Synthesis and Characterization of Antimony (V)-Polycobalticinium Esters

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ABSTRACT

Antimony (V) polycobalticinium esters, where the anion was
PF_6^-, Cl^-, Br^- and NO_3^-, were synthesized. A number of
factors were found to be important in the synthesis, including
anion exchange and pH. The products containing PF_6^- are
oligomeric ($\overline{DP}_w$ = 7) whereas the other products are di- and
trimeric. The products undergo oxidative degradation begin-
ning about 100 to 225°C. They are near semiconductors with
resistivities about 10^5 to 10^7 ohm-cm.

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INTRODUCTION

We continue to be actively pursuing the inclusion of metals within polymers. The present paper reports our efforts at synthesizing cobalticinium-containing polymers. Cobalticinium salts, unlike their isoelectronic ferrocene counterparts, are resistant to strong oxidizing agents such as potassium dichromate and fuming nitric acid [1, 2]. Neuse and Rosenberg [3] suggest possible uses of cobalticinium compounds to be applications requiring high thermo-oxidative stability. Gill and Mann [4] proposed the use of cobalticinium salts as haptens. Unlike their ferrocene counterparts, cobalticinium salts have not been extensively studied.

One of the easiest cobalticinium salts to synthesize is the dicarboxylic acid. Reaction of either the acid or neutralized form with typical organic acid chlorides employing low temperature condensation systems fail to give the desired condensation product. We recently reported the synthesis of cobalticinium polyesters by use of organometallic halides [Eq. (1)],

$$(1)$$
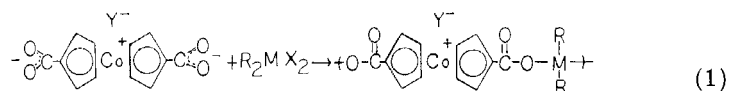
where M is Sn, Ti, or Zr [5, 6]. These products are electrical semiconductors. It was our intent to synthesize a number of cobalticinium products containing different anions for the purpose of evaluating the role of the anion in the electrical semiconductivity.

We have just begun the synthesis of Group V–containing products for a number of reasons, including first, 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 [7, 8]. Their toxicity is a disadvantage to human applications. Formation of a polymeric mixed chelate of antimony sodium tartrate with penicillamine gives a material which is considerably less toxic, yet that retains its antiparasitic action in schistosomiasis [9]. Synthesis of organic antimonials utilizing polar bond connections which are biologically hydrolizable could result in the synthesis of biologically useful control release agents.

Second, the reaction of organometallic antimony (V) compounds with typical Lewis bases to form the expected condensation product is well known [10-15]. Basic solutions of organic monoacids condense to form esters of the type 2 [12, 15]. Here we describe the initial synthesis of antimony polycobalticinium esters of the type 3 as a direct extension of the monoester synthesis.

$$R_3SbX_2 + RCO_2 \longrightarrow R_3Sb(O\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!R)_2 \qquad (2)$$

II

$$(3)$$
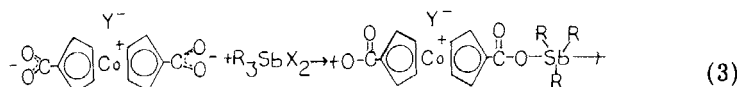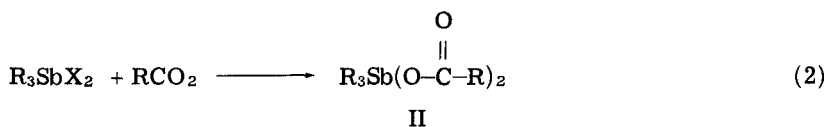
EXPERIMENTAL

Triphenylantimony dichloride, tributylantimony, trimethyl-antimony, and hexamethylphosphoramide were used as received from the Aldrich Chemical Co., Milwaukee, Wis. The cobalticinium acids were synthesized as described previously [5].

Polycondensation was conducted by utilizing equipment described previously [16]. Reactions were carried out in a 1-qt Kimex emulsifying jar placed on a Waring Blendor (Model 1120). The organic phase containing the antimony halide was added to stirred aqueous phases containing the diacid in water which had been previously neutralized by addition of sodium hydroxide. The product was obtained as a precipitate by use of suction filtration. Repeated washings with carbon tetrachloride and water assist in the purification of the product.

Elemental analysis was conducted as described elsewhere [17]. Results are consistent with that calculated for III. For the product from NO_3^- there was found 24.6% cobalt plus antimony; calculated was 27.1%. For the product from Br^-, 17.6% antimony was found; calculated was 17.8%. The product from PF_6^- showed a cobalt plus antimony content of 24.6%; calculated was 24.1%.

A Perkin-Elmer IR-237B spectrophotometer was used to obtain infrared spectra. The carbonyl band of the free acids shifted from about 1720 cm^{-1} to 1600 cm^{-1} characteristic of covalent-metal bond formation [18]. A band about 1280 cm^{-1} is characteristic of the Sb-O stretch. Products containing the $(Ph)_3Sb$ moiety exhibit bands at 1420 cm^{-1} (characteristic of the Sb-Ph stretching) and 680 and 730 cm^{-1} (characteristic of the C-H moiety within the phenyl moiety). Bands appear at about 860, 1015, 1050, and 1460 cm^{-1} and are characteristic of the cyclopentadienyl ring of the cobalticinium moiety. A strong band at about 820 cm^{-1} is found for products containing the PF_6^- anion and is characteristic of the P-F stretching [5, 6]. Weak bands at about $3325\text{-}3450 \text{ cm}^{-1}$ and $1700\text{-}1720 \text{ cm}^{-1}$ are found for most of the products (after acid wash) characteristic of the presence of carbonylic acid end-groups.

Viscometry was performed by utilizing a Cannon-Ubbelohde semi-micro dilution viscometer employing serial dilutions. Light scattering

studies were performed by using a Brice-Phoenix Universal Light Scattering Photometer (Model OM-2000), employing Kit Number K-CF-343 (Phoenix Precision Inst. Co., Phil., Penn.) for determination of fluorescence which was found to be absent in all systems.

Thermal stability of the product was determined by the use of differential scanning colorimetry (DSC) and thermal gravimetric analysis (TGA). The equipment used was a duPont 900 differential scanning calorimeter cell attached onto a duPont 950 thermal analyzer console and a duPont 900 thermal gravimetric analyzer. Both TGA and DSC studies were carried out under an air and nitrogen atmosphere with a gas flow rate of 0.2 to 0.3 liter/min.

DSC was conducted in open aluminum caps to allow volatile materials to leave, simulating the conditions of the TGA. A Mettler H20T semimicro balance was used for the weighing process for DSC.

Electrical properties were determined by utilizing a setup as described by Carraher [19]. Resistivity (specific bulk resistance) is the observed parameter for evaluating the electrical properties of the products.

Ultraviolet spectra were obtained with a Perkin-Elmer 202 ultraviolet-visible spectrophotometer using hexamethylphosphoramide as a solvent for products from Ph_3SbCl_2. All products gave a strong absorption in the 255 nm region. This is consistent with results obtained by Jaffé, who reported λ_{max} for Ph_3Sb at 256 nm and λ_{max} for Ph_3SbCl_2 of 218 nm [20].

RESULTS AND DISCUSSION

While reaction was general, only minimal product was forthcoming when organometallic antimony reactants other than $(Ph)_3SbCl_2$ or an associated anion other than PF_6^- (Table 1) were used. Thus a yield of only 2% was forthcoming from the condensation of $(CH_3)_3SbI_2$ with the PF_6^- acid salt whereas under similar conditions 70 to 80% yields are obtained from condensation with $(Ph)_3SbCl_2$.

Exchange of the anion can occur within the acid salts. For instance, there is a decrease in product yield if the diacid salts aqueous phase is prepared appreciably before the reaction is conducted. No product is found for PF_6^- systems if a 2-hr "aging" is allowed before the reaction is conducted. Under analogous conditions a yield about 75% is obtained if this "aging" is reduced to 10 min or less. As a general procedure, reaction phases are made up just prior (within 5 min or less) to attempted reaction. "Aging" is believed to be due to the dissociation of the anion, permitting water to become more "intimately" associated with the cobalticinium moiety which on reaction permits "wetting" and hydrolysis of the forming chain [5, 6].

TABLE 1. Results as a Function of Stirring Time[a]

Stirring time (sec)	Yield (%) for specified anionic species			
	PF_6^-	NO_3^-	Cl^-	Br^-
5	45, 50			
10	69, 68	7	7	13
15	75			6
20	80, 80			6
25	84			
30	80, 19[b]	3, 12[b]	3	5, 2[b]
40	80	3	3	
45	85			7
60	76, 53[c]			
120	75, 71[c]			

[a]Reaction conditions: triphenylantimony dichloride (1.00 mmole) in 25 ml carbon tetrachloride added to stirred (20,500 rpm) solutions of 1,1'-dicarboxycobalticinium PF_6^-, Br^-, Cl^- or NO_3^- in 25 ml aqueous solution neutralized by addition of an equivalance of sodium hydroxide for various stirring times at 25°C.
[b]Value for equivalent systems except each phase is 15 ml.
[c]Value for systems where each phase is 50 ml.

Anion exchange is the least rapid with the PF_6^- cobalticinium moiety and is rapid enough with the nitrate comonomer so as not to allow the recovery of unexchanged product. Infrared spectra of the product from the nitrate-containing comonomer show a marked decrease of bands due to the nitrate groups, namely, the 1480, 1350, 1275, and 1040 cm^{-1} bands. The chlorine ion, from the antimony dichloride, is the only other anion potentially present in moderate amounts. Elemental analysis of the product showed a chlorine content of about 4%. Total exchange would result in a 5.5% chlorine content. These products are di- and trimeric, with limiting viscosity numbers (LVN) about 3 ml/g and weight-average degrees of polymerization of the order of 3. Thus predicted degradation probably accompanies anion exchange, since products from the PF_6^- anion exhibit LVN's about 23 ml/g and $\overline{DP}_w$'s about 7 when PF_6^- exchange is not allowed.

Hydrolysis of the antimony halides is also believed to be important
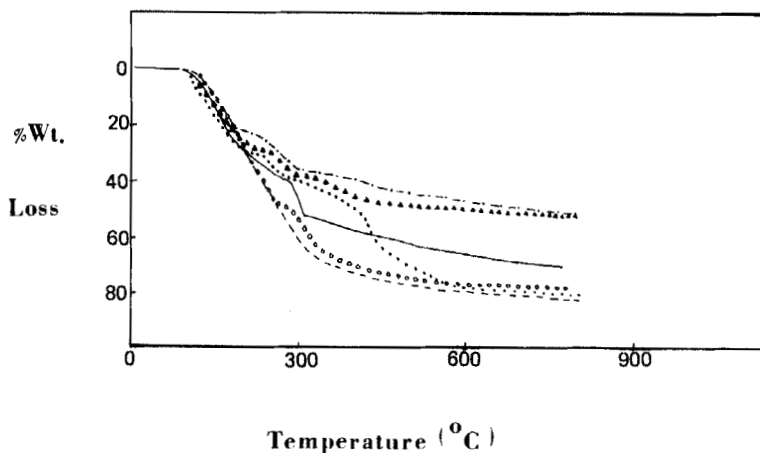
%Wt.

Loss

Temperature ($^\circ$C)

FIG. 1. TGA thermograms of products of $(C_6H_5)_3SbCl_2$ with various cobalticinium acids: (—) associated anion is PF_6^-, in air; (— · —) PF_6^-, in N_2; (···) Br^-, in air; ($\triangle$) Br^-, in N_2; ($\circ$) NO_3^-, in air; (- -) NO_3, in N_2. Heating rate, 20°C/min; gas flow rate, 0.2 liter/min.

Endo

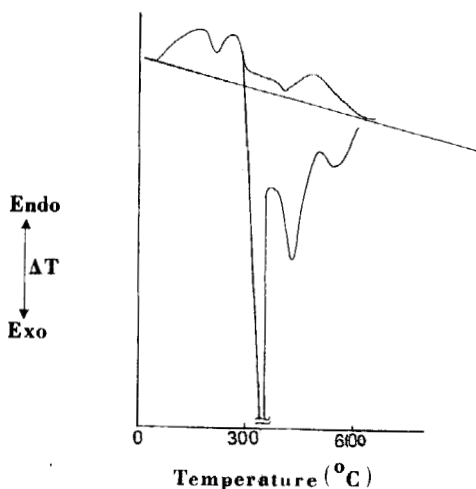ΔT

Exo

Temperature ($^\circ$C)

FIG. 2. DSC thermograms for the condensation product of $(C_6H_5)_3SbCl_2$ with the disodium salt of 1,1'-dicarboxycobalticinium hexafluorophosphate at a heating rate of 20°C/min and a gas flow rate of 0.2 liter/min (bottom) in air and (top) nitrogen for 1.00 ± 0.01 mg samples with the straight line being ΔT = 0.
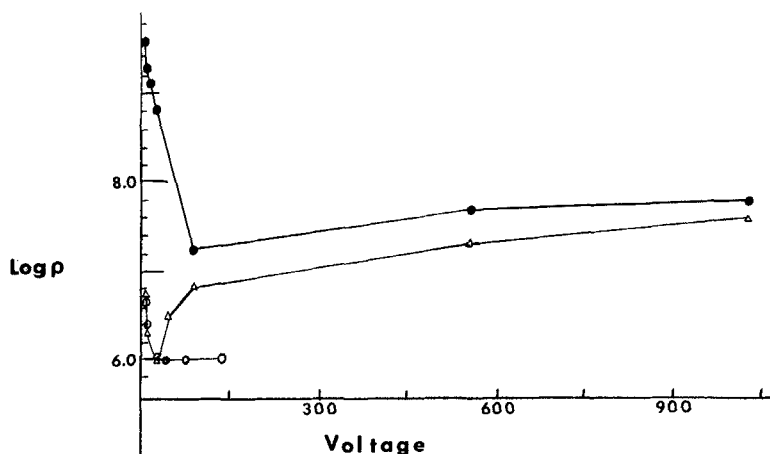
FIG. 3. Resistivity values ρ as a function of applied DC voltage for the condensation products of $(C_6H_5)_3SbCl_3$ with the disodium salts of 1,1'-dicarboxycobalticinium at 3000 lb applied pressure with the various associated anions: (●) NO_3^-; (△) Br^-; (○) PF_6^-.
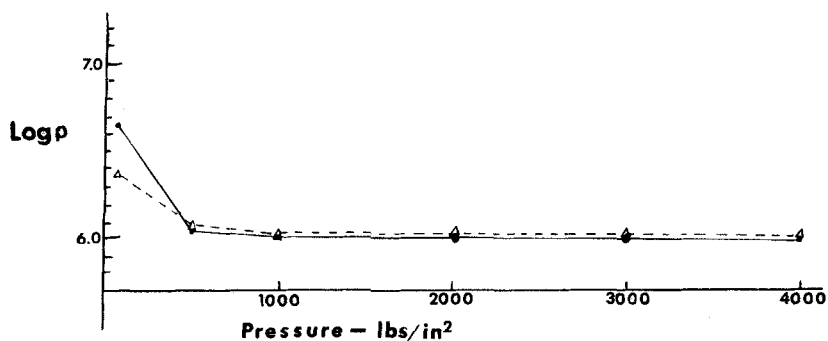

FIG. 4. Resistivity ρ for the condensation product of $(C_6H_5)SbCl_2$ with the disodium salt of 1,1-dicarboxycobalticinium hexafluoro-phosphate as a function of applied pressure at a DC applied voltage of (●) 10 V and (△) 100 V.

since little or no product is formed when employing the trimethyl-
or tributylantimony dihalides which are reported to hydrolyze at a
more rapid rate than the less aqueous soluble triphenylantimony
dichloride [21].

For $PF_6^{\ominus}$ cobalticinium comonomers reaction is rapid with yield
reaching a plateau after 20 sec stirring time. Product chain length
is about a weight average degree of polymerization of 7 ($\overline{M}_w \cong 5.2 \times 10^3$) with a viscosity in hexamethylphosphoramide about 23 ml/g.
Reproducibility of yield is good (Table 1).

For the other cobalticinium comonomers, where the anion is NO_3^-,
Br^- or Cl^-, yield reaches a maximum at a shorter stirring time (10
sec and less) with product yield being small. This marked decrease
for Br^- and NO_3^- compared with the PF_6^- comonomer has also been
observed in the synthesis of zirconacene poly(cobalticinium) esters
[22].

The importance of pH is evidenced by the narrow pH range suit-
able for product formation. Product is formed only over the pH range
of about 9 to 12.4. The diacid is not in the necessary salt form appre-
ciably below a pH of 9. Base-catalyzed hydrolysis appears to be
critical above a pH around 12.7 and above. This has also been ob-
served for other analogous cobalticinium systems when M is Ti, Zr,
or Sn (form I) [5, 6, 22, 23].

The cobalticinium products began to degrade in both air and
nitrogen within the 100-225°C range (Figs. 1 and 2). Degradation is
fairly rapid with only the metal oxide remaining by 600°C in air.
Degradation in air occurs through a complex of exothermic steps
whereas degradation in nitrogen occurs through endothermic steps.
These energy results are consistent with degradation occurring as
expected, through an oxidative route(s) in air.

The products are semiconductors with resistivity values about
10^5 to 10^7 ohm-cm. Resistivity slightly decreases as voltage increases
reaching a minimum and then generally rises while it remains approxi-
mately constant as pressure increases (Figs. 3 and 4). Resistivity
appears not to vary significantly with variation in anion nature indi-
cating that the nature of the anion (including anion mobility) appears to
play a minor role in determining the overall conductivity of the poly-
esters. A more comprehensive study is currently underway involving
analogous titanium polyesters involving both AC and DC measure-
ments.

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