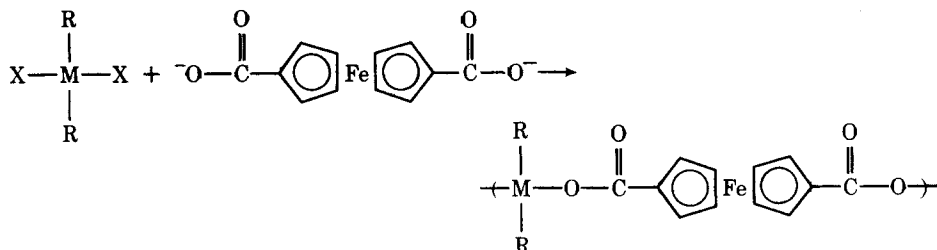


Synthesis of Oligomeric Group IVA Ferrocene Polyesters

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Synopsis

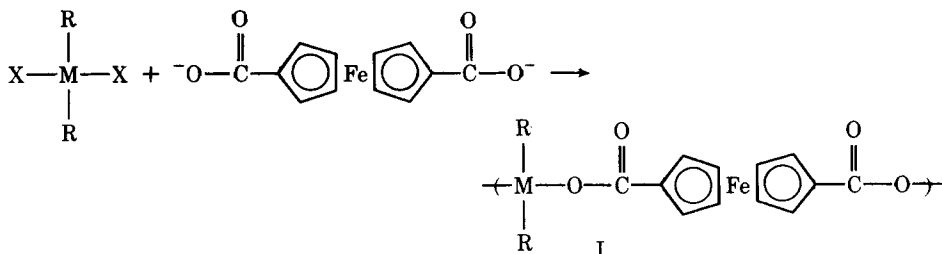
Oligomeric Group IVA ferrocene polyesters were synthesized utilizing the interfacial condensation technique. Yield decreases with increasing complexity of the aliphatic substituent; it decreases in the order of $I > Br > Cl$, and it decreases in the order of $Sn > Ge > Si$. Thus, initial attack by the nucleophile, steric requirements, and metal-halide bond breakage appear important:



where M = Si, Ge, or Sn.

INTRODUCTION

The inclusion of ferrocene-containing moieties into polymers enables the introduction of iron and the general better UV light stability of the products.¹ The inclusion of tin into polymers generally imparts antifungal and antibacterial properties to the product.² Exterior coatings (such as house and car paints) would benefit from a combination of these properties. Recently, we reported the initial synthesis of ferrocene-containing tin polyesters.³ Here, we report the further synthesis of such polyesters and the initial synthesis of the analogous germanium and silicon polyesters of form I:



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where M = Sn, Ge, or Si. The synthesis of tin polyesters and tin-ferrocene containing products is reviewed in references 3 to 5.

EXPERIMENTAL

The Group IVA organohalides were obtained from Alfa Inorganic, Inc. (Beverly, Mass.), except for dibutyltin diiodide, which was prepared as described by Alleston and Davies⁵ with physical properties in agreement with those reported by Seyferth and co-workers.⁷ The difluorides were all insoluble in suitable solvents precluding their use. Ferrocene dicarboxylic acid (FDA) was obtained from ROC/RIC Chemical Corp. (Sun Valley, Calif.). Disodium ferrocene dicarboxylate was generated just prior to reaction by addition of an equivalence of sodium hydroxide.

Polymerizations were conducted as described elsewhere.³ Briefly, the organometallic dihalide in an organic solvent was added to rapidly stirred solutions of the salt of FDA in water. Polymer precipitated rapidly from the reaction solution and was recovered by suction filtration.

Solubilities were determined using about 1 mg per 2 to 3 ml solvent. If the product appeared to be solubilized, the solvent was removed and an infrared spectrum obtained and compared to spectra of the original product for evidences of degradation. Viscosities were obtained utilizing serial dilutions of solutions contained in a Cannon-Ubbelohde semimicrodilution viscometer. Molecular weight was obtained from freezing-point lowering determination.

Infrared spectra were obtained utilizing the Perkin-Elmer 237B and Beckman IR-10 and 12 spectrophotometers utilizing KBr pellets. Spectra were in agreement with a repeating unit of form I. For instance, bands characteristic of the ferrocene unit are present at ca. 805, 1020 to 1030, and 1440 cm^{-1} ; bands characteristic of the M—Ph stretch at ca. 1480 and 1420 cm^{-1} are present; bands characteristic of the M—carbonyl (carbonyl stretching) at ca. 1660–1680 cm^{-1} are present. Elemental analysis was conducted utilizing usual "wet" semimicroqualitative sequences and were in agreement with a product of form I. For instance, for the condensation product with $(\text{Ph})_2\text{SnCl}_2$ — % Sn theory = 23, found = 24; % Fe-theory = 11, found = 10.

RESULTS AND DISCUSSION

Reaction is general occurring with all Group IVA R_2MX_2 reactants utilized. The products are generally light to dark (rust) red, the color presumably being derived from the ferrocene moiety. They are powders. As with other Group IVA products produced by us,^{4,5} solubility and solubility range are $\text{Si} > \text{Ge} > \text{Sn}$, with the tin polyesters soluble in only such dipolar aprotic solvents as DMF and triethyl phosphate. The products were all oligomeric, with degrees of polymerization between 2 and 5. This is disappointing but, as indicated by other studies of ours (for instance, refs. 4 and 5), may be due to the poor solubility of the product and/or rapid precipitation of oligomeric growing chains.

Several trends are evident. First, with aliphatic-substituted tin materials, yield decreases with increasing complexity of aliphatic substitution indicative of the importance of steric matters in product synthesis. Second, yield decreases in the order $\text{I} > \text{Br} > \text{Cl}$ for Sn—X monomers. This is in the order of

TABLE I
 Yield as a Function of Lewis Acid^a

Lewis acid	Yield M = Sn, % ^b	Yield M = Sn, % ^c	Yield M = Ge, % ^c	Yield M = Si, % ^c
Me ₂ MCl ₂	33	86	49	21
Me ₂ MBr ₂	58	90		
Et ₂ MCl ₂	23	79	41	
Et ₂ MBr ₂	38	85		
<i>t</i> -Bu ₂ MCl ₂	5	10		
<i>t</i> -Bu ₂ MBr ₂	5	11		
<i>t</i> -Bu ₂ MI ₂	6	18		
Ph ₂ MCl ₂	81	81	21	21
(PhCH ₂) ₂ MCl ₂	5	21		
(Ph)(CH ₂ =CH)MCl ₂	44			37
(<i>n</i> -C ₈ H ₁₇) ₂ MCl ₂		13		

^a LVN values ranged from 3 to 6 ml/g in DMSO representing number average degrees of polymerization of 2 to 5.

^b Reaction conditions: R₂MX₂ (0.50 mmole) contained in 30 ml CHCl₃ added to stirred (ca. 20,500 rpm no-load stirring rate) solutions containing 1,1'-ferrocene dicarboxylate (0.50 mmole) with NaOH (1.00 mmole) in 30 ml water at 25°C and 30 sec of stirring time.

^c Reaction conditions: same as a, except employing 1.25 mmoles of each reactant and 2.50 mmoles sodium hydroxide.

bond energy (Sn—I, 62 kcal/mole; Sn—Br, 76 kcal/mole; Sn—Cl, 85 kcal/mole)⁹ and bond polarizability and is indicative of the importance of metal halide bond breakage in the overall condensation process. Third, for the (few) runs made, yield generally is of the order Sn > Ge > Si. This trend has been found for other analogous Group IVA systems^{4,5} and is the direction of increasing electron density on the metal atom (and increasing participation of dπ—pπ bonding by the metal to a given electron (cf. ref. 4 for a short discussion of this topic) consistent with a more favorable nucleophilic attack on the more electron poor site.

Initial attack by the nucleophile, steric nature about the metal, and metal—halide bond breakage appear important in the present condensations. These results are consistent with an interchange mechanism. Caution must be exercised since other factors as monomer solubility, diffusion rates, etc., may be critical coincidentally leading to the observed trends.

Fourth, reactant concentration appears critical, with generally an increase in yield being seen for the systems containing reactant at the lower concentration (for instance, Table I, compare columns 1 and 2).

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