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

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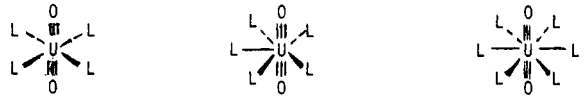
ABSTRACT: A series of polymeric bis(carboxylato)dioxouranium(VI) species have been synthesized via an equilibrium-controlled solution reaction where bis(acetato)dioxouranium(VI) dihydrate undergoes an acid interchange with a dicarboxylic acid. The solution synthesized species have number average molecular weights of up to 1.8×10^4 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 oxometal cation known.[1] The stereochemistry of dioxouranium(VI) compounds is derived from a basis of apical oxo ligands and an equatorial plane available to interact with four to six additional ligand donor atoms (L). This results in six, seven, and eight coordinate complexes of octahedral (1), pentagonal bipyramidal (2), and hexagonal bipyramidal (3) geometries, respectively.[2-4]



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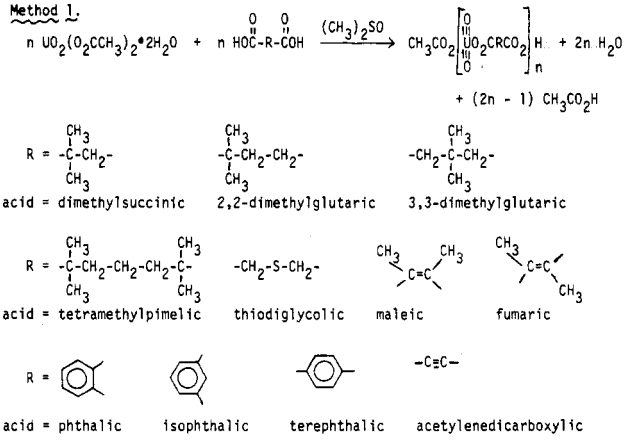
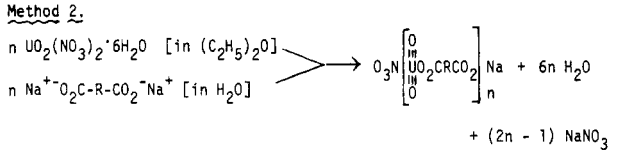
Most linear metal chelate polymers have been found to be intractable, and consequently, fundamental polymer properties, such as molecular weight, have been difficult to evaluate.[5-7] Coordination metal polymers containing dioxouranium(VI) centers generally appear to be more tractable materials.[8-15] Presumably this results from the disruption of interunit interactions by the apical oxo ligands. In addition, the tendency of uranium to extracoordination 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 extracoordinated species.[16-18] Despite the observation that certain dioxouranium(VI) coordination polymers are soluble in various aprotic donor solvents,[8-15] 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 sulfoxide and is driven to high conversion by removing acetic acid via



vacuum distillation 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.[8-15,19-21] **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 unusally high molecular weight condensation polymers,[22] but most of the materials we have prepared via this route are intractable and not subject to extensive characterization.



Experimental Section

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-tetramethylpimelic 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,

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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 & Jackson, was dried over calcium hydride under reflux conditions and distilled under vacuum.

Poly[(2,2-dimethylbutanedioato)(dimethyl sulfoxide)dioxouranium(VI)]. Two (2.0000) grams of 2,2-dimethylsuccinic acid (13.685 mmol) and 5.8053 g or uranyl acetate (13.687 mmol) were dissolved in 100 mL of dimethyl sulfoxide (Me_2SO). The solution was heated with a 45 °C oil bath, and the Me_2SO 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) gram of 2,2-dimethylglutaric acid (6.243 mmol) and 2.6484 g of uranyl acetate (6.244 mmol) were dissolved in 75 mL of Me_2SO. The solution was heated to 45 °C and Me_2SO 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 re-formed a yellow glass similar to the initial product. Elemental analysis of this material indicated that approximately 1.5 mol of Me_2SO was 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) gram of 3,3-dimethylglutaric acid (6.243 mmol) and 2.6484 g of uranyl acetate (6.244 mmol) were dissolved in 100 mL of Me_2SO. The solution was heated to 45 °C and Me_2SO 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 Me_2SO in a manner identical with the above preparation.

One-half (0.5000) gram of 3,3-dimethylglutaric acid (3.122 mmol) and 1.3904 g of uranyl acetate (3.278 mmol) 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 mmol) and 1.4566 g (3.434 mmol) 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 mmol) and 1.5890 g of uranyl acetate (3.746 mmol).

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 mmol) and 1.8539 g of uranyl acetate (4.371 mmol).

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 mmol) and 2.6484 g (6.244 mmol) 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, 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) gram of 2,2,6,6-tetramethylpimelic acid (2.312 mmol) and 0.9807 g uranyl acetate (2.312 mmol) were dissolved in 100 mL of Me_2SO. Gentle heat was required to completely dissolve the diacid. The solution was heated to 45 °C and Me_2SO 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[(2,2′-thiobis(acetato))bis(dimethyl sulfoxide)dioxouranium(VI)]. One (1.0000) gram of thiodiglycolic acid (6.660 mmol) and 2.8251 g of uranyl acetate (6.661 mmol) were dissolved in 100 mL of Me_2SO. The solution was heated to 45 °C, and Me_2SO was distilled under reduced pressure until no further solvent remained. The product residue was a clear pale-yellow glassy film deposited on the walls of the reaction vessel. The product was broken up into a powder and dried under reduced pressure, protected from light, at 100 °C for 15 h. The elemental analysis is consistent with 2 mol of Me_2SO being present for every mole of uranium, and the NMR spectra show that 2 mol of Me_2SO was present for a 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) grams of maleic acid (17.231 mmol) and 7.3092 g of uranyl acetate (17.233 mmol) were dissolved in 150 mL of Me_2SO. The mixture was stirred and, with gentle heating, formed a bright clear yellow solution. The solution was heated to 45 °C and Me_2SO 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 h. The elemental analysis is consistent with 1.75 mol of Me_2SO per mole of uranium, and the NMR spectra show there is 1.75 mol of Me_2SO 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) grams of fumaric acid (17.231 mmol) and 7.3092 g of uranyl acetate (17.233 mmol) were added to 150 mL of Me_2SO. The mixture was stirred and gentle heat applied until reagents were completely dissolved. The solution was heated to 45 °C and Me_2SO 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 mol of Me_2SO per mole of uranium, and the NMR spectra show an identical ratio of Me_2SO 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) gram of phthalic acid (6.019 mmol) and 2.5534 g of uranyl acetate (6.020 mmol) were dissolved in 100 mL of Me_2SO. The solution was heated to 45 °C and Me_2SO distilled under reduced pressure to dryness. The product stayed in solution until nearly all the solvent had been removed. As the last bit of Me_2SO 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 2 mol of Me_2SO per mole of uranium, and the NMR spectra show there is 2 mol of Me_2SO 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) gram of isophthalic acid (6.019 mmol) and 2.5534 g of uranyl acetate (6.020 mmol) were added to 150 mL of Me_2SO. The mixture was stirred and gentle heat was applied until both reagents were completely dissolved. The solution was heated to 45 °C and Me_2SO 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 powder. The product was dried at 100 °C under reduced pressure, protected from light, for 18 h. The elemental analysis is consistent with 1.25 mol of Me_2SO per mole of uranium, and the NMR spectra show that there is 1.25 mol of Me_2SO 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) gram of terephthalic acid (6.019 mmol) and 2.5534 g of uranyl acetate (6.020 mmol) were added to 150 mL of Me_2SO. The mixture was stirred and gentle heat applied until both reactants completely dissolved. The solution was heated to 45 °C and Me_2SO 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 2 mol of Me_2SO per mole of uranium, and the NMR spectra show that there is 2 mol of Me_2SO 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-butynedioato)bis(dimethyl sulfoxide)dioxouranium(VI)]. Initially 0.5892 g of acetylenedicarboxylic acid (5.166 mmol) and 2.0818 g of uranyl acetate (4.908 mmol) were added to 50 mL of Me_2SO. Both reactants readily dissolved to form a clear orange solution. The solution was heated to 45 °C and Me_2SO 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 fits of the elemental analysis data were achieved when one assumed that 2 mol of Me_2SO was present per mole of uranium.

Anal. Calcd for $[C_8H_{12}S_2O_8U]_n$: 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 millimoles 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 millimoles 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 re-formed 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 totaled 0.146 g, 6%. A substantial amount of material was unrecovered from the reactor surfaces.

Anal. Calcd for $[C_6H_{10}O_7U]_n$: 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 totaled 1.210 g, 51%.

Anal. Calcd for $[C_6H_{10}O_7U]_n$: C, 16.7; H, 2.3. Found: C, 13.5; H, 1.8.

Poly[(3,3-dimethylpentanedioato)(aquo)dioxouranium(VI)]. Two millimoles of 3,3-dimethylglutaric acid (0.3203 g) was dissolved in 50 mL of water along with 0.16 g of NaOH (4.0 mmol); 2.0 M NaOH was added dropwise until a neutral pH was achieved. Two millimoles 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 the dried at 100 °C under vacuum, protected from light, for 16 h; yield 0.511 g, 57%.

Anal. Calcd for $[C_7H_{12}O_7U]_n$: 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 millimoles 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 mmol). The mixture was stirred and gently heated until complete dissolution had occurred. NaOH (2.0 M) was added dropwise until a neutral pH was achieved. Two millimoles 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 mmol) was dissolved in 25.0 mL of 2.0 M NaOH. Additional NaOH solution was added dropwise to neutrality. Uranyl nitrate (12.5533 g, 25.000 mmol) 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 mmol) was added to 25.0 mL of 2.0 M NaOH. Additional NaOH solution was added dropwise to neutrality. Uranyl nitrate (12.5533 g, 25.000 mmol) 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 mmol) was dissolved in 25.0 mL of 2.0 M NaOH. Additional base was added dropwise to neutrality. Uranyl nitrate (12.553 g, 25.000 mmol) 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 mmol) was dissolved in 15 mL of deionized distilled water. NaOH (2.0 M) was added until neutrality was achieved. Uranyl nitrate (9.9507 g, 19.817 mmol) 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

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

bridging ligand (Me_2SO solvation)[a]	ratio acetate: bridging ligand[b]	dP[c]	M_n[d]
2,2-dimethylsuccinate(Me_2SO)	1:18	36	8900
2,2-dimethylglutarate(Me_2SO)	1:18	36	9300
3,3-dimethylglutarate(Me_2SO)	1:24	48	12200
2,2,6,6-tetramethylpimelate-(Me_2SO)	1:21	42	12400
thiodiglycolate($2Me_2SO$)	1:28	56	16200
maleate($1.75Me_2SO$)	1:8	16	4200
fumarate($2Me_2SO$)	1:24	48	13000
phthalate($2Me_2SO$)	1:30	60	17800
isophthalate($1.25Me_2SO$)	1:32	64	17100
terephthalate($2Me_2SO$)	1:26	52	15400

[a] Amount of Me_2SO solvation per bridging ligand determined by integration of respective NMR absorptions. [b] Determined by ratio of respective integrated NMR absorptions. [c] Degree of polymerization calculated assuming equal probability of acetate and bridging ligand end group. [d] Number average molecular weight based on one acetate and one bridging ligand end group.

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 200–4000 cm^{-1}. The samples were analyzed in a KBr glass.

Gel permeation chromatography was conducted on a 10^3-Å Ultrastyragel 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-μm PTFE membrane prior to use.

Nuclear magnetic resonance studies were conducted in Me_2SO-d_6 by using a Varian Model XL-300 spectrometer. Sample solutions were prepared by dissolving approximately 75 mg of polymer in 0.7 g of Me_2SO-d_6 with the aid of 1 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 No 75 capillary bore, equilibrated at 30.00 ± 0.02°. The solvent was NMP.

Thermal gravimetric analyses were conducted by 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 deg/min.

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 extracoordination invariably leads to strong retention of at least one solvent molecule per uranium in polymeric chelates where metal bridging is accomplished with dicarboxylates. By use of reaction solvents which contain a heteroatom, degrees of solvation can be easily estimated with elemental analysis. The degrees of Me_2SO solvation of the solution synthesized polymers are listed in Table I.

Table II
Dilute Viscosities[a] of Solution Synthesized Polymeric Dioxouranium Carboxylates

bridging ligand	viscosity: relative	viscosity: intrinsic, dL/g
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

[a] Viscosity data in NMP at 30.0 °C.

The *elemental analyses* indicate, after the degree of Me_2SO 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 discernible, 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 Me_2SO 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 by using Kraemer's approximation[23]

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

where $[\eta]_{inh}$ = inherent viscosity, c = concentration (in g/dL), t = time (in s).

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[24] 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 weights. 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 vs. 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[25]

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

Table III
Calibration of GPC with Dioxouranium(VI) 3,3-Dimethylglutarate Polymer

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

[a] Mole ratio of uranyl acetate to bridging ligand reactant used in a Me_2SO solution synthesis. [b] Intrinsic viscosity in NMP at 30.0 °C. [c] Ratio of acetate to bridging ligand in polymer as determined by NMR. [d] Probability of acetate end group based on the reactant ratio and an extent of reaction of 0.98. [e] Mean degree of polymerization based on the end group analysis. [f] Theoretical mean degree of polymerization based on the reactant ratio and an extent of reaction of 0.98. [g] Number average molecular weight based on the end group analysis. [h] Retention volume for the number average molecular weight; retention volume for the weight average molecular weight in parentheses.

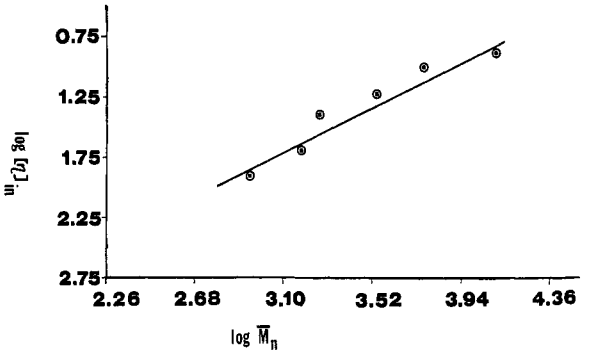

Figure 1. Plot of inherent viscosity (NMP; 30 °C) vs. $\bar{M}_n$ of poly[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)].

where r = Na/Nb = reactant mole ratio (Na < Nb) and 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 vs. monocomplexed bridging ligand, where

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

Infrared analyses show shifts in the carbonyl assymetric stretching frequency assigned to the bridging ligand to lower energies. Such shifts are characteristic of carboxylate–metal coordination.[26] 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 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.

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

bridging ligand	coord., cm^{-1}	free acid, 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)[a]	thermal behavior,[b] °C
2,2-dimethylsuccinate(Me_2SO)	loss of Me_2SO, 270; dec, 360
2,2-dimethylglutarate(Me_2SO)	loss of Me_2SO and dec, 240
3,3-dimethylglutarate(Me_2SO)	loss of Me_2SO, 185, 260; dec, 360
2,2,6,6-tetramethylpimelate-(Me_2SO)	loss of Me_2SO, 245; dec, 430
thiodiglycolate($2Me_2SO$)	loss of Me_2SO and dec, 225
thiodiglycolate(H_2O)	loss of H_2O, 100; dec, 270
maleate($1.75Me_2SO$)	loss of Me_2SO and dec, 170
fumarate($2Me_2SO$)	loss of Me_2SO, 165, 240; dec, 370
phthalate($2Me_2SO$)	loss of Me_2SO, 195, 295; dec, 420
isophthalate($1.25Me_2SO$)	loss of Me_2SO, 190, 300; dec, 480
terephthalate($2Me_2SO$)	loss of Me_2SO, 190, 275; dec, 475
acetylenedicarboxylate(H_2O)	loss of H_2O, 100; dec, 160
acetylenedicarboxylate (approx. $2Me_2SO$)	loss of Me_2SO and dec, 185

[a] Solvation with Me_2SO indicates solution synthesized material; solvation with water indicates interfacially synthesized material. [b] 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/min.

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 vs. retention volume as shown in Figure 2. Similarly, a plot of the product of the viscosities and the respective log molecular weight vs. 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.[7,27] The area of metal chelate polymers has been plagued with polymer intractability and low molecular

Table VI
GPC Data for Polymeric Dioxouranium(VI) Carboxylates

bridging ligand (solvating species)	mean retention vol[a]	$\bar{M}_n$,[b] (PS equiv)	$\bar{M}_w$[c] retention vol, mL	$\bar{M}_w$,[d] (PS equiv)
2,2-dimethylsuccinate(Me_2SO)	7.65	5600	6.67	16000
2,2-dimethylsuccinate(H_2O)[e,f]	6.29	25000	5.82	40000
2,2-dimethylsuccinate(H_2O)[g]	7.77	4900	6.80	14000
2,2-dimethylglutarate(Me_2SO)[e]	5.67	49000	5.32	68000
3,3-dimethylglutarate(Me_2SO)	7.46	6900	6.70	16000
2,2,6,6-tetramethylpimelate(Me_2SO)[e]	7.50	6500	5.90	38500
thiodiglycolate(Me_2SO)	7.80	4800	7.30	8100
thiodiglycolate(H_2O)	8.26	2900	7.32	8000
maleate(Me_2SO)	7.20	9300	6.33	23500
fumarate(Me_2SO)[e]	6.25	26000	5.48	57000
phthalate(Me_2SO)	7.40	7300	6.70	16000
isophthalate(Me_2SO)[e]	5.83	41000	5.53	55000
acetylenedicarboxylate(Me_2SO)	8.18	3200	7.42	7200
acetylenedicarboxylate(H_2O)	7.78	4900	7.02	11000

[a] Retention volume in mL on a 10^3-Å Ultrastyragel GPC column with NMP as the solvent. [b] Polystyrene equivalent number average molecular weight based on calibration with 11 standards. [c] $\bar{M}_w$ retention volumes are based on polystyrene retention times under comparable conditions. [d] Polystyrene equivalent weight average molecular weights. [e] The GPC curves for these species are quite nonideal, and the molecular weights calculated are less precise than the others, cf., the NMR results. [f] Precipitate formed at the interface in the best interfacial synthesis. [g] The soluble fraction of the same interfacial synthesis.

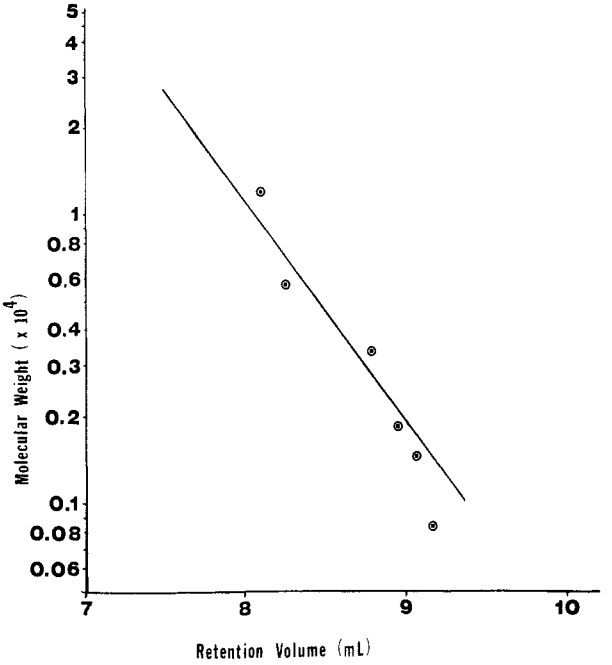

Figure 2. Plot of log $\bar{M}_n$ vs. GPC retention volume of poly-[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium-(VI)] in NMP.

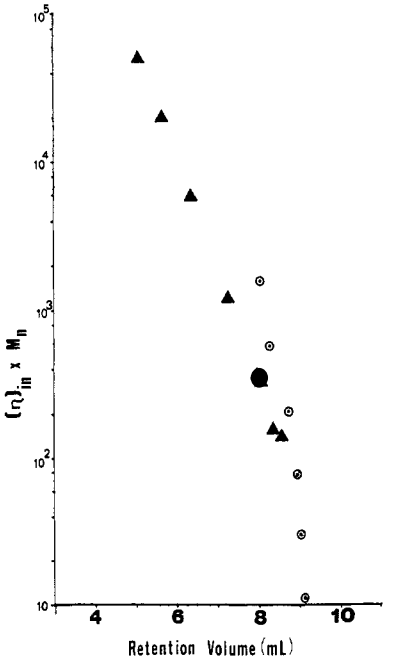

Figure 3. Universal calibration curve plot of the log ($\eta_{in}M_n$) vs. GPC retention volume for polystyrene standards (▲) and poly-[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium-(VI)] (⊙).

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.[28] 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 Me_2SO, which is known to be a good polymer solvent and to readily solvate dioxouranium(VI).[29] The steric bulk of Me_2SO appears to affect polymer tractability via the extracoordination of solvent by dioxouranium(VI). In fact we have found that all the aquo-solvated dioxouranium polymers are significantly less tractable than the corresponding Me_2SO solvates.[30]

The presence of a heteroatom in Me_2SO allows an assessment of the degree of solvation via elemental analysis. The amount of solvation is usually exactly 1 or 2 mol, or occassionally 1 and a fraction, of Me_2SO per uranium. The ratio of Me_2SO to the bridging ligand, which can be determined with NMR, is in agreement with the elemental analyses.[30] The TGA analyses reflect the high affinity of Me_2SO for uranium. Loss of 1 equiv of Me_2SO occurs at temperatures as high as 300 °C. Any solvation above 1 mol of Me_2SO per uranium is lost at or near the boiling point of Me_2SO.

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 the 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 by-products 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 assymetric stretch which are indicative of symmetrical carboxylate chelation.[26] The higher energy assymetric 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.[26] 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.[31]

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 vs. 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 g/dL 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 is plotted vs. the log of the respective inherent viscosities, a straight line is obtained. This finding is consistent with the Mark–Houwink relation[24] $[\eta] = KM^a$ 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.[32-34] This raises the intriguing possibility of new materials with unusual properties given the well-known photochemical and photocatalytic properties of dioxouranium(VI).[35-39]

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.[25] The evaluation of coordination polymers with SEC has seldom been accomplished.[40,41] Inorganic materials tend to suffer from secondary phenomena which exaggerate molecular size.[42] 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[30] (see Figure 4). This behavior suggests that large secondary effects are not inherent to the SEC of dioxouranium(VI) species.[42] However, secondary effects have been observed in several of the species reported here.

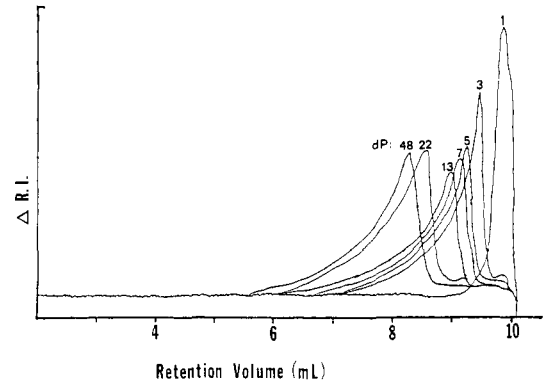

Figure 4. Gel permeation chromatograms of poly[(3,3-dimethylpentanedioato)(dimethyl sulfoxide)dioxouranium(VI)] with various mean degrees of polymerization.

A plot of SEC retention volume vs. 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 nonequilibrium-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 conformational 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 nonideal 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 tractability 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 γ radiation. We expect to report those results in the near future.

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Registry No. (2,2-Dimethylsuccinic acid)(uranyl acetate) (copolymer), 98971-90-5; (2,2-dimethylglutaric acid)(uranyl acetate) (copolymer), 98971-91-6; (3,3-dimethylglutaric acid)(uranyl acetate) (copolymer), 98971-92-7; (2,2,6,6-tetramethylpimelic acid)(uranyl acetate) (copolymer), 98971-93-8; (thiodiglycolic acid)(uranyl acetate) (copolymer), 98971-94-9; (uranyl acetate) (maleic acid) (copolymer), 98971-95-0; (uranyl acetate)(fumaric acid) (copolymer), 98971-96-1; (uranyl acetate) (phthalic acid) (copolymer), 98971-97-2; (uranyl acetate)(isophthalic acid) (copolymer), 98987-54-3; (uranyl acetate)(terephthalic acid) (copolymer), 98987-55-4; (acetylenedicarboxylic acid)(uranyl acetate) (copolymer), 98987-56-5; (2,2-dimethylsuccinic acid disodium salt)(uranyl nitrate) (copolymer), 107985-62-6; (3,3-dimethylglutaric acid disodium salt)(uranyl nitrate) (copolymer), 107985-64-8; (2,2,6,6-tetramethylpimelic acid disodium salt) (uranyl nitrate) (copolymer), 107985-66-0; (thiodiglycolic acid disodium salt)(uranyl nitrate) (copolymer), 107985-67-1; (maleic acid disodium salt)(uranyl nitrate) (copolymer), 107985-68-2; (fumaric acid disodium salt)(uranyl nitrate) (copolymer), 107985-69-3; (acetylenedicarboxylic acid disodium salt)(uranyl nitrate) (copolymer), 107985-70-6.

References and Notes

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 1015.
(2) Atoji, M.; McDermott, M. J. *Acta Crystallogr., Sect. B* **1970**, *B26*, 1540.
(3) Dewan, J. C.; Edwards, A. J.; Slim, D. R.; Guerchais, J. E.; Kergoat, R. *J. Chem. Soc., Dalton Trans.* **1975**, 2171.
(4) Reynolds, J. G.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1977**, *16*, 3357.
(5) Deshpande, U. G.; Shah, J. R. *J. Macromol. Sci.-Chem.* **1983**, *A20*, 355.
(6) Oh, J. S.; Bailar, J. C. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1225.
(7) Carraher, C. E., Jr.; Sheats, J. E.; Pittman, C. U., Jr. *Organometallic Polymers*; Academic: New York, 1978.
(8) Carraher, C. D., Jr.; Schroeder, J. A. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 215.
(9) Fenton, D. E.; Regan, C. M.; Casellato, U.; Vigato, P. A.; Vidali, M. *Inorg. Chim. Acta* **1982**, *58*, 83.
(10) Vigato, P. A.; Casellato, U.; Clemente, D. A.; Bandoli, G. *J. Inorg. Nucl. Chem.* **1973**, *35*, 4131.
(11) Barrientos, C.; Carbacho, H.; Contreras, J. G.f Lagos, G. *J. Inorg. Nucl. Chem.* **1978**, *40*, 926.
(12) Poddar, S. N.; Saha, N. *J. Indian Chem. Soc.* **1973**, *50*, 239.
(13) Irez, G.; Bekaroglu, O. *Synth. React. Inorg. Met. Org. Chem.* **1983**, *13*, 781.
(14) Degetto, S.; Baracco, L.; Faggin, M.; Celon, E. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2413.
(15) Battiston, G. A.; Degetto, S.; Sbrignadello, G.; Celon, E. *Gazz. Chim. It.* **1982**, *112*, 455.
(16) Toivonen, J.; Niinisto, L. *Inorg. Chem.* **1983**, *22*, 1557.
(17) Ruben, H.; Spencer, B.; Templeton, D.; Zalkin, A. *Inorg. Chem.* **1980**, *19*, 776.
(18) Serezhkin, V. N.; Soldatkina, M. A.; Trunov, V. K. *Koord. Khim.* **1981**, *7*, 1880.
(19) Maurya, P. A.; Agarwala, B. V.; Dey, A. K. *Indian J. Chem., Sect. A* **1978**, *16A*, 358.
(20) Cattalini, L.; Baracco, L.; Degetto, S.; Marangoni, G.; Maresca, L.; Sindellari, L *Gazz. Chim. It.* **1974**, *104*, 915.
(21) Nigam, H. L.; Pandeya, K. B.; Srivastava, P. C. *Curr. Sci.* **1971**, *40*, 600.
(22) Millich, F.; Carraher, C. E., Jr. *Interfacial Synthesis*; Marcel Dekker: New York, 1977.
(23) Kraemer, E. O. *Ind. Eng. Chem.* **1938**, *30*, 1200.
(24) Houwink, R. *J. Prakt. Chem.* **1940**, *157*, 15.
(25) Flory, P. J. *J. Am. Chem. Soc.* **1936**, *58*, 1877.
(26) Alcock, N. W.; Tracy, V. M.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1976**, 2238.
(27) Sheats, J. E.; Carraher, C. E., Jr.; Pittman, C. U., Jr. *Metal-Containing Polymeric Systems*; Plenum: New York, 1985.
(28) Glebov, V. A. *Koord. Khim.* **1982**, *8*, 1377.
(29) Lincoln. S. F. *Pure Appl. Chem.* **1979**, *51*, 2059.
(30) Hardiman, C. J. Ph.D. Dissertation, University of Massachusetts, Amherst, 1985.
(31) Lee, A. Y. Ph.D. Dissertation, University of Massachusetts, Amherst, 1986.
(32) Berry, G. C. *Contemporary Topics in Polymer Science*; Plenum: New York, 1977; Vol. 2, p 55.
(33) Kurata, M.; Tsunashima, Y.; Iwama, M.; Kamada, K. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975; p iv–1.
(34) Rabinowitch, E.; Belford, R. L. *Spectroscopy and Photochemistry of Uranyl Compounds*; Pergamon: New York, 1964.
(35) Noda, I.; Tsuge, T.; Nagasawa, M. *J. Phys. Chem.* **1970**, *74*, 710.
(36) Burrows, H. D.; Kemp, J. *Chem. Soc. Rev.* **1974**, *3*, 139.
(37) Greatorex, D.; Hill, R. J.; Kemp, T. J.; Stone, T. J. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 2059.
(38) Rehorek, D.; Puaux, J. P. *Radiochem. Radioanal. Lett.* **1982**, *52*, 29.
(39) Brittain, H. G.; Konteatis, Z.; Janusz, S.; Perry, D. L. *Inorg. Chem. Acta* **1981**, *51*, 39.
(40) Archer, R. D.; Illingsworth, M. L.; Rau, D. N.; Hardiman, C. J. *Macromolecules* **1985**, *18*, 1371.
(41) Pittman, C. U., Jr.; Hirao, A. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1677.
(42) Shibukawa, M.; Saito, M.; Kuroda, R. *Z. Anal. Chem.* **1984**, *319*, 410.

Possible Helical Shapes of the Polycarbonate Chain and Their Influence on the Unperturbed Dimensions

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ABSTRACT: The helical parameters corresponding to the various skeletal conformations of the bisphenol A polycarbonate chain have been calculated. Combining these results with the conformational energy calculations shows that both flat-helical and extended conformations are of equal energy for this chain. In addition, cyclic structures are also found to be stereochemically possible. The small values of the characteristic ratio of the unperturbed end-to-end distance and its temperature coefficient are attributed to the equal energy of the flat-helical and extended-helical, as well as the nonhelical, conformers.

Introduction

The analysis of the conformations accessible to a segment of the bisphenol A polycarbonate chain (BPAC) has been reported previously.[1,2] The schematic of the chain is shown in Figure 1. The preferred conformations of the carbonate group with respect to the contiguous phenyl moiety and those of contiguous phenyl groups with respect to each other were described.[1,2]

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