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Synthesis and Characterization of Antimony (V) Polyoximes

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Synthesis and Characterization of Antimony (V) Polyoximes

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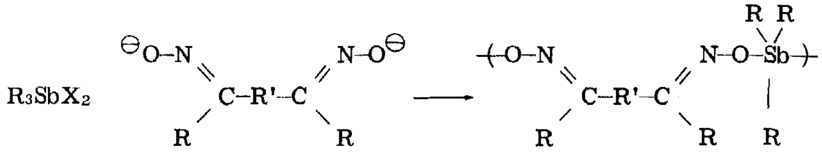
ABSTRACT

Antimony (V) polyoximes were synthesized by utilizing the interfacial technique. Reaction occurs only over the limited pH range of 11-13. Yield reaches a plateau after about 180 sec stirring time, with product chain length decreasing with increasing stirring time. The products exhibit low LVN/$\overline{M}_w$ ratios, probably due to a combination of factors including chain stiffness, poor solubility, and presence of the metal atom. Thermal degradation occurs above 300°C through the oxidative route(s) in air. The products exhibit only moderate thermal stability.

INTRODUCTION

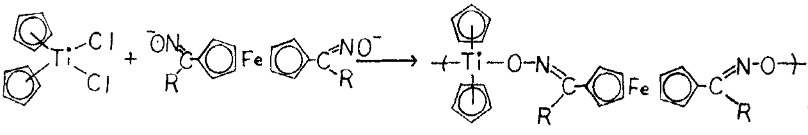
We have just begun the synthesis of polymers containing Group VA elements as an extension of our continuing efforts of synthesis of organometallic polymers. Here we present the initial synthesis of antimony (V) polyoximes of form I.



I (1)

Our reasons for desiring the synthesis of products of form I include synthesis of antimony-containing polymers for biological testing. Most antimony-containing products exhibit some biological activity. Antimony potassium and sodium tartrate, stibophen, sodium antimonyl gluconate, and sodium α,α-dimercaptosuccinate are used to control filariasis, leishmaniasis, and schistosomiasis [1, 2]. Their high toxicity is a disadvantage to human applications. Formation of a mixed chelate of antimony sodium tartrate with penicillamine gives a considerably less toxic material that retains its antiparasitic action in schistosomiasis [3]. Inclusion of organic antimonials by polar bond connections which are potentially biologically hydrolyzable could result in the synthesis of medically useful control release agents.

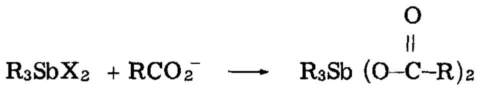
Second, there has been only one other reported utilization of dioximes in the synthesis of polymers. Carraher and Christensen [4] reported the synthesis of titanium-containing polyferroceneoximes utilizing the interfacial technique of polycondensation [Eq. (2)]. The present work is intended to further illustrate the use of oximes as Lewis bases in polycondensation reactions.



(2)

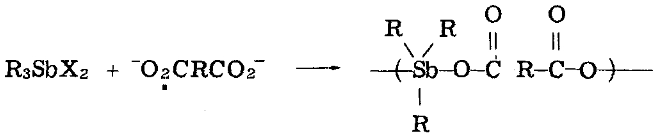
II

Third, while reactions of antimony(V) dihalides with oximes have not yet been reported, reactions with analogous mono- and diacid salts are known [Eqs. (3) and (4)] and occur in typical Lewis acid-base manner [5-10]. Thus condensation with dioximes can be considered an extension of previous work.



$$R_3SbX_2 + RCO_2^- \longrightarrow R_3Sb(O{-}\overset{O}{\overset{\|}{C}}{-}R)_2 \qquad (3)$$

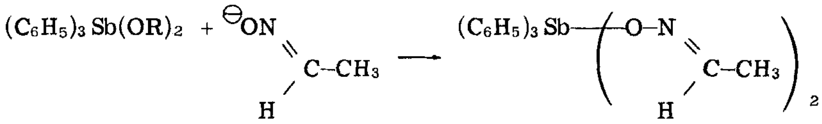
III



(4)

IV

Harrison and Zuckerman [5] note that monomeric antimony oximes are formed from reaction with dialkoxytriphenylantimony [Eq. (5)].



V

(5)

EXPERIMENTAL

The following chemicals were used as received without further purification: triphenylantimony dichloride, benzoquinone dioxime, terephthaldicarboxaldehyde, hexamethylphosphoramide, anthraquinone, terephthaldicarboxaldehyde, duroquinone (Aldrich Chemical Co., Milwaukee, Wis.); Sulfolane-W (gift from Shell Chemical Co., New York). The dioximes were prepared as described by Vogel [11], and physical characteristics were comparable to those cited in the literature.

Polycondensation was carried out by utilizing equipment previously described [12]. Reactions were conducted in a 1-qt Kimax emulsifying jar or water-jacketed semimicro aluminum jar. The jar was placed on a Waring Blendor, model 1120, which was connected through a Powerstat, type 116, to control blender speed. The organic phase containing the antimony-containing compound was added to the aqueous phase containing the dioxime which was neutralized by addition of an equivalence of sodium hydroxide. The product was recovered as a precipitate by suction filtration. Repeated washings with water and chloroform were employed to assist in the purification of the product.

Elemental analysis was conducted as described elsewhere [13]. Results are consistent with calculated values for I. For instance, the product from the condensation of triphenylantimony dichloride with benzoquinone dioxime showed 24.8% antimony (calculated 24.9%); condensation with terephthaldehyde dioxime gave a product with 23.6% antimony (calculated 23.6%), both products with less than 10^{-2}% chlorine.

Infrared spectroscopy was conducted by utilizing Beckman IR-10 and Perkin-Elmer 237B spectrophotometers. The N–O bond in oximes is reported to be in the range of 870 to 1050 cm^{-1} [14]. For the unreacted dioximes this occurs about 1000 ± 10 cm^{-1}. For the disodium salt of the dioxime there is a slight upward shift to 1030 ± 10 cm^{-1}, indicative of the ionic character of the $NO^{\ominus}$, Na bond. Condensation products exhibit a strong down field band about 960 cm^{-1}, the downfield shift characteristic of the covalent Sb–O–N moiety. Broad bands about 3300 to 2700 cm^{-1} characteristic of the O–H stretch in the N–O–H are absent for the products indicative of the absence of infrared detectable N–O–H end groups. The band characteristic of the Sb–O moiety occurs as a weak band about 980 cm^{-1}. Bands characteristic of the $(C_6H_5)_3Sb$ moiety are present in the product about 1420 to 1440 cm^{-1} (characteristic of the $Sb–C_6H_5$ stretch), 850 cm^{-1} and 870 cm^{-1}. Other bands characteristic of both comonomers are present.

Viscometry was performed by utilizing a Cannon-Ubbelohde semimicro dilution viscometer employing serial dilutions.

Light scattering was performed using a Brice-Phoenix Universal Light Scattering Photometer (Model 2000) employing Kit Number K-CF-343 (Phoenix Precision Inst. Co., Phil., Penn.) for determination of fluorescence.

Thermal gravimetric analysis (TGA) was conducted by use of a duPont 950 TGA instrument. Differential scanning calorimetry was carried out with a duPont 900 DSC cell fitted on a duPont thermal analyzer console employing a linear baseline compensator to insure a constant energy baseline. A Mettler HT 20 semimicro balance was employed for weighing the DSC samples. Measurements were obtained on samples contained in open aluminum cups to allow volatized gases to freely flow from the cup more closely simulating the conditions under which TGA studies were conducted.

RESULTS AND DISCUSSION

Reaction generally occurs only with benzoquinone dioxime and terephthaldehyde dioxime (Table 1). The reason(s) for this is unknown. Further attempts utilizing other reaction conditions have thus far failed to achieve polycondensation with additional oximes. Further work is planned in this regard.

Reaction of benzoquinone dioxime with $(C_6H_5)_3SbCl_2$ was carried out as a function of pH. At pH 11 and below, the unreacted dioxime is obtained as the principal precipitate product. Hydrolysis of the

TABLE 1. Results as a Function of Dioxime[a]

Dioxime	Yield (%)	Molecular weight (light scattering)	LVN (ml/g)	Solvent
p-Benzoquinone dioxime	25	6.9×10^5	6	Hexamethylphosphoramide
p-Benzoquinone dioxime		7.0×10^5	10	Triethyl phosphate
Terephthaldicarboxaldehyde dioxime	24	5.6×10^5	4	DMSO
Terephthaldicarboxaldehyde dioxime			39	Sulfolane-W

[a] Reaction conditions: triphenylantimony (V) chloride (0.01 mole) in 10 ml of chloroform added to stirred (20,500 rpm) solutions of dioxime (0.01 mole) in 10 ml of water with NaOH (0.03 mole) at 25°C with 15.0 min stirring time.

triphenylantimony dichloride occurs at a pH in excess of 13. Thus the desired product is formed only in the limited pH range between 11 and 13. Polymer synthesis utilizing the analogous condensation of dioximes with organic diacid chlorides was unsuccessful, probably due to extensive hydrolysis of the acid chloride; interfacial polycondensation with fully charged anions typically occurs within the aqueous layer, where extensive hydrolysis is possible [15]. This is a distinct advantage for a number of organometallic halides, where hydrolysis can occur at a slower rate than for organic acid chlorides or where the organometallic halide forms an aqueous stable, but reactive, condensation Lewis acid such as the Group IVB Cp_2MCl_2 compounds, where a stable, aquated Cp_2M^{+2} moiety is formed. Analogous interfacial condensation of dioximes with similar R_3AsX_2 reactants has thus far been unsuccessful probably due to their greater hydrolysis rate relative to R_3SbX_2 compounds.

Yield reaches a plateau after about 180 sec stirring time, with product molecular weight decreasing with increase in time, presumably due to base-catalyzed hydrolysis (Table 2). The latter is observed for a number of organometallic polycondensation systems [15] and is demonstrated by addition of known product to stirred reaction systems and observing both a decrease in product chain length and amount of product.

One reason for desiring the synthesis of antimony polyoximes is to investigate the solvent properties of such products which are

TABLE 2. Results as a Function of Stirring Time[a]

Stirring time (min)	Yield (%)	LVN (ml/g)[b]
0.15	8	18
0.60	9	12
3.00	24	
8.00	25	9
15.00	25	6

[a] Reaction conditions as in Table 1, except that p-benzoquinone dioxime was used.

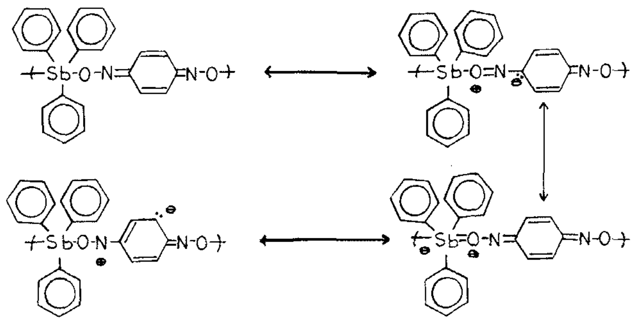
[b] Values obtained in hexamethylphosphoramide.

indicated (through construction of space-filling models) to be particularly "rigid". Following is a discussion of the results of such studies and a comparison and discussion of an overall viscosity-chain length trend becoming apparent in many of the presently synthesized organometallic polymers.

One object for our synthesis of new polymers is the evaluation of their obedience to general polymer theories. A common characteristic of polymers is the relatively large drag effect in dilute solution resulting from the polymer chain lying in several flow planes. A number of our products have exhibited unusually low viscosities compared with molecular weight determined by light scattering.

At least four factors may contribute to the low viscous drag to chain length observation. First, many of the organometallic polymers synthesized by our group can be thought of as offering resonance throughout (large segments) the chain, leading to what is called fluorescence whereby light is absorbed and reemitted equally in all directions, unlike "pure" light scattering where scattering envelopes are formed with light intensity varying with angle. For the present system, only products from p-benzoquinone dioxime exhibited fluorescence determined as described in the operating manual to the Brice-Phoenix 0M2000 light scattering photometer. Correction for fluorescence resulted in a decrease in weight-average molecular weight from 1.5×10^8 (before correction or fluorescence) to 6.9×10^5 (after correction) for one product from triphenylantimony dichloride and p-benzoquinone dioxime.

Second, many products which have exhibited unusually low viscosity: molecular weight ratios are semirigid, which permits them to be more easily accommodated within a small number of shear planes, resulting in a relatively low drag. Products from both terephthaldicarboxaldehyde dioxime and p-benzoquinone dioxime (even after correction due



to fluorescence) exhibit unusually low viscosity:molecular weight ratios (Table 1), and molecular models of both appear semirigid. As previously noted, attempts at the synthesis of less rigid or nonrigid polyoximes has failed thus far, preventing a better testing of the parameter of rigidity. Additionally, a number of dioximes were not sufficiently soluble to permit reaction.

A third factor which should be considered for materials exhibiting an unusual viscosity:light scattering - molecular weight relationship is anomalous scattering due to color or absorption. The routine for such determination is also included in the Operations Manual for the light scattering photometer. The present products do not exhibit such anomalous scattering.

The fourth factor concerns the relatively high weight of the metal atoms per occupied volume. For instance the (atomic) volume occupied by antimony is about five times that of carbon, yet the mass is about ten times as great.

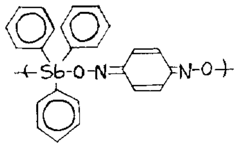
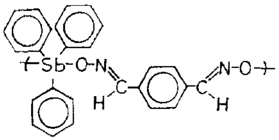
Both resonance and sterically restricted motion contribute to overall chain stiffness. This "semirigid" nature present for many of the organometallic products thus far studied may permit the chains to be more easily accommodated within a small number of shear planes contributing to a relatively low viscous drag.

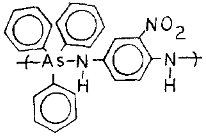
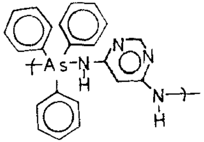
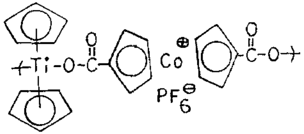
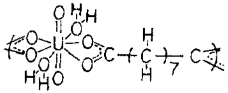
Chain stiffness alone is not responsible for the low drag observed as evidenced by low LVN/$\overline{M}_w$ values observed for several somewhat flexible organometallic polymers such as the zirconium thio group-containing polyester noted in Table 3 with a LVN/$\overline{M}_w$ ratio of 1.2×10^{-4}.

Another consideration is the typical poor solubility of organometallic polymers both in the low number of solvents in which the polymers are soluble and in the low extent of solubility in solvents where solubility is effected [34]. This limited solubility may "assist" portions of the polymer chain to reside between flow planes to minimize polymer-solvent interaction.

There currently is no direct experimental evidence to substantiate this "interflow plane" suggestion, but factors related to poor polymer solubility may be indicated by the generally low a values observed for

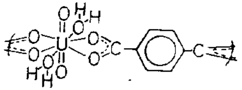
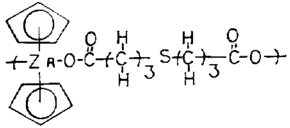
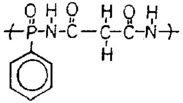
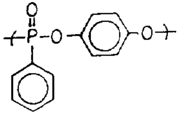
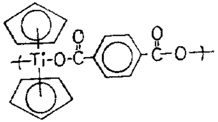
TABLE 3. LVN/$\overline{M}_w$ Ratios and K and a Values for Selected Polymers[a]

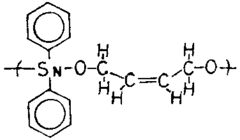
Polymer (name or structure)	Solvent	LVN/ $\overline{M}_w \times 10^4$	$K \times 10^3$ (ml/g)	a	Reference
Polystyrene	Benzene	8.4	9.2	0.74	[16]
Polyethylene	p-Xylene	333	16	0.83	[17]
Polypropylene	Decalin	17	11	0.80	[18]
Polyacrylonitrile	DMF	24	24	0.75	[19]
Poly(vinyl chloride)	Cyclohexanone	27	170	0.55	[20]
Poly(ethylene terephthalate)	Phenol/tetrachlorophenol	25	47	0.68	[21]
Poly(hexamethylene adipamide)	90% Aqueous formic acid-2 M KCl	24	140	0.56	[22]
Polydimethylsiloxane	Bromobenzene	7.6	76	0.5	[23]
	Hexamethylphosphoramide	0.087	2.2	0.4	[24]
	Triethyl phosphate	0.14			[24]
	DMSO	0.071	.71	.5	[24]
	Sulfolane-W	0.70			[24]

	DMSO	0.40			[25]
	DMSO	0.14			[25]
	2-Chloroethanol	5.0	15	0.63	[26]
	DMSO	48	300	0.55	[27]
Poly(sodium acrylate)	1.5 M Aqueous NaBr	12	124	0.5	[28]
Poly(benzyl methacrylate)	Benzene	2.0	1.03	0.82	[29]
Poly(4,4'-isopropylidene carbonate)	Chloroform	28	277	0.5	[30]

(continued)

TABLE 3 (continued)

Polymer (name or structure)	Solvent	LVN/ $\overline{M}_w \times 10^4$	$K \times 10^3$ (ml/g)	a	Reference
	Triethyl phosphate	0.73	25	0.53	[27]
	2-Chloroethanol	1.2			[31]
	DMSO	0.22			[32]
	DMSO	5.5	20	0.61	[31]
	2-Chloroethanol	1.8	21	0.48	[32]

	Octanethiol	0.25	6.2	0.4	[33]

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[a] $\overline{M}_w$ determined by light scattering photometry. The ratio LVN/M_w is "normalized" using $\overline{M}_w = 10^4$.

TABLE 4. LVN/$\overline{M}_w$ Ratios for Theta and Nontheta Systems

Polymer	K × 10^3 (ml/g)	a	LVN/$\overline{M}_w$	Reference
Poly-1-butene				
Theta	123	0.50	12	[35]
Nontheta	7.3	0.80	12	[35]
Polystyrene				
Theta	80	0.50	8	[36]
Nontheta	22	0.64	8	[30]
Poly(vinyl chloride)				
Theta	156	0.50	16	[37]
Nontheta	16	0.77	19	[38]
Poly(vinyl acetate)				
Theta	82	0.50	8	[30]
Nontheta	32	0.65	12	[39]
Poly(methyl acrylate)				
Theta	54	0.50	5.4	[29]
Nontheta	4.5	0.78	5.9	[30]
Polytetrahydrofuran				
Theta	206	0.49	19	[30]
Nontheta	42	0.65	17	[30]
Nylon 66				
Theta	253	0.50	25	[22]
Nontheta	142	0.56	25	[22]

for the organometallic products. Further, a product from the condensation of triphenylantimony (V) dichloride with terephthaldicarboxaldehyde dioxime near its theta point in DMSO exhibits very little slope in the plots of η_{rel}/c (k = 0.004) versus concentration (k values based on units of concentration of g/dl) yielding a LVN of 4 ml/g. In sulfolane, a better solvent as indicated by greater slopes in the η_{sp}/c (k = 0.22) and ln η_{rel}/c (k = 0.1), the LVN increased to 39 ml/g.

Poor polymer solubility alone is not responsible for the low drag. This is based on data such as those given in Table 4 where the LVN/$\overline{M}_w$ ratios are approximately constant for a number of polymer systems when comparing theta with nontheta polymer-solvent combinations. It presently appears that it takes both chain stiffness and poor solubility to account for the observed low drags, with both factors acting to force the chains into a small number of flow planes.

Table 3 also contains a listing of Mark-Houwink K and a values.

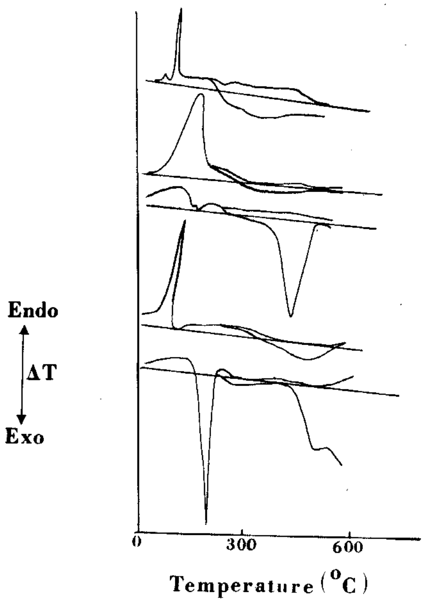

FIG. 1. DSC thermograms (from top to bottom) ($(C_6H\ )_3SbCl_2$; benzoquinone dioxime; condensation product of $(C_6H_5)_3SbCl_2$ and benzoquinone dioxime; terephthaldehyde dioxime; condensation product of $(C_6H_5)_3SbCl_2$ and terephthaldehyde dioxime obtained at a heating rate of 20°C/min with a gas flow rate of 0.2 lpm for 1.00 ± 0.02 mg samples. The straight line is the $\Delta T = 0$ line. After the thermogram recordings split, the lower portion represents results obtained in air, the upper portion results obtained in nitrogen.

Neither the a or K values alone appear to signal the unusual $LVN/\overline{M}_w$ ratio, but, considered as a pair, they appear lower for most of organometallic polymers when compared with typical organic polymers. The low a values probably result from the characteristic poor solubility of the organometallic polymers (as previously noted). The K term can be further subdivided in accordance with the Flory-Fox approach, giving

$$K = \phi\,(\overline{r}_0{}^2/M)$$

The low K may in part be due to the high M (factor four) value per $\overline{r}_0$ unit due to the presence of the metal atom. This has yet to be tested but should be demonstrable by synthesis of analogous families of organometallic polymers where only the M is varied (with relatively little change in the atomic volume of the metal, such as with Zr and

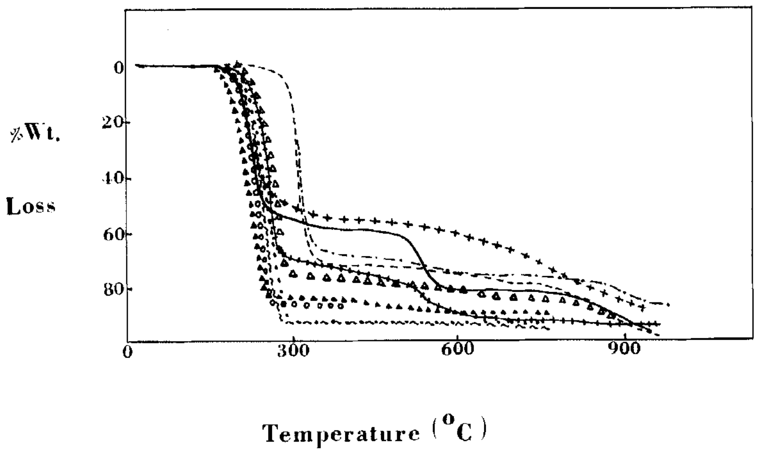

FIG. 2. TGA thermograms of: $(C_6H_5)_3SbCl_2$ (· · ·) in air and (~~) in N_2; benzoquinone dioxime (▲) in air and (○) in N_2; condensation product of $(C_6H_5)_3SbCl_2$ and benzoquinone dioxime (—) in air and (+) in N_2; terephthaldehyde dioxime (+ +) in air and (△) in N_2; condensation product of $(C_6H_5)_3SbCl_2$ and terephthaldehyde dioxime (· - ·) in air and (- -) in N_2. All thermograms obtained at a heating rate of 20°C/min with a gas flow rate of 0.2 liter/min.

Hf) and comparing the K values. Poor solubility of synthesized Zr and Hf products have thus far prevented investigation of this.

Thermograms were obtained on all products and starting materials. Degradation of the products to 300°C is similar (DSC, TGA thermograms, Figs. 1 and 2) in air and nitrogen. Above 300°C degradation occurs through an endothermic route(s) in nitrogen but an exothermic route(s) in air indicative of oxidative degradation occurring in air. Initial weight loss begins about 250°C for the products in both air and nitrogen. Degradation occurs through a series of kinetically controlled (time-dependent) stability plateaus typical of organometallic polymers [15].

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