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Olefin Polymerization and Copolymerization with Alkylaluminum-Initiator Systems. VII. Initiation by Electrophilic Halogens*

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ABSTRACT

The discovery of initiation of cationic polymerization of isobutylene and styrene by electrophilic chlorine generated by the reaction of chlorine and trimethylaluminum in the temperature range -40 to -100° is reported. Bromine and trimethylaluminum is a very poor initiating system, and iodine and trimethylaluminum does not initiate the polymerization of either isobutylene or styrene. Polymerization of isobutylene initiated by chlorine and trimethylaluminum shows a linear plot of log $\overline{M}_v$ vs 1/T with an overall E_{DP} of ~1.9 kcal/mole. The molecular weights ($\overline{M}_w$) of polystyrene obtained with the Cl_2/Me_3Al system appear to be the highest ever reported for cationic polymerization of this monomer under comparable conditions. The mechanism of initiation has been investigated by model

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*For Part VI of this series, see J. P. Kennedy, Abstracts, 23rd International Congress of Pure and Applied Chemistry, Boston, 1971, Vol. 1, p. 105.

experiments: The reaction between Cl_2/Me_3Al and 2,2,4-trimethyl-1-pentene gave three chlorinated products (2-chloromethyl-4,4-dimethyl-1-pentene, 1-chloro-2,4,4-trimethyl-1-pentene, and 2-chloromethyl-2,4,4-trimethylpentane). The position of chlorine in these compounds indicate initiation by electrophilic chlorine, $Cl^{\oplus}$. Some preliminary results obtained using diethylaluminum chloride-halogens as coinitiator-initiator systems are also described.

INTRODUCTION

Lewis-acid-catalyzed addition of halogens to carbon-carbon multiple bonds are generally thought to proceed through the following steps [1]:

$$Cl_2 + MCl_3 \longrightarrow [Cl^{\oplus} MCl_4^{\ominus}] \xrightarrow{C=C} [Cl-C-C^{\oplus} MCl_4^{\ominus}]$$

$$\longrightarrow Cl-C-C-Cl + MCl_3$$

where MCl_3 is a Friedel-Crafts halide such as $FeCl_3$. We theorized that the mechanism of this reaction and that of initiation of a cationic polymerization are similar. Therefore we postulated that halogens in the presence of an appropriate Lewis acid would function as effective initiators of cationic polymerization. Previous investigation in this area has established that alkylaluminum compounds in the presence of suitable protogens (HX) [2] or cationogens (RX) [3] are efficient coinitiator-initiator systems for cationic polymerization.

Our present study shows that chlorine in conjunction with trimethylaluminum is indeed a powerful initiator system of cationic polymerization. This paper concerns the scope and limitations of the new coinitiator-initiator system. The species responsible for initiation in this system is an electrophilic chlorine atom.

Prior to this study very little has appeared in the literature regarding the reaction of halogens with trialkylaluminums. It has been reported that the reaction between chlorine and trialkylaluminum compounds occurs very vigorously, often accompanied by spontaneous ignition even at -60°C [4]. The reaction was proposed to be a radical chain process. Ziegler and Weyer [5] considered an ionic process for the reaction of alkylaluminum compounds with halogens; however, because of the uncontrollable nature of the reaction, a definitive characterization of products proved impossible.

EXPERIMENTAL

All experiments were carried out under nitrogen atmosphere (<50 ppm moisture level) in a stainless steel enclosure [6]. The purity and analysis of isobutylene and methyl chloride have been previously described [6]. Styrene was dried over calcium hydride and freshly distilled before use. Trimethylaluminum (Texas Alkyls, Inc.) was freshly distilled under reduced pressure. Diethylaluminum chloride was treated with NaCl at 80°C for 2 hr to remove ethylaluminum dichloride and distilled in vacuo. Chlorine gas (<99.5% pure, Linde specialty gases) was passed through a glass column (12 × 1 in. i.d.) packed with barium oxide and molecular sieves (powder, 3A) before condensation. t-Butyl chloride and 2,4,4-trimethyl-1-pentene (Aldrich Chemical Co.) were dried over molecular sieves and freshly distilled. Bromine was purified by distillation under an inert atmosphere, and iodine by vacuum sublimation.

Polymerizations were carried out in Pyrex glass tubes covered by a stopper. A 2.8-3.0 M solution of monomer in methyl chloride was cooled to the selected temperature and a dilute methyl chloride solution of alkylaluminum compound was added. Rapid polymerization ensued upon addition of dilute methyl chloride solution of the initiator (chlorine or t-butyl chloride) to the quiescent system. Polymerization was quenched by the addition of prechilled methanol. The precipitated polymer was washed and dried for 24 hr in a vacuum oven (45°, ~1 Torr).

The viscosity-average molecular weights of polyisobutylene were obtained from viscosity measurements of 0.1% polymer solutions in diisobutylene at 20°C. The viscosity-average molecular weight was calculated from [7]:

$$\ln \overline{M}_v = 12.48 + 1.565 \ln[\eta]$$

The molecular weights of polystyrene ($\overline{M}_w$, $\overline{M}_n$) were determined by gel permeation chromatography with a Waters Associates instrument and an 1/8% solution of the polymer in degassed THF.

Model Compound Studies

Gas chromatographic analysis was carried out with an HP 5750 gas chromatograph equipped with flame ionization detector. Molecular weights were determined using a Chromalytics MC-2 Mass Chromatograph employing SF_6 and CO_2 carrier gases and a dual channel Mosely recorder. NMR analysis was done using a Varian A-60 spectrometer equipped with a low-temperature probe.

Reaction of 2,4,4-Trimethyl-1-pentene with Cl_2/Me_3Al

In a round-bottom flask equipped with a thermometer well were placed 3.2 ml (20.4 mmoles) 2,4,4-trimethyl-1-pentene and 5 ml methyl chloride. The flask was cooled to -65° and 2.0 ml (21 mmoles) trimethylaluminum were added with stirring followed by 2.2 mmoles chlorine in methyl chlorine solution. n-Nonane was added as an internal standard for GC analysis. The reaction mixture was stirred for 30 min. The reaction was quenched by dropwise addition of prechilled methanol.

The aluminum alkoxides were coagulated by the addition of a saturated aqueous solution of sodium potassium tartarate. The organic layer was diluted with pentane, washed, and dried. GC analysis (5% carbowax, 12 ft × 1/8 in. on Chromosorb W, 80-175°, 6°/min He flow 35 ml/min) showed 15 ± 2% conversion based on monomer disappearance. A scaled up version of the above reaction was performed for product characterization.

The reaction product was distilled and separated into three fractions. The first fraction was mainly unreacted monomer. The second fraction (low boiler) consisted of four components and the third, the high boiler, was a complex misture of five components. No attempt was made to identify these high boiling fractions. (See Discussion.) The major peak (66%) from the low boiler was identified as 2-chloromethyl-4,4-dimethyl-1-pentene, MW 147.9 [MW (calc) for $C_8H_{15}Cl$, 146.8]; NMR (CCl_4), δ 0.92 ($C-C\underline{H}_3$, 10H), 2.08 ($-C\underline{H}_2-$, 2H), 4.92 and 5.25 ($=C\underline{H}_2$, 1H each). The NMR spectrum was identical to that reported in the literature [8].

The product present in intermediate proportions in the low boiling fraction (~23%) appeared as two peaks of approximately equal areas. However, under conditions used in mass chromatographic and preparative chromatographic analyses (less sensitive thermal conductivity detector), the two peaks appeared to be merged into a single peak. This component had MW 145.4 (expected for $C_8H_{15}Cl$, 146.8) and its NMR spectrum showed in CCl_4 (δ) a singlet at 0.92 ($C-C\underline{H}_3$, 10H), singlets with unresolved fine structures at 1.8 and 2.01 ($=C{\diagup}^{C\underline{H}_3}$, 3H, and $-C\underline{H}_2-$, 2H, respectively) and a broad multiplet at 5.7 ($=C\underline{H}Cl$, 1H) consistent with the structure $ClCH=C(CH_3)(CH_2-t\text{-}C_4H_9)$.

It proved impossible to isolate preparatively sufficient quantities of the minor component (6%) of the low-boiling fraction for NMR spectroscopy. From the mass chromatographic analysis of the product mixture, its MW was found to be 161.0, close to the MW expected for 2-chloromethyl-2,4,4-trimethylpentane (162.5). This compound was independently synthesized by the reaction of 2,2,4,4-tetramethylpentane with N-chlorosuccinimide in refluxing CCl_4 in the presence of a catalytic amount of benzoyl peroxide. The major product of this reaction was isolated by preparative gas chromatography. Its NMR spectrum showed in CCl_4 (δ) a singlet at 3.33 ($Cl-C\underline{H}_2-$, 2H), a singlet at 1.46 ($-C\underline{H}_2-$, 2H), and two singlets at 1.08 and 1.0 ($C-C\underline{H}_3$, 6H and 9H, respectively), and had a MW of 165.0 as determined by mass chromatography, consistent with the structure of the expected 2-chloromethyl-2,4,4-trimethylpentane. Comparison (peak superposition method) of this authentic material with the minor component (6%) of the low-boiling fraction using gas chromatography (5% carbowax 20 M, 12 ft × 1/8 in. and 5% SE-30, 12 ft × 1/8 in.) showed them to be identical.

RESULTS AND DISCUSSION

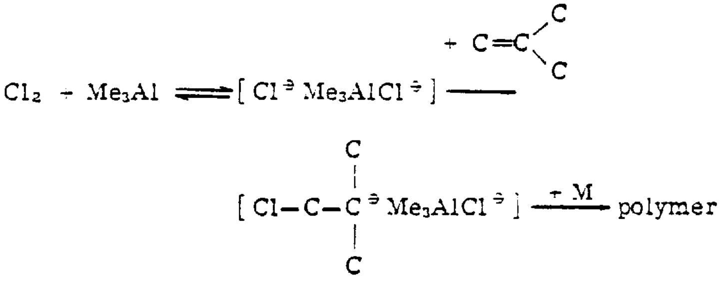
Polymerization of Styrene and Isobutylene with Chlorine/Trimethylaluminum Initiator System

Olefins such as isobutylene and styrene dissolved in methyl chloride can be stirred in the presence of certain alkylaluminum compounds such as trimethylaluminum and diethylaluminum chloride without any reaction. However, instantaneous polymerization occurs when small amounts of cationogenic initiator HX or RX are introduced into the quiescent system. Depending on the nature and amount of cationogen added, smooth, controlled polymerization or fast, even explosive, reactions can be obtained [2, 9].

In the course of fundamental studies on the mechanism of cationic polymerization we have investigated the initiation of isobutylene with trialkylaluminum compounds and various cationogens, and we have discovered that the polymerization can be efficiently initiated by chlorine. This discovery was made by theorizing that the hypothetical ion-counter ion pair that is involved in the chlorination of trimethylaluminum

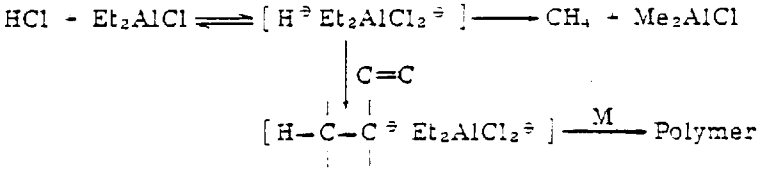
$$Cl_2 + Me_3Al \rightleftharpoons [Cl^{\oplus} Me_3AlCl^{\ominus}] \longrightarrow Me_2AlCl + MeCl$$

could also initiate the polymerization of cationically active monomers, e.g., isobutylene:



$$Cl_2 + Me_3Al \rightleftharpoons [Cl^{\oplus} Me_3AlCl^{\ominus}] \xrightarrow{+\ C=C(C)C} [Cl-C-C(C)_2^{\oplus} Me_3AlCl^{\ominus}] \xrightarrow{+M} \text{polymer}$$

This expectation was based on the finding that a small amount of HCl, in conjunction with Et_2AlCl, is an efficient cationic initiator, possibly by the following mechanism [2]:



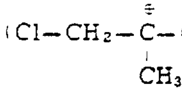
$$HCl + Et_2AlCl \rightleftharpoons [H^{\oplus} Et_2AlCl_2^{\ominus}] \longrightarrow CH_4 + Me_2AlCl$$

$$[H^{\oplus} Et_2AlCl_2^{\ominus}] \xrightarrow{C=C} [H-C-C^{\oplus} Et_2AlCl_2^{\ominus}] \xrightarrow{M} \text{Polymer}$$

These thoughts led to our experiments in which chlorine in methyl chloride solutions was added to quiescent isobutylene-trimethylaluminum mixtures in the same solvent in the temperature range -40 to -100°C. Polymerization started immediately (flash polymerization) and attained limiting conversions within 5-10 min. Table 1 summarizes our data. For comparison, t-butyl chloride (t-BuCl) was also used as an initiator under identical conditions, and the results from these studies are included in Table 1.

Two observations stand out from an examination of Table 1: 1) Under comparable conditions, Cl_2 is a more active initiator of cationic polymerization than t-BuCl, and 2) chlorine is by far the best initiator among the three halogens studied.

It has been postulated that initiator efficiency is determined by a judicious balance of the availability of the initiating ion and its stability [9]. Since the highest initiator efficiency for isobutylene was previously observed with t-BuCl, it was concluded that herein these two effects compensate each other. However, the present study shows that chlorine possesses greater initiating efficiency than t-BuCl under comparable conditions (15,000 g PIB/mole for Cl_2 vs 5,000 g PIB/mole for t-BuCl; similarly, 28,000 g PSty/mole for Cl_2 vs 1,500 g PSty/mole for t-BuCl). Note that in these cases the initiator efficiencies for Cl_2 are minimum values because conversions in these experiments were quite high so that the initiator efficiency was probably limited by the availability of unconverted monomer ("catalyst starvation"). It is conceivable that the low concentration (availability) of the initiating species (postulated as $Cl^{\oplus}$-counter ion pair) is more than compensated for by its extreme reactivity toward initiation of styrene or isobutylene polymerization. Propagation in these systems is probably by the more stable styryl ($Cl—CH_2—\underset{\oplus}{C}H—\phi$) or t-alkyl



$(Cl—CH_2—\overset{\oplus}{\underset{CH_3}{C}}—CH_3)$ ion-counterion pair.

The ability of the three halogens to initiate polymerization in conjunction with Me_3Al varies in the order $Cl_2 > Br_2 \gg I_2$. All attempts to initiate the polymerization of isobutylene or styrene using I_2/Me_3Al have proven unsuccessful. The reasons for this are at present purely a matter of speculation. Steric effects of the halogens to complexation with alkylaluminum compounds might play a part in determining the reactivity of various halogens toward polymerization. In this connection recent results from our laboratories are of interest. It was found that the reactivity of t-butyl halides toward trimethylaluminum to form neopentane varies in the order t-BuCl > t-BuBr ≫ t-BuI [10, 11].

TABLE 1. Polymerization of Styrene and Isobutylene with Me_3Al/X_2 and Me_3Al/t-BuCl Initiator Systems[a]

Temp (°C)	Initiator	Me_3Al [moles × 10^5]	Initiator [moles × 10^5]	Me_3Al/Initiator	Time (min)	Yield (g)	Conversion (%)	$\overline{M}_n \times 10^{-4}$	$\overline{M}_v \times 10^{-3}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
Isobutylene											
-40	Cl_2	60	20	3	60	3.1	89		46.4		
-40	t-BuCl	60	20	3	60	3.3	94		44.2		
-50	Cl_2	20	20	1	5	2.6	74.5				
-50	Cl_2	20	20	1	30	3.1	89		72.8		
-50	Cl_2	20	20	1	60	3.2	91.5				
				(Initiator efficiency[b] ~15,000 g/mole)							
-50	Cl_2	60	20	3	5	3.1	89				
-50	t-BuCl	20	20	1	60	1.0	28		63.3		
				(Initiator efficiency[b] ~5,000 g/mole)							
-50	Cl_2	60	20	3	60	2.5	71.5				
-50	Cl_2	120	20	6	60	3.2	91.5				
-50	Br_2	60	20	3	60	0	0				
-50	Br_2	120	20	6	60	0	0				
-50	Br_2	120	120	1	60	0	0				

-50	I_2^c	60	20	3	60	0	0				
-50	I_2^c	120	120	1	60	0	0				
-75	Cl_2	120	20	6	60	3.1	89		118.3		
-75	t-BuCl	120	20	6	60	2.9	82.5		100.3		
-100	Cl_2	120	20	6	60	0.2	6		182.4		
-100	t-BuCl	120	20	6	60	0.25	7		189.1		
Styrene											
-50	Cl_2	20	0.4	50	5	0.07	1				
					60	0.24	4	24.4		43.7	1.8
-50	Cl_2	20	20	1	5	5.6	90	6.1		29.3	4.8
-50	Cl_2	20	20	1	60	5.7	90				
(Initiator efficiency[b] ~28,000 g/mole)											
-50	Cl_2	60	20	3	5	2.8	45	15.8		45.1	2.9
					60	3.7	60				
-50	Cl_2	120	20	6	5	2.8	45				
					60	3.6	60				
-50	t-BuCl	20	20	1	60	1.8	30	13.2		25.8	1.9
(Initiator efficiency[b] ~9,000 g/mole)											

(continued)

TABLE 1. Polymerization of Styrene and Isobutylene with Me_3Al/X_2 and Me_3Al/t-BuCl Initiator Systems[a] (Continued)

Temp (°C)	Initiator	Me_3Al [moles $\times 10^5$]	Initiator [moles $\times 10^5$]	Me_3Al/Initiator	Time (min)	Yield (g)	Conversion (%)	$\overline{M}_n \times 10^{-4}$	$\overline{M}_v \times 10^{-3}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
Styrene (Continued)											
-50	t-BuCl	60	20	3	5	1.4	22	12.8		35.0	2.75
					60	3.7	60				
-50	t-BuCl	120	20	6	60	6.2	100				
-50	Br_2	60	20	3	60	0	0				
-50	Br_2	60	60	1	60	0	0				
-50	Br_2	120	120	1	60	1.3	20	12.4		32.6	2.6
-50	I_2[c]	20	20	1	60	0	0				
-50	I_2[c]	60	20	3	60	0	0				
-50	I_2[c]	120	20	6	60	0	0				
-50	I_2[c]	120	120	1	60	0	0				

[a] Conditions: Each charge consisted of 4.8 ml (60×10^{-3} mole) of isobutylene or 6.85 ml (60×10^{-3} mole) of styrene in 15 ml methyl chloride (~2.8-3.0 M). The calculated amount of Me_3Al was added as methyl chloride solution and stirred at the preselected temperature. Dilute initiator solution in methyl chloride was introduced to this system.

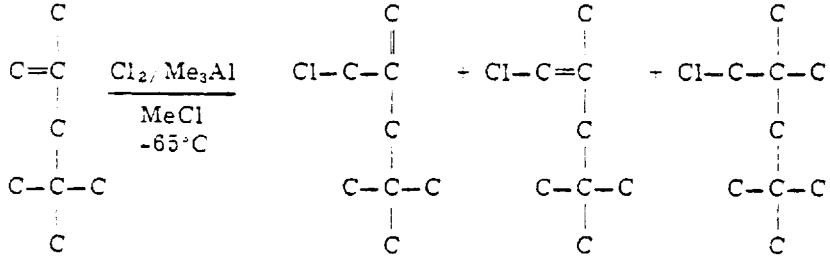
[b] Initiator efficiency is defined as grams of polymer formed per mole of initiator added (Cl_2 or t-BuCl).

[c] Because of the poor solubility of iodine in methyl chloride, solutions were made up in ethyl chloride.

Mechanism of Initiation with $Cl_2 \cdot Me_3Al$. Model Compound Studies

To characterize the nature of the initiating species, we undertook model polymerization studies. It was mandatory that propagation be minimized so as to facilitate product characterization. We chose as our model 2,4,4-trimethyl-1-pentene (I), a monomer structurally similar to isobutylene except that it is unable to propagate because of its bulky substituents. The suitability of this substrate as a model for isobutylene polymerization has been established [12].

Experimentally, 2,4,4-trimethyl-1-pentene was dissolved in methyl chloride containing Me_3Al at -65°. Reaction was initiated by the introduction of a methyl chloride solution of chlorine initiator. After ~30 min of stirring, the reaction was quenched by the introduction of cold methanol. The products were separated and characterized. The low-boiling fraction of the reaction product was found (see Experimental) to consist of a mixture of 2-chloromethyl-4,4-dimethyl-1-pentene (II), 1-chloro-2,4,4-trimethyl-1-pentene (III), and 2-chloromethyl-2,4,4-trimethylpentane (IV) in the relative proportion 66:28:6. Two peaks were observed in GC for Component III, although preparatively only the mixture could be isolated and characterized. Tentatively we assign the two peaks to the geometrical isomers of Olefin III. No evidence for the existence of the third isomeric olefin, 2-chloromethyl-4,4-dimethyl-2-pentene, was found. This appears consistent with the reported reluctance of the $C_8^{\oplus}$ ion (dimethyl neopentyl carbenium ion) to deprotonate to 2,4,4-trimethyl-2-pentene [12].



In an independent experiment we mixed equal amounts of a 3-M solution of chlorine and trimethylaluminum in methylene chloride at -50°C in an NMR tube and recorded its spectra. We detected two peaks, one corresponding to methyl chloride protons (2.34 δ upfield of CH_2Cl_2 protons) and the other assigned to the methyl groups attached to aluminum (5.67 δ upfield of CH_2Cl_2 protons) in a relative intensity of 1:5.7. This is consistent with the stoichiometry for the reaction between chlorine and trimethylaluminum:

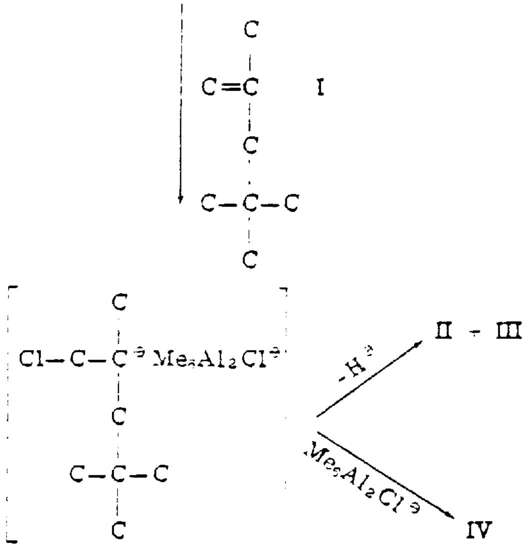
$$Cl_2 + (Me_3Al)_2 \longrightarrow CH_3Cl + Me_5Al_2Cl$$

This reaction is analagous to the reaction between t-BuCl and trimethylaluminum which yields neopentane [10]:

$$\text{t-BuCl} + (Me_3Al)_2 \longrightarrow \text{neopentane} + Me_5Al_2Cl$$

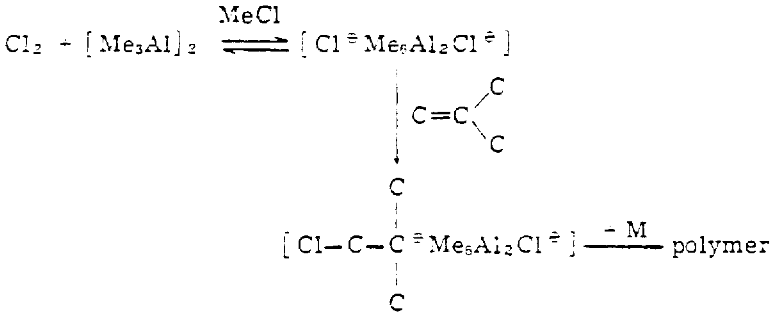
On the basis of these results we propose the following scheme for the reaction of 2,4,4-trimethyl-1-pentene with Cl_2/Me_3Al:

$$Cl_2 + (Me_3Al)_2 \rightleftharpoons [Cl^{\oplus} Me_6Al_2Cl^{\ominus}] \longrightarrow MeCl + Me_2AlCl.Me_3Al$$



Although Olefins II and III could also arise by a simple addition of chlorine to 2,4,4-trimethyl-1-pentene in the absence of trimethylaluminum, we believe that our scheme is consistent with all observations. The reaction of the chlorocation with the counterion ($Me_5Al_2Cl^-$) to give IV represents a 'termination' reaction. Expulsion of the proton from the carbenium ion to give II and III can be regarded as a "chain transfer" process. This eliminated proton can either add to cholorolefins (II and III) or the monomer (I) to give a new C_8^+ cation which in turn can add to another monomer to give C_{16}^+ cations. The products arising from such cations were assumed to be present in the higher-boiling fractions of the reaction between I and Cl_2 Me_3Al and no attempts were made to identify these products. For purposes of establishing the end group it appears sufficient to characterize only the products arising from the first-formed carbenium ion.

Cationic initiation of olefin polymerization by Cl_2 and Me_3Al can then be postulated as



The role of MeCl solvent in these polymerizations appears quite similar to that postulated for olefin polymerization using Me_3Al and t-BuCl as initiator and has been described in detail elsewhere [13].

We have also shown that 1,2-dichloro-2-methylpropane, which could presumably arise as a result of an initial addition of chlorine to isobutylene, is not an initiator of polymerization in conjunction with trimethylaluminum. Under conditions wherein chlorine or t-butyl chloride in the presence of trimethylaluminum rapidly and explosively initiates the polymerization of isobutylene (>80% conversion in less than 5 min), 1,2-dichloro-2-methylpropane is totally inert. No polymer was obtained even after 2 hr of reaction at -50°. The relative inertness of 1,2-dichloro-2-methylpropane to solvolytic substitution and elimination [14] as well as its inability to initiate polymerization in the presence of titanium tetrachloride as the coinitiator [15] have been described previously.

For the sake of simplicity we have represented the initiation process as a stepwise reaction, the first step involving the reaction between Cl_2 and Me_3Al, followed by addition to olefin. We recognize that this might be an oversimplification of what is probably a complex reaction involving the halogen, alkylaluminum, and olefin in the same transition state leading to the intermediate chlorocarbenium ion-counterion pair. Consequently the exact nature of the attacking species is a matter of conjecture and we view the chlorine simply as an electrophilic reagent that is able to provide "chlorine cations." However, just as free protons in solutions, free halogen ions should also be considered fictional. Even ion-counterion pairs such as $[Cl^{\oplus}\ Me_6Al_2Cl^{\ominus}]$ might have only a fleeting existence and are probably present in extremely small concentrations. Since no polymerization occurs in the absence of alkylaluminum compounds in these systems, it is conceivable that Lewis acids such as Me_3Al and other alkylaluminum compounds "solvate" the chloride ion by complexation, thus rendering the carbenium ion sufficiently stable to enter successfully in the propagation reaction.

Effect of Temperature on the Molecular Weight of Polyisobutylene

The viscosity-average molecular weights of polyisobutylenes obtained from the Cl_2/Me_3Al and t-BuCl/Me_3Al initiator systems at -40, -50, -75, and -100°C were determined. The plots of log molecular weight vs 1/T were linear in both cases and are shown in Fig. 1. The experimental points representing both the Cl_2/Me_3Al and t-BuCl/Me_3Al systems fall on the same straight line with the overall activation energy (E_{DP}) calculated from the slope of ~1.9 kcal/mole. This is in excellent agreement with a value of E_{DP} ~ 1.7 kcal/mole observed previously for the t-BuCl/Me_3Al system by Kennedy and Milliman [13]. This points to the similarity in the overall polymerization mechanism with the two systems Cl_2/Me_3Al and t-BuCl/Me_3Al. An explanation for this similarity could be that except for the initiation step, the counterion associated with the propagating carbenium ion determines to a large degree the mechanism of propagation, transfer, and termination reactions. The counterion produced

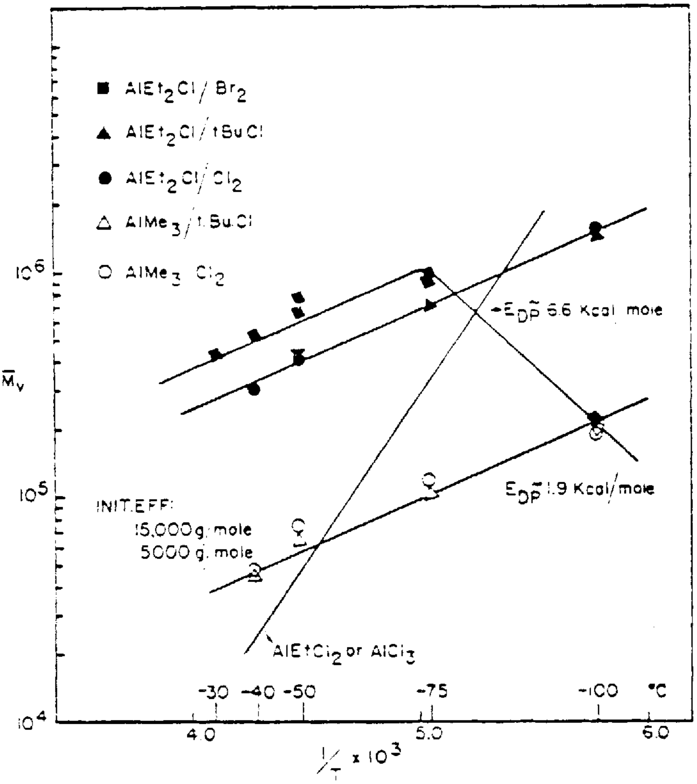


FIG. 1. The effect of temperature on $\overline{M}_v$ of polyisobutylene obtained with alkylaluminum initiator systems ([isobutylene] ~3.0 M in methyl chloride).

in both systems, Cl$_2$ Me$_3$Al and t-BuCl Me$_3$Al, might be the same, i.e., Me$_6$Al$_2$Cl$^+$.

For purposes of comparison the slope of the line obtained with AlCl$_3$ or EtAlCl$_2$ is also indicated in Fig. 1. These Lewis acids do not require the explicit addition of an initiator for polymerization, and their log $\overline{M}_v$ vs 1 T plot is characterized by an overall $E_{DP} \sim 6.6$ kcal/mole [13]. Less acidic Lewis acids such as Et_2AlCl, Me_3Al, and $(iBu)_3Al$ require the addition of a suitable cationogenic compound for initiation. In the log $\overline{M}_v$ vs 1/T plot, these alkylaluminum compounds constitute a family of parallel lines with an overall E_{DP} of ~1.7 kcal/mole. The fact that the Cl_2/Me_3Al initiator system fits in with the latter group once again shows that in this system the initiation is indeed controlled and that the stronger Lewis acids, such as $MeAlCl_2$ and $AlCl_3$, which can conceivably arise from the successive reactions of Me_3Al and Cl_2, are not involved in the initiation mechanism.

Table 2 summarizes the results obtained using halogen and diethylaluminum chloride. It is clear that even Br_2 is able to initiate isobutylene polymerization with a more powerful Lewis acid such as diethylaluminum chloride. The initiator efficiency (defined as grams of PIB formed per mole of initiator) of bromine is lower than those of both chlorine and t-butyl chloride under comparable conditions at -50°C. As observed with Me_3Al, chlorine possesses greater initiator efficiency than t-BuCl. Iodine, even in conjunction with Et_2AlCl, appears to be a very inefficient initiator of isobutylene polymerization. The ability of halogens to initiate cationic polymerization in conjunction with Et_2AlCl follows the same order as that observed with Me_3Al, i.e., $Cl_2 > Br_2 \gg I_2$.

The viscosity-average molecular weights of polyisobutylene, obtained in these studies in the range -30 to -100°C, are shown in Fig. 1. The results from the Cl_2/Et_2AlCl and the t-BuCl/Et_2AlCl initiator systems define a single line displaced upwards but parallel to the line defined by Me_3Al and the same two initiators. This once again points to the essential similarity in the polymerization mechanism between the two initiators Cl_2 and t-BuCl. The upward displacement of the Et_2AlCl line relative to the Me_3Al line has been previously observed [13]. Both the slope of the log $\overline{M}_v$ vs 1/T line and the absolute values of $\overline{M}_v$ of polyisobutylene obtained during the present study using t-BuCl/Et_2AlCl agree very well with the values reported earlier by Kennedy and Milliman [13]. However, using t-BuCl/Me_3Al initiator system we could only reproduce the slope of the line; the absolute values of the molecular weights were lower by a factor of 2.5 when compared with the previously reported values. The reason for this discrepancy is not clear at the present time.

The molecular weights of polyisobutylene obtained with the Br_2/Et_2AlCl system are consistently higher than those obtained with either the Cl_2/Et_2AlCl or the t-BuCl/Et_2AlCl systems in the range -30 to -75°C. The reason for this is not entirely clear. It may be that the relatively larger size of the counterion (presumably $Et_4Al_2Cl_2Br^{\ominus}$) enhances the ability of the ion pair to dissociate further. It has been observed before that among the three Lewis acids, $EtAlCl_2$, $AlCl_3$, and BF_3, $EtAlCl_2$ produces the highest molecular weight polymer [16]. This has been attributed to the larger size of the counterion that is presumably formed with $EtAlCl_2$ relative to the other two Lewis acids.

The $\overline{M}_v$ of polyisobutylene obtained using the Br_2/Et_2AlCl at -100°C drops to approximately 200,000. At these low temperatures the initiating efficiency of this initiator-coinitiator system drops drastically and the rate of polymerization (as observed visually from the rate of precipitation of polymer from solution) is also considerably slowed down. Consequently, to realize reasonable conversions to polymer, one is forced to use 100-200 times more bromine than what was used at higher temperatures. Therefore it may be that this excess bromine enters into unwanted side reactions (such as termination and transfer), leading to lower molecular weight of the product. The same appears true even in the very few cases where iodine could be used as an initiator of polymerization in conjunction with Et_2AlCl. Only low molecular weight, oily polyisobutylene could be obtained.

Polymerization of Styrene with Cl_2/Me_3Al: $\overline{M}_w$, $\overline{M}_n$, and MWD

Molecular weights ($\overline{M}_w$, $\overline{M}_n$, and MWD) of polystyrene are summarized in Table 1. These molecular weights are among the highest ever reported for polystyrene by cationic mechanism under comparable conditions. These values are all the more remarkable since we have made no attempt to optimize our molecular weights.

Examination of Table 1 reveals two trends: 1) Molecular weights decrease with increasing conversion, and 2) the molecular weight distribution broadens with increasing conversion. These two trends have been observed before [17].

TABLE 2. Polymerization of Isobutylene with Et_2AlCl/Initiator System[a]

Temp (°C)	Initiator	Initiator [moles × 10^7]	Et_2AlCl/initiator	Yield (g)	Conversion (%)	Initiator efficiency × 10^{-5} g PIB/moles of initiator	$\overline{M}_v \times 10^{-3}$
-30	Br_2	10	200/1	0.33	9.4	3.3	416
-40	Cl_2	4	500/1	1.4	40	35	297
-40	t-BuCl	4	500/1	1.0	29	25	
-40	Br_2	4	500/1	0.2	5.7	5	
-40	Br_2	10	200/1	0.35	10.0	3.5	501
-40	I_2	10	200/1	0	0		
-40	I_2	20	100/1	0	0		
-40	I_2	40	50/1	0	0		
-40	I_2	2000	1/1	2.6	74	0.13	
-50	Cl_2	10	200/1	2.6	74.5	26	408
-50	Cl_2	4	500/1	1.7	48.5	40	
-50	t-BuCl	10	200/1	1.3	37	13	392
-50	t-BuCl	4	500/1	0.8	23	20	
-50	Br_2	10	200/1	0.8	23	8	654
-50	Br_2	10	200/1	0.6	17		649
-50	Br_2	4	500/1	0.35	10	9	

-50	I_2	10	200/1	0	0		
-50	I_2	20	100/1	0	0		
-50	I_2	40	50/1	0	0		
-50	I_2	2000	1/1	2.9	83	0.15	161
-75	Cl_2	10	200/1	2.5	71.5	25	
-75	t-BuCl	10	200/1	1.3	37	13	
-75	Br_2	10	200/1	0.2	5.7	2	828
-75	Br_2	20	100/1	0.9	25	4.5	904
-75	Br_3	20	100/1	0.6	17	3	970
-75	I_2	2000	1/1	0	0		
-100	Cl_2	20	100/1	3.0	84	15	1453
-100	t-BuCl	20	100/1	3.0	84	15	1392
-100	Br_2	20	100/1	0	0		
-100	Br_2	40	50/1	0	0		
-100	Br_2	2000	1/1	0.3	8.6	0.015	223
-100	Br_2	2000	1/1	0.5	14	0.025	211.5

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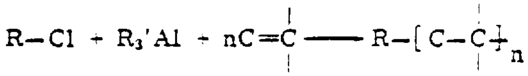
[a] Conditions: Each charge consisted of 4.8 ml (60×10^{-3} mole) of isobutylene in 15 ml methyl chloride (~3.1 M solution); Et_2AlCl (20×10^{-5} mole) was added as dilute methyl chloride solution and the mixture stirred at the preselected temperature. The appropriate amount of dilute methyl chloride solution of the initiator was added to this mixture. The reaction was allowed to proceed for 30 min (at -100°C for 60 min). Polymerization was terminated by adding 5 ml of prechilled methanol.

These observations point to a polymerization involving relatively slow initiation and rapid propagation and termination (or chain transfer). The relatively low molecular weight at high conversion can be qualitatively explained on the basis of predicted proportional dependence of DP on monomer concentration. A molecular weight distribution of 2, the most probable MWD, indicates a conventional chain propagation mechanism with probably one well-defined catalyst species as the growing site. This also represents the expected value for a conventional cationic chain-growth mechanism in which chain transfer is the dominant chain-breaking event. The broadening of MWD with conversion is also consistent with the fact that in a typical cationic polymerization the molecular weights are primarily determined by chain transfer. Broadness of distribution can also arise as a result of multiplicity of propagating ion pairs (tight or solvent separated) and the multiplicity of counterions ($R_3AlCl^{\ominus}$, $R_2AlCl_2^{\ominus}$, etc.). Chain branching arising as a result of transfer to the polymer has also been proposed to explain the unusually large MWD values (~5) obtained at high conversion [18].

In conclusion, our continuing study in the cationic initiation of olefin polymerization with the alkylaluminum-initiator systems has provided derivatized polymers with partially well-defined end-groups for the first time.



$$\mathrm{R{-}Cl + R_3'Al + nC{=}\overset{|}{\underset{|}{C}} \longrightarrow R{-}[C{-}\overset{|}{\underset{|}{C}}]_n}$$

where R = t-alkyl, allyl, benzyl, or chloro. This is impossible to achieve using the conventional Lewis acids such as BF_3 and $AlCl_3$.

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