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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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To cite this Article Carraher Jr., Charles E. and Jambaya, Leonard M.(1974) 'Reaction Species in the Aqueous Solution and Interfacial Synthesis of Zirconium Polyethers', *Journal of Macromolecular Science, Part A*, 8: 7, 1249 – 1259

To link to this Article: DOI: 10.1080/00222337408068628

URL: <http://dx.doi.org/10.1080/00222337408068628>

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Reaction Species in the Aqueous Solution and Interfacial Synthesis of Zirconium Polyethers

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ABSTRACT

The following tentative identifications are made from the study of variations in pH and substituted hydroquinones in the synthesis of zirconium polyethers: active species for aqueous solution systems, $\text{Cp}_2\text{Zr}^{2+}$ and RO^\ominus ; active species for interfacial systems, Cp_2ZrCl_2 and R-OH with reaction occurring near the interface or in the organic phase. Yield increases as stirring rate increases throughout the stirring range of 13,000 to 24,500 rpm. Decent yields can also be obtained utilizing "inverse interfacial" systems where the Cp_2ZrCl_2 is originally contained in water and the diol and added base in the organic layer. No product is found utilizing organic solution systems.

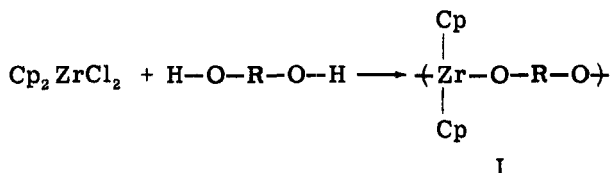
*Taken from thesis of Leonard M. Jambaya, University of South Dakota, 1973.

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INTRODUCTION

Relatively little work has been reported on the synthesis of organo-metallic polymers due in large part to a lack of suitable preparative methods. We have been engaged in the synthesis of organometallic polymers utilizing low temperature condensation techniques, namely the solution and interfacial techniques (for instance, Refs. 1-6). Such techniques avoid or limit undesirable thermally dependent competing reactions. Recently we reported the synthesis of zirconium polyethers of Form I [1].



Much of our work is based largely on the Lewis acid (the metal atom site)-Lewis base (diamine, diol, etc.) concept. Even so, the Lewis acids and bases can exist in several forms. Also, several reaction sites are possible for interfacial synthesis. The present paper presents evidence aimed at tentatively identifying the active metal and diol species for both polyether synthesis being effected by the solution and interfacial techniques as well as the site of polymerization for interfacial systems. Also, results from studying other reaction variables are presented.

EXPERIMENTAL

Polymerization procedures are similar to those described in detail elsewhere [2, 5]. Briefly, solutions of Cp_2ZrCl_2 are added to stirred aqueous solutions containing diol and any added base. For interfacial systems Cp_2ZrCl_2 is contained in a water immiscible solvent whereas for aqueous solution systems Cp_2ZrCl_2 is contained in water. The reaction apparatus is similar to that described elsewhere [7]. Reaction occurs under rapidly stirred conditions in a 1 pint Kimax Emulsifying Mill jar placed on a Waring Blendor with a recorder rotor speed of 23,500 rpm (no load). Solutions are added through a large mouthed funnel placed in a hole in the jar lid. Addition is rapid such that 100 ml of solution can be added in less than 3 sec. A second hole in the jar lid acts as a vent. Timing for each reaction is begun after the second phase has been introduced into the stirring jar. Syntheses employing hydroquinone or substituted hydroquinone or substituted hydroquinones were accomplished under a nitrogen atmosphere utilizing equipment described elsewhere [7].

An Instrumentation Laboratories, Inc. pH meter (Model 205) was used to measure the pH's of aqueous solutions.

Polymerizations where stirring speed was varied were conducted on a blender where the stirring rate was standardized using a Strobotac, Type 1531-A (General Radio Company, Concord, Massachusetts). The blender was connected to a Powerstate, Type 116 (Superior Electric Co., Bristol, Connecticut), and the "no-load" speed was measured as a function of powerstate reading.

DISCUSSION AND RESULTS

While we have spent considerable effort in the synthesis of organometallic polymers, results aimed at describing the active species have been quite limited. This is mainly due to the following: 1) rapidity of reaction—most reactions are complete within 60 sec; 2) complexity of reaction system—rapidly stirred and for interfacial reactions the reaction system is heterophasic; 3) lack of prior similar and/or credulous research in analogous condensations; and 4) most of the organometallic products are insoluble in all solvents thus precluding determinations requiring solution of the products. Synthesis of the zirconium polyethers suffers from all of the above, making identification of the reactive species and site(s) speculative.

The exact form of the aqueous solubilized Cp_2ZrCl_2 is unknown. Various structures have been suggested for the analogous aqueous solubilized Cp_2TiCl_2 which include $\text{Cp}_2\text{Ti}^{2+}$ and Cp_2TiOH^+ [8-10]. Aqueous solutions are acidic, exhibiting a pH in the range of 1 to 3. This is indicative of the occurrence of hydrolysis which would favor the presence of species such as Cp_2ZrOH^+ . (Previous work has established that Cp_2ZrCl_2 subsequently is dihydroxylated to yield solid $\text{Cp}_2\text{Zr}(\text{OH})_2$ [3]). A 0.1 M aqueous solution of Cp_2ZrCl_2 exhibits a pH of 1.4. Assuming the two most prevalent species to be $\text{Cp}_2\text{Zr}^{2+}$ and Cp_2ZrOH^+ , this would indicate the ratio of $\text{Cp}_2\text{Zr}^{2+}:\text{Cp}_2\text{ZrOH}^+$ to be 1.5:1. For simplicity, Cp_2ZrCl_2 solubilized in water will be designated as $\text{Cp}_2\text{Zr}^{2+}$. Other characteristics of aqueous solutions of Group IVB Cp_2MCl_2 compounds have already been described [3].

Synthesis of zirconium polyethers was general for the interfacial syntheses but was effected with only aromatic diols utilizing aqueous solution systems [1]. This suggests that the active form(s) of reactants may be different for the two synthetic systems. The lack of polymer formation in aqueous solutions with aliphatic diols may be due to the difference in acidity between aromatic and aliphatic diols. For instance, hydroquinone is 99% monoionized at pH's > 12, and over 99% diionized at pH's > 13.8 (for hydroquinone $\text{p}K_{a1} = 10$ [11] and $\text{p}K_{a2} = 12$ [12]). Aliphatic diols remain largely un-ionized even at a

TABLE 1. Yield as a Function of pH-Aqueous Solution Systems^a

Buffer pairs (amount)	Average pH ^b	Yield (%)
KCl (0.004 mole) NaOH (0.0016 mole)	13	83
NaOH (0.0016 mole) NaHCO ₃ (0.00128 mole) NaHPO ₄ (0.00012 mole)	11.8	2
NaOH (0.0012 mole) Na ₂ HPO ₄ (0.00012 mole)	9.4	0.0
KCl (0.004 mole) NaHCO ₃ (0.00128 mole)	8.2	0.0
Na ₂ CO ₃ (0.00072 mole) Na ₃ PO ₄ · 12H ₂ O (0.00072 mole)	5.4	0.0
NaOH (0.004 mole) NaH ₂ PO ₄ (0.002 mole)	8.5	0.0

^aReaction conditions: Cp₂ZrCl₂ (0.001 mole) in 50 ml of water added to stirred solutions of hydroquinone in 50 ml of water containing added buffer at 23,000 rpm (no load) stirring rate for 30 sec stirring time at 25°C.

^bAverage pH is the initial pH + final pH divided by 2. The change in pH ranged from 1 unit to no more than 2.5 units.

pH of 14 (for instance, ethylene glycol has a pK_{a1} of 15.1 [12, 13]). It is possible that polycondensation is only effected in aqueous solution with deprotonated diols whereas other criteria are critical for interfacial systems. If the aqueous synthesis involve the deprotonated diol, then one might expect an increase in the rate of condensation with pH assuming competing factors, as Cp₂Zr²⁺ hydroxylation, etc. remain relatively unchanged. To evaluate this, yield was studied as a function of pH utilizing buffered aqueous solutions with hydroquinone (Table 1). There is a direct correlation between pH and percentage monoionized and diionized hydroquinone with product being formed only where a large amount of the diol is deprotonated. This is consistent with the idea that the predominating active diol species, at least for condensations with Cp₂ZrCl₂, is the deprotonated diol.

A similar pH profile study was made for the interfacial condensation of hydroquinone with Cp₂ZrCl₂ (Table 2). There is an obvious difference in the pH yield trend in comparison to that observed in the

TABLE 2. Yield as a Function of pH-Interfacial Systems^a

Buffer pairs (amount)	Average pH	Yield (%)
Na ₂ HPO ₄ (0.0012 mole) NaHCO ₃ (0.00128 mole)	12.8	36
NaHCO ₃ (0.008 mole) Na ₂ CO ₃ (0.00072)	12.7	36
Na ₃ PO ₄ ·12H ₂ O (0.00072 mole) Na ₂ HPO (0.000128 mole)	10.5	30
Na ₃ PO ₄ ·12H ₂ O (0.0014 mole) Na ₂ HPO ₄ (0.00012 mole)	7.5	65
NaHCO ₃ (0.0016 mole) Na ₂ CO ₃ (0.00072 mole)	6.4	58

^aReaction conditions same as Table 1 except that buffer was used as indicated. Average pH is the summation of the initial and final pH divided by 2. Variation was no more than 3 pH units. Cp₂ZrCl₂ was in 50 ml of CHCl₃ instead of water.

aqueous solution synthesis. Medium yields of product are achieved even at low pH's. In fact, better yields are achieved in the pH ranges where little diol is deprotonated than where most of the diol is deprotonated. (It must be noted that no product is formed in the absence of added buffer or base, thus the presence of added buffer or base is essential to polycondensation.) This is consistent with the active species for interfacial synthesis to be the un-ionized hydroquinone. This might also imply that reaction occurs in the organic phase since if the reaction occurs in the aqueous phase one should expect reaction with the more active RO[⊖] to occur at the expense of the slower reaction with ROH, resulting in a trend similar to that found in the aqueous solution systems rather than the observed trend.

A similar pH profile study was made for the interfacial condensation of phenylphosphonic dichloride and hydroquinone where the active hydroquinone is believed to be the ion [12]. No product was formed at pH's below 9. Product yield increased with pH in a manner directly related to the increase in the amount of ionized hydroquinone. The obvious difference between the yield-pH relationship found for the reaction between phenylphosphonic dichloride and hydroquinone and the present system is consistent with the reactive species being different for the two systems.

Further supportive evidence as to the active species was sought by

comparing the relative reactivity trends for interfacial and aqueous solutions as a function of substituents on hydroquinone. We can argue that if the reactive species in both systems is the same, 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_2ZrCl_2 , i.e., the active zirconium species in both systems is the $\text{Cp}_2\text{Zr}^{2+}$ formed in the interfacial systems by migration from the organic layer to the aqueous layer. Further, the active diol species would be either RO^\ominus or ROH with reaction occurring in the aqueous phase to allow hydrolysis of Cp_2ZrCl_2 .

TABLE 3. Yield as a Function of Substituted Hydroquinone^a

	Aqueous solution		Interfacial	
	Yield (%)	DP_N^b	Yield (%)	DP_N^b
Methylhydroquinone	12	35	14	41
2,5-Diterbutylhydroquinone	40	45	21	-
Hydroquinone	40	-	61	-
Bromohydroquinone	14	34	18	41
Chlorohydroquinone	5	34	50	-
2,5-Dichlorohydroquinone	15	37	21	-
Tetrachlorohydroquinone	31	67	46	-
2,3-Dicyanohydroquinone	51	56	45	46

^aReaction conditions: same as Tables 1 and 2 except NaOH (0.002 mole) base was employed.

^bDerived from IR spectra of products as described in the Discussions section.

The trends are dissimilar (Table 3). Solubility, etc. trends were established and found to be unrelated in determining the relative reactivity trends (Table 5). Thus the reactive species are probably not the same for the two systems. Several observations are apparent. First, steric hindrance appears to be less important for the aqueous system. This is expected if the reactive species are $\text{Cp}_2\text{Zr}^{2+}$ and RO^\ominus for the aqueous solution systems with reaction occurring by a simple, highly energetically favored, addition reaction and Cp_2ZrCl_2 and ROH for the interfacial systems with the reaction presumably occurring by a less energetically favored bi-molecular transition state where steric considerations are more important. Second, the

TABLE 4. Yield as a Function of Diol for Systems Employing Et_3N as the Added Base^a

Diol	Yield (%)	
	Aqueous solution	Interfacial
Chlorohydroquinone	15	18
1,4-Benzenedimethanol	27	36
1,4-Dichlorohydroquinone	39	
Methylhydroquinone	56	70
2,5-Diterbutylhydroquinone	66	26
2,3-Dicyanohydroquinone	81	30
2-Butyne-1,4-diol	0	5

^aReaction conditions were the same as in Tables 1 and 2 except that Et_3N (0.002 mole) was used instead of NaOH.

TABLE 5. Summary of Solubilities and Distribution Ratios

	Solubility in water ^a (g/ml)	Solubility in CHCl_3 ^a (g/ml)	Distribution ratio ^b moles in CHCl_3 : moles in H_2O
2,5-Diterbutylhydroquinone	0.043	0.039	64
Dicyanohydroquinone	0.0031	0.013	1.1
Tetrachlorohydroquinone	0.012	0.012	7.1
Chlorohydroquinone	0.11	0.10	0.19
Methylhydroquinone	0.025	0.025	0.19
Hydroquinone	0.0040	0.0091	17

^aAt room temperature, 25°C.

^bDetermined using 0.001 mole of diol, 50 ml CHCl_3 , and 50 ml of H_2O to which 0.002 M NaOH had been added at 25°C.

electronic nature of the hydroquinones appears to be of secondary importance in both systems. (Table 3 is arranged according to the general hydroxyl bond polarity.)

An analogous study was made but this time Et_3N was employed as

the added base. The trend for the aqueous solution system is essentially the same as that obtained for the NaOH added base systems. There exist several differences in the trends for interfacial systems. These differences do not appear to be related to such criteria as bond polarity or steric requirements. The reason(s) for these observed differences may be due to the fact that Et_3N is soluble in the organic phase and thus may exert some added influence during the reaction, but as of yet this is unknown. The difference in trends between the aqueous solution and interfacial systems is again quite evident, indicating a difference in reactive species between the two systems.

While the direct identification of particular reactive species has yet to be made, the following observations are consistent with the experimental results reported above: active species for aqueous solution systems, $\text{Cp}_2\text{Zr}^{2+}$, and $\text{R}-\text{O}^-$; active species for interfacial systems, Cp_2ZrCl_2 and $\text{R}-\text{OH}$, with reaction occurring near the interface or in the organic phase.

Yield was studied as a function of the stirring rate of the blender (Table 6). For both systems, yield increased with increase in stirring rate. Smirhoya et al. [14] refer to such situations as being indicative of diffusion-controlled processes, i.e., differences in the diffusion rates of reactants are responsible for the variations in yield with stirring rate. Diffusion effects are generally apparent only for systems where the activation energy for reaction is in the low to medium range (generally 20 kcal/mole or less). While the activation energy of the current reactions is unknown, it is reasonable to assume that such reactions exhibit activation energies in the low to medium range since many Schotten-Baumann reactions exhibit activation energies in this range [12, 15].

TABLE 6. Yield as Function of Stirring Rate^a

Stirring rate (rpm)	Yield (%)	
	Interfacial	Aqueous solution
13,000	59	24
14,700	66	31
17,700	71	42
21,400	75	47
23,400	92	51
24,500	93	58

^aReactions conditions: Same as Tables 1 and 2 except for stirring rate and with NaOH (0.002 mole) as the base.

Since the Cp_2ZrCl_2 and diols are soluble in both organic and aqueous solutions, at least four low temperature condensation systems can be devised. Results from two of these have already been given, i.e., the "usual" interfacial and aqueous solution systems. An additional organic solution system and additional interfacial system designated as an "inverse" interfacial system (since the Cp_2ZrCl_2 is contained in the aqueous phase and the diol and added base in the organic phase) can also be devised. For best results the added base should be contained in the phase containing the Lewis base (diol). Thus an organic base such as triethylamine, Et_3N , should be employed. Et_3N has been found to be a satisfactory substituent for sodium hydroxide [1] and was employed as the added base for all four systems. The inverse system gave product at a satisfactory level, but the organic solution system did not give any detectable product (Table 7).

Three end groups are possible/ the R-OH (maximum occurring in the 3000 to 3500 cm^{-1} region), Zr-Cl (280 to 305 cm^{-1}), and Zr-OH (maximum occurring in the 3300 cm^{-1} region) occurring from the hydrolysis of Zr-Cl. No IR-detectable Zr-Cl end groups are found (except as noted below). Most products show both Zr-OH and R-OH end groups. Certain products synthesized utilizing NaOH as

TABLE 7. Yield for Inverse Interfacial and Organic Solution Synthesis^a

Diol	Yield (%)	
	Organic solution	Inverse interfacial
Hydroquinone	0	56
1,4-Benzenedimethanol	0	31
2,5-Ditertbutylhydroquinone	0	28
2,3-Dicyanohydroquinone	0	62
4,4-Isopropylenediphenol	0	35
Ethylene glycol	0	
1,4-Butanediol	0	

^aReaction conditions: For inverse reactions, Cp_2ZrCl_2 (0.001 mole) in 50 ml H_2O was added to diol (0.001 mole) in 50 ml CHCl_3 . For organic solution, Cp_2ZrCl_2 (0.001 mole) in 50 ml CH_2Cl_2 was added to diol (0.001 mole) in 50 ml CHCl_3 . Base, NEt_3 (0.002 mole) was added to the diol-containing phase. Other conditions as described in Tables 1 and 2.

the added base exhibit only (detectable) Zr—OH end groups. From comparison of the Zr—OH band at 3300 cm^{-1} to the Cp- π band at 1440 cm^{-1} [standard product $\text{Cp}_2\text{Zr}(\text{OH})_2$], it is possible to generate a crude number-average degree of polymerization, $\overline{\text{DP}}_N$. Results are cited in Table 3. The capability of identifying such relatively large $\overline{\text{DP}}_N$'s is possible because of the high intensity of the Zr—OH band at 3300 cm^{-1} . Such values must be viewed as upper estimates at best since small R—OH peaks may be "hidden" by the intense Zr—OH band. Because of the uncertainty of such $\overline{\text{DP}}_N$'s, no emphasis was placed on the results.

Spectra of products from NEt_3 systems show no evidence of end groups formed from reaction with NEt_3 but contained mostly R—OH end groups with a small amount of Zr—OH end groups (Table 4). The greater presence of Zr—OH end groups in NaOH systems is consistent with the observed rapid hydroxylation of Cp_2ZrCl_2 in sodium hydroxide solutions. As expected, the relative number of Zr—OH:R—OH end groups increases with a pH increase, with the Zr—Cl end groups present at lower pH's (Tables 1 and 2). There is no change in the relative Zr—OH:R—OH end groups for either the interfacial or aqueous solutions systems as the stirring rate is varied (Table 6).

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Accepted by editor March 25, 1974

Received for publication April 10, 1974