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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Charles E. Carraher JR.^a; Jana L. Lee^a

^a Department of Chemistry, University of South Dakota, Vermillion, South Dakota

To cite this Article Carraher JR., Charles E. and Lee, Jana L.(1975) 'Tentative Identification of the Reactive Species in the Reaction of Cp_2TiCl_2 with Salts of Diacids', *Journal of Macromolecular Science, Part A*, 9: 2, 191 – 198

To link to this Article: DOI: 10.1080/00222337508068656

URL: <http://dx.doi.org/10.1080/00222337508068656>

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Tentative Identification of the Reactive Species in the Reaction of Cp_2TiCl_2 with Salts of Diacids

CHARLES E. CARRAHER, JR. and JANA L. LEE

Department of Chemistry
University of South Dakota
Vermillion, South Dakota 57069

ABSTRACT

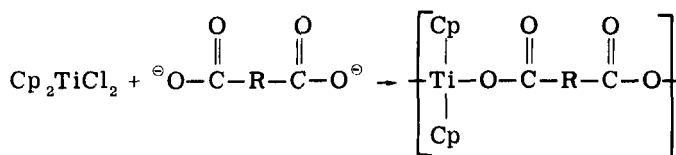
The tentative identification of the reactive species in the condensation of Cp_2TiCl_2 with salts of diacids to form titanium polyesters is made. The reactive species are believed to be the same for both aqueous solution and interfacial systems, i.e., R-CO_2^- and $\text{Cp}_2\text{Ti}^{2+}$ with reaction occurring in the aqueous phase. The condensation of Cp_2TiCl_2 with disodium terephthalate in interfacial systems occurs via a pseudo-first-order reaction:

$$\text{Rate} = k[\text{Cp}_2\text{TiCl}_2]$$

The rate-determining step(s) is believed to be diffusion of Cp_2TiCl_2 into the aqueous layer and/or hydrolysis of Cp_2TiCl_2 .

INTRODUCTION

We have previously reported the initial synthesis of titanium polyesters of Form I utilizing both interfacial and solution techniques [1, 2]. More recently we reported the thermal stability and "anomalous fiber formation" for some of the products [3]. We now report on several reaction variables associated with the synthesis of the polyesters. Reasons for desiring the synthesis of such products are cited elsewhere as is previous work involving titanium esters [1, 2].



I

EXPERIMENTAL

The following reagents were used without further purification: dicyclopentadienyltitanium dichloride (Alfa Inorganics, Inc., Beverly, Massachusetts); all of the diacids were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin.

Polymerization procedures are given elsewhere [1, 2]. Briefly, solutions of Cp_2TiCl_2 are added to stirred solutions containing salts of diacids. For interfacial systems, Cp_2TiCl_2 is contained in an organic solvent, whereas for aqueous solution systems it is contained in water.

Light scattering, elemental analysis, IR spectroscopy, viscometry, and solution techniques are the same as those employed previously [1, 2]. Elemental analysis and IR spectra are in agreement with a product of repeating unit 1. Many of the products are insoluble in all attempted solvents. Viscosity and/or weight-average molecular weight results are reported for those which are soluble.

Condensations were carried out using a blender whose "no-load" speed was standardized using a strobotac, type 1531-A (General Radio Company, Concord, Maryland). The blender was connected to a Powerstat, Type 116 (Superior Electric Co., Bristol, Connecticut) and the speed measured as a function of powerstat reading.

RESULTS AND DISCUSSION

The purpose of this research was to tentatively identify the reactive species and site for the interfacial systems, and to evaluate particular reaction parameters for which other similar systems have shown dependencies.

Results aimed at determining the kinetic behavior, active species, and site(s) of polycondensation for interfacial systems have been quite limited mainly due to 1) rapidity of reactions, many being completed in less than 60 sec; 2) complexity of reaction, reaction pathways, and reaction species; 3) complexity of reaction system, rapidly stirred and heterophasic; 4) lack of prior similar and/or credulous research in analogous organometallic condensations; and 5) many of the organometallic products are insoluble in all solvents precluding determinations requiring solution of the products [4]. The present system suffers to some degree from all of these problems, necessitating the speculative nature of the results.

The exact form of the aqueous solubilized Cp_2TiCl_2 is unknown. Various structures have been suggested which include Cp_2TiOH^+ and $\text{Cp}_2\text{Ti}^{2+}$ [5-7]. Aqueous solutions probably contain several species with the relative abundance varying with pH. Aqueous solutions of Cp_2TiCl_2 are acidic, exhibiting pH's in the range of 1 to 2. This is indicative of hydrolysis of Cp_2TiCl_2 which favors the presence of species such as Cp_2TiOH^+ . A 0.08 M solution of Cp_2TiCl_2 gives a pH of 1.7 corresponding to a $\text{Cp}_2\text{Ti}^{2+}:\text{Cp}_2\text{TiOH}^+$ of 3:1 assuming these to be the most prevalent species. At high pH's, insoluble $\text{Cp}_2\text{Ti}(\text{OH})_2$ is formed. Aqueous solutions of Cp_2TiCl_2 can be evaporated to dryness to give Cp_2TiCl_2 back again quantitatively. Thus solubilization of Cp_2TiCl_2 to form various ions is reversible. Other characteristics of aqueous solutions of Cp_2TiCl_2 have been reported elsewhere [1, 2]. For simplicity, Cp_2TiCl_2 solubilized in water will be designated as $\text{Cp}_2\text{Ti}^{2+}$. The active form of the salt is presumably the anion, RCO_2^- for aqueous solution systems.

Evidence as to the active species was sought by comparing the relative reactivity trends for interfacial and aqueous solution systems as a function of substituted terephthalic acid. If the reactive species is the same for both systems, then the orders and/or general dependencies should be the same for both systems, the only difference being the presence of an organic layer which supplies a constant supply of Cp_2TiCl_2 , i.e., the active titanium species in both systems is the $\text{Cp}_2\text{Ti}^{2+}$ formed in the interfacial systems via migration from the organic layer to the aqueous layer and the active acid form is the salt, RCO_2^- , with the reaction occurring in the aqueous phase to allow

hydrolysis of Cp_2TiCl_2 . All systems were run to completion, i.e., 1 min stirring time is greater than the reaction time; thus yield is a measure of the overall efficiency of polyester formation.

The trends are similar and follow a trend tetramethylterephthalate > dimethylterephthalate > terephthalate > bromoterephthalate > dichloroterephthalate > nitroterephthalate which is the trend of decreasing basicity of the RCO_2^- [8]. This is consistent with reaction occurring via a simple addition pathway and also with reaction occurring in the aqueous phase for the interfacial systems. The latter is not unexpected since the solubility of the salt in the organic phase should be quite low.

A similar comparative study has been carried out between the reaction of Cp_2TiCl_2 with substituted hydroquinones to form polyethers [9]. For these systems yield trends were dissimilar with steric hindrance being a critical factor for interfacial systems, which was consistent with a more sterically dependent bimolecular reaction between R-OH and Cp_2TiCl_2 occurring in interfacial systems. Other evidence was consistent with polyesterification occurring via different pathways for interfacial and solution systems with reaction occurring in the organic layer, near the interface for interfacial systems.

Reactions in aqueous solution systems are too rapid to follow using conventional techniques. Reaction in interfacial systems is somewhat slower, and a kinetic study was attempted using terephthalic acid and Cp_2TiCl_2 . Addition of the reactants to one another was rapid and controlled such that addition of 100 ml of solution required less than 5 sec. Reaction time was begun after addition of the two phases. Treatment of the data is open to discussion. Concentrations are calculated based on the amount of reactant present compared to the total volume of both phases. Reaction rates and concentrations of reactants are based on the amount of polymer formed. This is believed to be valid since an investigation of the species present does not indicate the presence of other nonpolymer using products.

The data were treated in the usual manner and yield linear plots of $\log [\text{Cp}_2\text{TiCl}_2]_{\text{initial}} / [\text{Cp}_2\text{TiCl}_2]$ as a function of time and rate as a function of reactant concentration, i.e., first-order relationships (Fig. 1). Further work was done. By varying the amounts of reactants, it was found that the rate is primarily dependent on the concentration of the Cp_2TiCl_2 but not greatly affected by the concentration of the disodium terephthalate (range tested = 0.015 to 0.045 $\underline{\text{M}}$), being in agreement with the expression

$$\text{Rate} = k[\text{Cp}_2\text{TiCl}_2]$$

The reaction is believed to be pseudo-first-order since 1) it is apparent that yield is dependent on the nature of the diacid (cf., for instance, Table 1), and 2) the plots of rate vs $[\text{Cp}_2\text{TiCl}_2]$ and \log

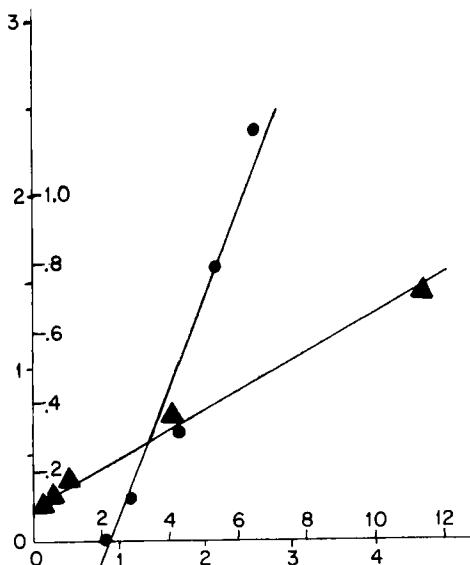


FIG. 1. Kinetic data for the condensation of Cp_2TiCl_2 (0.00125 mole) in 30 ml chloroform and disodium terephthalate (made from the addition of 0.00250 mole of sodium hydroxide to 0.00125 mole of terephthalate acid) in 10 ml of water at 27°C with a stirring rate of 17,500 rpm plotted for first-order kinetic relationships. Outside ordinate values: Rate [moles/(liter)(sec) $\times 10^{-4}$] (●). Outside abscissa values: $[\text{Cp}_2\text{TiCl}_2] \times 10^2$ (●). Inside abscissa values: $\log \frac{[\text{Cp}_2\text{TiCl}_2]_0}{[\text{Cp}_2\text{TiCl}_2]_{\text{time}}}$ (▲). Inside abscissa values: Reaction time time (min) (▲).

$[\text{Cp}_2\text{TiCl}_2]_{\text{initial}}/[\text{Cp}_2\text{TiCl}_2]$ vs time do not pass through the ordinate as true first-order plots should.

Product molecular weight appears to be constant with reaction time for this system with an average limiting viscosity number of 0.15 dl/g and a weight-average molecular weight of 3×10^5 via light-scattering photometry. This is consistent with a chain-type mechanism proposed for many interfacial condensations (for instance, Refs. 4 and 10).

A similar kinetic behavior was reported for the interfacial condensation of Cp_2ZrCl_2 with the disodium salt of 1,1'-ferrocene dicarboxylic acid [11]. To further evaluate the kinetic behavior, the

TABLE 1. Yield as a Function of Substituted Terephthalic Acid^a

Acid	Yield (%)	
	Interfacial	Aqueous solution
Tetramethylterephthalic acid	76	59
Dimethylterephthalic acid	65	47
Terephthalic acid	55 ^b	48 ^c
Bromoterephthalic acid	33	43
Dichloroterephthalic acid	30	32
Nitroterephthalic acid	28	27

^aReaction conditions: For interfacial systems the sodium salts of dicarboxylic acids (prepared from addition of 0.00125 mole of diacid to 0.00375 mole of NaOH) in 30 ml of H₂O were added to rapidly stirred (rpm = 21,500) solutions of Cp₂TiCl₂ (0.00125 mole) in 30 ml of CHCl₃ at 27°C for 1 min stirring time. Aqueous solution systems were prepared in the same way except Cp₂TiCl₂ was contained in 30 ml of H₂O.

^bLVN = 0.15/dl/g and \bar{M}_w via light scattering of 3×10^5 , both in 2-chloroethanol at 30°C.

^cLVN = 0.08 dl/g in 2-chloroethanol at 30°C.

system was studied as a function of stirring rate. Yield remains essentially constant throughout the stirring range of 10,100 to 24,400 rpm. According to Smirhova [12], a constancy of yield as stirring rate is varied means the reaction is "kinetically controlled."

The Cp₂TiCl₂ possesses two color sites, the yellow Cp-Ti and the red Ti-Cl [1, 2]. Interfacial reactions progress through a series of color changes from red to pink to yellow. The appearance of the yellow color was always found experimentally to coincide with the completion of the reaction and can be utilized as a crude measure of the rates of reaction. The time required for onset of the yellow coloration is listed in Tables 2 and 3 as the "color change time." Color change time decreases (i.e., reaction rate increases) with an increase in stirring rate (Table 2). Such reactions should then be viewed as diffusion controlled (i.e., differences in yield and/or rate are brought about by differences in diffusion, assuming that increased stirring rates effect only increases in interfacial surface area [12, 13]) and not as "kinetically controlled." (The systems utilized in the kinetic studies did not exhibit the onset of yellow coloration.)

TABLE 2. Yield as a Function of Stirring Rate for Interfacial Systems^a

Stirring rate (rpm)	Yield (%)	Color change time ^b (sec)
10,000	50	60
15,200	64	55
18,100	54	45
21,500	55	25
22,400	55	25
24,400	55	20

^aReaction conditions the same as given in Table 1 for terephthalic acid except for stirring rate.

^bReported to the nearest 5 sec.

TABLE 3. Yield as a Function of Organic Volume^a

CHCl_3 volume	Yield (%)	Color change time ^b (sec)
30	55	25
60	52	35
120	5	60
150	3	60

^aReaction conditions the same as given in Table 1 for terephthalic acid except for volume of CHCl_3 .

^bReported to the nearest 5 sec.

It is currently believed that the rate-determining reaction is the diffusion of the Cp_2TiCl_2 through the interface into the aqueous layer and/or the hydrolysis of the Cp_2TiCl_2 , either or both responsible for 1) the pseudo-first-order rate dependence on Cp_2TiCl_2 and 2) the color changes observed as a function of stirring rate.

The importance of diffusion and/or hydrolysis of Cp_2TiCl_2 is further borne out by the dependence of yield and "color change time" on the volume of the organic phase with color change time becoming

less and yield becoming greater as chloroform volume is decreased (Table 3).

ACKNOWLEDGMENT

J.L.L. was supported by American Chemical Society Operations Catalysts-SEED during the summer of 1973.

REFERENCES

- [1] C. Carraher, J. Polym. Sci., A-1, **9**, 3661 (1971).
- [2] C. Carraher, Org. Coatings Plast. Chem., **31**, 330, 338 (1971).
- [3] C. Carraher, Chem. Technol., 1972, 741.
- [4] C. Carraher and F. Millich, eds., Interfacial Polymerizations, Dekker, New York, 1975.
- [5] K. Andra, Z. Chem., **7**, 318 (1967).
- [6] F. Calderazzo, Organometallic Chem. Rev., **B-5**, 547 (1969).
- [7] G. Doyle and R. Tobias, Inorg. Chem., **7**, 2484 (1968).
- [8] H. Jaffe, Chem. Rev., **53**, 191 (1953).
- [9] C. Carraher and S. Bajah, Polymer, **15**, 9 (1974).
- [10] P. Morgan, Condensation Polymers: By Interfacial and Solution Methods, Wiley, New York, 1965.
- [11] C. Carraher and J. Reimer, Polymer, **13**, 153 (1972).
- [12] O. Smirhova, El Ali Khasan, I. Loser, and G. Kulesnikov, Vysokomol. Soedin., **7**, 503 (1965).
- [13] C. Carraher and R. Frary, Makromol. Chem., **175**, 2307 (1974).

Accepted by editor July 18, 1974

Received for publication July 31, 1974