195, 295; decomp: 420
Isophthalate(1.25 DMSO)	loss of DMSO: 190, 300; decomp: 480
Terephthalate(2 DMSO)	loss of DMSO: 190, 275; decomp: 475
Acetylenedicarboxylate(H <sub>2</sub> O)	loss of water: 100; decomp: 160
Acetylenedicarboxylate (approx. 2 DMSO)	loss of DMSO and decomp: 185

<sup>a</sup>Solvation with DMSO indicates solution synthesized material;  
solvation with water indicates interfacially synthesized material.

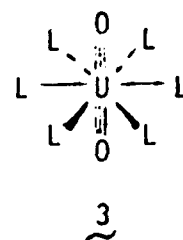
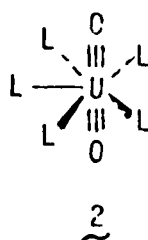
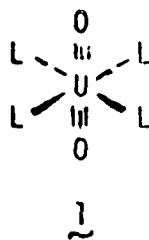
<sup>b</sup>Thermal behavior based on correspondence of observed weight loss to  
known material composition. TGA performed on a Perkin-Elmer TGS-2 with  
a temperature increase of 20 °C per minute.

Table VI. GPC Data for Polymeric Dioxouranium(VI) Carboxylates.

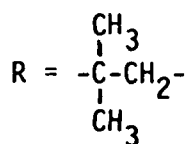
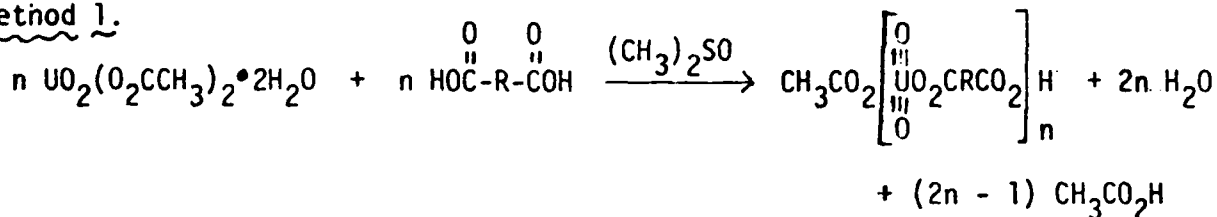
Bridging ligand and (solvating species)	Mean retention volume <sup>a</sup>	$\bar{M}_n^b$ (PS equivalent)	$\bar{M}_w^c$ retention volume (mL)	$\bar{M}_w^d$ (PS equivalent)
2,2-Dimethylsuccinate(DMSO)	7.65	5600	6.67	16000
2,2-Dimethylsuccinate(H <sub>2</sub> O) <sup>e, f</sup>	6.29	25000	5.82	40000
2,2-Dimethylsuccinate(H <sub>2</sub> O) <sup>g</sup>	7.77	4900	6.80	14000
2,2-Dimethylglutarate(DMSO) <sup>e</sup>	5.67	49000	5.32	68000
3,3-Dimethylglutarate(DMSO)	7.46	6900	6.70	16000
2,2,6,6-Tetramethylpimelate(DMSO) <sup>e</sup>	7.50	6500	5.90	38500
Thiodiglycolate(DMSO)	7.80	4800	7.30	8100
Thiodiglycolate(H <sub>2</sub> O)	8.26	2900	7.32	8000
Maleate(DMSO)	7.20	9300	6.33	23500
Fumarate(DMSO) <sup>e</sup>	6.25	26000	5.48	57000
Phthalate(DMSO)	7.40	7300	6.70	16000
Isophthalate(DMSO) <sup>e</sup>	5.83	41000	5.53	55000
Acetylenedicarboxylate(DMSO)	8.18	3200	7.42	7200
Acetylenedicarboxylate(H <sub>2</sub> O)	7.78	4900	7.02	11000

<sup>a</sup>Retention volume in mL on a 10<sup>3</sup> Angstrom Ultrastyrigel GPC column with NMP as the solvent. <sup>b</sup>Polystyrene equivalent number average molecular weight based on calibration with eleven standards.

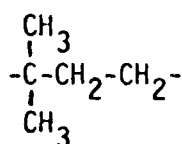
<sup>c</sup> $\bar{M}_w$  retention volumes are based on polystyrene retention times under comparable conditions. <sup>d</sup>Polystyrene equivalent weight average molecular weights. <sup>e</sup>The GPC curves for these species are quite non-ideal and the molecular weights calculated are less precise than the others; cf. the NMR results. <sup>f</sup>Precipitate formed at the interface in the best interfacial synthesis. <sup>g</sup>The soluble fraction of the same interfacial synthesis.



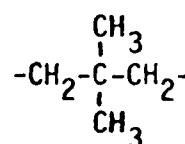
Method 1.



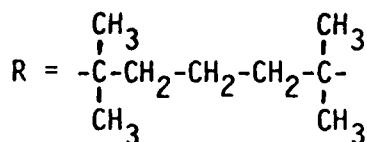
acid = dimethylsuccinic



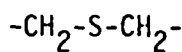
2,2-dimethylglutaric



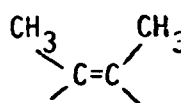
3,3-dimethylglutaric



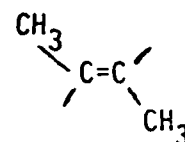
acid = tetramethylpimelic



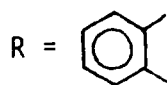
thiodiglycolic



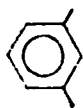
maleic



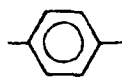
fumaric



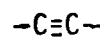
acid = phthalic



isophthalic

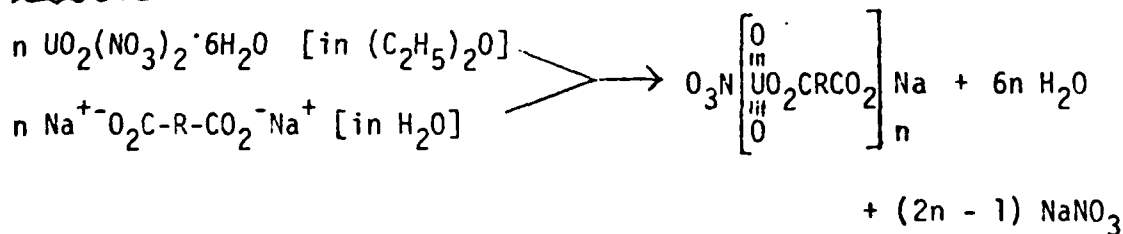


terephthalic



acetylenedicarboxylic

Method 2.



### CAPTIONS FOR FIGURES

Figure 1. Plot of inherent viscosity (NMP; 30°C) vs.  $\bar{M}_n$  of poly-[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)].

Figure 2. Plot of  $\log \bar{M}_n$  vs. GPC retention volume of poly[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)] in NMP.

Figure 3. Universal calibration curve plot of the  $\log (\eta_{in} \times M_n)$  vs. GPC retention volume for polystyrene standards ( $\blacktriangle$ ) and poly[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)] ( $\odot$ ).

Figure 4. Gel permeation chromatograms of poly[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)] with various mean degrees of polymerization.

Fig. 1

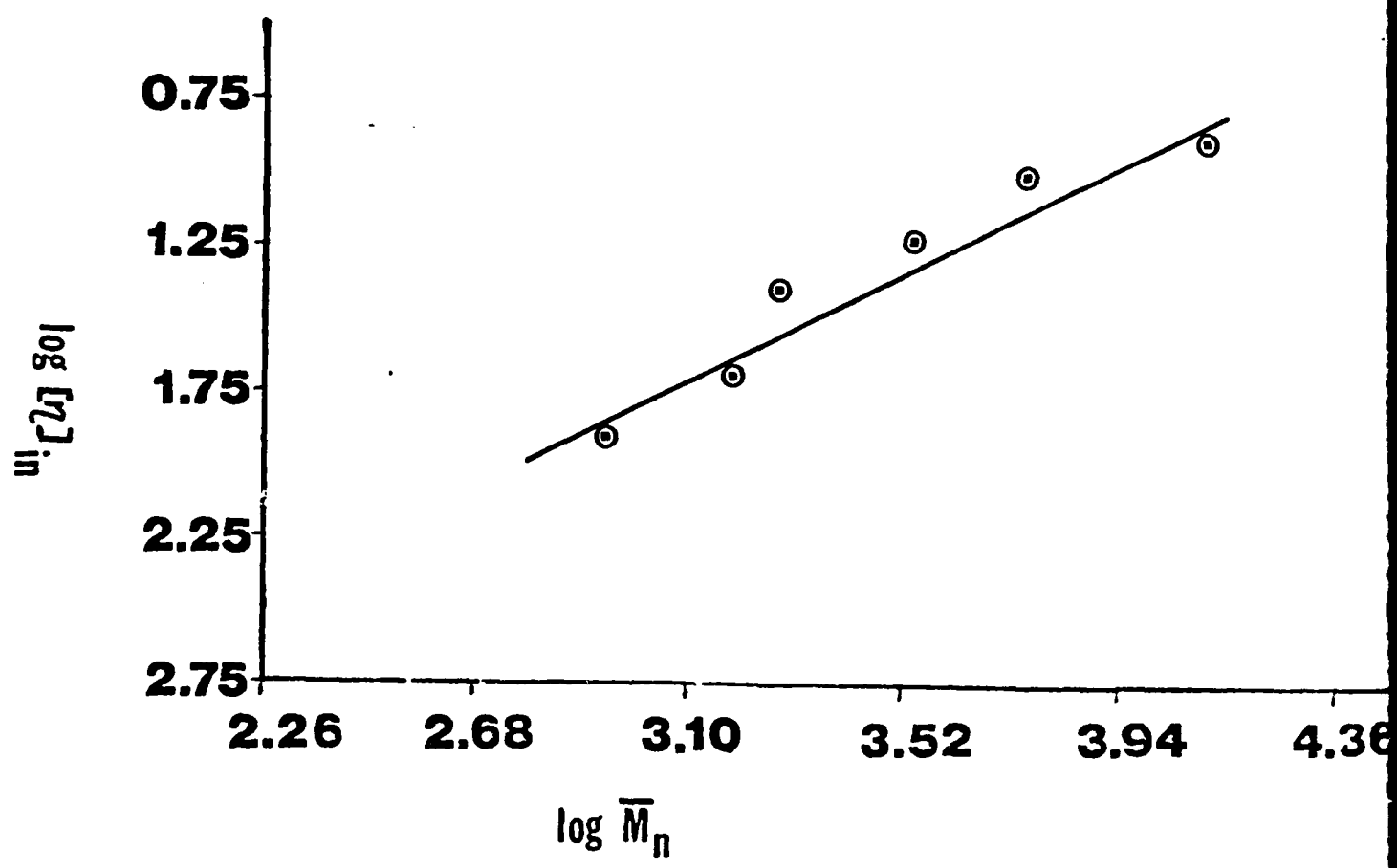


Fig. 1

Fig. 2

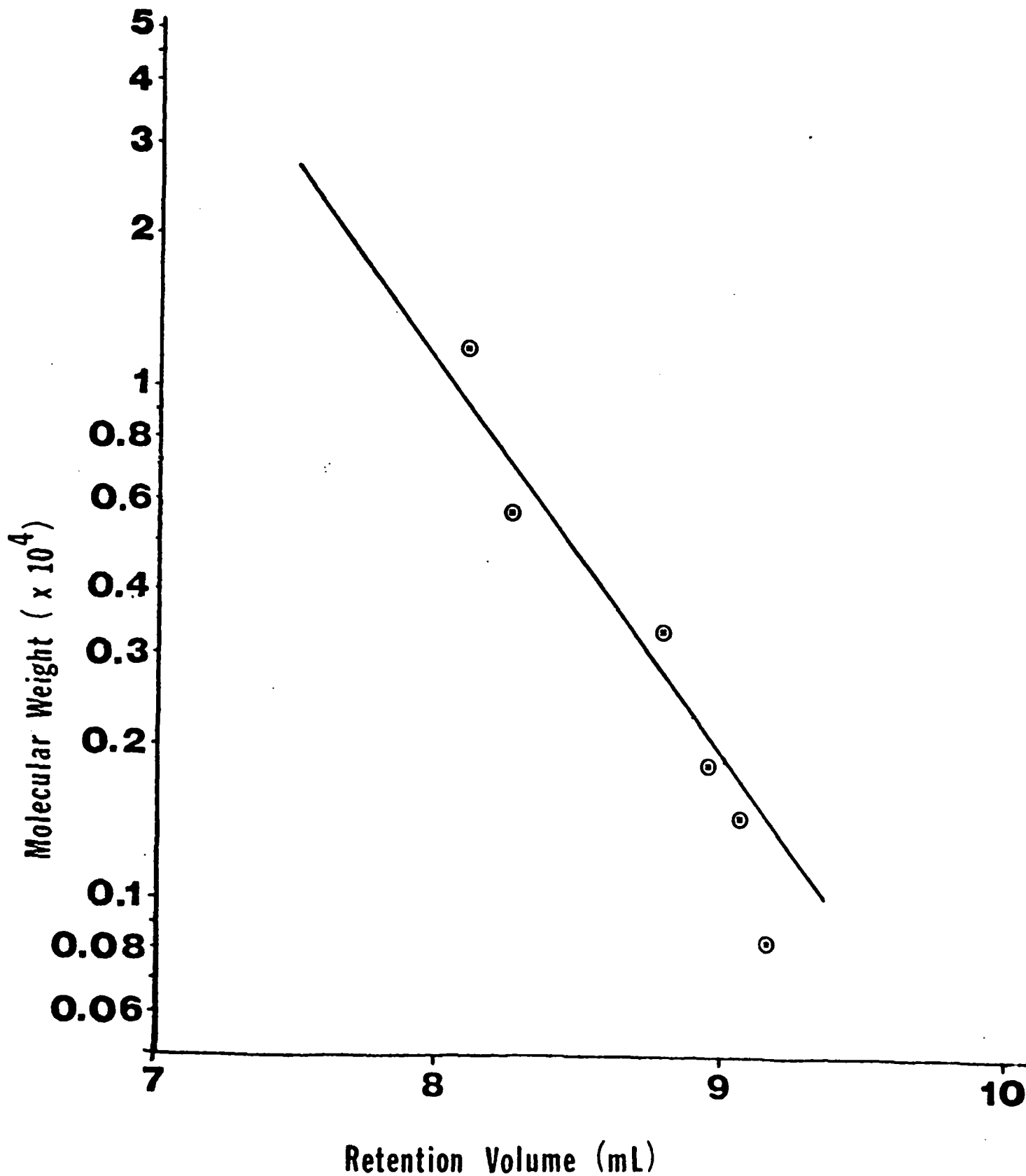


Fig. 2



Fig. 3

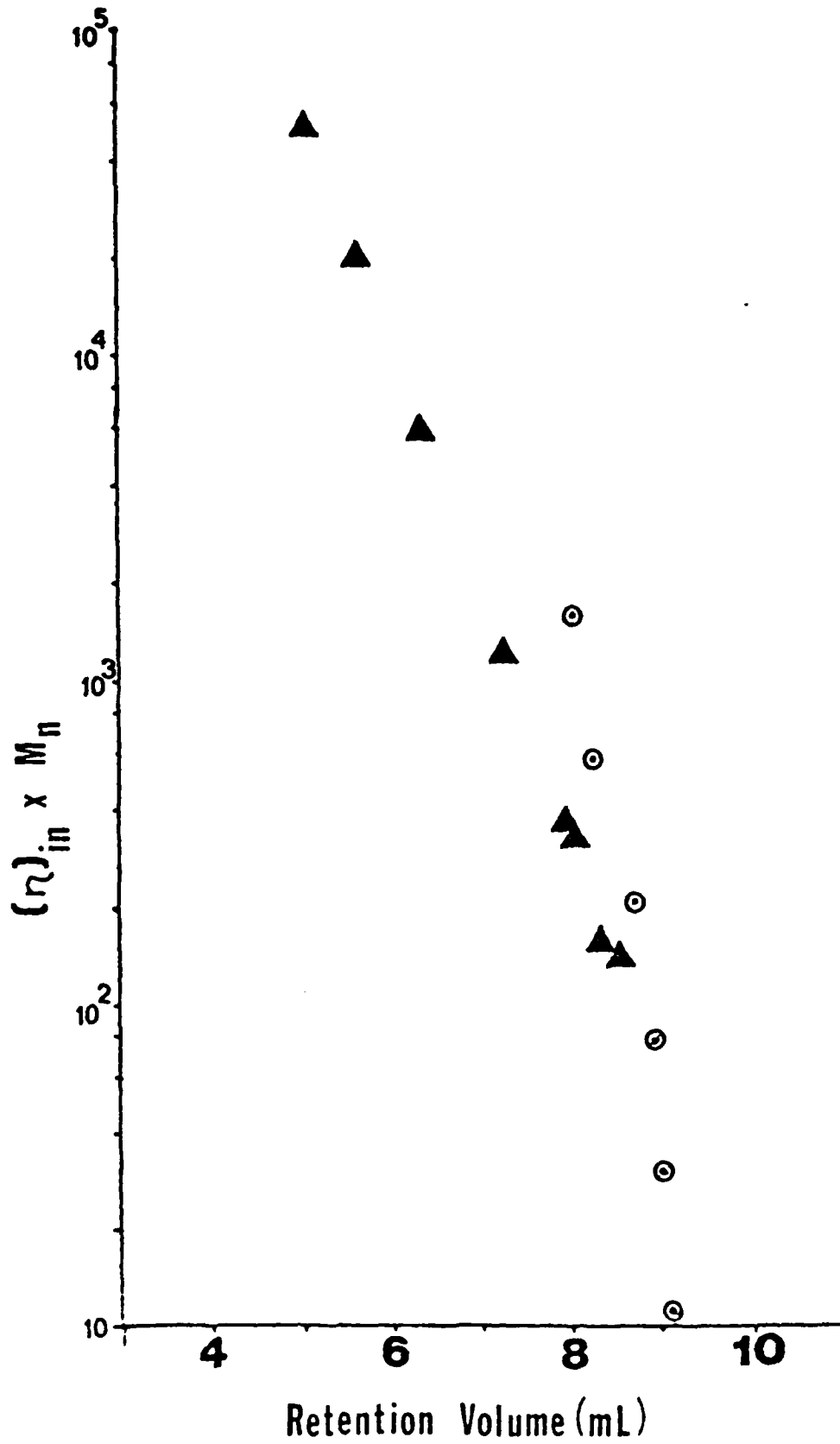


Fig. 3

Fig 4

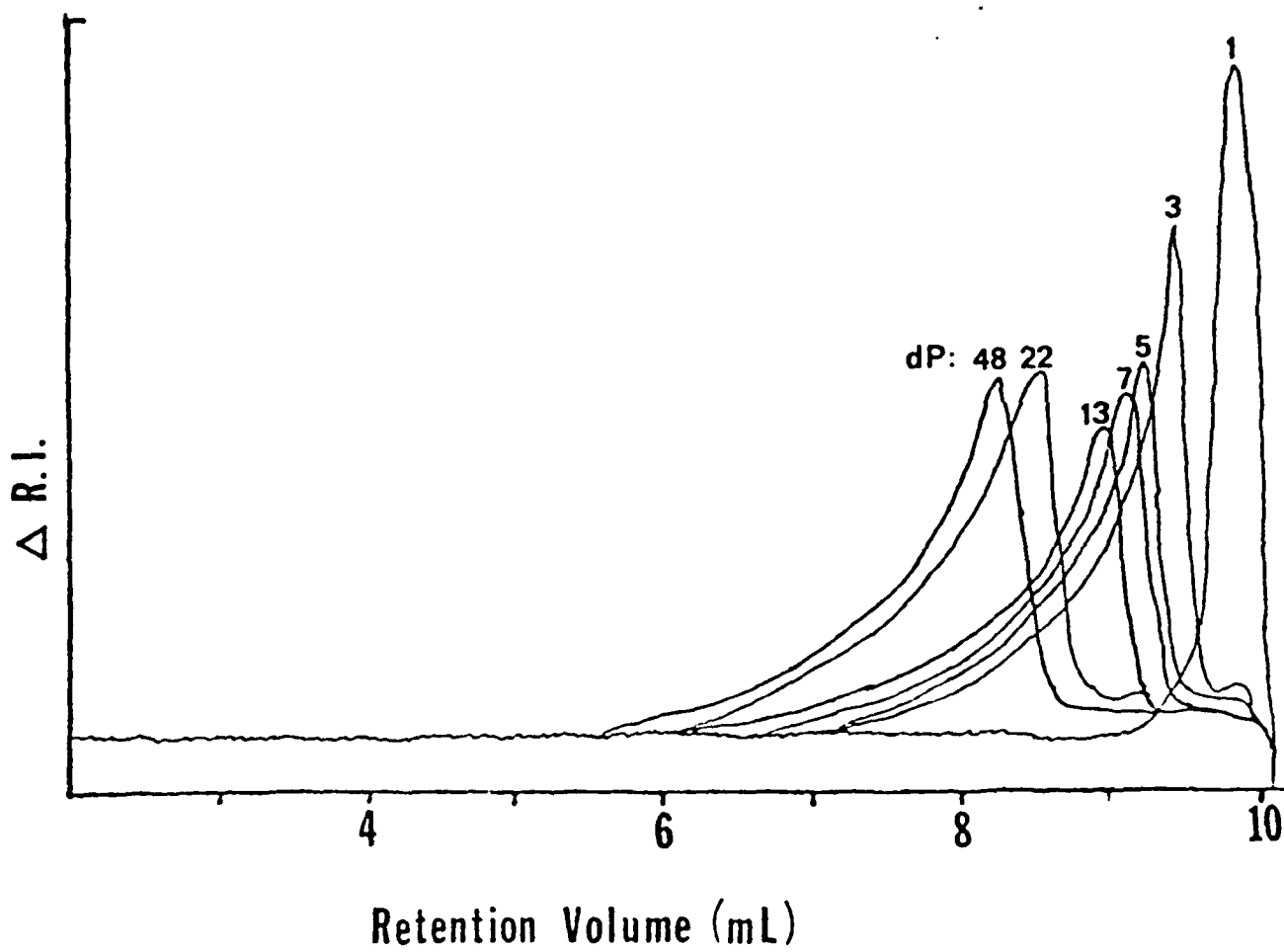


Fig. 4

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