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ORGANOALUMINUM CHEMISTRY AND ITS APPLICATION TO THE INITIATION OF CARBENIUM ION POLYMERIZATION *

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Summary

Organoaluminum compounds are weak Lewis acids, which specifically react with a number of reagents (or bases) and generate an electrophile (initiator)-gegenion pair, reminiscent of classical Friedel—Crafts complexes. These complexes, under suitable reaction conditions, initiate polymerization of cationically polymerizable monomers producing useful high molecular weight polymers. In recent years a number of such organoaluminum-initiator systems have been systematically explored and their chemistry unravelled. As a consequence new insights have been gained which has led to newer applications of organoaluminum compounds in organic as well as new polymer synthesis.

The present paper briefly summarizes the results in this area, especially from the point of view of initiator generation. Some recent results on the initiation of carbenium ion polymerizations using the oxyhalides of sulfur and phosphorous in conjunction with organoaluminum compounds are discussed.

Introduction

The serendipitous discovery by Ziegler and his coworkers [1] that organoaluminum compounds in the presence of transition metal salts can polymerize ethylene at atmospheric pressures to high molecular weight linear polyethylene established for the first time the commercial utility of organoaluminum chemistry. The discovery of stereospecific polymerization of 1-olefins by Natta [2] based on a catalyst system comprising an organoaluminum compound and titanium halides gave further impetus to this branch of organometallic chemistry. Since that time a number of investigations have attempted to elucidate the nature of these catalysts and the role of organoaluminum compounds in

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* Dedicated to Professor H.C. Brown in recognition of his contributions to chemistry.

these polymerizations. These have been summarized in a number of incisive reviews [3,4,5].

More recently the utility of organoaluminum compounds have been extended to an entirely new class of polymerization reactions, namely those involving carbenium ions as propagating ends. This paper reviews recent progress in this new area of application of organoaluminum chemistry.

Terminology

Trivalent carbocations, the parent of which is CH_3^+, will be described as carbenium ions. In general carbenium ion polymerizations are initiated by a combination of Lewis acid (example, classical Friedel—Crafts halides) and Bronsted acid. Further it is now accepted that pure Friedel—Crafts halides are unable to initiate carbenium ion polymerizations, unless suitable proton sources are present [6]. Such combinations for example, HF/BF_3, $HBr/AlBr_3$, $H_2O/TiCl_4$ are amongst the strongest acids known and are most effective initiators. In these cases it has been shown that the true initiator is a proton (from Bronsted acid) and the function of the Friedel—Crafts halide is to only help remove and stabilize by coordination the halide ion (eq. 1). Accordingly the correct terminology

$$HF + BF_3 \rightarrow H^+BF_4^- \underset{C=C}{\rightleftarrows} H{-}C{-}C^+BF_4^- \underset{C=C}{\rightleftarrows} \text{Polymer} \qquad (1)$$

is to designate the Friedel—Crafts halide as the coinitiator and the source of the initiating species as initiator. The term "syncatalysts" originally proposed by Plesch [7] for such coinitiator/initiator pairs has also been recently renewed [8].

Carbenium ion polymerizations: mechanism

The mechanism of carbenium ion polymerizations may be discussed in terms of five basic steps: priming or cation formation, initiation, propagation, chain-transfer and termination (eq. 2—6).

$$MX_n + HX \rightarrow H^+MX_{n+1}^- \qquad (2)$$

$$H^+ + C{=}C \rightarrow H{-}C{-}C^+ \qquad (3)$$

$$H{-}C{-}C^+ + C{=}C \rightarrow H{-}C{-}C{-}C{-}C^+ \rightarrow \rightarrow \text{Polymer} \qquad (4)$$

$$H{-}C{-}C{-}C{-}C^+ + C{=}C \rightarrow H{-}C{-}C{-}C{=}C + H{-}C{-}C^+ \qquad (5)$$

$$H{-}C{-}C{-}C{-}C^+ + Y^- \rightarrow H{-}C{-}C{-}C{-}C{-}Y \qquad (6)$$

Priming is the process in which an active electrophilic species, e.g., proton, carbenium ion, is produced from the initiator molecule. Priming should be distinguished from initiation proper, the process in which the electrophile attacks the monomer. Propagation is the repititive addition of the monomer to carbenium ion. Chain transfers interrupts the kinetic chain by transferring the electrophilic site from a growing polymer to a nucleophilic species in the system. Depending on the nature of nucleophile (monomer, solvent, polymer, counterion) various types of chain-transfer steps can arise. The most important chain-transfer step is that of to the monomer. Since the relative rates of chain-transfer to propagation usually determine the molecular weights, chain-transfer is undesirable if high molecular weight polymers are to be prepared. To reduce the rate of chain-transfer whose activation energy is relatively high, polymerizations are carried out at very low temperatures, generally in the range of 0 to —100° C. Termination, the least understood of all steps, is the ultimate destruction of the propagating activity of chain and limits conversions in a given polymerization reaction.

In spite of intensive research on the various intricacies of this mechanism over the past three decades, much remains to be learnt about these fundamental steps. The present status of our understanding is summarized in a number of excellent reviews [9,10].

Organoaluminum compounds as coinitiators in carbenium ion polymerizations

Conventionally strong Lewis acids such as aluminum chloride, boron trifluoride, and titanium tetrachloride have been used as coinitiators in carbenium ion polymerizations. More recently, the trialkylaluminum and dialkylaluminum halides have been extensively investigated as representative classes of weaker Lewis acids capable of initiating carbenium ion polymerizations.

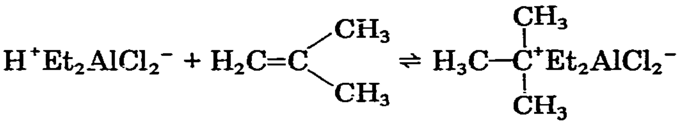
Extensive studies have revealed significant differences between these two classes of Lewis acids. The stronger Lewis acids are capable of initiating polymerizations without the purposeful addition of an electrophile, whereas the weaker Lewis acids require specific addition of an initiator. Further, it has been observed that polymerization initiated by an alkylaluminum/initiator system is less susceptible to common impurities compared to Lewis acids such as $AlCl_3$ etc., enabling "bench top" experimentation. In contrast, experimental study of initiation with conventional (strong) Lewis acids has to be carried out under high vacuum to obtain meaningful results.

These two factors render alkylaluminum compounds as ideal candidates for research into many aspects of initiation in carbenium ion polymerizations. Studies during the past decade or so have led to the discovery of entirely new classes of initiators for carbenium ion polymerizations which possess major advantages. In addition the polymerization mechanism has been brought into sharper focus which in turn has led to significant developments in synthetic polymer chemistry.

The alkylaluminum—Bronsted acid system

The first significant results on the utility of organoaluminum compounds as coinitiators in carbenium ion polymerizations were revealed in a patent issued to ESSO Research and Engineering Company in 1967 [11]. The results established that isobutylene or mixtures of siobutylene and isoprene (3 vol-%) can be polymerized in polar solvents such as methyl chloride to high molecular weight polyisobutylenes or butyl rubbers in high conversion using diethylaluminum chloride in conjunction with Bronsted acids. A variety of Bronsted acids were explored and the following approximate order of reactivity was established: HCl, HBr >> HF, H_2O > Cl_3CCO_2H >> CH_3OH > CH_3COCH_3. The sequence follows approximately the acid strength of initiators involved. An initiation mechanism consistent with the experimental observations was proposed (eq. 7, 8).

$$HCl + Et_2AlCl \rightleftharpoons H^+Et_2AlCl_2^- \qquad (7)$$



$$H^+Et_2AlCl_2^- + H_2C{=}C(CH_3)_2 \rightleftharpoons H_3C{-}\overset{CH_3}{\underset{CH_3}{C^+}}Et_2AlCl_2^- \qquad (8)$$

The alkylaluminum/alkyl halide system

The first formed carbenium ion in isobutylene polymerization from the alkylaluminum/Bronsted acid system is a t-butyl cation (eq. 8) which can in principle be generated from the corresponding t-butyl halide and dialkylaluminum halide. Therefore it was predicted that t-butyl chloride in conjunction with alkylaluminums could also prove to be an efficient initiator for the polymerization of cationically polymerizable monomers such as isobutylene, styrene, etc. The prediction has been confirmed by detailed experimentation [12,13]. The following initiation mechanism has been proposed for the Et_2AlCl/t-BuCl system (eq. 9):

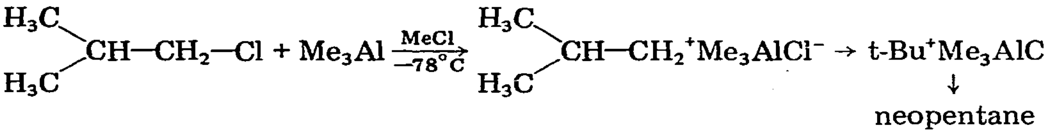
$$\text{t-BuCl} + Et_2AlCl \rightleftharpoons \text{t-Bu}^+Et_2AlCl_2^- \xrightarrow[+M]{} \text{Polymer} \qquad (9)$$

Fundamental studies on this basic reaction using model nonpolymerizable olefins have confirmed the essential correctness of this mechanism [14]. Although t-BuCl shows the greatest efficiencies in polymerization, a host of other alkyl halides capable of forming stable carbenium ions (e.g. allyl chloride, benzyl chloride, trityl chloride) have also proved to be efficient initiators. The relative efficiencies have been shown to depend on a subtle balance between carbenium ion stability (thermodynamic) and carbenium ion availability (kinetic) factors.

The study of alkylaluminum/alkyl halide system in depth has led to new uses for alkylaluminum compounds in organic synthesis. It was found that when trimethylaluminum was mixed with alkyl and aryl halides at −78° C in methyl chloride solvent, an instantaneous alkylation reaction occurred which was explained in terms of eq. 10 [15]:

$$R{-}Cl + Me_3Al \overset{MeCl}{\rightleftharpoons} R^+Me_3AlCl^- \rightarrow R{-}Me + Me_2AlCl \qquad (10)$$

A series of organic chlorides were examined and it was found that (a) the reactivity of alkyl halides follows the order $3° > 2° > 1°$, corresponding to the known stability of carbenium ions and (b) with triethyl- and triisobutyl-aluminum, hydride transfer competes effectively with alkylation. The intermediacy of carbenium ions in these alkylation reactions is evidenced by the fact that isobutyl chloride gives exclusively neopentene upon alkylation with trimethylaluminum (eq. 11) and optically active α-phenylethyl chloride gives only racemic 2-phenylbutane upon alkylation with triethylaluminum (eq. 12). It has also been shown that t-olefins (e.g. 1-methylcyclohexane) can also be alkylated (to 1,1-dimethylcyclohexane) in the presence of trimethylaluminum and hydrogen chloride [16].



$$(CH_3)_2CH{-}CH_2{-}Cl + Me_3Al \xrightarrow[-78^\circ C]{MeCl} (CH_3)_2CH{-}CH_2^+Me_3AlCl^- \rightarrow t\text{-}Bu^+Me_3AlCl^- \downarrow \text{neopentane} \quad (11)$$

$$(-)Ph\overset{*}{C}H(Me)Cl + Et_3Al \xrightarrow[-65^\circ C]{EtCl} (\pm)\text{-}PhCH(Me)(Et) + PhCH(Me)H \qquad (12)$$

An attempt has been made to elucidate the finer points of this alkylation reaction. From a study of kinetics of alkylation of t-BuX (X = Cl, Br, I) in MeX (X = Cl, Br, I) and cyclopentane as solvents it was found that [17]: (a) the alkylation rate follows the order t-BuCl > t-BuBr > t-BuI, (b) the alkylation decreases in the order MeCl > MeBr > MeI >> cyclopentane and (c) the activation energies in the range —20 to —80° C are ~11 kcal/mol in all methyl halide solvents and ~16 kcal/mol in cyclopentane. The alkylation rates span a wide range and are given in Table 1.

The results bear out the specific role of solvent in these reactions. Trimethylaluminum is known to be dimeric in the solid [18], liquid [19] and gaseous states [20]. It has also been shown that a rapid exchange of the bridge and terminal methyl groups occur at room temperature which can be frozen at around —40° C. The precise mechanism of exchange is still a matter of speculation. Both inter- and intra-molecular mechanisms have been proposed [21,22]. It was found by Kennedy and Milliman [23] that addition of MeCl to a 0.3 *M* solution of trimethylaluminum in cyclopentane at —40° C caused the two NMR signals due to bridge and terminal methyl groups to coalesce. This implies that the methyl exchange on aluminum is catalyzed by MeCl. Since dimer bridge opening is a necessary requisite for facile reaction at the aluminum, methyl halide is a superior solvent than cyclopentane. It has been further shown by NMR that the rate of bridge to terminal methyl exchange in $(Me_3Al)_2$ is fastest in MeCl, followed by MeBr and MeI. This implies that exchange is slowed down as a result of increasing size and decreasing bascity of the halogen in the methyl halide series. The next step in alkylation envisages the displacement of the methyl halide coordinated to the aluminum by the t-butyl halide. Since the coordinate bond strength increases in the order Al←I > Al←Br > Al←Cl (the order of decreasing polarizabilities of halogens being I > Br > Cl), the reaction is expected to be most sluggish with MeI. The overall reaction for the specific case Me_3Al/t-BuCl/MeCl is summarized in Fig. 1 (path a).

It is therefore reasonable to conclude that solvents play a dominant role in determining the activity of the alkylaluminum compound in the alkylation reac-

TABLE 1

RATES OF ALKYLATION OF t-BUTYL HALIDES WITH TRIMETHYLALUMINUM AT —40°C

t-BuX	k (l mol^{-1} sec^{-1}) × 10^6			
	MeCl	MeBr	MeI	Cyclopentane
t-BuCl	$>10^9$	4100	2000	1.2
t-BuBr	13 000	1800	100	0.7
t-BuI	75	15	3.2	0.005

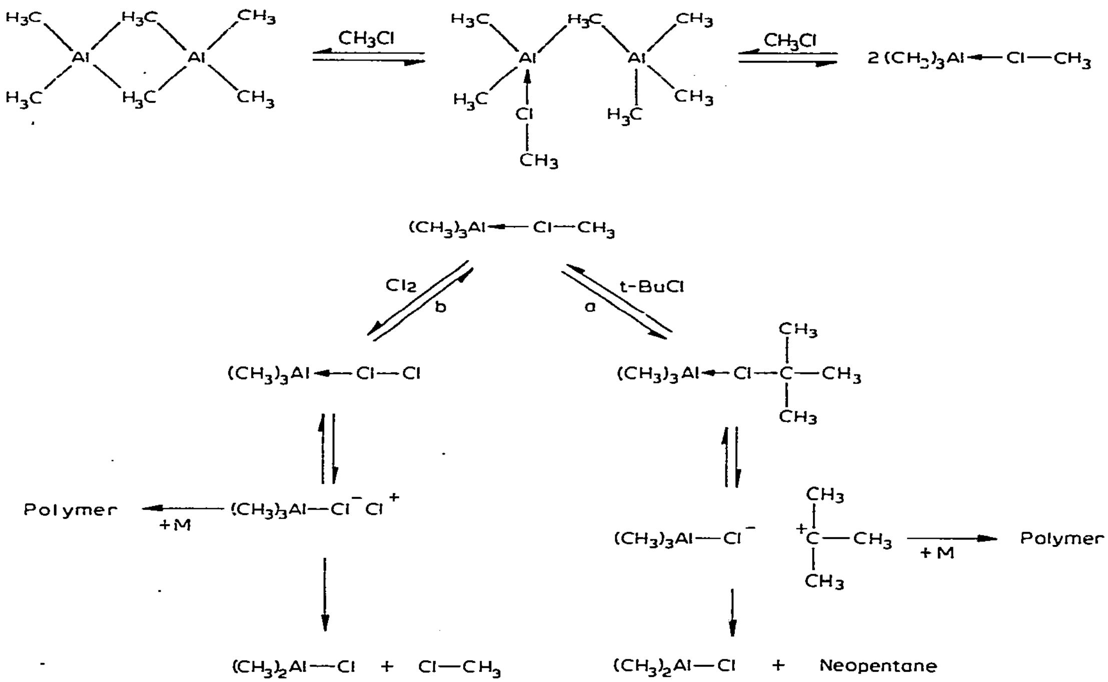


Fig. 1. Proposed mechanism of alkylation and polymerization with trimethylaluminum/t-BuCl or Cl_2 in MeCl as solvent.

tion. The slow rates observed with cyclopentane could be due to the absence of a suitable agent that can function as a "bridge opener". These conclusions are confirmed by a study of isobutylene polymerization with Me_3Al/t-BuCl in MeCl, MeBr, MeI and cyclopentane solvents. The efficiency of polymerization decreases in the order MeCl > MeBr and no polymerization was observed in MeI and cyclopentane [24].

The alkylaluminum/halogen systems

Recently it has been found that halogens and interhalogen compounds in conjunction with alkylaluminum compounds are efficient initiators for carbenium ion polymerizations [8,25]. Based on extensive data from two independent laboratories, the following conclusions can be reached: 1. The initiating species is best regarded as an electrophilic halogen cation formed by the interaction of halogen with alkylaluminum compound. 2. The role of the organoaluminum compound is to specifically solvate the chloride anion by complexation, thus rendering the carbenium ion sufficiently stable to enter successfully in the propagation reaction. 3. The efficiency of the polymerization increases in the order $Cl_2 > ICl >> IBr > Br_2 > I_2$. 4. The dialkylaluminum halides are more reactive than trialkylaluminums. 5. Some of these initiators yield substantially higher molecular weight polyisobutylene and isobutylene-coisoprene polymers at higher temperatures when compared with conventional catalysts such as $AlCl_3$, BF_3, etc. A mechanism for halogen initiation has been proposed (Fig. 1, path b).

TABLE 2

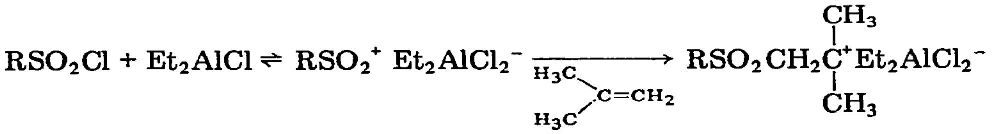
POLYMERIZATION OF ISOBUTYLENE USING THE Et_2AlCl/CH_3SO_2Cl INITIATOR SYSTEM [a]

Et_2AlCl (mol × 10^5)	CH_3SO_2Cl (mol × 10^5)	Yield (g)	Conversion (%)	$\bar{M}_v \times 10^{-3}$
20	0.2	0.6	17	323
20	0.4	1.0	29	—
20	20	0.9	28	360
60	20	2.2	63	314
60	60	3.6	100	—

[a] Conditions: each charge consisted of 4.8 ml (60 × 10^{-3} mol) of isobutylene in 15 ml methyl chloride (~3 *M*). The calculated amount of Et_2AlCl was added as dilute solution in methyl chloride followed by initiator solution at −50° C. Reaction time: 30 min.

The alkylaluminum/sulfonyl halide system

In a continuing search of novel electrophilic species capable of initiating polymerizations we have studied the alkylaluminum/sulfonyl halide system for isobutylene polymerization. In the presence of Lewis acids, sulfonyl chlorides are known to form sulfonilium cations [26] which we hypothesized could initiate polymerization (eq. 13). Some representative results are shown in Table 2. The relative efficiencies of a number of initiators are compared in



$$RSO_2Cl + Et_2AlCl \rightleftharpoons RSO_2^+\ Et_2AlCl_2^- \xrightarrow[\substack{H_3C \\ \quad C=CH_2 \\ H_3C}]{} RSO_2CH_2\overset{CH_3}{\underset{CH_3}{C^+}}Et_2AlCl_2^- \qquad (13)$$

Table 3. An independent study has shown that thionyl chloride and sulfuryl chloride in conjunction with diethylaluminum chloride are also capable of initiating carbenium ion polymerizations [27]. Presumably the initiators are electrophilic species such as $ClSO^+$ and $ClSO_2^+$.

The alkylaluminum/acid halide system

Organic acid halides (e.g., oxalyl chloride, acryloyl chloride, acetyl chloride, etc.) have been shown to initiate isobutylene and styrene polymerization in con-

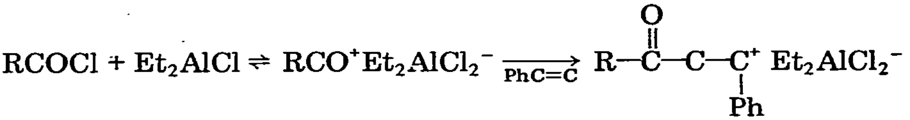
TABLE 3

COMPARISON OF INITIATOR EFFICIENCIES [a]

Initiator	Efficiency × 10^{-5} (g polymer/mol of initiator)
Cl_2	16
tBuCl	10
Br_2	7
CH_3SO_2Cl	3
I_2	0

[a] Conditions: monomer/isobutylene, 3.1 *M* in MeCl; coinitiator, Et_2AlCl, 10^{-2} *M* in MeCl; initiator approx. 10^{-4} *M* in MeCl; temperature −50° C.

junction with alkylaluminum compounds [27,28]. The initiating species in these cases are best described as an acylium ion (eq. 14). In the absence of a polymerizable monomer organoaluminum compounds are known to convert acid

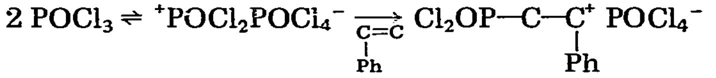


$$RCOCl + Et_2AlCl \rightleftharpoons RCO^+Et_2AlCl_2^- \xrightarrow[PhC=C]{} R-\overset{\overset{O}{\|}}{C}-C-\underset{\underset{Ph}{|}}{C^+}\ Et_2AlCl_2^- \qquad (14)$$

halides to ketones [29], a reaction characteristic of other organometallic alkylating agents. Under identical conditions, for copolymerization of isobutylene with 3 vol.% isoprene using diethylaluminum chloride as coinitiator, the initiator efficiencies of a series of acid halides at —40° C varied as $SO_2Cl_2 > COClCOCl > SOCl_2 > CH_2{=}CHCOCl > CH_3COCl$.

The alkylaluminum/phosphorous oxychloride system

It has been reported recently that phosphorous oxychloride is capable of polymerizing α-methylstyrene at high monomer/$POCl_3$ ratios (10/1) through a carbenium ion mechanism [30]. The major limitations of this initiator were that (a) it was not sufficiently active to polymerize styrene and (b) even with α-methylstyrene only low molecular weight oligomers could be obtained. Evidence for the presence of Cl_2OP- end group in polymer was presented. Although no mechanisms were specifically indicated, it is possible that the electrophile $^+POCl_2$, generated presumably by a self-dissociation mechanism of $POCl_3$ could be responsible for initiation of polymerization (eq. 15). Such self-dissociation wherein $POCl_3$ functions both as acceptor and donor is well documented [31]. It is



$$2\,POCl_3 \rightleftharpoons {}^+POCl_2POCl_4^- \xrightarrow[\underset{\underset{Ph}{|}}{C=C}]{} Cl_2OP-C-\underset{\underset{Ph}{|}}{C^+}\ POCl_4^- \qquad (15)$$

therefore reasonable to expect that in presence of a stronger acceptor such as an alkylaluminum compound, the dissociation process could be facilitated leading to more efficient initiation. We have recently confirmed this prediction by successfully polymerizing both styrene and α-methylstyrene with $Et_2AlCl/POCl_3$ initiator system to high molecular weight polymers. The initiator efficiency (g polystyrene formed/mole of initiator) for $POCl_3$ is ~30,000 compared to ~90,000 for t-BuCl under identical conditions (2.5 *M* styrene in chlorobenzene, 0.025 *M* Et_2AlCl and 0.03 *M* initiator at —20° C). Full details of this study will be published elsewhere.

Phosphorous trichloride has also been reported to be an inefficient initiator for carbenium ion polymerizations [32,33]. However, our results from $POCl_3$ would appear to indicate that the activity of this initiator could also be improved by using it in conjunction with suitable alkylaluminum compounds.

Miscellaneous alkylaluminum/initiator systems

A number of other reagents capable of generating an initiating electrophilic species in conjunction with alkylaluminum compounds has been reported in the literature. These are $Et_2AlCl/NOCl(NO^+)$ [34], Et_2AlCl/*N*-bromosuccinimide (Br^+) [27] and Et_3Al/CH_3OCH_2Cl ($CH_3OCH_2^+$) [28]. Plausible electrophiles capable of functioning as initiator in these systems have been indicated in parenthesis. However, no in depth study is yet available on these systems. Although trimethylchlorosilane has been reported to be an initiator in conjunction with Lewis acids such as $HgCl_2$ and $FeCl_2$ for styrene polymerization [35], the evidence is not clear as to whether an alkylsiliconium ion is indeed the initiating species [36].

Conclusions

The fundamental discovery that trialkylaluminum and dialkylaluminum halides are capable of initiating carbenium ion polymerizations only in the presence of a specifically added source of electrophiles, gave the impetus to this new area of application of organoaluminum chemistry to polymer science. These developments provided for the first time derivatized polymers with partially well defined end groups which could be used in post-polymerization and polymer modification reactions. Results from this area have also significantly contributed to the expanding horizons of polymer synthesis via cationic techniques and are summarized in detail elsewhere [37,38].

Our studies in this area have also provided new insights into the interaction of organoaluminum compounds with a variety of reagents capable of generating electrophilic species via a classical Lewis acid/base reaction. Today alkylaluminums can be routinely handled in the laboratory (with suitable precautions), and they possess many desirable properties such as ease of purification and good solubility in common organic solvents. Consequently they may also prove to be the Lewis acids of choice in many classical Friedel—Crafts reactions. Systematic studies in this area are clearly warranted.

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References

1 K. Ziegler, E. Holkamp, H. Breil and H. Martin, Angew Chem., 67 (1955) 541.
2 G. Natta, J. Polym. Sci., 16 (1955) 143.
3 J. Boor, Jr., Macromol. Rev., 2 (1967) 115.
4 W.L. Carrick, Advan. Polym. Sci., 12 (1973) 65.
5 S. Sivaram, Ind. Eng. Chem., Prod. Res. Dev., 16 (1977) 121.
6 Z. Zlamal, in G.E. Ham (Ed.), Kinetics and Mechanism of Polymerization, Vol. 1, Marcel Dekker, New York, 1969, p. 231.
7 P.H. Plesch, Progr. High Polymers, 2 (1968) 137.
8 A. Priola, G. Ferraris, M. di Maina and P. Guisti, Makromol. Chem., 1976 (1975) 2271.
9 J.P. Kennedy, Cationic Polymerization of Olefins. A Critical Inventory, Wiley—Interscience, New York, 1975.
10 P.H. Plesch (Ed.), The Chemistry of Cationic Polymerization, Pergamon, London, 1963.

11 J.P. Kennedy, U.S. Pat. 3,349,065, 1967, to ESSO Research and Engineering Company.
12 J.P. Kennedy, J. Makromol. Sci.,-Chem. A, 3 (1969) 861.
13 J.P. Kennedy, in J.P. Kennedy and E. Tornqvist (Eds.), Polymer Chemistry of Synthetic Elastomers, Part I, Wiley—Intersceince, New York, 1968, p. 291.
14 J.P. Kennedy and S. Rengachary, Advan. Polym. Sci., 14 (1974) 1.
15 J.P. Kennedy, J. Org. Chem., 35 (1970) 532.
16 J.P. Kennedy and S. Sivaram, J. Org. Chem., 38 (1973) 2262.
17 J.P. Kennedy, N. Desai and S. Sivaram, J. Amer. Chem. Soc., 95 (1973) 6386.
18 P.H. Lewis and R.E. Rundle, J. Chem. Phys., 21 (1953) 986.
19 K.S. Pitzer and H.S. Gutowsky, J. Amer. Chem. Soc., 68 (1946) 2204.
20 A.W. Laubengayer and W.F. Gilliam, J. Amer. Chem. Soc., 63 (1941) 477.
21 K.C. Williams and T.L. Brown, J. Amer. Chem. Soc., 88 (1966) 5460.
22 N. Muller and D.E. Pritchard, J. Amer. Chem. Soc., 82 (1960) 248.
23 J.P. Kennedy and G.E. Milliman, Advan. Chem. Ser., 91 (1969) 287.
24 P.D. Trivedi, Ph.D. Thesis, The University of Akron, 1976.
25 J.P. Kennedy and S. Sivaram, J. Macromol. Sci.,-Chem. A, 7 (1973) 969.
26 H. Reinheckel, K. Haage and D. Jahnke, Organometal. Chem. Rev., A, 4 (1969) 47.
27 M. Baccaredda, M. Bruzzone, S. Cesca, M. DiMaina, G. Ferraris, P. Guisti, P.L. Magagnini and A. Priola, Chim. Ind. (Milano), 55 (1973) 109.
28 T. Saegusa, H. Imai and J. Furukawa, Makromol. Chem., 79 (1964) 207.
29 T. Mole and E.A. Jeffery, Organoaluminum Compounds, Elsevier, Amsterdam, 1972, p. 311.
30 M. Biswas and P.K. Mishra, Polymer, 16 (1975) 621.
31 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, New York, 1962, p. 389.
32 T. Taninaka and Y. Minoura, J. Polym. Sci., Chem. Ed., 14 (1976) 685.
33 T. Tananika, K. Iwamoto, Y. Minoura, J. Polym. Sci., Chem. Ed., 15 (1977) 2219.
34 J.P. Kennedy (The University of Akron), personal communication.
35 Y. Minoura and H. Toshima, J. Polym. Sci., A1, 11 (1972) 1109.
36 R.J.P. Corriu and M. Henner, J. Organometal. Chem., 74 (1974) 1.
37 J.P. Kennedy and R.R. Smith, in L.H. Sperling (Ed.), Recent Advances in Polymer Blends, Grafts and Blocks, Plenum Press, New York, 1974, p. 303.
38 J.P. Kennedy and E.G. Melby, J. Polym. Sci. Chem. Ed., 13 (1975) 29.