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Condensation of Cp_2TiCl_2 with Tetraamines

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ABSTRACT

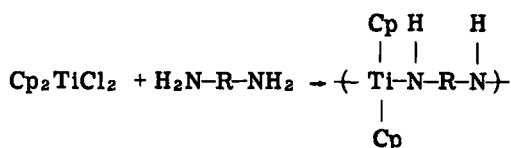
The synthesis of titanium polyamines from tetraamines is general and rapid. Systems utilizing equimolar quantities of reactants produce linear products, whereas tri- and tetra-substitution occurs when excess Cp_2TiCl_2 is used. The products exhibit moderate high-temperature stability but poor low-temperature stability, with degradation occurring via nonoxidative routes to ca. 200° C, and by oxidative routes in air at higher temperatures.

INTRODUCTION

Our group is responsible for the synthesis of a number of organo-metallic polymers [1-3]. Recently we began the synthesis of titanium-containing polymers, including the synthesis of titanium polyamines [4]. Several of these products exhibited moderately

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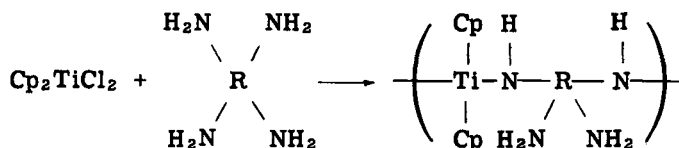
†Operation Catalyst-SEED Student, Summer 1975.



I

good weight retention (for instance ca. 80% weight retention at 600°C for the product from methyl-p-phenylenediamine) in air and nitrogen.

This led us to speculate on the thermal stability of products from tetrafunctional Lewis bases where internal crosslinking may occur to produce a thermally stable product. Here we report the synthesis and initial thermal characterization of titanium polyamines of form II.



II

EXPERIMENTAL

3,3'-Diaminobenzidine, 3,3',4,4'-tetraaminobenzophenone, and 1,2,4,5-tetraaminobenzene were utilized as received from Burdick & Jackson Labs, Muskegon, Mich. Dicyclopentadienyltitanium dichloride was also utilized as received from Alfa Inorganics, Beverly, Mass. Reaction procedures are similar to those described in detail elsewhere [4, 5]. Briefly, Cp_2TiCl_2 in an organic solvent is added to stirred aqueous solutions of the tetraamine with added base. Polymer rapidly precipitates from the reaction mixture and is obtained by suction filtration. It is then repeatedly washed with portions of water and the organic solvent, dried, and weighed.

IR spectra of the polymeric products and reactants were obtained by utilizing Perkin-Elmer 237B and Beckman IR-10 spectrophotometers. The products exhibited bands consistent with repeating units of form II. Bands characteristic of secondary and primary amine N-H stretching appear in the 3200-2500 cm^{-1} region. Band(s) at ca. 860-690 cm^{-1} characteristic of substituted aromatic rings are

present. For products from 3,3',4,4'-tetraaminobenzophenone a carbonyl band at ca. 1560 cm^{-1} is present. Bands characteristic of the cyclopentadienyl (Cp) groups are present at ca. 1440, 1015, and $810\text{--}850\text{ cm}^{-1}$ (in some instances certain of these bands are obscured by stronger bands). Elemental analysis (by both "wet analysis" and thermal techniques) are consistent with products of form II, where equimolar amounts of reactants are employed. Representative results appear in Tables 2 and 3.

Solubility tests were performed by adding ca. 1 mg of the material to 3 ml of the liquid. Liquids tested included water, chloroform, triethyl phosphate, dimethyl sulfoxide (DMSO), dimethylformamide, Sulfolane-W, acetone, carbon tetrachloride, and benzene. The products were insoluble in all solvents except DMSO, in which solubility was less than 0.1%, thus eliminating product characterization requiring polymer solution.

Thermal gravimetric analysis (TGA) was conducted by employing a 950 du Pont TGA instrument. Differential scanning calorimetry (DSC) was carried out by using a du Pont DSC cell fitted on a 900 du Pont thermal analyzer console employing a linear baseline. Gas flows of ca. 0.3 liter/min were employed. A Mettler H20T semimicro balance was employed for the weighing of DSC samples. DSC measurements were obtained on samples ground to a powder contained in open aluminum cups to allow the free flow away from the solid of volatilized gas, thus more closely simulating the conditions under which TGA studies were conducted.

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

Stirring time (sec)	Diamino-benzidine yield (%) ^b	Tetraamino-benzophenone yield (%) ^b	Tetraamino-benzene yield (%) ^b
5	33	—	—
15	26	—	—
60	23	—	—
180	27	67	4
300	26	66	4

^aReaction conditions: Cp_2TiCl_2 (1.00 mmole) in 25 ml chloroform added to diamine (1.00 mmole) with triethylamine (2.00 mmole) in 100 ml water at 25°C ; stirring rate 20,500 rpm for 180 sec.

^bElemental analyses within 1% of values given in Table 3.

TABLE 2. Results as a Function of Amine Concentration^a

DAB (mmole)	Yield (%)	Ti found (%) ^b
0.50	40	17
1.00	27	12
2.00	20	13

^aReaction conditions: Cp_2TiCl_2 (1.00 mmole) in 25 ml chloroform added to stirred solutions of diaminobenzidine (DAB) in 100 ml of water containing a twofold molar amount of triethylamine at a stirring ratio of 20,500 rpm (no load) at 25°C for 180 sec stirring time.

^bTi content: calculated for form II, 12%; calculated for form III, 17%.

TABLE 3. Results as a Function of Amine and Reactant Concentrations^a

Reactant concentration (mmole)	Diaminobenzidine yield (%) ^b	Tetraamino-benzophenone yield (%) ^c	Tetraamino-benzene yield (%) ^d
0.50	14	30	3
1.00	27	67	4
2.00	17	29	2
10.00	5	6	1

^aReaction conditions: Cp_2TiCl_2 in 25 ml chloroform added to stirred solutions of amine containing two-fold molar amounts of triethylamine in 100 ml of water at a stirring rate of 20,500 rpm (no load) at 25°C for 180 sec stirring time.

^bTi: Calcd, 12%; found, 13%.

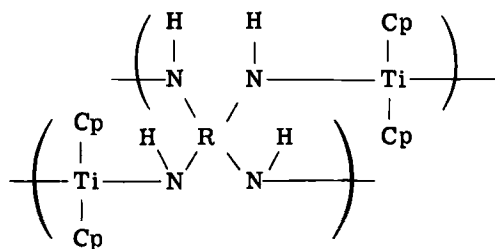
^cTi: Calcd, 11%; found, 12%.

^dTi: Calcd, 15%; found, 17%.

RESULTS AND DISCUSSION

Reaction appears general and rapid (Table 1). This rapidity of reaction is characteristic of most of the organometallic polymer-producing systems employing the interfacial technique [6, 7].

There exist four potentially reactive nucleophilic sites per Lewis base molecule. While systems employing 1:1 molar ratios of Cp_2TiCl_2 : amine appear to react in a 1:1 ratio, yielding products of form II, excess molar amounts of amine appear to give products containing more than one Cp_2Ti moiety per repeating unit—in theory capable of yielding products of form III.



III

For instance, the product from a 2:1 ratio of diaminobenzidene: Cp_2TiCl_2 (Table 2) contains 17% Ti compared with theoretical values of 12% (form II) and 17% form III). Infrared spectra contain higher intensity bands related to secondary amines and lower intensity bands characteristic of primary amines when compared with compounds prepared from systems employing a 1:1 ratio of reactants.

This behavior is similar to that exhibited by diamidoximes, which also contain four nucleophilic sites per Lewis base molecule. Diamidoximes, on reaction with excess Cp_2TiCl_2 , form crosslinked, tri- and tetra-substituted amidoxime moieties [8-10].

Thus while a predominance of the product is of form II, a small amount of crosslinking may occur for all products, evidencing itself in general insolubility in all solvents, though poor solubility of organometallic polymers appears to be a characteristic of such products [6, 7]. Such insolubility precludes physical characterizations (such as determination of molecular weight) and fabrication procedures requiring polymer solution.

Results as a function of amount of reactant appear in Table 3. Yield maximizes about a 0.08 M concentration (calculated on the basis of moles of reactant per total system). This is within the usual favorable concentration region experienced for interfacial systems [6, 7].

Thermograms appear as Figs. 1-3. While several products exhibit moderate high temperature weight retention (greater than 80% at $> 500^\circ\text{C}$), all show poor low temperature stabilities, most

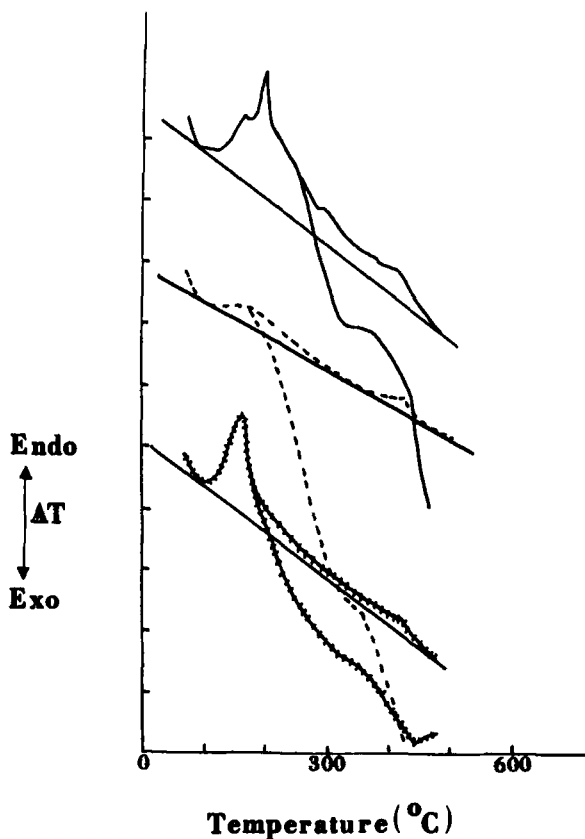


FIG. 1. DSC thermograms for condensation products of Cp_2TiCl_2 with (—) tetraaminobenzophenone, (++) tetraaminobenzene, and (--) diaminobenzidine, in air (lower plot) and in nitrogen (upper plot). Gas flow rate, 0.3 liter/min; heating rate, $30^\circ\text{C}/\text{min}$; Y-axis setting of $0.2^\circ\text{C}/\text{in}$, for 1.00-mg samples; the straight solid line represents $\Delta T = 0$.

beginning to degrade below 100°C . Additionally the weight retention plateaus are kinetically controlled, i.e., dependent on the heating ratio, with ca. 10% additional weight loss at isothermal times of ca. 30 min at 500°C . Initial degradation to ca. 200°C occurs via similar routes in air and nitrogen, but after this oxidative degradation occurs in air.

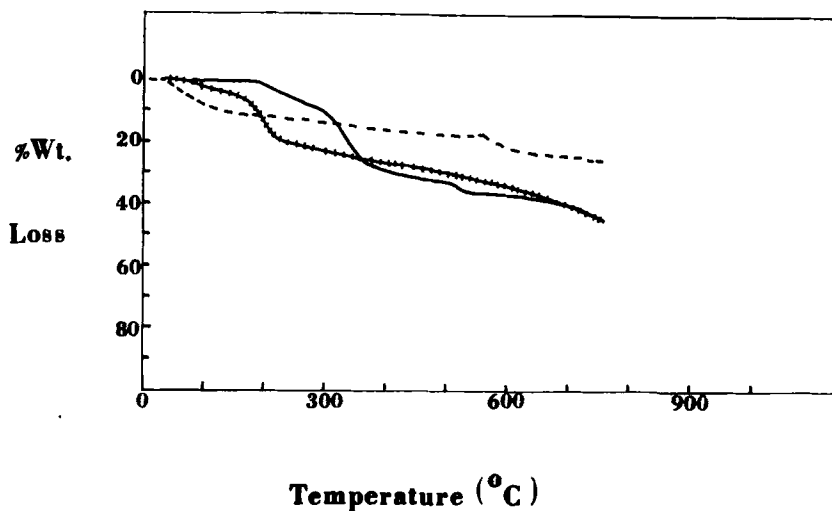


FIG. 2. TGA thermograms in nitrogen for products described in Fig. 1.

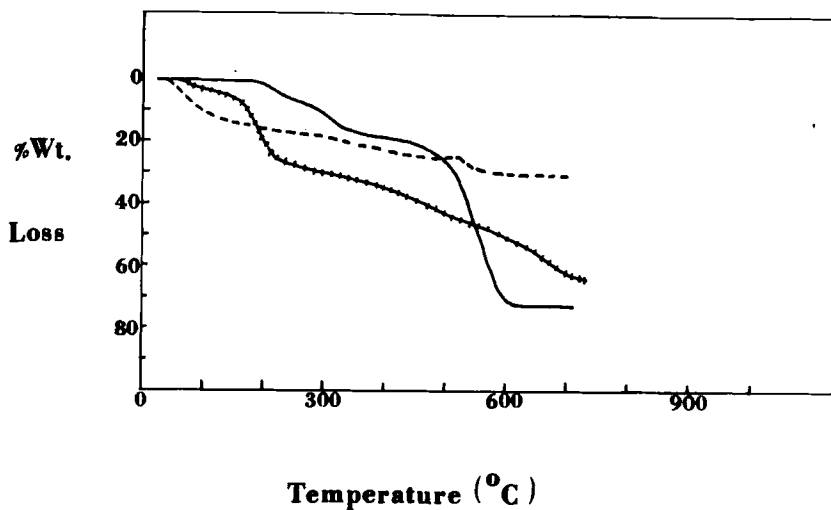


FIG. 3. TGA thermograms in air for products described in Fig. 1.

Thus, hoped-for internal cyclization and/or crosslinking appears either not to occur or to be insignificant in formation of truly high temperature-stable products. In terms of weight retention, the tetraamino products do not appear to offer advantages over titanium polyamines of form I.

Degradation begins to occur by solid-state routes before the T_g occurs, preventing attempted solution of the products by heating the products to the T_g in favorable solvents (such as dipolar aprotic solvents).

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