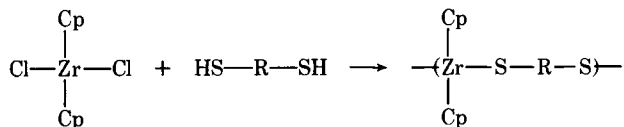


## Synthesis of Oligomeric Zirconium Polythioethers

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### Synopsis

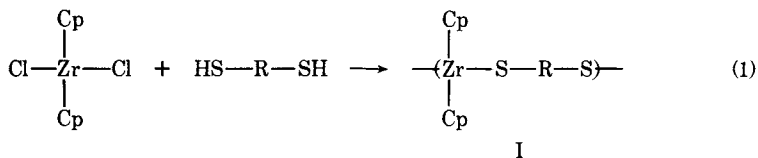
Synthesis of zirconium oligomeric polythioethers was effected using aqueous solution and interfacial techniques:



The products are insoluble in all tried solvents and possess Zr—OH endgroups but no detectable quantities of R—SH, Zr—Cl, or Zr—N—Et-endgroups.

### INTRODUCTION

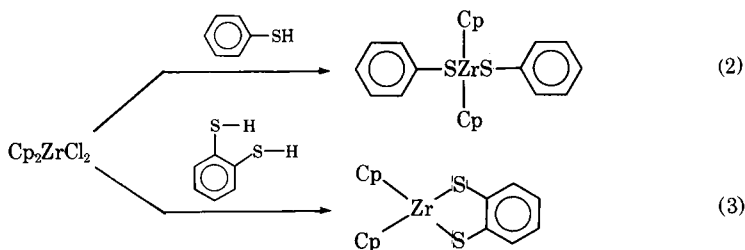
Recently, we reported the synthesis of Group IVB polyesters and titanium polyamines and polyethers.<sup>1-4</sup> The basis for such synthesis involves the Lewis acid-base concept where the dihalo Group IVB cyclopentadiene is the electrophile and the amine, carboxylate anion, or alcohol is the nucleophile. A reasonable extension would be the synthesis of zirconium polythioethers of form I: We now report such synthesis. The



synthetic routes chosen are the interfacial and aqueous solution techniques since many organometallic reactants and products are unstable at elevated temperatures and many undesirable reactions can occur at high temperatures.

Synthesis of the M-S bond (where M is a Group IVB metal) is known.<sup>5-9</sup> For instance, Cp<sub>2</sub>ZrCl<sub>2</sub> reacts with benzene thiol and 1,2-dithiolbenzene in benzene in the presence of Et<sub>3</sub>N to give products containing the Zr-S bond<sup>7</sup>:

\* Portions of this paper were taken from the thesis of R. J. N., 1971.



The zirconium-containing compound chosen was dicyclopentadienylzirconium dichloride,  $\text{Cp}_2\text{ZrCl}_2$ , for several reasons. Unlike many organometallic halides which rapidly hydrolyze to form hydroxides or oligomeric polyoxides when exposed to water,  $\text{Cp}_2\text{ZrCl}_2$  ionizes to form  $\text{Cp}_2\text{Zr}^{2+}$  which is stable for periods longer than 15 min.<sup>1,4</sup>  $\text{Cp}_2\text{ZrCl}_2$  is commercially available, air stable, and a proven catalyst in many reaction systems. Such catalytic activity may be transferred to a polymer containing the  $\text{Cp}_2\text{Zr}$  moiety.

### EXPERIMENTAL

Dicyclopentadienylzirconium dichloride ( $\text{Cp}_2\text{ZrCl}_2$ ) was obtained from Alfa Inorganics, Inc. (Beverly, Mass.). Ethylenebis(3-mercaptopropionate) (EMPAT) was obtained as a gift from Evans Chemetics, Inc. (Darien, Conn.). (Trade name for EMPAT is Glycol Dimercaptopropionate.) All the other dithiols were obtained from Aldrich Chemical Co. (Milwaukee, Wis.). All reactants were used as obtained without further purification.

Reactions were carried out in a 1-pt Kimax emulsifying jar placed on a Waring Blendor (Model 1120) with a listed "no load" rotor speed of 23,000 rpm. The apparatus is described in detail elsewhere.<sup>10</sup>

The general polymerization procedure is essentially the same as that employed by us in the synthesis of Group IVB-containing polyesters.<sup>1,4</sup> Briefly, two types of polymerization procedures were used: solution and interfacial. In both procedures the phase containing the base and dithiol was added through the large-mouthed funnel to the stirred dicyclopentadienylzirconium dichloride solution. The solvents used were water and chloroform. Each phase consisted of 25 ml of solution. All reactions were run at room temperature.

Infrared spectroscopy was conducted using a Beckman IR-10 infrared spectrophotometer with the use of KBr pellets for solids and KBr pellet plates as described elsewhere for liquids.<sup>11</sup> Elemental analyses were consistent with a repeating unit of form I. For instance, the zirconium analysis for the product with EMPAT was 26% calculated, 26% found; for the product with 1,2-ethanedithiol it was 28% calculated, 30% found; for the product with 1,6-hexanedithiol it was 24% calculated, 25% found.

Assignments of the infrared peaks were made by comparing the peaks of the polymer spectra with those of the known monomers and with band assignments recorded in the literature.<sup>12-17</sup> The following absorption bands (present in all spectra) are attributed to the presence of the cyclo-

pentadienylzirconium moiety: bands around 830–800, 1025–1010, and 145–1440  $\text{cm}^{-1}$ , characteristic of the Cp- $\pi$  ring. In addition to these bands, the aliphatic polythioethers show bands around the 3000–2900  $\text{cm}^{-1}$  region which are characteristic of their C—H stretching modes. The dimercaptpropionate shows band in the 1750–1735  $\text{cm}^{-1}$  region which is characteristic of the carbonyl stretching vibration. In addition, the spectra of all the pure dithiols used show bands around 2600–2500  $\text{cm}^{-1}$  due to the S—H stretch and a band in the 720–680  $\text{cm}^{-1}$  region which can be attributed to the C—S stretching vibration. In the polythioethers, the former band does not appear and the latter is shifted toward lower wave numbers (in the 660–640  $\text{cm}^{-1}$  range when detectable). The lowering of the C-S vibration is consistent with observations made for bondings to metals by Lewis bases such as diols, thiols, and amines. The absence of a new band (i.e., bands not directly derived from the inclusion of either the Cp<sub>2</sub>Zr or S-R-S moieties) in the 1050–1200  $\text{cm}^{-1}$  region is proof of the absence of detectable amounts of Zr-O-Zr bonding. Thus, both infrared spectroscopy and elemental analysis are in agreement with a repeating structure depicted by form I.

All of the spectra contained at least some absorption bands in the 3550–3000  $\text{cm}^{-1}$  region. There are three possible explanations: the presence of —OH endgroups in the polymer, water being entrapped in the polymer chains, or structures resulting from hydrolysis of the Cp<sub>2</sub>ZrCl<sub>2</sub>. This topic will be dealt with in the discussion.

The products did not melt to 300°C with the use of a Fisher-Johns melting point apparatus at an approximate heating rate of 5°C/min. The products did change color in this temperature range, generally to a brown tan, at temperatures greater than 200°C.

Attempts were made to dissolve the polythioethers in numerous and varied solvents by the following method. Samples of approximately 0.001 g were placed in small test tubes to which about 2 ml of the solvents was then added. The tubes were stoppered and periodically shaken by hand over a two- to three-week interval. In cases where polymer solubilization was believed to occur (due to the disappearance of the solid), it was shown that solubilization did not occur but rather polymer degradation had taken place. This presents a major obstacle to determining molecular weights (and other solution characterizations) which requires the solution of the product. Kopf and Schmidt<sup>8</sup> noted a similar lack of solubility of the titanium-containing oligomeric thioethers they prepared. Kopf and Schmidt obtained their molecular weights via elemental analysis for end-groups.

Many of the products are initially tacky, but all dry to yield white, powdery solids. The products, as expected, are electrostatic.

## DISCUSSION

Synthesis results for zirconium polythioethers are recorded in Table I. Utilization of water-containing systems is possible because, unlike the

TABLE I  
Yield as a Function of Dithiol, Reaction System, and Concentration

Dithiol	Yield— interfacial, %	Absorbance <sup>d</sup> Zr—OH	Absorbance <sup>d</sup> Zr—Cp	$\bar{DP}^d$	Yield— aqueous sol., %	Absorbance <sup>d</sup> Zr—OH	Absorbance <sup>d</sup> Zr—Cp	$\bar{DP}^d$
EMPAT <sup>a</sup>	6	—	—	—	5	—	—	—
1,6-Hexanedithiol <sup>a</sup>	4	—	—	—	3	0.11	0.12	4
1,2-Ethanedithiol <sup>a</sup>	1	0.30	0.30	4	5	0.40	0.38	4
EMPAT <sup>b</sup>	6	0.28	0.41	6	9	0.14	0.22	6
1,6-Hexanedithiol <sup>b</sup>	31	0.70	0.74	4	36	0.50	0.29	3
1,3-Propanedithiol <sup>b</sup>	6	0.58	0.54	4	5	0.66	0.40	3
EMPAT <sup>c</sup>	4	—	—	—	0	—	—	—
1,6-Hexanedithiol <sup>c</sup>	31	—	—	—	0	—	—	—
1,2-Ethanedithiol <sup>c</sup>	7	—	—	—	0	—	—	—

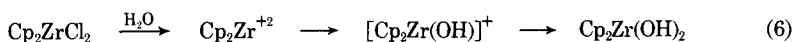
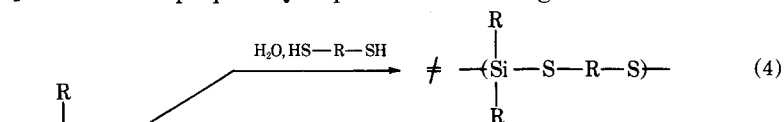
<sup>a</sup> Reaction conditions: Dithiol (0.0005 mole) with triethylamine (0.001 mole) in 15 ml water added to a stirred solution of  $Cp_2ZrCl_2$  (0.0005 mole) in 15 ml  $CHCl_3$  for the interfacial systems or 15 ml water for the aqueous solution systems at 25°C, 23,000 rpm stirring rate for 1 min, unless otherwise noted.

<sup>b</sup> Reaction conditions: same as (a), except volumes are 25 ml instead of 15 ml and mole amounts of reactants are 0.001 mole and for triethylamine, 0.002 mole.

<sup>c</sup> Reaction conditions: same as (b), except NaOH is used in place  $Et_3N$ .

<sup>d</sup> Determined as described in discussion, with the following absorbances determined from  $Cp_2Zr(OH)_2$ : Zr—OH, 0.26; Cp—Zr, 0.09.

corresponding Group IVA dihalides which undergo hydrolysis to form oligomeric polyoxides,<sup>18</sup> dicyclopentadienyl Group IVB dichlorides ionize to form  $\text{Cp}_2\text{M}^{2+}$  ions. These ions are stable for periods greater than 15 min under reaction conditions.<sup>1-4</sup> Hydroxylation of the  $\text{Cp}_2\text{M}^{2+}$  ion is of the order  $\text{Hf} > \text{Zr} > \text{Ti}$ .<sup>19</sup> To avoid such hydroxylations, shown in eq. (6),  $\text{Cp}_2\text{ZrCl}_2$  solutions are prepared just prior to conducting the reaction:



Triethylamine and NaOH were evaluated as added bases. The former was employed for several reasons. Previous evaluations of organic and inorganic bases in the synthesis of Group IVB polyamines and polyethers have shown it to be an effective base in scavenging HCl.<sup>2-4</sup> It is easily removable since both  $\text{Et}_3\text{N}$  and  $\text{Et}_3\text{NHCl}$  are water soluble. Also, it does not appreciably compete with the diol or diamine for the  $\text{M}-\text{Cl}$  site, presumably because of its steric hindrance.<sup>2-4</sup> Synthesis of polymer was general for  $\text{Et}_3\text{N}$ , but either no yield or low yield of polymer was found when NaOH was the employed base in the aqueous solution systems.

As noted previously, the products are insoluble in all tested solvents. This precludes absolute molecular weight determination. Poor or nonsolubility has characterized all Group IVB polymers synthesized by ourselves and others.<sup>1-4, 18, 19</sup> This is unfortunate and presents a major obstacle to characterization of the products and evaluation of the effects of particular reaction variables on molecular weight. Even so it does not eliminate their use where solution is not necessary.

Yield is constant with stirring time (for instance, see Table II) but is greatly dependent on monomer concentration and/or volume of the phases (Table I). Both techniques appear capable of producing product in poor to medium yield, with neither system offering consistently better yields.

There are four possible endgroups. They are the  $\text{Zr}-\text{OH}$ , formed via hydroxylation of the  $\text{Zr}-\text{Cl}$  endgroup;  $\text{Zr}-\text{Cl}$ ,  $\text{R}-\text{SH}$ , and an endgroup formed from the condensation of  $\text{Zr}-\text{Cl}$  with  $\text{Et}_3\text{N}$ . Detectable quantities of the latter are eliminated because of the absence of characteristic  $\text{N}-\text{Et}$  bonds in infrared spectra of the products. All the products exhibit broad bands in the  $3400-3000 \text{ cm}^{-1}$  region. The presence of water is excluded since the bands remain even after extensive vacuuming following a procedure shown to eliminate occluded water from polymer matrices.<sup>20, 21</sup>  $\text{Cp}_2\text{Zr}(\text{OH})_2$  shows an intense broad band in the  $3550-3100 \text{ cm}^{-1}$  region

TABLE II  
Yield as a Function of Stirring Time<sup>a</sup>

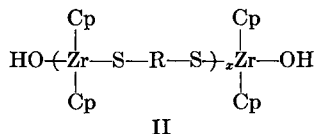
Stirring time, sec	Yield, %	
	Interfacial	Aqueous solution
30	7	4
60	6	9
120	8	
180	6	6
300		9

<sup>a</sup> Reaction conditions: EMPAT (0.001 mole) and triethylamine (0.002 mole) in 25 ml water added to stirred solutions of  $\text{Cp}_2\text{ZrCl}_2$  (0.001 mole) in 25 ml  $\text{CHCl}_3$  or  $\text{H}_2\text{O}$  at 25°C, 23,000 rpm stirring rate for varying times.

which corresponds with the broad band found in the products. Thus, the products possess detectable quantities of Zr-OH endgroups. There is no noticeable difference in the intensity of this band whether synthesis was effected via the aqueous solution or interfacial routes utilizing  $\text{Et}_3\text{N}$  as the added base. Generally, the OH bands are more intense for products produced with NaOH as the added base, indicating added importance of Zr-Cl hydroxylation in such systems.

The S-H stretching band is assigned the region 2600–2500  $\text{cm}^{-1}$ .<sup>12</sup> None of the products exhibits bands in this region. Thus, the presence of detectable amounts of R-S-H endgroups is excluded. The Zr-Cl stretching, symmetric and asymmetric, is tentatively assigned as 365 and 335  $\text{cm}^{-1}$ , respectively. There are no detectable sharp bands in this region for the products. Caution must be exercised since there is a broad band in the products throughout the region of 600–300  $\text{cm}^{-1}$  (due to the thiol moiety) which may obscure the Zr-Cl bands.

The average degrees of polymerization recorded in Table I were calculated using the Zr-OH band about 3500–3100  $\text{cm}^{-1}$  and the Zr-Cp band about 1600–1620  $\text{cm}^{-1}$  assuming that only Zr-OH endgroups exist generating a product of form where the value given in Table I corresponds to the  $x$  value in form II:



From such calculations it can be assumed that the products are generally oligomeric, not polymeric.

Since yields are so low, it is of interest to determine the form of the remaining reactants. This was partially done. For example, in the interfacial reaction of  $\text{Cp}_2\text{ZrCl}_2$  (0.001 mole) with 1,2-ethanedithiol (0.001 mole), only 7% (0.0190 g) of material was collected via initial filtration of the reaction mixture. The two reaction phases were separated and evaporated to dryness at room temperature.  $\text{Cp}_2\text{ZrClOH}$  (0.508 g) was recovered

from the chloroform layer. This would account for about 17% of the zirconium.

Product precipitated from the aqueous phase as the liquid was evaporated. This product was separated and additional liquid evaporated, with subsequent precipitation of material. All of the material present in the aqueous phase (0.1974 g) appeared via infrared spectroscopy to be identical and consisted of units of form II where  $x = 1$  and 2 (average  $\overline{DP} = 2$ ), identified using the technique described previously for determination of molecular weight. This would account for about an additional 68% of the  $Cp_2Zr$  moiety. Whether such products formed during the initial stirring or subsequent to the stirring is unknown. Even so, these materials are water soluble while higher molecular weight products are not water soluble, thus forming the basis for separation of materials listed in Tables I and II as products. Additionally, the fact that all of the materials having the thiol moiety included within themselves have Zr-OH endgroups suggests that chain termination, i.e., termination of reaction, occurs via hydroxylation of the zirconium moiety. Such hydroxylation appears to be the limiting molecular chain length factor. It may also account for the absence of products for many of the attempted aqueous solution systems since it is presumed that hydroxylation would be of greater importance in such systems.

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