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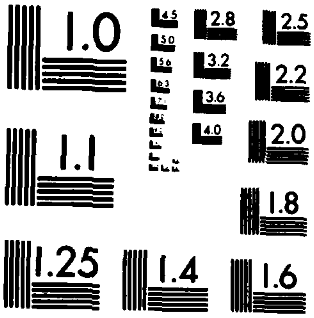

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Polymers containing metal ions can exhibit properties quite different from the parent polymers from which they are derived. Metal ions added to preformed polymers can produce marked property changes, especially when the metal modifies the polymer backbone, as is the case in some of the polymeric hydrazones we have been investigating. When polymer syntheses are designed to place the metal ion directly in the backbone, even more pronounced differences are possible. Classically, planar arrays with conjugated ligands were used for thermal stability but they tend to produce intractability and yield

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20 Abstract (continued)

only low molecular weight species. We are evaluating several methods which can minimize such intractability, including: 1) oxo metal ions, such as uranyl(VI); 2) bulky ligands, such as alkyl substituted ligands; and 3) nonrigid eight-coordinate centers, such as tungsten(IV).

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METAL-CHELATE POLYMERS: STRUCTURAL/PROPERTY RELATIONSHIPS AS A FUNCTION OF THE METAL ION

by

Ronald D. Archer, Christopher J. Hardiman,
Kong S. Kim, Edward R. Grandbois and Madeline Goldstein

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METAL-CHELATE POLYMERS: STRUCTURAL/PROPERTY RELATIONSHIPS AS A FUNCTION OF THE METAL ION

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INTRODUCTION

Metal ions chelated to preformed polymers can produce marked property changes, especially when the metal ion is bonded directly to the polymer backbone. Such metal-chelate polymers can show superior properties over their organic counterparts in certain applications,[1] although properties such as thermal stability are quite polymer and metal ion dependent.[2] A good example of improved thermal stability is provided by the zinc chelate of PTO; i.e., poly(terephthaloyloxalic-bis-amidrazone).[3,4] This metal-chelate polymer and many others are also good fire retardants. The existance of polymer-anchored metal catalysts is well documented, too.[1,5-11] However, superiority is not always the case. Brittleness and intractability are two properties often associated with metal-

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containing polymers.[12] We are attempting to modify polymers through metal ion chelation and to vary the metal ions therein, in order to learn more about how such chelation modifies the properties of the polymers. The polymeric hydrazones under investigation in our laboratory provide examples of the changes which are possible.

When the metal ion is a part of the backbone itself, even more drastic property changes are possible. However, intractibility is often very severe in such polymers. In order to overcome the intractibility problems, we are synthesizing ligands and polymers with

1) oxo metal ions,
2) bulky ligands, and/or
3) non-rigid coordination centers.

Our initial studies using the latter have already been published.[13] This paper notes our progress in obtaining oxo-metal ion polymers for film-forming applications. To date these studies have concentrated on uranyl polymers. Ligand syntheses related to the other two methods are also noted.

EXPERIMENTAL

Synthesis

Poly(terephthaloyloxalic-bis-amidrazone), PTO, was obtained commercially and poly(terephthaloylbutane-2,3-dihydrazone), PTBH, was synthesized from butane-2,3-dihydrazone and terephthaloyl chloride in dimethylacetamide with a triethylamine catalyst. Anal. Calcd for $C_{12}H_{12}N_4O_2$: C, 59.0; H, 4.9; N, 22.9. Calcd for

$C_{12}H_{12}N_4O_2\ H_2O$: C, 55.0; H, 5.3; N, 21.4. Found*: C, 56.5; H, 5.1; N, 21.5. For GPC of product see Fig. 1. The butanedihydrazone was synthesized by slowly adding a methanolic solution of 2,3-butanedione (diacetyl) to 64% aqueous hydrazine. The model ligand dibenzoylbutane-2,3-dihydra- zone was prepared from benzoyl chloride and butane-2,3-dihydrazone in an analogous manner.

The metallated chelate polymers of PTO and PTBH were synthesized for several metals from aqueous ammonia solutions of the metal salts and the respective polymer. For less labile metal ions, e.g., nickel(II), elevated temperature reactions under pressure were used to avoid the loss of ammonia and to obtain stoichiometric metal content. Although a few hours at room temperature suffices for metal ions as labile as zinc(II), longer time periods at 90^o are necessary for nickel(II). Chelation with PTBH requires longer times as the polymer is not swelled by concentrated aqueous ammonia like PTO. See Table 1.

Bis(8-quinolinol) was prepared by modifications of a published procedure of Bratz and von Niementowski.[14] A warm (40^o) solution of ferric sulfate (210 g [0.5 mol] in 1400 mL H_2O) was added rapidly to a 40^o solution of 8-quinolinol (70 g [0.5 mol] in 1400 mL H_2O). After 15 min of stirring, a NaOH solution (75.6 g in 700 mL H_2O was added over a period of an hour. After standing overnight, the black pasty material was filtered and dried. The paste was dissolved in 240 mL conc HCl and 320 mL glacial acetic acid via vigorous stirring and

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*Elemental analyses by the University of Massachusetts Microanalysis Laboratory.

Table 1. PTO and PTBH Metal Chelate Polymers[a]

Polymer	Metal Ion[b]	Temp.	Time	$[NH_3]$	Satn[c]
PTO	Zn^{++}	25°	1 da	6 M	100 %
		25°	1 da	15 M	100 %
		90°	2 hr	15 M	100 %
PTO	Ni^{++}	25°	2 da	6 M	80 %
		90°	2 hr	15 M	80 %
		90°	2 da	15 M	100 %
PTO	Cu^{++}	25°	4 da	15 M	100 %
PTO	Cd^{++}	25°	3 da	15 M	100 %
PTO	Pb^{++}	25°	3 da	15 M	75 %
PTBH	Zn^{++}	25°	1 da	15 M	70 %
		90°	2 da	15 M	100 %
PTBH	Ni^{++}	90°	3 da	15 M	95 %
PTBH	Cu^{++}	90°	3 da	15 M	55 %
PTBH	Cd^{++}	90°	3 da	15 M	75 %
PTBH	Pb^{++}	90°	3 da	15 M	100 %

[a] PTO = poly(terephthaloyloxalic-bis-amidrazone);
PTBH = poly(terephthaloylbutane-2,3-dihydrazone).
[b] Metal ions in 5 to 10 fold excess during reactions.
[c] Satn = % saturation for 1 metal ion/polymer unit.

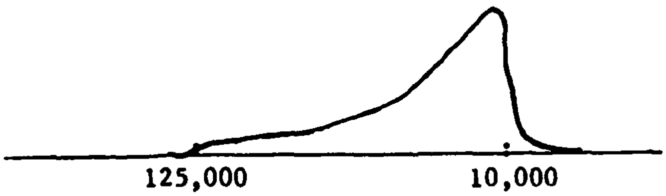


Fig. 1. GPC of PTBH vs polystyrene standards in NMP on Ultrastyragel

heating. Acetone (6.4 L) was used to precipitate the bright yellow dihydrochloride salt; yield, 22%. Addition of conc. aqueous ammonia to pH = 8 was followed by 1 hour stirring, filtering, washing with water, and drying in vacuo. Two recrystallizations from dimethylformamide, dissolution in HCl/H_2O and reprecipitation with conc. aqueous ammonia as before provided a yield of 12%. Anal. Calcd for $C_{18}H_{12}N_2O_2$: C, 75.0; H, 4.2; N, 9.7. Found: C, 74.7; H, 4.2; N, 9.8.

Bis(7-propyl-8-quinolinol) was prepared by treating 7-allyl-8-quinolinol[15] with two equivalents of p-toluenesulfonhydrazide[16] in diglyme under reflux conditions, precipitated with water, dissolved in CH_2cl_2, concentrated, ether added and HCl salt precipitated with HCl gas. The salt was dissolved in water, neutralized to pH = 7.6, extracted with ether, dried with Na_2SO_4, concentrated to dryness at room temperature, and distilled (126°/5 mm Hg). The alkyl quinolinol was obtained in a 73% yield and was oxidatively coupled by adding an ethanolic solution to a basic aqueous solution of $K_3Fe(CN)_6$. The coupled product, alternatively designated as 8,8'-dihydroxy-7,7'-dipropyl- 5,5'-biquinolyl, was obtained in a 21% yield after recrystallization from dimethylformamide. Anal. Calcd for $C_{24}H_{24}N_2O_2$: C, 77.4; H, 6.4; N, 7.5. Found: C, 76.8; H, 5.8; N, 7.5.

1,5-Diazaanthraquinone has been prepared through a simplified synthesis of a 1,5-diazaanthracene derivative. First, 2,6-dimethyl-1,2,3,4-tetrahydro-1,5-diazaanthracene-2,4,8-tricarboxylic acid was prepared from p-phenylenediamine and pyruvic acid according to the procedure of Giuliano and Stein;[17] yield, 39%. This compound was simultaneously decarboxylated and dehydrogenated with palladium on charcoal in 1,2,4-trichlorobenzene under reflux for three hours. The crude 2,6—dimethyl-1,5-diazaanthracene was heated with concentrated nitric acid for seven hours. Upon cooling, 1,5-diazaanthraquinone-2,6-di-carboxylic acid crystallized as the dihydrate, yield, 14%. After removing the water of hydration, this diacid was decarboxylated by mixing it with twice its weight of calcium oxide and then heating the mixture rapidly in an evacuated sublimator. After one crystallization of the sublimate, 1,5-diazaanthraquinone was obtained as yellow/brown flakes; yield 15%, net yield overall, 1%. Anal. Calcd. for $C_{12}H_6N_2O_2$: C, 68.6; H, 2.9; N, 13.3. Found: C, 68.2; H, 3.0; N, 13.2.

Uranyl polymers have been synthesized through solution reactions as follows: A donor solvent such as dimethyl sulfoxide (DMSO) was used to dissolve stoichiometric quantities of a bridging ligand and uranyl acetate dihydrate. Typically, 100 mL of DMSO is sufficient for a one gram reaction. The DMSO/acetic acid azeotrope was distilled from the solution in vacuo using a minimum amount of heat and then taken to dryness. The progress of the reaction was monitored via NMR examination of the distillate. Drying the product overnight at 100° in vacuo typically gave analyses consistent with one to two moles DMSO per mole of the uranyl cation. See Table 2.

Uranyl polymers have also been synthesized interfacially based on the work of Carraher and Schroeder.[18] Initially, 0.02 mol of an appropriate bridging ligand, such as a dicarboxylic acid, was added to 100 mL of water, neutralized with a quantitative amount of NaOH, and placed in a high-speed blender. A solution of 0.02 mol uranyl

Table 2. Uranyl Polymers of Dicarboxylic Acids

Ligand	M_n[a]	Empirical Formula/Analyses
2,2-Dimethylsuccinate[b]	7,000	$\mathrm{UO_2[O_2CC(CH_3)_2CH_2CO_2](C_2H_6SO)}$ Calcd: C, 19.5; H, 2.9; S, 6.5; U, 48.4 Found: C, 19.6; H, 2.9; S, 6.6; U, 48.3
2,2-Dimethylglutarate	30,000	$\mathrm{UO_2[O_2CC(CH_3)_2CH_2CH_2CO_2](C_2H_6SO)}$ Calcd: C, 21.4; H, 3.2; S, 6.3; U, 47.0 Found: C, 21.4; H, 3.2; S, 6.9; U, 46.1
3,3-Dimethylglutarate	10,000	$\mathrm{UO_2[O_2CCH_2C(CH_3)_2CH_2CO_2](C_2H_6SO)}$ Calcd: 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
2,2,6,6-Tetramethylpimelate[c]	6,000	$\mathrm{UO_2[O_2C(CH_3)_2(CH_2)_3C(CH_3)_2CO_2](C_2H_6SO)}$ Calcd: 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
Thiodiglycolate	4,000	$\mathrm{UO_2(O_2CCH_2SCH_2CO_2)(C_2H_6SO)_{1.5}}$ Calcd: C, 15.7; H, 2.5; S, 15.0 Found: C, 16.0; H, 2.6; S, 15.1
Maleate	8,000	$\mathrm{UO_2(\underline{cis}\text{-}O_2CCH{=}CHCO_2)(C_2H_6SO)_{1.75}}$ Calcd: C, 17.3; H, 2.3; S, 10.8; U, 45.8 Found: C, 17.5; H, 2.5; S, 10.5; U, 45.4
Fumarate	10,000	$\mathrm{UO_2(\underline{trans}\text{-}O_2CCH{=}CHCO_2)(C_2H_6SO)_2}$ Calcd: 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
Phthalate	10,000	$\mathrm{UO_2(\underline{o}\text{-}O_2CC_6H_4CO_2)(C_2H_6SO)_2}$ Calcd: 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
Isophthalate	lim solb	$\mathrm{UO_2(\underline{m}\text{-}O_2CC_6H_4CO_2)(C_2H_6SO)_{1.25}}$ Calcd: 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
Terephthalate	insolb	$\mathrm{UO_2(\underline{p}\text{-}O_2CC_6H_4CO_2)(C_2H_6SO)_2}$ Calcd: 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
Acetylenedicarboxylate	6,000	$\mathrm{UO_2(O_2CC{\equiv}CCO_2)(C_5H_9NO)_{1.75}}$ Calcd: C, 27.6; H, 2.9; N, 4.4; U, 42.8 Found: C, 26.9; H, 3.5; N, 4.6; U, 44.4

[a–c] Footnotes at the top of the next page

Table 2. (continued)

[a] M_n values based on GPC & viscosity in NMP relative to polystyrene.

[b] The uranyl polymer of dimethylsuccinate was also synthesized in pyridine (the monopyridine product requires N, 2.8; found: N, 2.5) and interfacially (the diaqua product requires C, 16.0; H, 2.7; found: C, 15.8; H, 2.1).

[c] The uranyl polymer of tetramethylpimelate was also synthesized in pyridine (the monopyridine product requires N, 2.5; found: N, 2.4) (the diaqua product requires C, 25.4; H, 4.3; found: C, 25.8; H, 3.9).

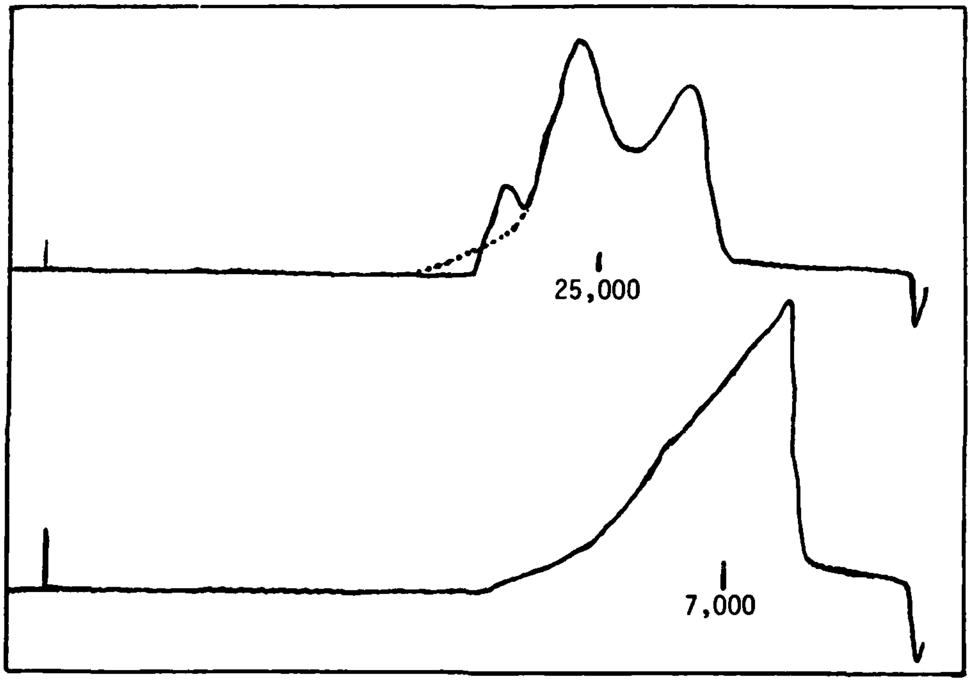


Fig. 2. GPC spectra (in NMP on 10^3 A Ultrastyragel) of UO_2(2,2-dimethylsuccinate)$\cdot 2H_2O$ polymer isolated during an interfacial polymerization. The Upper curve is the precipitate formed at the interface during the polymerization (M_n ca. 25,000 vs. polystyrene). The dotted line represents an estimate for the polymer which exceeds the exclusion limit of the column. The Lower curve represents the precipitate which occurs from the aqueous layer upon cooling (M_n ca. 7,000 vs. polystyrene).

nitrate hexa- hydrate in diethyl ether was also placed in the blender and the two phase system was mixed at high velocity for 30 seconds and the product was filtered from the solution. Drying overnight at 100° *in vacuo* typically provided analyses consistent with diaquo species.

Properties

Standard methods were used for all studies. Of particular note are the gel permeation studies of the uranyl polymers. Since they are generally insoluble in tetrahydrofuran, the usual solvent of choice, the polymers could not be easily studied until the recent availability of columns compatible with N-methyl-2-pyrrolidone (NMP) (Ultrastyragel/Waters).

RESULTS AND DISCUSSION

PTO and PTBH Polymers

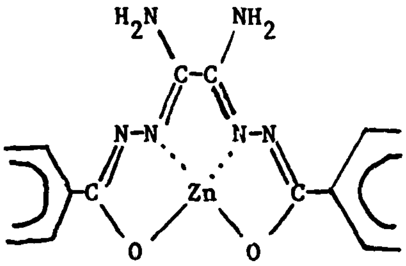
Metallated PTO polymers show that extreme differences in behavior which can result from the direct attachment of metal ions directly onto a polymeric backbone. Whereas the zinc derivative is appreciably more thermally stable than the parent polymer,[2,3] we find that the nickel(II) and copper(II) derivatives are less thermally stable than the parent polymer. See Table 3. This modification thermal stability is dependent on saturation of the polymer by the metal ion; e.g., Frank and coworkers[19] have claimed no enhanced stability for the zinc PTO derivative, in direct opposition to the results of van Krevelen[2] and ourselves. Similarly, the mechanical properties of the zinc PTO derivative are excellent, but the nickel-

Table 3. Decomposition Temperatures for PTO and PTBH Metal Polymers

Polymer	Metal-free	Zn(II)	Ni(II)	Cu(II)	Cd(II)	Pb(II)
PTO	325°C	500°	300°	300°	450°	unsatd
PTBH	290°C	350°	330°	unsatd	unsatd	340°

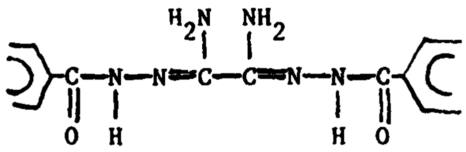
[a]unsatd = unsaturated.

(II) derivative is very brittle after annealing at 100° for the normal drying period of several hours. One potential bonding mode for the zinc PTO derivative is shown in structure 1.



1

Note that the coordination of zinc to four of the donor atoms leaves four other nitrogen donors free as potential crosslinking sites. Our choice of 1 as the mode of coordination is based on the loss of carbonyl stretching transitions in the infrared upon coordination of zinc, and the other metal ions as well. The mode of coordination had been in dispute previously,[2,3,19,20] although Frank *et al.*[19] had come to a similar conclusion. The electronic spectra of the metallate PTO species show large bathochromic (red) shifts as expected for a more conjugated system. The parent polymer backbone of PTO ,2, lacks total conjugation.



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The brittleness of nickel(II) derivative coupled with the knowledge *that nickel(II) is often six-coordinate* led us to synthesize the PTBH polymer, in which the amine groups in 1 are replaced with methyl groups. We felt that this substitution should minimize the crosslinking possibilities for the nickel ions. To our surprise, the nickel(II) derivative is once again appreciably less stable than the analogous zinc derivative. The stability of the nickel derivative relative to the parent polymer appears to be dependent on the stoichiometry of the product. Again the copper(II) derivative is similar in stability to the nickel species. Cadmium and lead derivatives, even when not fully stoichiometric, are better than the transition elements. Together these results suggest the rigid stereochemistry of the partially filled *d* level ions (tetragonal planar for four coordination for these types of ligands) causes the rigidity. The d^{10} ions have no favored angles (although ligand donor donor atom repulsions favor movement toward a tetrahedron). The lower thermal stability was unexpected, but as noted by Carraher,[18] each system of chelated polymeric materials appears different.

Bridging Ligands

Conjugated bridging ligands have been synthesized in order to prepare thermally stable metal chelate polymers which might show electron transport properties. 5,5'-Bis(8-quinolinol) is difficult to obtain pure. The coupling reaction involves iron(III), which stays coordinated except in strongly acidic or basic media. Unfortunately, after being purified by sequential treatment with acid and then base, the product exhibited low solubility and was difficult to use in polymer synthesis. However, it is known that alkyl substitution often increases the solubility of 8-quinolinol derivatives quite markedly, and 5,5'-bis(7-propyl-8-quinolinol) is no exception. Its solubility is much greater than the non-alkyl substituted species. Although we had hoped to oxidize these to quinone forms so we could oxidize and polymerize tungsten(II) precursors as we had done with quinoxaline-5,8-dione,[13] such oxidations have been unsuccessful to date. An alternative ligand, 1,5-diaza-anthra-9,10-quinone, has been synthesized for analogous purposes. The synthesis is much improved over the literature procedure for its precursor, 1,5-diazaanthracene.[21] The earlier procedure has several more steps and an even poorer yield. The reaction of the quinone with $W(CO)_3(PPh_3)_2Cl_2$ is negligible thermally, but photochemical activation allows some product formation, although the details have not been worked out as yet. Thus, although the oxidizing ability of diazaanthraquinone is appreciably less than that of quinoxalinedione, photochemical activation may allow its use in successful polymer synthesis.

Uranyl Polymers

Polymeric species with the metal ions directly in the backbone can alter the polymer properties significantly, even when cross-linking is not taking place. To minimize chain stacking forces, we are using the dioxouranate(VI) ion. We have synthesized a wide variety of amorphous, film-forming, uranyl dicarboxylate polymers. On the other hand, Beilstein[22] lists a large number of metal derivatives of 2,2-dimethylsuccinic acid, maleic acid, and fumaric acid as crystalline. Although fewer derivatives of the other acids have been listed,[23] in general, the metal ion derivatives of the dicaroxylates have been isolated as micro-crystalline species. Our success in producing non-crystalline polymers may be related to the careful control of stoichiometry in the solution polymerizations of the diacids with uranyl acetate (equation 1) in polar solvents.

$$UO_2(C_2H_3O_2)_2 + HOOC\text{-}R\text{-}COOH \longrightarrow [UO_2(OOC\text{-}R\text{-}COO)]_n + 2\ HC_2H_3O_2 \qquad (1)$$

The acetic acid is removed *in vacuo* to drive reaction 1 to the right. Although we have had some success in pyridine, DMSO appears to be the solvent of choice in most cases. The sulfur analysis provides unambiguous evidence for the degree of solvation in the products. Pyridine can be similarly analyzed for nitrogen, but the lower solubilities of the polymers in pyridine causes precipitation before adequate chain lengths had been obtained. The amorphous nature of the products is probably aided by the dioxouranate(VI) ion, which interacts strongly with the carboxylates, and even crosslinks in the absence of coordinating solvents, but has enough bulk to minimize chain interactions. The number-average molecular weights of the uranyl polymers relative to polystyrene range from 4000 to 30,000, consistent with expectations for step-growth condensation polymerizations which are stoichiometrically limited. Ligand purity varied from acid to acid, and the thiodiglycolic was the poorest in quality.

Interfacial polymerizations, as in equation 2, have also been used, where the uranyl nitrate, dissolved in diethyl ether, and the disodium salt of the diacid, dissolved in water, were stirred together at high speeds for up to 30 seconds.

$$UO_2(NO_3)_2 + {}^{-}OOC\text{-}R\text{-}COO^{-} \longrightarrow [UO_2(OOC\text{-}R\text{-}COO)]_n + 2\ NO_3^{-} \qquad (2)$$

The procedure is analogous to that used by Carraher and Schroeder.[18] Molecular weight improvement occurred by interfacial synthetic procedures for 2,2-dimethylsuccinate. However, the lower solubility of the product and the necessity of finding the proper concentration conditions for enhanced molecular weights, not necessarily stoichiometric, caused us to continue with solution polymerizations for most of our studies.

Infrared spectra are consistent with coordinated carboxylate with very weak bands due to uncoordinated carbonate occasionally observed at intensities low enough to suggest that the molecular weight estimates are real. In other samples weak methyl NMR signals suggest acetate end groups.

These yellow polymers display good glass adhesion and are being evaluated for radiation sensitivity for lithography. Preliminary results are very encouraging.

Conclusion

Overall, the prospects for significant improvements in polymers through the appropriate incorporation of metal ions is evident. The properties of such polymers are very metal-ion dependent. Minor changes in metal ion content can also make significant differences in the resulting properties of the polymeric materials produced. Modification of the coordination sphere of a given metal provides another pathway to property modification that remains to be explored.

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REFERENCES

1. J. E. Sheats, Kirk-Othmer Ency. Chem. Tech., 3rd ed., 15, 184 (1981).

2. C. E. Carraher, Jr., J. Macromol. Sci.-Chem. A17, 1293 (1982).

3. D. W. van Krevelen, Chem. and Ind., 49, 1396 (1971); Angew. makromol. Chem., 22, 133 (1972).

4. Anon., Textile Progr., 8, 124, 156 (1976).

5. C. U. Pittman, Jr., "Polymer-Supported Reactions in Organic Synthesis (P. Hodge and D. C. Sherrington, Eds.), Wiley, New York, 1980, Chpt.5.

6. C. Carlini and G. Sbrana, J. Macromol. Sci.-Chem., A16, 323 (1981).

7. D. W. Slocum, B. Conway, M. Hodgman, K. Kuchel, M. Moronski, R. Nobel, K. Webber, S. Duraj, A. Siegel, and D. A. Owen, J. Macromol. Sci.-Chem., A16, 357, (1981).

8. Y. Chauvin, D. Commereuc and F. Dawans, Progr. Polym. Sci., 5, 95 (1977).

9. J. P. Collman and L. S. Hegedus, "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley, CA, 1980, p. 370.

10. F. R. Hartley and P. N. Vezey, Adv. Organomet. Chem., 15, 189 (1977).

11. J. C. Bailar, Jr., Catal. Rev.-Sci. Eng. 10, 17, (1974).

12. J. C. Bailar, Jr., "Organometallic Polymers" (C. E. Carraher, Jr., J. E. Sheats, and C. U. Pittman, Jr., Eds.) Academic Press, N. Y., 1978, p. 313.

13. R. D. Archer, W. H. Batschelet and M. L. Illingsworth, J. Macromol. Sci.-Chem., A16, 261 (1981).

14. L. T. Bratz and S. von Niementowski, Ber., 52B, 189 (1919).

15. B. Mander-Jones and V. M. Trikojus, J. Proc. Roy. Soc. N. S. Wales, 66, 300 (1932).

16. R. S. Dewey and E. E. vanTamelin, J. Am. Chem. Soc., 83, 3729 (1961).

17. R. Giuliano and M. L. Stein, Gazz. Chim. Ital., 84, 284 (1954).

18. C. E. Carraher, Jr. and J. A. Schroeder, J. Polym. Sic. Polym. Lett. Ed., 13, 215 (1975).

19, V. D. Frank, W. Dietrich, J. Dehnke, A. Kobook, G. Schuch and M. Wallrahe, Angew. Makromol. Chem., 40, 445 (1974).

20. D. W. van Krevelen, Chem. Eng. Tech., 47, 793 (1975).

21. P. Ruggli and E. Preiswerk, Helv. Chem. Acta, 22, 478 (1939).

22. Beilstein, II, 662, 740, 751 (and analogous pages in suppl. 1 - 4).

23. Beilstein, II, 677, 684, 728, 802 (and analogous pages in suppl. 1 - 4).

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