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Kinetic Investigation of the Living Cationic Polymerization of Isobutylene Using a *t*-Bu-*m*-DCC/$TiCl_4$/2,4-DMP Initiating System

Robson F. Storey* and Kim R. Choate, Jr.[†]

The University of Southern Mississippi, Department of Polymer Science, P.O. Box 10076, Hattiesburg, Mississippi 30406

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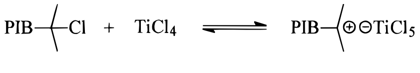
ABSTRACT: A kinetic and mechanistic study of the living cationic polymerization of isobutylene was conducted using 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC)/$TiCl_4$ initiating system with 2,4-dimethylpyridine (DMP) as an electron donor in 60/40 (v/v) hexane/methyl chloride cosolvents. The complex between $TiCl_4$ and DMP was observed to be largely soluble in this medium in the temperature range −50 to −80 °C. Over the same temperature range using a $[t\text{-Bu-}m\text{-DCC}]_o$:$[TiCl_4]_o$ ratio of 1:20, polymerizations were free of termination and chain transfer reactions, up to monomer conversions in excess of 95%, and molecular weight distributions were narrow. It was observed that the concentration of DMP had to be maintained in excess of the concentration of protic impurities to obtain living polymerizations. At −80 °C, the kinetic order of the rate of polymerization was unity with respect to both monomer and initiator concentrations, approximately 2 with respect to $[TiCl_4]_{eff}$, defined as $[TiCl_4]_o - [DMP]$, and −0.25 with respect to DMP. These results were similar to those obtained using pyridine as an electron donor, which forms an insoluble complex with $TiCl_4$. Similar polymerization rates were obtained for various polymerizations in which the same $[TiCl_4]_{eff}$ was obtained from different combinations of $[TiCl_4]_o$ and [DMP], demonstrating that the fractional, negative kinetic order of the rate with respect to DMP reflects the reduction in $[TiCl_4]_o$ caused by complexation. The apparent activation energy for the rate of polymerization was observed to be negative, attributed to an equilibrium between dormant and active growing chains. It was proposed that the observed second-order kinetic dependency on the $TiCl_4$ concentration results from the fact that propagation takes place predominantly through chains possessing dimeric gegenions and that the latter must form by reaction of additional $TiCl_4$ with monomeric gegenions, rather than direct ionization of chains by neutral, dimeric Ti_2Cl_8.

Introduction

In a recent paper, we reported the kinetics of the cationic polymerization of isobutylene (IB) initiated by 1,4-*bis*(2-chloro-2-propyl)benzene (dicumyl chloride) (DCC)/$TiCl_4$, in the presence of pyridine, using 60/40 (v/v) hexane/methyl chloride cosolvents.[1] This system is representative of carbocationic polymerizations in which living characteristics are brought about by the presence of an externally added electron donor (ED), a general technique that was developed for IB polymerization principally by Kennedy *et al.*[2−4] Our results showed that the system displays living characteristics in the temperature range $-50 \geq T \geq -80$ °C, and that the kinetic orders with respect to monomer and initiator are unity. It was proposed that propagation in this system occurs through a simple bimolecular reaction between nondissociated ion pairs and monomer. These same conclusions were reached by other authors who dealt with a similar polymerization system.[5]

It was further reported[1] that the DCC/$TiCl_4$/pyridine system yields an apparent negative energy of activation for propagation, which was attributed to the operation of a dynamic equilibrium between dormant, *tert*-alkyl chloride chain ends and active, ion-paired chain ends:



(1)

The same reversible activation-deactivation equilibrium was postulated for the early quasiliving[6,7] and living polymerizations of IB[3,4] reported by Kennedy *et al.* However, the observed kinetic orders of the propagation with respect to the Lewis acid and pyridine, approximately +2 and −0.28, respectively, suggested a considerably more complicated mechanism. The second-order dependence on $TiCl_4$ has also been observed by others[8] and attributed to the predominant participation of dimeric $Ti_2Cl_9^-$ gegenions in the propagation reaction. Formation of a $TiCl_4$/pyridine complex, visible in the polymerization reactor as a precipitate, was suggested to be responsible for the negative fractional dependency on the pyridine concentration. Due to the obvious complexation of $TiCl_4$ by the Lewis base, we introduced a quantity termed the effective $TiCl_4$ concentration, defined as $[TiCl_4]_{eff} = [TiCl_4]_o - [pyr]$, which represents the amount of free $TiCl_4$ that is available to coinitiate the polymerization, assuming a 1:1 complex between Lewis acid and Lewis base.

The mechanistic role of pyridine and other electron donors in living carbocationic polymerizations remains obscure and the subject of controversy. For example, Kaszas *et al.*[3] proposed that the Lewis acid/ED complex interacts with the growing PIB chain ends, leading to carbocation stabilization. More recently, Faust *et al.*[8] proposed that the main function of externally added EDs is to react with protic impurities in the polymerization system. The effectiveness of an insoluble complex such as $TiCl_4$/pyridine would seem to contradict the carbocation stabilization theory since it is difficult to envision stabilization by a solid complex which has precipitated from the reaction; however, a small portion of the complex may be in solution, and conceivably only a small amount would be required to stabilize the very low concentration of active chain ends.

[†] Present address: General Electric Company, 1 Lexan Lane, Mount Vernon, IN 47620−9364.

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As a result of the ambiguities associated with the partially insoluble $TiCl_4$:pyridine complex, we have employed a different ED, 2,4-dimethylpyridine (DMP) which forms a largely soluble complex with $TiCl_4$. This paper describes kinetic and mechanistic investigations of an IB polymerization system consisting of 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC) as initiator, $TiCl_4$ as the coinitiator, and DMP as the electron donor in 60/40 (v/v) hexane/methyl chloride cosolvents. A comparison to the previously reported heterogeneous $TiCl_4$/pyridine system will be made, and a more detailed interpretation of the observed kinetic dependencies on the Lewis acid and electron donor will be presented.

Experimental Section

Materials. *t*-Bu-*m*-DCC was prepared from 5-*tert*-butylisophthalic acid (Amoco Chemical Co.) *via* esterification with methanol, followed by a Grignard reaction to form the *tertiary* alcohol, and then chlorination *via* reaction with gaseous HCl using a modification of procedures previously described.[9,10] Hexane (Aldrich Chemical Co.) was dried prior to use by distillation from calcium hydride. Isobutylene and methyl chloride (AIRCO) were dried by passing the gaseous material through a column packed with BaO and $CaCl_2$. $TiCl_4$ (99.9%, packaged under nitrogen in SureSeal bottles), 2,4-lutidine (99%, 2,4-dimethylpyridine, DMP), and anhydrous methanol were used as received from Aldrich Chemical Co.

Instrumentation. Gel permeation chromatography (GPC) was performed on PIB samples to determine number average molecular weights (M_n) and molecular weight distributions (MWD) (M_w/M_n) relative to PIB standards with narrow MWD (Storey Research Group). A Waters Associates high-pressure system was employed, equipped with a model 510 solvent delivery module, a Model 410 differential refractometer operating at 33 °C, and a Model 484 ultraviolet detector operating at 265 nm. The system also included an Alcott Chromatography Model 728 autosampler utilizing a Valco Model EQ60AL injector, and two Polymer Laboratory PLgel 5 μm Mixed-D columns. Tetrahydrofuran (THF), freshly distilled from CaH_2, served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were approximately 0.5% (w/w) in THF, with an injection volume of 50 μL.

Procedures. Polymerizations were carried out in a glovebox under dry nitrogen. Specific reaction conditions are listed in the figure captions and tables. A representative polymerization procedure used to construct a single first-order plot was as follows: 600 mL of hexane, 400 mL of methyl chloride, 1.09 mol of IB, 1.35×10^{-3} mol of *t*-Bu-*m*-DCC, and 2×10^{-3} mol of DMP were added sequentially to a chilled 2 L three-necked round-bottomed flask, equipped with mechanical stirrer. Methyl chloride and IB were condensed into chilled graduated cylinders before addition to the flask. The mixture was stirred for 0.5 h; then, 50 mL portions were transferred to chilled, 25 × 200 mm culture tubes *via* a 50 mL volumetric pipette, and the tubes were capped with teflon-lined screw caps. With vigorous shaking, neat $TiCl_4$ (1.35×10^{-3} mol, unchilled) was injected into each culture tube using a Hamilton CR-700 constant rate syringe. Polymerizations were terminated by the injection of 10 mL of prechilled methanol.

The terminated polymer solutions were removed from the drybox and immediately poured into approximately 100 mL of methanol contained in tared 9 oz. glass jars. The samples were allowed to stand open to the atmosphere, generally overnight, causing evaporation of the hexane and slow precipitation of the polymer. The supernatant solution was decanted, and the precipitate was washed three times by pouring approximately 100 mL of methanol into the jars, swirling, and decanting. The jars were then placed in a vacuum oven at 50 °C until a constant weight was obtained. The fractional yield (Y) of polymer was determined gravimetrically, and the quantity $[M]_o/[M]$ was calculated as $1/(1 - Y)$.

Results and Discussion

The kinetics of the living polymerization of isobutylene using the *t*-Bu-*m*-DCC/$TiCl_4$/DMP initiating system were determined by gravimetrically monitoring polymer yield as a function of reaction time. The initial monomer concentration (1.0 M), solvent polarity (60/40, v/v), and polymerization volume (50 mL) were held constant in all cases except where specifically noted otherwise, and $TiCl_4$ was always the final component to be added. Since DMP forms a soluble complex with $TiCl_4$, the polymerization mixtures were mostly homogeneous, except for a minute amount of precipitate that was attributed to 2,4-dimethylpyridinium salts, created by the scavenging of protic impurities (HA) by the $TiCl_4$:DMP complex. Faust *et al.*[8] have observed this same phenomenon for the onium salts of 2,6-di-*tert*-butylpyridine.

The data were interpreted in terms of the kinetic rate law for a living polymerization with fast initiation:

$$r_p = -\frac{d[M]}{dt} = k_p[R^{\oplus}][M] = k_{app}[M] \qquad (2)$$

where r_p is the rate of polymerization, k_p is the second-order rate constant for propagation, $[R^{\oplus}]$ is the concentration of instantaneously active growing chains (constant), k_{app} is the apparent first-order rate constant for propagation and [M] is the concentration of monomer. Plots of the integrated form of eq 2, $\ln([M]_o/[M])$ vs time, were utilized to determine the value of k_{app} for each particular set of polymerization conditions. Linearity of these first-order kinetic plots demonstrated the expected first-order dependency on the monomer concentration and indicated that the number of growing chains remained constant (no absolute termination). The slopes of these plots, k_{app}, include $[R^{\oplus}]$, whose value is directly proportional to the overall concentration of growing chain ends, and [CE], which in turn, is equal to the original concentration of initiating sites, $[I]_o = 2[t\text{-bu-}m\text{-DCC}]_o$).

Linearity of M_n(GPC) vs monomer conversion plots was used to demonstrate the absence of chain transfer during the polymerization. It is a necessary and sufficient condition that both of the aforementioned plots demonstrate linearity for the polymerizations to be considered living.[11]

Initiating System Concentration. It has been standard practice in our laboratory to treat the initiating system, i.e. initiator, coinitiator, and electron donor, as one unified system. Typically, the ratio $[CE]:[TiCl_4]_o:[ED]$ was set at 1:10:1. This large excess of coinitiator is not absolutely necessary, but previous results have proven this to be a convenient ratio, yielding living polymerizations to high monomer conversions (90+%). Thus, using a $[t\text{-Bu-}m\text{-DCC}]_o:[TiCl_4]_o:[DMP]$ ratio of 1:20:2, the kinetics of polymerization were determined as a function of the concentration of the unitized initiating system at −80, −50, and −30 °C.

The apparent rate constants, k_{app}, obtained for various initiating system concentrations at these three temperatures are listed in Table 1. The values at −80 and −50 °C agreed well with, but were consistently slightly lower than, those measured at the same temperatures in the previous study involving pyridine as the ED.[1] Thus, the degree of solubility of the $TiCl_4$:ED complex does not significantly affect the overall rate of polymerization. The plots of $\ln([M]_o/[M])$ vs time for the polymerizations at −80 °C are shown in Figure 1 and are representative of the behavior observed at both -80 and −50 °C. At a given initiating system concentration the apparent rate constant of propagation was constant, indicating a constant number of growing chains, *i.e.*, absence of

Table 1. Effect of Initiating System Concentration and Temperature on the Rate of Isobutylene Polymerization[a]

temp (°C)	[*t*-Bu-*m*-DCC]$_o$ × 10^3 (M)	k_{app} × 10^4 (s^{-1})
−80	0.70	0.70
	0.95	1.6
	1.25	3.2
	1.90	8.6
	2.60	25
−50	0.70	0.041
	0.95	0.086
	1.25	0.18
	1.90	0.58
	2.60	1.3
−30	1.90	0.089
	2.60	0.19
	4.00	0.87
	6.00	2.9
	8.00	8.0
−40	1.90	0.22
−70	1.90	4.9

[a] [*t*-Bu-*m*-DCC]$_o$:[$TiCl_4$]$_o$:[DMP] = 1:20:2; [IB]$_o$ = 1M; hexane/MeCl, 60/40 (vol/vol).

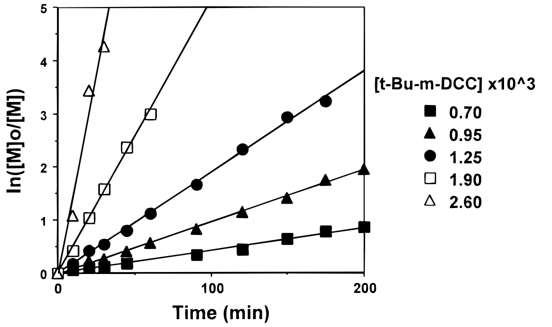

Figure 1. Effect of initiating system concentration on the rate of polymerization of IB at −80°C. [IB]$_o$ = 1 M; [*t*-Bu-*m*-DCC]$_o$:[$TiCl_4$]$_o$:[DMP] = 1:20:2; hexane/MeCl = 60/40 (vol/vol).

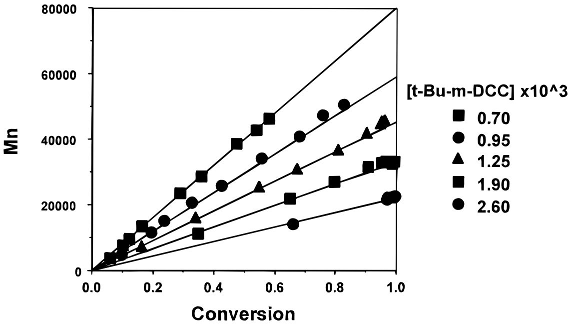

Figure 2. M_n vs conversion plots for IB polymerizations at −80°C. Lines are theoretical: p[IB]$_o$56 (g/mol)/[*t*-Bu-*m*-DCC]$_o$ vs *p*, where *p* = conversion. [IB]$_o$ = 1 M; [*t*-Bu-*m*-DCC]$_o$:[$TiCl_4$]$_o$:[DMP] = 1:20:2; hexane/MeCl = 60/40 (vol/vol).

irreversible termination, up to essentially complete conversion of the monomer for some runs. As expected, an increase in the initiating system concentration caused a large increase in the k_{app}; this reflects an increase in the overall number of growing chains (higher [CE]) and in the fraction of chains that are instantaneously active (higher [$TiCl_4$]$_{eff}$). Plots of M_n vs conversion for the same −80 °C polymerizations are shown in Figure 2. The absence of chain transfer in the polymerizations is clearly demonstrated through the linearity of the data points and their excellent agreement with the theoretical lines.

Figure 3 shows the ln([M]$_o$/[M]) vs time plots obtained at −30 °C, the highest temperature studied. Although the rates were considerably lower at the higher temperature, the same trend of increasing rate with increasing initiating system concentration was observed. However, at this relatively high temperature, the curves do not pass through the origin, but instead exhibit a finite *y*-intercept, suggesting a higher apparent rate constant during the initial stage of the polymerization. Conceivably this could reflect a higher ionization equilibrium constant for the *tert*-benzylic chloride initiator, and for short chains in which the ionization reaction can still be affected by the presence of the initiator residue. It is interesting that positive *y*-intercepts were observed at −30 °C but not at lower temperatures.

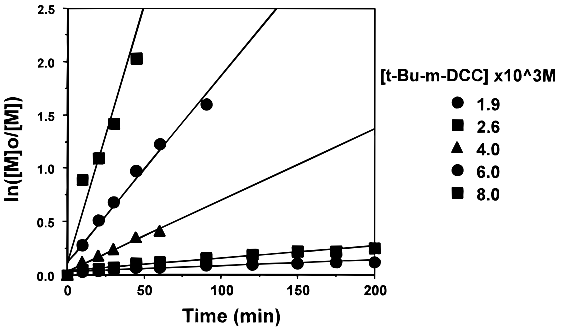

Figure 3. Effect of initiating system concentration on the rate of polymerization of IB at −30°C. [IB]$_o$ = 1 M; [*t*-Bu-*m*-DCC]$_o$:[$TiCl_4$]$_o$:[DMP] = 1:20:2; hexane/MeCl = 60/40 (vol/vol).

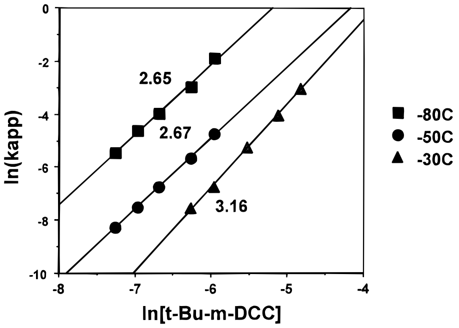

Figure 4. Reaction order of initiating system concentration for polymerization of IB (k_{app} in min^{-1}). [IB]$_o$ = 1 M; [*t*-Bu-*m*-DCC]$_o$:[$TiCl_4$]$_o$:[DMP] = 1:20:2; hexane/MeCl = 60/40 (vol/vol).

By plotting ln(k_{app}) vs ln[*t*-Bu-*m*-DCC]$_o$ for the reactions at each of the three temperatures studied, the kinetic order of the reaction with respect to the initiating system was determined as shown in Figure 4. It must be remembered that although ln([*t*-Bu-*m*-DCC]$_o$) was plotted on the *x*-axis, the other two components were changed in the appropriate amounts to retain a 1:20:2 ratio of [*t*-Bu-*m*-DCC]$_o$:[$TiCl_4$]$_o$:[DMP]. From Figure 4, the kinetic orders with respect to the initiating system at −80, −50, and −30 °C were found to be 2.65, 2.67, and 3.16 respectively. The value of approximately 2.7 for the two lower temperatures is in good agreement with previous results obtained for IB polymerizations at −80 °C with pyridine as ED.[1,12] The higher overall kinetic order measured at −30 °C may be anomalous since other studies have suggested lower orders at higher temperatures.[1,13] This issue requires further study.

Effect of Initiator Concentration on the Rate of Polymerization. First-order kinetics were measured for polymerizations conducted at −80°C using several *t*-Bu-*m*-DCC concentrations while holding the concentration of all other components the same. The resulting first-order plots were linear and passed through the origin. Table 2 lists the k_{app}s obtained for each initiator

Table 2. Effect of [*t*-Bu-*m*-DCC]$_o$, [TiCl$_4$]$_o$, and [DMP] on the Rate of Isobutylene Polymerization[a]

[*t*-Bu-*m*-DCC]$_o$ $\times 10^3$ (M)	[TiCl$_4$]$_o$ $\times 10^2$ (M)	[DMP] $\times 10^3$ (M)	k_{app} $\times 10^4$ (s^{-1})
0.40	3.95	2.00	3.4
0.60			5.2
0.80			7.0
1.10			9.6
1.30			12
1.24	2.48	0.62	8.1
		1.86	6.2
		3.11	5.4
		4.35	4.9
	0.73	2.48	0.20
	1.61		1.7
	1.73		2.0
	2.11		3.0
	2.91		6.1
	4.00		14

[a] [IB]$_o$ = 1 M; hexane/MeCl = 60/40 (vol/vol); temp = −80 °C.

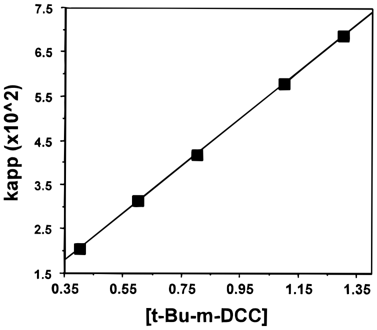

Figure 5. Plot of k_{app} (min^{-1}) vs [*t*-Bu-*m*-DCC]$_o$ for polymerization of IB at −80°C. [IB]$_o$ = 1 M; [TiCl$_4$]$_o$ = 3.95×10^{-2} M; [DMP] = 2×10^{-3} M; hexane/MeCl = 60/40 (vol/vol).

concentration, and, as shown in Figure 5, a linear relationship between k_{app} and [*t*-Bu-*m*-DCC]$_o$ was observed. This shows that [$R^{\oplus}$] in eq 2 is proportional to [CE] = 2[*t*-Bu-*m*-DCC]$_o$ over the entire range of *t*-Bu-*m*-DCC concentrations studied. The same result was observed in our earlier investigations using the DCC/TiCl$_4$/pyridine system[1] and by other authors for similar IB[5,14] and vinyl ether[15] polymerization systems. The direct proportionality between rate and chain end concentration suggests that propagation occurs overwhelmingly through ion-paired species. Even though it has recently been shown that ion pairs and free ions demonstrate similar reactivity toward olefins,[16,17] it is still to be expected that a significant dissociation equilibrium would upset the otherwise linear relationship between concentration of active species and overall concentration of chain ends, and one would observe an increase in k_{app}/[CE] with decreasing [CE]. Puskas *et al.*[5] reached a similar conclusion for IB polymerizations coinitiated by TiCl$_4$.

Effect of TiCl$_4$ and Effective TiCl$_4$ Concentration on the Rate of Polymerization. The effect of the TiCl$_4$ concentration on the rate of polymerization was determined by measuring the apparent rate constant of polymerization at −80 °C using various TiCl$_4$ concentrations while holding the concentration of all other components constant. First-order kinetic plots constructed for the polymerizations were linear and passed through the origin. The k_{app}s obtained from these plots are listed in Table 2. A plot of ln(k_{app}) vs ln[TiCl$_4$]$_o$ showed that the polymerization rate varied with the 2.3 power of the [TiCl$_4$]$_o$. This value is slightly higher than, but in good agreement with, values of 2.0 and 2.2, obtained for the previously reported pyridine-containing system using either 1,4-*bis*(2-chloro-2-propyl)benzene[1] or 2-chloro-2,4,4-trimethylpentane[12] initiators, respectively.

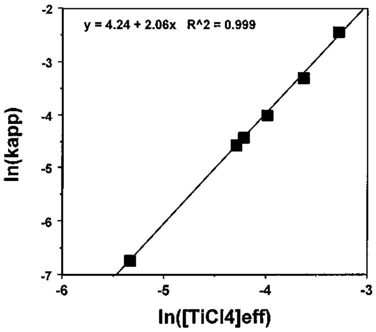

Figure 6. Reaction order of [TiCl$_4$]$_{eff}$ for polymerization of IB at −80°C (k_{app} in min^{-1}). [IB]$_o$ = 1 M; [*t*-Bu-*m*-DCC]$_o$ = 1.24×10^{-3} M; [DMP] = 2.48×10^{-3} M; hexane/MeCl = 60/40 (vol/vol).

Due to complexation between TiCl$_4$ and the electron donor, the use of the nominal concentration of TiCl$_4$, [TiCl$_4$]$_o$, in the kinetic expressions for the polymerization is probably invalid. Therefore, we have employed a quantity which represents the amount of free TiCl$_4$ in the polymerization mixture available to coinitiate the polymerization, assuming essentially quantitative formation of a 1:1 TiCl$_4$:ED complex. This quantity, termed the effective TiCl$_4$ concentration, is defined as [TiCl$_4$]$_{eff}$ = [TiCl$_4$]$_o$ − [ED] and scales inversely with the amount of ED present in the system. It should be noted that the concentration of protic impurities, [HA], may also affect [TiCl$_4$]$_{eff}$, because the precipitation of onium salts decreases both [TiCl$_4$]$_0$ and [ED]. If the salt is $EDH^+TiCl_4OH^-$, then [TiCl$_4$]$_{eff}$ remains unchanged. If the negative ions consist of $TiCl_5^-$, $Ti_2Cl_8OH^-$, $Ti_2Cl_9^-$, or some combination thereof, then [TiCl$_4$]$_{eff}$ is reduced. In practice, [HA] may be neglected in the calculation of [TiCl$_4$]$_{eff}$ if [ED] ≥ the concentration of protic impurities. Previous results for the DMP-[18] and pyridine-containing systems[1] have demonstrated that *n*th-order kinetic plots of the type ln(k_{app}) vs ln[TiCl$_4$]$_{eff}$ show a deviation from linearity, *i.e.*, a strong rise in the k_{app}, when [ED] is lowered below [HA]. This was attributed to the superposition of very fast propagation due to protic impurity initiation onto the slow propagation due to purposely added initiator, thereby dramatically increasing the overall polymerization rate. However, if the condition [ED] ≥ [HA] is maintained, a plot of ln(k_{app}) vs ln[TiCl$_4$]$_{eff}$ is characteristically linear, as demonstrated in Figure 6 for the DMP-containing system under typical polymerization conditions. The slope of approximately 2.0 represents the kinetic order of the polymerization rate with respect to [TiCl$_4$]$_{eff}$. This is in good agreement with the previously studied pyridine-containing systems[1,12] which both yielded a dependency of 1.9 with respect to [TiCl$_4$]$_{eff}$.

Since linearity of the plot in Figure 6 gives strong evidence that the ED removes Lewis acid from the polymerization mixture through complexation, studies were employed in which various combinations of [TiCl$_4$]$_o$ and [DMP] were used to yield the same [TiCl$_4$]$_{eff,}$ with the concentration of all other components held constant. Figure 7 shows ln([M]$_o$/[M]) vs time plots for the resulting polymerizations, and it may be observed that a constant polymerization rate was obtained for all the various polymerizations. This clearly demonstrates that the ED complexes with TiCl$_4$, at approximately one-to-one stoichiometry, to remove it from the polymerization mixture.

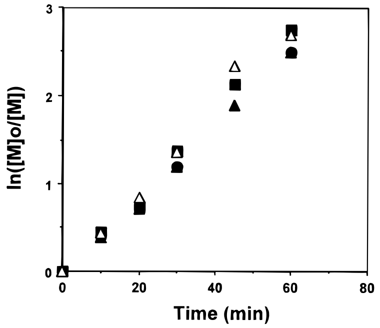

Figure 7. First-order plots for polymerization of IB at constant $[TiCl_4]_{eff}$ at −80°C. $[IB]_o$ = 1M; $[t\text{-Bu-}m\text{-DCC}]_o = 1.0 \times 10^{-3}$ M; $[TiCl_4]_{eff} = 3.2 \times 10^{-2}$ M; hexane/MeCl = 60/40 (vol/vol).

Effect of Electron Donor Concentration on the Rate of Polymerization. The effect of the electron donor concentration on the rate of polymerization was determined by measuring the first-order kinetics at −80 °C for polymerizations at various 2,4-dimethylpyridine concentrations while holding the concentration of all other components constant. The data, listed in Table 2, show that the polymerization rate decreased with increasing [DMP]. First-order plots constructed to obtain the k_{app}s were all linear and passed through the origin. From a plot of $\ln(k_{app})$ vs ln[DMP], the kinetic dependency with respect to [DMP] on the polymerization rate was determined to be −0.25. This agrees well with the value of −0.28 reported previously for systems utilizing pyridine.[1] The negative sign reflects the decrease in $[TiCl_4]_{eff}$ caused by complexation of Lewis acid with ED. The absolute value is governed by changes in the quantity $[TiCl_4]^m_{eff}$ brought about by a given change in [ED], where m is the kinetic dependency of the rate with respect to $[TiCl_4]_{eff}$. For example, if changes in [ED] are expressed relative to some reference concentration, $[ED]_{ref}$, then it is obvious that if $[ED]_{ref} << [TiCl]_o$, small changes in [ED] will have very little effect on $[TiCl]_{eff}$, which remains virtually equal to $[TiCl]_o$, and the order with respect to the ED will be negative but quite close to zero (i.e., a negative fraction). This relationship can be quantified as follows, using the definition of $[TiCl]_{eff}$, where n is the apparent kinetic order with respect to the ED.

$$\left\{\frac{[TiCl_4]_o - [ED]}{[TiCl_4]_o - [ED]_{ref}}\right\}^m = \left\{\frac{[ED]}{[ED]_{ref}}\right\}^n \qquad (3)$$

It is noteworthy that insertion into eq 3 of the values $[TiCl_4]_o = 2.5 \times 10^{-2}$ M, $[ED]_{ref} = 2.5 \times 10^{-3}$ M, and $m = 2$, which are typical of the polymerizations investigated in this work, yields n in the range −0.21 to −0.23 for ED concentrations within the range of $[ED]_{ref} \pm 10\%$. This is very close to the value of −0.25 actually measured for DMP within this range of concentrations, suggesting that eq 3 represents the correct interpretation of the observed kinetic order for the ED.

The foregoing discussion indicates that if a complexing ED is used, any excess ED over the minimum necessary to impart living characteristics to the polymerization will unnecessarily retard the rate of polymerization and will be wasteful of both Lewis acid and ED. Since earlier discussions indicated that it is desirable to set [ED] ≥ [HA], we may state therefore that the "correct," *i.e.*, technologically optimal, ED concentration is [ED] = [HA] + slight excess. This is a departure from the early practice, by many investigators including ourselves, of setting [ED] = [CE]. In a recent paper,[19] we reported a simple method for estimating [HA] which employs a Lewis base such as 2-ethylhexyl *p*-(dimethylamino)benzoate which forms a colored complex with $TiCl_4$. Since the complex is rapidly and quantitatively decomposed by protic impurities, such a base may be used to titrate protic impurities within a cationic polymerization mixture, with the end point indicated by persistence of color due to accumulation of undecomposed complex. Using this method, we observed that the protic impurity concentration in our drybox, in polymerization mixtures identical to the ones in this paper except for the identity of the Lewis base, was within the following range: $1 \times 10^{-3} < [HA] < 2 \times 10^{-3}$ M. As a further demonstration of proton scavenging, Figure 8 shows representative GPC traces for polymerizations at −30 °C containing [ED] equal to zero, 0.25×10^{-3} M (just below the concentration of protic impurities), and 3.8×10^{-3} M (well above the concentration of protic impurities). It is clearly apparent that DMP, when added to the polymerization system in excess of protic impurities, suppressed uncontrolled initiation and yielded PIBs with a narrow MWD. The use of a slight excess of ED is a necessary safeguard to account for the uncertainty in the measurement of [HA] and the higher efficiency of protic initiation at higher temperatures. For example, Figure 9 shows GPC traces (RI and UV detectors) for two identical polymerizations carried out at −30 and −80 °C, with [ED] just below [HA]. The −30 °C RI trace contains a broad, high molecular weight peak, whereas the −80 °C trace does not. This peak was attributed to protic initiation since it is visible in the RI but not the UV trace (no aromatic initiator residue). These results suggest that initiation by protic impurities is reduced at lower temperatures. This "freezing out" of protic impurity initiation at low temperatures for isobutylene polymerization has also been observed by Kaszas *et al.*[3]

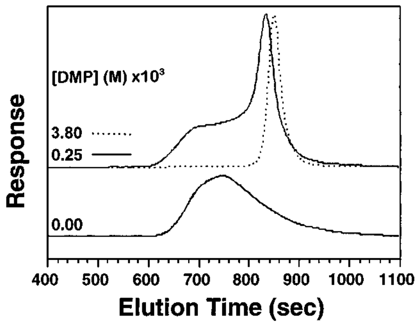

Figure 8. GPC traces demonstrating effect of [DMP] on MWD of PIB at −30°C. $[IB]_o$ =1 M; [DMP] (M) × 10^3 = as shown; $[TiCl_4]_o = 2.48 \times 10^{-2}$ M; hexane/MeCl = 60/40 (vol/vol).

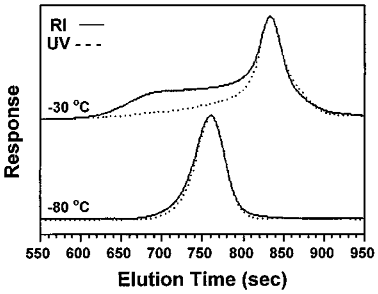

Figure 9. GPC traces demonstrating the incidence of initiation of IB by protic impurities at −30 and −80°C. $[IB]_o$ =1 M; $[t\text{-Bu-}m\text{-DCC}]_o = 1.9 \times 10^{-3}$ M; $[TiCl_4]_o = 3.8 \times 10^{-2}$ M; [DMP] = 0.25×10^{-3} M; hexane/MeCl = 60/40 (vol/vol).

Mechanism of $TiCl_4$-Coinitiated Isobutylene Polymerization. For all of the polymerizations investigated, linearity of both kinetic and M_n vs conversion plots was obtained to very high conversions (95+%) under a wide range of conditions. This demonstrated an absence of absolute termination and chain transfer, respectively, during the effective lifetime of the polymerizations. Linearity of the kinetic plots demonstrated first-order dependency of rate on [IB]. The rate of polymerization was also shown to be directly proportional to the concentration of the initiator, *t*-Bu-*m*-DCC, which validates the use of eq 2 and implies that the active chain end concentration, $[R^{\oplus}]$, is proportional to $[t\text{-Bu-}m\text{-DCC}]_o$ over the entire range investigated. These results suggest that propagation is a simple bimolecular reaction between monomer and activated chain ends, which are thought to be predominantly paired ions based on the absence of a dilution effect (i.e., no increase in k_{app}/[CE] with decreasing [CE])[1] and other considerations.[5]

A large body of evidence exists, however, which indicates that for living IB polymerizations the overwhelming majority of the growing PIB chains, at any given instant, are dormant (reversibly chlorinated) and in dynamic equilibrium with a much smaller concentration of active ion pairs. Among this evidence is the fact that *tert*-alkyl chloride end-capped PIBs are almost always produced regardless of the quenching agent used to terminate the polymerization,[20,21] and pre-formed *tert*-alkyl chloride PIBs can be used as initiators for the polymerization of IB.[3] Perhaps the two most convincing indications of this equilibrium are (1) the relatively low rates of these polymerizations in spite of the extremely large rate constants characteristic of the reaction of carbocation ion pairs with olefins[5] and (2) the increase in the rate of polymerization with decreasing temperature presumably caused by a shift in the equilibrium in favor of the ionized species.[1,9] The latter effect can be appreciated from the k_{app} data in Table 1 for identical polymerizations ($[t\text{-Bu-}m\text{-DCC}]_o = 1.9 \times 10^{-3}$ M) carried out over a range of temperatures from −30 to −80 °C. The apparent rate constant for the −80 °C polymerization was 15 times greater than that of the same polymerization at −50 °C and approximately 100 times greater than that at −30 °C. This data is fitted quite well by an Arrhenius equation, and the apparent activation energy for the rate was calculated to be −8.5 kcal/mol.

In principle, the dormant−active chain end equilibrium would pose no special problem with regard to formulation of a mechanism and kinetic model for these polymerizations, particularly in view of the uncomplicated kinetic orders of the polymerization rate with respect to monomer and living chain end concentration, *i.e.*, unity in both cases. Thus, for example, Kaszas and Puskas[14] have developed such a model that predicts the rate of polymerization to be described by eq 2, with $[R^{\oplus}] = K_1[I]_o[TiCl_4]_o$, where K_1 is the constant for the activation-deactivation equilibrium shown in eq 1, $[TiCl_4]_o = [TiCl_4]_{eff}$ (based upon the use of the noncomplexing ED, 2,6-di-*tert*-butylpyridine), and $[I]_o$ = the original concentration of initiating sites. The predicted first-order dependency of the rate with respect to the Lewis acid concentration was demonstrated by these authors using the TMPCl/$TiCl_4$ initiating system in 60/40 (v/v) hexane/methyl chloride cosolvents. It should be noted, however, that their data included only three different $[TiCl_4]_o$, and the systems were somewhat unusual in that $[TiCl_4]_o/[TMPCl]_o \leq 1$, caused by relatively high $[TMPCl]_o$. In contrast, a more complex situation is indicated by the approximately second-order dependence of the rate on $[TiCl_4]_{eff}$, which was observed for the systems reported in this paper and in others.[1,8,12,22] It has been suggested that second-order dependency on $TiCl_4$ results when propagation is carried overwhelmingly by chains possessing dimeric gegenions,[1,8] that is,

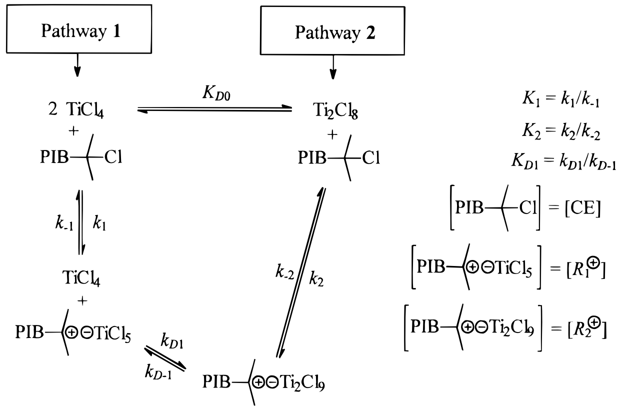

Figure 10. Equilibria among dormant and ionized chain ends in $TiCl_4$-coinitiated, living polymerization of IB.

$$r_p = \{k_{p1}[R_1^{\oplus}] + k_{p2}[R_2^{\oplus}]\}[M] \cong k_{p2}[R_2^{\oplus}][M] \qquad (4)$$

where, k_{p1} and k_{p2} represent the second-order rate constants for propagation, and $[R_1^{\oplus}]$ and $[R_2^{\oplus}]$ the concentrations, of instantaneously active chains carrying monomeric and dimeric gegenions, respectively. The formation of dimeric gegenions is supported by the known tendency for halogenated titanium compounds to form dimers as shown in eqs 5 and 6.[23−25]

$$2TiCl_4 \overset{K_{D0}}{\rightleftharpoons} Ti_2Cl_8 \qquad (5)$$

$$TiCl_5^- + TiCl_4 \overset{K_{D1}}{\rightleftharpoons} Ti_2Cl_9^- \qquad (6)$$

However, eqs 5 and 6 suggest that dimeric gegenions may be formed *via* at least two competing pathways, as shown in Figure 10 for a $TiCl_4$-coinitiated IB polymerization. In pathway **1**, monomeric $TiCl_4$ ionizes a dormant *tert*-alkyl chloride chain end to create an activated chain with a monomeric gegenion; the latter then reacts with another molecule of $TiCl_4$ to form a dimeric gegenion. In pathway **2**, neutral, dimeric Ti_2Cl_8 ionizes a dormant chain end to form a dimeric gegenion directly. It is obvious that the value of K_{D0} will largely determine the predominance of one or the other pathway. It will be shown below that dimeric gegenions will cause second-order dependency on $[TiCl_4]_{eff}$ only if they form *via* pathway **1**.

The following analysis is based upon the mechanism shown in Figure 10. The fact that the ionization equilibria are shifted extensively toward the dormant species allows two simplifications: (1) the combined concentration of active chain ends, $[R_1^{\oplus}] + [R_2^{\oplus}]$, is sufficiently small that the concentration of dormant chain ends, [PIB−Cl], is approximately equal to the overall concentration of chains ends, [CE], and (2) the amount of Lewis acid that exists as negatively charged gegenions is negligible, and thus the total original effective concentration of Lewis acid, $[TiCl_4]_{eff}$, is essentially equal to the combined concentration of neutral monomeric and dimeric species as follows (higher aggregates are neglected).

$$[\mathrm{TiCl_4}]_{\mathrm{eff}} \cong [\mathrm{TiCl_4}] + 2[\mathrm{Ti_2Cl_8}] \tag{7}$$

Application of the steady-state approximation to both $[R_1^{\oplus}]$ and $[R_2^{\oplus}]$ yields the following equation in which the concentration of active chains with dimeric gegenions is defined in terms of the various rate and equilibrium constants in Figure 10:

$$[R_2^{\oplus}] = [\mathrm{CE}] \times \frac{K_1K_{\mathrm{D1}}[\mathrm{TiCl_4}]^2 + \frac{k_2}{k_{\mathrm{D-1}}}[\mathrm{Ti_2Cl_8}] + K_{\mathrm{D1}}\frac{k_2}{k_{-1}}[\mathrm{TiCl_4}][\mathrm{Ti_2Cl_8}]}{1 + \frac{k_{-2}}{k_{\mathrm{D-1}}} + K_{\mathrm{D1}}\frac{k_{-2}}{k_{-1}}[\mathrm{TiCl_4}]} \tag{8}$$

Equation 8 predicts the observed proportionality between the active, ionized chain end concentration (and hence the rate) and the overall chain end concentration, [CE]. In the numerator, the leftmost term represents the contribution of pathway **1**, the center term represents the contribution of pathway **2**, and the rightmost term is a cross term that becomes negligible whenever one pathway or the other predominates. Since the term involving $[\mathrm{TiCl_4}]$ in the denominator is generally $<<1$, the denominator is approximately constant.

Combining the definition of K_{D0} with eq 7 yields the following expressions for $[\mathrm{TiCl_4}]$ and $[\mathrm{Ti_2Cl_8}]$:

$$[\mathrm{TiCl_4}] = \frac{-1 + \sqrt{1 + 8K_{\mathrm{D0}}[\mathrm{TiCl_4}]_{\mathrm{eff}}}}{4K_{\mathrm{D0}}} \tag{9}$$

$$[\mathrm{Ti_2Cl_8}] = \frac{1 + 4K_{\mathrm{D0}}[\mathrm{TiCl_4}]_{\mathrm{eff}} - \sqrt{1 + 8K_{\mathrm{D0}}[\mathrm{TiCl_4}]_{\mathrm{eff}}}}{8K_{\mathrm{D0}}} \tag{10}$$

For a typical effective Lewis acid concentration of $[\mathrm{TiCl_4}]_{\mathrm{eff}} = 10^{-2}$ M, all values of $K_{\mathrm{D0}} \leq 1$ L/mol yield negligible $[\mathrm{Ti_2Cl_8}]$, and thus within this regime of K_{D0}, dimeric gegenions must form overwhelmingly *via* pathway **1** since the concentration of neutral dimers is virtually zero. Thus for low K_{D0}, the terms in eq 8 involving $[\mathrm{Ti_2Cl_8}]$ are insignificant, $[\mathrm{TiCl_4}]_{\mathrm{eff}} \cong [\mathrm{TiCl_4}]$ according to eq 7, and the following equation results, which predicts, in agreement with experiment, that the concentration of instantaneously active carbocations, and hence the rate constant for propagation, is proportional to $[\mathrm{TiCl_4}]_{\mathrm{eff}}^2$:

$$[R_2^{\oplus}] = [\mathrm{CE}]\frac{K_1K_{\mathrm{D1}}[\mathrm{TiCl_4}]_{\mathrm{eff}}^2}{1 + \frac{k_{-2}}{k_{\mathrm{D-1}}}} \tag{11}$$

Large values of K_{D0} ($\geq 10^5$ L/mol) cause the concentration of monomeric $\mathrm{TiCl_4}$ to drop essentially to zero, and thus eq 7 predicts $[\mathrm{TiCl_4}]_{\mathrm{eff}} \cong 2[\mathrm{Ti_2Cl_8}]$, and eq 8 reduces to the following, which predicts first-order dependency of the rate on $[\mathrm{TiCl_4}]_{\mathrm{eff}}$:

$$[R_2^{\oplus}] = [\mathrm{CE}]\frac{K_2[\mathrm{TiCl_4}]_{\mathrm{eff}}}{2\left(\frac{k_{\mathrm{D-1}}}{k_{-2}} + 1\right)} \tag{12}$$

This prediction is clearly contrary to the experimental observation of second-order dependency; thus K_{D0} cannot be so large, and pathway **2** cannot predominate under these conditions. It is possible that for intermediate values of K_{D0}, dimeric gegenions could be formed *via* both pathways. However, the predicted apparent kinetic order with respect to $[\mathrm{TiCl_4}]_{\mathrm{eff}}$ was calculated empirically from eq 8, using reasonable values for the various rate and equilibrium constants, and found to change smoothly from a value of 2 at $K_{\mathrm{D0}} = 1$ L/mol, to a value of unity at $K_{\mathrm{D0}} = 10^5$ L/mol. Thus, any significant participation of pathway **2** predicts a reduction in the kinetic order toward unity. Obviously, the external kinetic order for $[\mathrm{TiCl_4}]_{\mathrm{eff}}$ will also be decreased toward unity if significant propagation proceeds *via* chains carrying monomeric gegenions.

As a final note, it is appropriate to discuss the value of K_1K_{D1} in eq 11, since this product apparently represents the effective ionization equilibrium constant in many $\mathrm{TiCl_4}$-coinitiated IB polymerizations. For the purposes of discussion, the rate constant for cationic propagation of a contact ion pair, in this case k_{p2} in eq 4, is taken to be approximately 10^4 L/mol-s, based upon the assumption of similar reactivity between ion pairs and free ions.[16,17] If a typical experimental k_{app} of 1.7×10^{-4} s^{-1} is selected (entry 11 in Table 2: $[\mathrm{CE}] = 2.48 \times 10^{-3}$ M, $[\mathrm{TiCl_4}]_{\mathrm{eff}} = [\mathrm{TiCl_4}]_{\mathrm{o}} - [\mathrm{DMP}] = 1.36 \times 10^{-2}$ M), it then follows that $[R_2^{\oplus}] \cong 10^{-8}$ M under these conditions. Thus, according to eq 11, the quantity $K_1K_{\mathrm{D1}}(1 + k_{-2}/k_{\mathrm{D-1}})^{-1}$ is on the order of 10^{-2} L^2/mol^2. If $k_{-2}/k_{\mathrm{D-1}} << 1$, *i.e.*, if the chain end deactivation process is also *via* pathway **1**, then $K_1K_{\mathrm{D1}} \cong 10^{-2}$ L^2/mol^2. Individual values for K_1 and K_{D1} may also be postulated in view of the apparent nonparticipation of chains carrying monomeric gegenions. One explanation for this phenomenon is that their concentration is vanishingly low, *i.e.*, $[R_1^{\oplus}] << [R_2^{\oplus}]$. This would dictate that K_1 is quite small, say 10^{-6}–10^{-5} L/mol, and that K_{D1} is relatively much larger, e.g. 10^3–10^4 L/mol. Under these conditions, monomeric gegenions would rapidly react with additional $\mathrm{TiCl_4}$, and $[R_2^{\oplus}]$ would be 10–100 times greater than $[R_1^{\oplus}]$.

Conclusions

The kinetics of the living polymerization of isobutylene using the *t*-Bu-*m*-DCC/$\mathrm{TiCl_4}$/2,4-dimethylpyridine initiating system were investigated. DMP was specifically chosen as an electron donor because it affords a soluble complex with $\mathrm{TiCl_4}$, compared to other strongly complexing electron donors, such as pyridine, which do not. The essential features of the polymerization, *i.e.*, the observed kinetic orders with respect to the various components, were found to be the same regardless of the solubility of the Lewis acid/electron donor complex; however, the apparent rate constants for polymerization were consistently observed to be slightly lower for the soluble $\mathrm{TiCl_4}$:DMP complex compared to the insoluble $\mathrm{TiCl_4}$:pyridine complex. It is unclear, however, whether the lower rate is due to the solubility of the complex; recent work has shown that consistent differences in rate may be observed between two EDs, even when both form soluble complexes.[19]

The presence of the electron donor was observed to be crucial in eliminating undesirable initiation by protic impurities in the system. Living cationic polymerizations of IB initiated solely by the purposely added initiator *t*-Bu-*m*-DCC were obtained only in those cases where the ED concentration exceeded that of the protic impurity concentration. These results tend to validate the proton scavenging theory of Faust *et al.*[8] for systems employing very strongly complexing EDs. However, their model is oversimplified and fails to account for differences in polymerization rate and molecular weight distributions of polymers formed in the presence of different EDs.[26]

On the basis of a number of observations, including a strong increase in rate with decreasing temperature, it was concluded that the concentration of active chain ends is much lower than the overall chain end concentration, due to the existence of an equilibrium between the ionized, active chain ends and dormant *tert*-alkyl chloride chain ends. The position of this equilibrium is affected by temperature and solvent polarity and particularly by the concentration of Lewis acid. If the observed second-order dependence of the polymerization rate on the effective Lewis acid concentration is assumed to result from the predominant participation of dimeric gegenions in propagation, then it was concluded that dimeric gegenions must form by reaction of additional $TiCl_4$ with monomeric gegenions, rather than direct ionization of chains by neutral, dimeric Ti_2Cl_8.

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