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Synthesis and Initial Thermal Characterization of Titanium Polyferrocene Ethers

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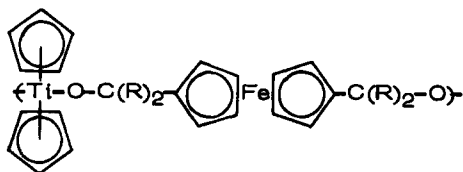
ABSTRACT

Titanium polyferrocene ethers were synthesized by the interfacial technique. Reaction is rapid and general. Synthesis can be effected by utilizing either NaOH or Et₃N but not without added base. Reactant molar ratio yield trends vary with the nature of the diol, indicative of the sensitivity of the system, at least to this variable. Decomposition to ca. 150° C occurs via a nonoxidative mode(s). Above 150° C, degradation occurs through an oxidative route(s) in air.

INTRODUCTION

We have been active in the synthesis of organometallic polymers often utilizing low temperature condensation processes. Recently we reported [1] the synthesis of titanium polyethers. Here we report synthesis of the analogous ferrocene-containing polyethers (I). While we have included the ferrocene moiety into a number of polymers

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I

utilizing salts of the diacid [2-4], the present paper reports our initial efforts at its inclusion through condensation as a diol. Since it is our initial experience with such ferrocene-containing compounds, we were interested in not only obtaining the products but also determining its potential usefulness in other systems and certain reaction dependencies. (The use of diol containing ferrocene-containing reactants will become more prevalent because of their recent commercial availability.)

Reasons for desiring inclusion of either titanium or ferrocene into polymers have been covered previously [1-7].

EXPERIMENTAL

Dicyclopentadienyltitanium dichloride, Cp_2TiCl_2 , was obtained from Alfa Inorganics (Beverly, Mass.). 1,1'-Dihydroxymethylferrocene (HMF) was obtained from Research Organic/Inorganic Chemical Corp. (Sun Valley, Calif.) and 1,1'-bis(A-hydroxyisopropyl)ferrocene (HIF) and 1,1'-bis(A-hydroxyethyl)ferrocene (HEF) were obtained from Wind River Chemicals (Opelika, Alabama). All were utilized as received.

Polymerization and recovery procedures are analogous to those reported elsewhere. Briefly, solutions of Cp_2TiCl_2 are added to stirred solutions containing the diol. Polymer precipitates rapidly from the reaction system and is recovered by suction filtration after suitable organic solvent and water washes.

Spectra were obtained by use of Beckman IR-10 and Perkin-Elmer 237 B spectrophotometers. All spectral samples were prepared with potassium bromide pellets. Spectra of the products exhibited the bands at 1415, 1040 and 815 cm^{-1} characteristic of the Cp group, at

TABLE 1. Yield as a Function of Diol and Stirring Time^a

	Yield (%)		
	HMF	HEF	HIF
Stirring time (sec)			
15	45	51	27
30	58	51	66
45	58	51	66
180	62	53	—
Fe (%)			
Calcd	13.2	12.4	11.7
Found	13.0	12.4	12.7
Ti (%)			
Calcd	11.4	10.6	10.0
Found	11.8	10.6	10.7
TiO ₂ + Fe ₂ O ₃ (%)	39.7	35.5	33.4

^aReaction conditions: Cp₂TiCl₂ (1.00 mmole) in 25 ml chloroform added to stirred solutions containing diol (1.00 mmole) and Et₃N (7.0 mmole) in 25 ml of water at 25° C and 23,500 rpm (no load) stirring rate. Diols: HMF = 1,1'-dihydroxymethylferrocene; HEF = 1,1'-bis(A-hydroxyethyl)ferrocene; HIF = 1,1'-bis(A-hydroxyisopropyl)ferrocene.

1150-1180 cm⁻¹ characteristic of the Ti-O-C moiety (tentative); a weak band about 3500-3200 cm⁻¹ due to Ti-OH and/or R-OH end groups, and bands 2850-3000 cm⁻¹ characteristic of C-H aliphatic stretching. Other bands are present and are also consistent with repeating unit I.

Elemental analyses were determined by means of both thermal and wet analysis techniques. Results are in agreement with a repeating unit of form I and are given in Table 1.

Solubility tests were carried out by addition of ca. 1 mg of polymer to 2 ml of liquid with regular viewing for two weeks. The products were insoluble in all liquids, degrading in concentrated HNO₃ and

concentrated H_2SO_4 after 3 hr. The products were stable and insoluble in such liquids as concentrated H_3PO_4 , concentrated NH_3 , triethylamine, diethylamine, pyridine, hexane, chloroform, chlorophenol, benzene, nonane, carbon tetrachloride, dioxane, dimethylformamide, dimethyl sulfoxide, acetone, water, nitrobenzene, 1,2,3-trichloropropane, 2,4-pentanedione, ethyl acetate, m-cresol, acetonitrile, and trichloroethylene. This lack of solubility precludes characterizations (such as molecular weight measurements) requiring polymer solution. While disappointing, it does not exclude product uses not requiring polymer solution. This insolubility is analogous to that previously reported for other titanium polyethers.

Thermal analyses were conducted by utilizing the du Pont 900 Thermal Analyzer console fitted with a DSC cell employing a linear baseline compensator and a 950 du Pont TGA apparatus. Procedures are described in detail elsewhere [8].

DISCUSSION AND RESULTS

Yield was studied as a function of base type. Representative results appear in Table 2. No product is formed in the absence of added base, indicating the importance of neutralizing HCl formed from condensation of the diol with Cp_2TiCl_2 . Product is formed both in the presence of NaOH (illustrative of a soluble inorganic base) and triethylamine

TABLE 2. Yield as a Function of Base^a

Run	Base	Amount of base (mole)	Yield (%)
1	None	0	0
2	NaOH	0.004	35
3	NaOH	0.008	40
4	Et_3N	0.008	1
5	Et_3N	0.018	40
6	Et_3N	0.036	61
7	Et_3N	0.144	25

^aReaction conditions: Cp_2TiCl_2 (4.00 mmole) in 50 ml chloroform added to stirred solutions containing 1,1'-dihydroxymethylferrocene (1.00 mmole) and base in 25 ml of water at 25°C, 23,500 rpm stirring rate for 30 sec.

TABLE 3. Results as a Function of Mole Ratio of Reactants^a

Mole ratio Cp ₂ TiCl ₂ :diol	Diol	Yield (%)
2:1	HMF	62
1:1	HMF	58
1:2	HMF	33
2:1	HEF	43
1:1	HEF	51
1:2	HEF	75
2:1	HIF	57
1:1	HIF	66
1:2	HIF	80

^aReaction conditions: same as for Table 1 for 1:1 systems at 30 sec stirring time. For other systems only the mole amount of reactant is varied.

(exemplifying a soluble organic base); triethylamine is utilized because of previous success in employing it in analogous interfacial condensation and because of the steric hindrance exhibited by it, minimizing effective competition for the titanium-containing moiety). Fairly large excesses can be tolerated giving acceptable yields. Large excesses (run 6, Table 2) give products exhibiting end groups containing portions of the triethylamine, and even larger excesses (run 7, Table 2) cause a decrease in product. Thus syntheses should not utilize excessive amounts of base.

Titanium polyferrocene ether formation is general, occurring with all ferrocene diols utilized, and rapid, occurring within 30 sec stirring time (Table 1). Reaction is also rapid and general when employing sodium hydroxide as the added base.

Steric hindrance at the diol is not critical to product yield, since product yield with HIF is about that of HMF.

Results of yield as a function of molar amount of reactants appear in Table 3. Yields are reproducible to $\pm 2\%$. The trend varies with diol. This is unusual [2], indicative of the sensitivity of the reaction system. For HMF, yield is more dependent on the diol and less dependent of Cp₂TiCl₂ concentration; for the other two diols, yield is sensitive to the concentrations of both reactants, decreasing with excess Cp₂TiCl₂ and increasing with excess diol.

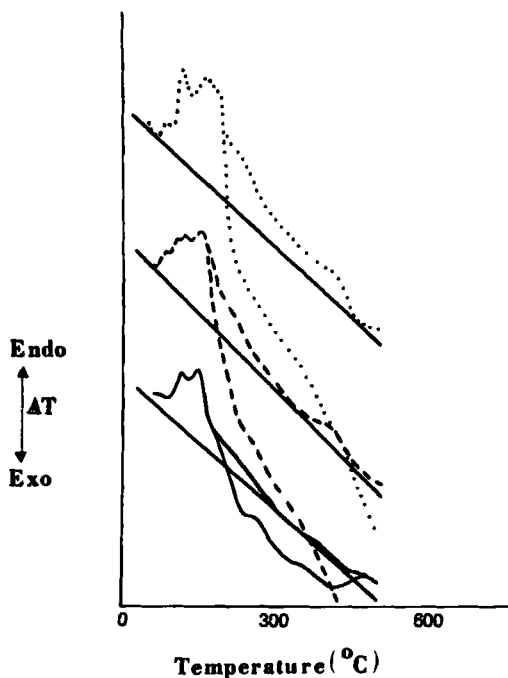


FIG. 1. DSC thermograms for products of Cp_2TiCl_2 with (--) HIF, (—) HMF, and (···) HEF: (lower portion of plot) in air after ca. 150°C and (upper portion of plot) in nitrogen. Gas flow rate, 3 liter/min; heating rate, $30^\circ\text{C}/\text{min}$; Y-axis setting, 0.1 C/in. (0.0040 mV/in.); the straight solid line represents $\Delta T = 0$.

Explanations are possible utilizing variations in reactive site and species and differences in diffusion rates and inherent diol reactivity. While rational explanations consistent with the results could be given they will not be, since definitive results have not been obtained. This variance of trend with diol points out the caution that must be exercised in inferring general trends from studies of single systems.

The results indicate that ferrocene diols should be useable in analogous interfacial condensation systems.

DSC and TGA thermograms appear in Figs. 1-3. Comparisons of the thermograms show that initial degradation to ca. 150°C occurs through an identical nonoxidative mode(s) in both air and nitrogen. Above 150°C degradation occurs through an oxidative mode(s) in air.

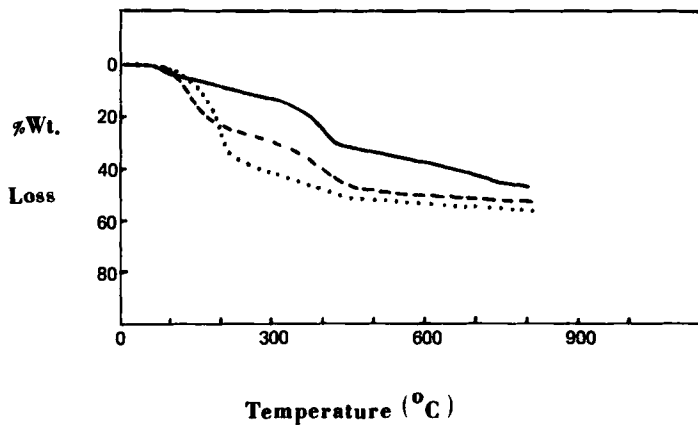


FIG. 2. TGA thermograms in air of products. Conditions and symbols as given in Fig. 1, in air.

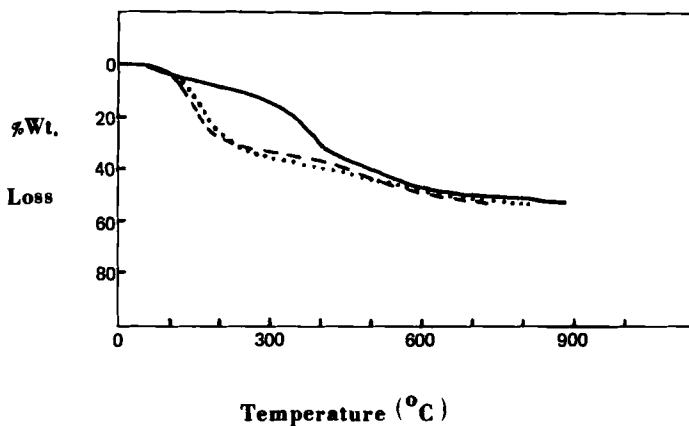
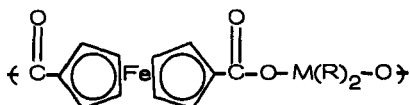


FIG. 3. TGA thermograms in N₂ for products. Conditions and symbols as given in Fig. 1, in nitrogen.

Unlike other ferrocene-containing polymers synthesized by us [2-4], the iron remains as residue. Probably the difference lies in the nature of the ferrocene to metal bonding. Previous products were linked through a carboxyl moiety which may decompose to carbon monoxide and carbon dioxide, freeing the ferrocene moiety or volatilization with (probable) accompanying further decomposition. The



ferrocene polyethers are not directly attached to the metal but are connected through a methylene bridge. Heating to ca. 1000° C for several hours yields Fe₂O₃ quantitatively.

The products actually exhibit both poor low and high temperature weight retention of the organic moiety. Metal oxides of Fe₂O₃ and TiO₂ compose most of the remaining residue after ca. 800° C in air. Percentages of TiO₂ plus Fe₂O₃ are given in Table 1 for ready comparison with the TGA thermograms. Thus, for the product with HIF at 600° C there remains 50% residue, of which all but 16% may be simply metal oxides.

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