

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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

Self-Initiation in Cationic Polymerization

J. P. Kennedy^a

^a Institute of Polymer Science, The University of Akron, Akron, Ohio

Online publication date: 29 September 2010

To cite this Article Kennedy, J. P.(1972) 'Self-Initiation in Cationic Polymerization', Journal of Macromolecular Science, Part A, 6: 2, 329 – 346

To link to this Article: DOI: 10.1080/0022233X.1972.10131859

URL: <http://dx.doi.org/10.1080/0022233X.1972.10131859>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

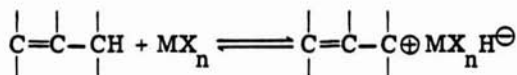
Self-Initiation in Cationic Polymerization

J. P. KENNEDY

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325

ABSTRACT

A critical examination of polymerization, dimerization, and isomerization experiments carried out under carefully controlled (anhydrous) conditions leads to the conclusion that polymerization, etc. may proceed in purest monomer/Friedel-Crafts halide systems in the absence of cointiators. Thus the well-entrenched view that Friedel-Crafts halides always require cointiator (protogenic impurities) for initiation of cationic polymerizations has to be modified. It is postulated that initiation in purest olefin/Friedel-Crafts halide systems might proceed by a self-initiation mechanism involving the abstraction of an allylic H from the monomer by the Friedel-Crafts halide MX_n :



The chemistry and evidence for this mechanism are discussed in detail.

INTRODUCTION

It is a well-entrenched notion that for the initiation of cationic polymerizations with Friedel-Crafts halides (BF_3 , AlCl_3 , TiCl_4 , etc.) the presence of a third species, commonly called the coinitiator (H_2O , HCl , RCl , etc.), is required. In the light of recent evidence this view is erroneous and must be modified. In this paper the author critically examines the limitations of the earlier hypothesis, organizes new findings, and presents a new theory of self-initiation with Friedel-Crafts halides.

Table 1 is a comprehensive compilation of polymerization and related systems in which initiation cannot be explained by published theories. Only work that was carried out under rigorously anhydrous conditions (high vacuum plus other precautions such as sodium mirror and prepolymerization technique) has been considered in Table 1. For example, Czechoslovak authors found that AlBr_3 [1] or AlEtCl_2 [2] initiate the polymerization of isobutylene in *n*-heptane in the absence of protogens or cationogens, and that the rate obeyed

$$-d[M]/dt = k[\text{MX}_n]^2[\text{isobutylene}]$$

where MX_n is AlBr_3 or AlEtCl_2 . In subsequent publications $\text{AlBr}_3 \cdot \text{TiCl}_4$ mixed systems were described to be more active initiators than AlBr_3 alone [5], while TiCl_4 alone was found to be completely inactive. Many Friedel-Crafts halides and binary Friedel-Crafts halide combinations have been examined in conjunction with isobutylene. Certain Friedel-Crafts halides were found to be active initiators (AlBr_3 , AlI_3 , GaCl_3 , GaBr_3) whereas others were unable to induce polymerization per se (TiCl_4 , SnCl_4) but accelerated polymerizations induced by active metal halide catalysts [3, 5].

Similarly, it has been found that purest AlBr_3 or AlEtCl_2 were able to polymerize isoprene [11, 12] and that as soon as isoprene was contacted with AlBr_3 , ionization occurred as indicated by electrical conductivity and UV spectroscopy.

The authors theorized [3] that initiation with the AlBr_3 and the $\text{AlBr}_3 \cdot \text{TiCl}_4$ systems was due to AlBr_2^+ and TiCl_3^+ , respectively, formed by the self-dissociation

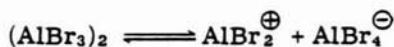


TABLE 1. Polymerization of Olefins by Self-Initiation in Two-Compound Systems

Monomer	Catalyst	Solvent	Temp range (°C)	Remarks	Refs.
Isobutylene	AlBr ₃	n-Heptane	+20 to -60	H ₂ O is retarder; $-d[M]/dt = k[I]^2 [M]$	1
Isobutylene	AlEtCl ₂	n-Heptane	+21 to -55	H ₂ O is inhibitor; $-d[M]/dt = k[I]^2 [M]$	2
Isobutylene	AlBr ₃ , TiCl ₄ , etc.	n-Heptane	-13	Rate increases on TiCl ₄ addition	3
Isobutylene	AlBr ₃ , TiCl ₄ , etc.	n-Heptane	-13	Nonsteady state kinetics proposed	4
Isobutylene	AlBr ₃ , TiCl ₄ , etc.	n-Heptane	-14	"Active and "inactive" Friedel-Crafts halides investigated	5
Isobutylene	AlI ₃	n-Heptane	-14		6
Isobutylene	GaCl ₃	n-Heptane	-14		5
Isobutylene	GaBr ₃	n-Heptane	-14		5
Isobutylene	TiCl ₄	CH ₂ Cl ₂ or bulk	-72 to -78	"Polymerization condensation"	7-9
Isobutylene	SnCl ₄	C ₂ H ₅ Cl	-78.5	Measurable polymerization rate even after exhaus- tive drying	10

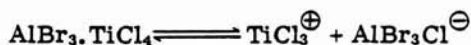
(continued)

TABLE 1. Polymerization of Olefins by Self-Initiation in Two-Compound Systems (Continued)

Monomer	Catalyst	Solvent	Temp range (°C)	Remarks	Refs.
Isoprene	AlEtCl ₂	n-Heptane	+20 to -18	$-d[M]/dt = k[IM][M]$	11
		Benzene	+20		
Isoprene	AlBr ₃	Benzene, toluene, and n-heptane	+21	Electrical conductivity and UV spectra	12
Isoprene	AlEtCl ₂	n-Heptane	+21		13
Isoprene	AlBr ₃	n-Heptane or toluene or benzene	+21		13
Isoprene	AlCl ₃	n-Heptane	+21	Initiator in suspension	13
Isoprene	AlCl ₃	n-Heptane or benzene	+21	Resublimed AlCl ₃	14
Indene	TiCl ₄	CH ₂ Cl ₂	-70	TiCl ₄ is active alone, rate increases in presence of H ₂ O or HCl	15
Indene	SnCl ₄	CH ₂ Cl ₂	-30	SnCl ₄ is active alone, rate increases in presence of H ₂ O	16, 17

α -Methylstyrene	TiCl_4	CH_2Cl_2	+10 to -72	TiCl_4 is active alone, rate increases in presence of H_2O , HCl , or added TiCl_4	18
α -Methylstyrene	SnCl_4	$\text{C}_2\text{H}_5\text{Cl}$	+55	Questionable dryness	19
α -Methylstyrene	AlEt_2Cl	CH_3Cl	-50	Controls: isobutylene and styrene need initiator under the same conditions	20
Cyclopentadiene	TiCl_3OBu	CH_2Cl_2	-43 to -70	TiCl_3OBu is active alone, rate increases in the presence of H_2O , and strongly increases with HCl , second TiCl_3OBu addition also positive	21, 22
Cyclopentadiene	AlEt_2Cl	CH_3Cl	-50	Controls: isobutylene and styrene need initiator under the same conditions	20
5-Methyloxyindene	BF_3	CH_2Cl_2	> -30°		23
Propylene	BF_3	CH_2Cl_2	-35	$d[M]/dt = k[\text{BF}_3]$	24
β -Methylstyrene	BF_3	$(\text{CH}_2\text{Cl})_2$	+25	$[\text{BF}_3 \cdot \text{CH}_3\text{OH}]^{3/2} [M]$	25
2-Butene	BF_3	$(\text{CH}_2\text{Cl})_2$	+25	Dimerization is first order in both olefin and BF_3	26, 27, 39
1-Methylcyclopentene	BF_3	n-Hexane	0	Isomerization rate = $k[\text{BF}_3][\text{BF}_3 \cdot \text{H}_2\text{O}]$	48

or, in the case of $\text{AlBr}_3 \cdot \text{TiCl}_4$, by self-dissociation of the mixed halide



Evidence for this proposal was the finding of titanium residues in purified polyisobutylene samples synthesized by $\text{AlBr}_3 \cdot \text{TiCl}_4$. This evidence is unacceptable since the purification involved multiple precipitations of a polyisobutylene in heptane solution into aqueous sulfuric acid; it is inconceivable that moisture-sensitive Ti-C bonds could have survived such a work-up. Rather, the presence of Ti in the polymer indicates the unsatisfactory removal of hydrolyzed titanium residues. The self-dissociation mechanism has also been criticized from the thermochemical point of view [28]. Finally, in their last paper [5] the original authors themselves repudiated their self-dissociation proposal and left the question of initiation open for further exploration [5].

Sigwalt and his school investigated the polymerization details in the isobutylene- TiCl_4 , indene- TiCl_4 , indene- SnCl_4 , α -methylstyrene- TiCl_4 and cyclopentadiene- $\text{TiCl}_3\text{O}i\text{Bu}$ systems, all in CH_2Cl_2 solvent [15-17, 21, 22, 29-32]. The isobutylene- TiCl_4 system exhibited a strange phenomenon. It was found that TiCl_4 polymerized isobutylene when the TiCl_4 was condensed from the vapor phase, but not in the liquid phase. The experiment was carried out in an H-shaped reactor by first prepolymerizing isobutylene with TiCl_4 at -78° to scavenge all possible impurities; the absence of impurities was demonstrated by the fact that no further polymerization occurred on admitting a second aliquot of TiCl_4 into the prepolymerized ($\sim 30\%$ conversion) system. Similarly, no further polymerization took place upon agitating the contents of the reactor or on tipping the liquid over into an adjoining compartment. However, polymerization occurred when the volatile components in the system were distilled over from the first arm of the H-shaped reactor into the second arm. Polymerization occurred on distillation even when the walls of the second compartment were coated with a sodium mirror, or in the absence of CH_2Cl_2 (i.e., in an experiment with neat isobutylene), or in the absence of light, or when the vaporization-condensation rate was changed from a relatively slow to a fast process. The French workers coined the term "polymerization by condensation" [29] for this phenomenon, but did not propose a mechanism to explain the observations.

Sigwalt [15-17, 21, 22] also found that slow polymerization occurred in driest indene-TiCl₄, indene-SnCl₄, α -methylstyrene-TiCl₄, and cyclopentadiene-TiCl₃OBu systems. In the α -methylstyrene-TiCl₄ and cyclopentadiene-TiCl₃OBu systems, the rate of polymerization increased upon a second addition of TiCl₄ and TiCl₃OBu, respectively. In line with the classical cointiation theory, the rates strongly increased upon the addition of protogens (H₂O or HCl).

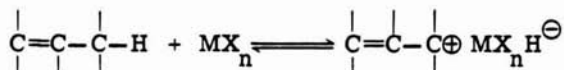
The work of the Czechoslovak and French schools are only two sets of examples among the many listed in Table 1 that suggest the cationic polymerization of certain olefins can be initiated with certain Friedel-Crafts halides alone, in the absence of any protogenic (or cationogenic) impurities. It is unlikely that further drying could have stopped the reactions listed in Table 1: the available rate and other information are excellently reproducible and self-consistent. For the same reason the data cannot be dismissed [33] by assuming that, for example, AlBr₃ may require different kinds and/or different concentrations of impurities than BF₃ and/or TiCl₄ for initiation. In view of the consistency of data, the time has come to abandon the hypothesis that the presence of a third species (coinitiator) is always needed to initiate cationic polymerizations by Friedel-Crafts halides. A theory, together with a new classification of cationic initiators, will now be proposed to explain initiation by Friedel-Crafts halides of cationic polymerization in the absence of protogens or cationogens.

SELF-INITIATION AND COINITIATION

Cationic initiation with Friedel-Crafts halides may proceed by two mechanisms:

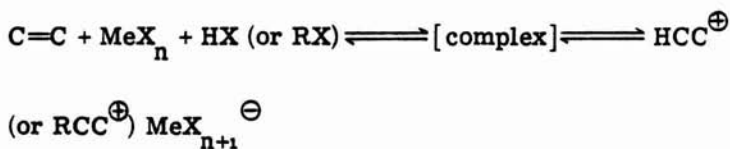
(1) Self-initiation in two-component (monomer-initiator) systems. In this class belong monomer/metal halide systems capable of initiation in the absence of extraneous cationogens.

It is proposed that self-initiation in two-component systems occurs by the removal of an allylic H in the form of an hydride ion from the nucleophilic monomer by strong Lewis acids MX_n:



The allylic hydrogen is provided by the monomer itself, e.g., isobutylene, isoprene, indene; hence the term self-initiation.

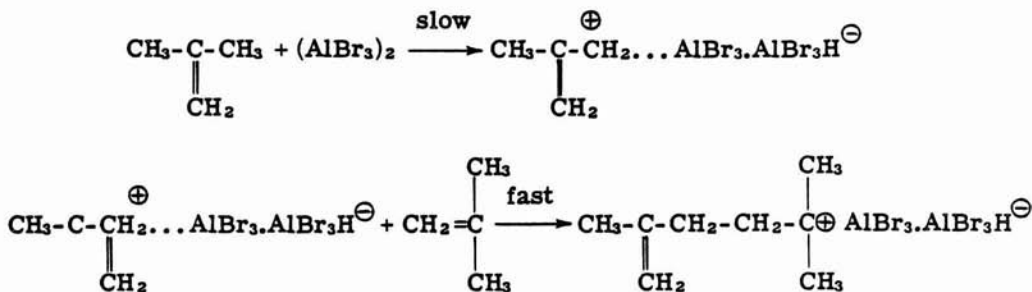
(2) Cointiation in three-component (monomer-initiator-cointiator) systems. In this class belong monomer/metal halide systems which for initiation require the presence of a third chemical (commonly called the cointiator, hence the term: cointiation). Conveniently this class can be subdivided into (a) cointiation with protogens, e.g., Bronsted acids such as HCl, H₂O, and CCl₃COOH, and (b) cointiation with cationogens, e.g., alkyl halides such as tert-BuCl:



The cointiation mechanism is, of course, the classical view that has been used successfully by a generation of workers since its introduction by the Evans-Polanyi school [34]. This now conventional view has been summarized, examined, and reviewed many times, for example, Refs. 35 and 36, and falls outside the scope of this paper. A detailed discussion of the self-initiation concept follows.

SELF-INITIATION IN OLEFIN/FRIEDEL-CRAFTS HALIDE SYSTEMS: INTERPRETATION OF PUBLICATIONS

Isobutylene can be polymerized by pure AlBr₃ in n-heptane [1] and the rate is second order in AlBr₃ and first order in isobutylene. As AlBr₃ is a dimer in hydrocarbons, these observations are in line with the self-initiation concept:



Similarly, self-initiation can readily be assumed in the isoprene- AlBr_3 system [12] particularly, since in this case the appearance of electrical conductivity and characteristic UV spectra indicate ionization immediately after mixing these chemicals. Indeed, all the various findings of the Czechoslovak workers may be explained by allylic self-initiation.

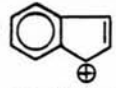
Marek's intriguing observation [3] that the rate of a relatively slowly proceeding isobutylene polymerization initiated by AlBr_3 is suddenly enhanced by the addition of TiCl_4 , a per se inactive chemical, is explained by assuming that the TiCl_4 helps in breaking up the

$$\begin{array}{c} \text{Br} \quad \text{Br} \quad \text{Br} \\ \diagdown \quad \diagup \quad \diagdown \\ \text{Al} \quad \text{Al} \\ \diagup \quad \diagdown \quad \diagup \\ \text{Br} \quad \text{Br} \quad \text{Br} \end{array}$$

into monomeric AlBr_3 , thus producing a stronger Lewis acid, a suitable hydride acceptor.

The findings of the French researchers can also be explained by the self-initiation concept. The most intriguing observation to be explained is that TiCl_4 appears to be active only when condensed from the vapor phase. Cheradame and Sigwalt emphasize this [29]: "...the catalyst is associated with itself in solution and it dissociates when in the vapor phase. From this it can be assumed that the TiCl_4 monomer molecule is able to induce direct initiation" (emphasis by this author). They further state that unpublished evidence is available to prove self-association in solution [29]. On the basis of these facts self-initiation can readily be invoked and the only assumption one has to make is that the unassociated TiCl_4 is a sufficiently strong Lewis acid for hydride abstraction, whereas the associated (less acidic) titanium tetrachloride which exists in the condensed phase is not.

Sigwalt's other findings with indene, α -methylstyrene, and cyclopentadiene in the liquid phase at low temperatures are also in agreement with the self-initiation concept. As mentioned above, in purest indene- TiCl_4 , indene- SnCl_4 , α -methylstyrene- TiCl_4 , and cyclopentadiene- TiCl_3OBu systems, polymerization occurs in the liquid phase and in these cases one does not need to resort to "polymerization-condensation" to obtain polymer. The problem here is to explain why the isobutylene- TiCl_4 system is inactive in the liquid phase but indene and α -methylstyrene polymerize under essentially identical conditions. The explanation may reside in the differing nucleophilicities of these monomers: indene, α -methylstyrene, and cyclopentadiene are most likely more nucleophilic than isobutylene and are better allylic H donors than the latter monomer. The stability of the allylic carbenium ions

$$\begin{array}{c} \oplus \\ | \\ \text{CH}_2 \\ | \\ \text{C} \end{array}$$


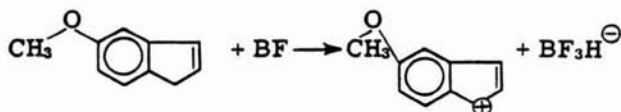
and

$$\begin{array}{c} \oplus \\ | \\ \text{CH}_2 \\ | \\ \text{C}-\text{C}_6\text{H}_5 \end{array}$$

are greater than that of $\text{CH}_2-\text{C}-\text{CH}_3$ so that even the less-acidic,

associated TiCl_4 or SnCl_4 are able to remove hydride ions from indene or α -methylstyrene, whereas a more acidic "free" TiCl_4 is necessary to abstract an allylic H from isobutylene. Similarly, TiCl_3OBU is probably still a sufficiently strong Lewis acid to abstract a hydride ion from cyclopentadiene and produce the initiating carbenium ion C_5H_5^+ [21, 22].

Marechal reports [23] but does not explain the observation that a complex is formed and no polymerization occurs between BF_3 and 5-methoxyindene below $\sim 30^\circ$; however, rapid polymerization takes place upon heating above this temperature. In line with the self-initiation postulate, it is possible that above -30° the complex dissociates and that the free BF_3 initiates the polymerization by hydride abstraction:



Marechal also found that 3,4-dimethoxystyrene, a monomer which does not have allylic H, required a protogen HCl , HF , or CCl_3COOH for initiation.

Sauvet et al. [37] studied the dimerization of 1,1-diphenylethylene (DPhE) with TiCl_4 in CH_2Cl_2 in the 0 to -78° range at various DPhE/ TiCl_4 ratios. Dimerization did not occur when this ratio was higher than ~ 100 ; however, rapid dimerization could be initiated upon the introduction of HCl or H_2O . These results are in complete agreement with those by Evans and co-workers who published a series of papers on the dimerization of DPhE in the presence of TiCl_4 , SnCl_4 , and SbCl_5 and an added protogen [38]. In contrast to these findings, Sauvet et al. [37] also observed that dimerization of DPhE proceeded even in the absence of added protogens when the DPhE/ TiCl_4 ratio was less than ~ 10 . This cannot be explained by any existing initiation theory. A possibility may be that with this olefin a mechanism of the Hunter-Yohe type obtains:

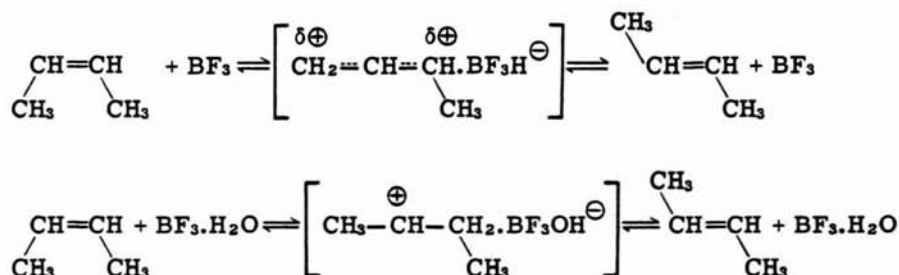


and that it is driven by the stable tertiary carbenium ion, whereas higher complexes such as $\text{TiCl}_4 \cdot 2, 3, \text{DPhE}$ are unfavorable and do not arise.

Eastham published a series of 10 papers [26] on the dimerization of 2-butene and polymerization of propylene with BF_3 and complexes. Significantly, slow $\text{cis} \rightleftharpoons \text{trans}$ isomerization of 2-butene proceeded with BF_3 alone in carefully dried systems. The rate of isomerization greatly accelerated in the presence of water and obeyed the equation [26, 27]

$$d[\text{isomer}_B]/dt = k[\text{BF}_3][\text{BF}_3 \cdot \text{H}_2\text{O}][\text{isomer}_A]$$

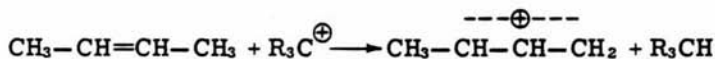
This process can be interpreted to be a composite of a self-initiated and cointiated mechanism:



in which the first process is slower than the second.

On close reading, Eastham's data also show [24] that propylene slowly polymerizes with BF_3 alone (Fig. 1 in Ref. 24) and that the rates are faster in the presence of $\text{BF}_3 \cdot \text{CH}_3\text{OH}$ complexes. In line with the self-initiation postulate, BF_3 might be a sufficiently strong Lewis acid to abstract a hydride ion from propylene.

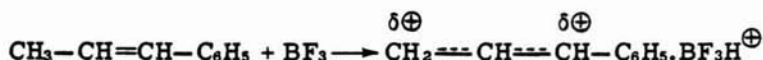
It was also observed that UV [40] and visible [41] chromophores were slowly formed when butenes in ethylene dichloride were mixed with BF_3 and $\text{BF}_3 \cdot \text{CH}_3\text{COOH}$. The conclusion was that the colored ionic species were allyl carbenium ions which formed by hydride transfer from the butenes to adventitious carbenium ion impurities:



In line with the self-initiation proposal, it may also be that BF_3 was the allylic hydride abstractor.

The dimerization of β -methylstyrene with BF_3 was also studied

by Eastham and co-workers [25]. The dimerization rate was very sensitive to impurities and became reproducible only after the reactor was baked at 500° for extended periods in vacuum. Significantly, dimerization could not be suppressed even under driest conditions. The authors theorized that non-scavengable protons ($-\overset{|}{\text{Si}}-\text{OH}$) could have been involved in initiation. Another possibility is self-initiation:



In line with this proposition, the rate of dimerization was first order in both olefin and BF_3 .

Fontana and Kidder [42] reported some 20 years ago that propylene and 1-butene polymerized with AlBr_3 only in conjunction with added "promoters," e.g., HBr . In this report HBr was truly a promoter because on closer reading of Ref. 42 it becomes apparent that polymerizations proceeded also in the absence of promoters, albeit slower (Table 1, Ref. 42). In contrast, in the Introduction the authors state that "...in one experiment no reaction occurred at low temperatures under anhydrous conditions and in the absence of added promoter"; however, no experimental details were given. This contradiction cannot now be resolved and a reexamination of this system is needed.

There is also an ambiguous report [13] from which it could be interpreted that isoprene is initiated by SnCl_4 alone. However, on careful reading of Ref. 13, this author concluded that the pertinent experiment was probably carried out in moist heptane and therefore the results have little diagnostic value.

EVIDENCES FOR SELF-INITIATION

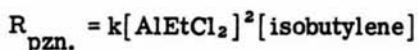
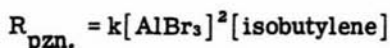
While there is no direct proof for the self-initiation mechanism, several circumstantial evidences corroborate this proposition.

The formation of allylic carbenium ions from olefins (e.g., 1-butene, 2-butene) on the surface of Lewis acidic solids has recently been proven spectroscopically [43]. For example, the vibrational spectrum of the species formed from 1-butene on silica-alumina was indistinguishable from the spectra of the

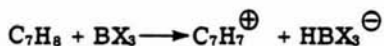
⊕

butenyl ion $\text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3$ obtained from 3-chloro-1-butene in fused SbCl_5 [43]. It was proposed that the surface, the strong Lewis acid, abstracted a hydride ion from the olefin.

Reliable quantitative information (e.g., the rate laws of polymerization of isobutylene with AlBr_3 [1] or AlEtCl_2 [2], the dimerization of β -methylstyrene with BF_3 [25]) are in agreement with the self-initiation mechanism:

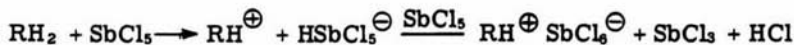


The basic proposition of hydride abstraction for certain carbenium ion precursors by Lewis acids such as BBr_3 and BI_3 has been well documented in small molecule organic chemistry. For example, Harmon and associates have shown (49-52) that boron tribromide or triiodide readily abstracts allylic hydride from cycloheptatriene and generates the tropylium ion:

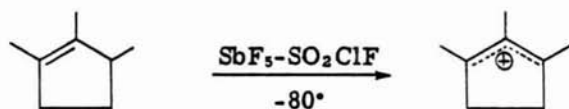


Hydride transfer to boron is independently supported by Parnes et al.'s work (53) who found evidence for the presence of B-H bonds in the reduced boron compound.

In a similar vein, Holmes and Pettit (54) abstracted hydride ions from cycloheptatriene and 9,10-dihydroanthracene by treatment with SbCl_5 in carbon disulfide or benzene solution at 0° and proposed the following reaction sequence:



Very recently Olah et al. [44] have described the formation of allyl cations by hydride abstraction from an olefin in "super acid" media at low temperatures:



These authors raised but could not answer the question of whether or not the actual H abstractor is the SbF_5 itself or "the strong protic super acid which is always present in 'neat' SbF_5 due to unavoidable impurities."

As carbenium ions are able to remove hydride ions from olefins, and since carbenium ions and Friedel-Crafts halides are both acids in the Lewis sense, it is conceivable that certain metal halides could also abstract hydride ions from suitable donors, such as olefins. For example, BF_3 may remove the hydride ion from NaH : in this manner NaBF_3H has been prepared from NaH and BF_3 in ether at -70° [45]. The B-H and Al-H bonds are fairly strong (79 and 68 kcal/mole, respectively) and contribute to the stability of compounds such as NaBH_4 and LiAlH_4 .

Thermochemical calculations are of little diagnostic value for the self-initiation proposal, as the effect of solvation (with the monomer) and/or aggregation of charged species of various structures is impossible to assess. Also, the ultimate fate of the hydride ion is a matter of conjecture. It is conceivable that the $\text{AlBr}_3\text{H}^\ominus \cdot \text{AlBr}_3$ could, for example, be involved in the deprotonation of carbenium ions (R^\oplus) to give H_2 and olefin (R^\ominus) by



This possibility could be examined by careful H_2 analysis. Olah's above cited paper may hold an important clue in this regard: these authors state that "...[hydride abstractions]... are always accompanied by formation of some H_2 ..." [44].

Following this line of thought, this author has carried out some experiments with α -methylstyrene and cyclopentadiene with AlEt_2Cl as the Lewis acid in methyl chloride solvent at -50°C [20]. Rapid polymerization occurred when either of these monomers were mixed with AlEt_2Cl ; however, no polymerization took place with isobutylene and/or styrene. It could be that with α -methylstyrene and cyclopentadiene self-initiation via H^\ominus transfer is favorable because of the

formation of relatively stable allylic carbenium ions $\text{CH}_2=\overset{\oplus}{\text{C}}(\text{CH}_2)\text{-C}_6\text{H}_5$ and $\text{C}_6\text{H}_5\text{-CH}^+\text{-CH}_2$, but initiating species do not form in the less favorable

isobutylene case.

Self-initiation via H^\ominus transfer gives unsaturated end-groups that are structurally very similar to and indeed almost indistinguishable from end groups arising in chain transfer to monomer (proton transfer). For example, in case of self-initiation with isobutylene,

the head group would be $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-$

a structure which is very similar to the end group $-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$

that is formed on conventional chain transfer to monomer.

Self-initiation via H^\ominus transfer to Friedel-Crafts halides is most likely a slow process, particularly in nonpolar media, and may easily be masked (outcompeted) by the more facile coinication mechanisms with H_2O , HX , or suitable RX . Therefore, self-initiation experiments should be carried out for extended periods (for hours, perhaps for days) particularly with propylene which gives the least-stabilized unsubstituted allylic carbenium ion ($\text{C}=\text{C}-\text{C}^\oplus$). Isobutylene is better in this respect: while the center-substituted allylic carbenium ion arising from isobutylene is probably not much more stable than the unsubstituted one obtained from propylene, the propagating species is a very stable tertiary cation. 1-Butene is also more

reactive than propylene because the butenyl ion $\text{CH}_2=\text{CH}-\overset{\oplus}{\text{C}}\text{H}-\text{CH}_3$ is relatively stable. Obviously isoprene, α -methylstyrene, indene, and cyclopentadiene, the other monomers which show self-initiation, are superior hydride sources. This is in agreement with the observations that α -methylstyrene and indene self-initiate with TiCl_4 in the condensed phase whereas isobutylene does not, and that cyclopentadiene self-initiates with the presumably low-acidity TiCl_3OBu [21, 22].

Only correct predictions will establish the value of the self-initiation theory. For this theory to be valid only monomers which

contain at least one available allylic hydrogen atom could provide their own initiator. Thus styrene, its ring substituted derivatives, 3,3-dimethyl-1-butene, etc., should not initiate by this route. Indeed, workers who studied the polymerization behavior of styrene under carefully dry conditions (for example, styrene- $\text{BF}_3\text{-CCl}_4$ [46], styrene- AlCl_3 [47]) state that this monomer cannot be polymerized with Friedel-Crafts halides except in the presence of a protogen or cationogen. The geometric availability of the allylic hydrogen atom could also be of import, and it is conceivable that in monomers such as 3,3-diphenyl-1-propene the allylic H is sterically unavailable and self-initiation is prohibited.

If the theory of self-initiation is correct, small amounts of good hydride donors in conjunction with Friedel-Crafts halides could initiate the polymerization of less favorable hydride donors. For example, cyclopentadiene or indene added to a quiescent isobutylene/ TiCl_4 system in the liquid phase could initiate the polymerization of the latter. In these cases cyclopentadiene and indene function as initiators. Experiments along these lines are being carried out in the author's laboratory.

ACKNOWLEDGMENTS

The author is grateful to Mr. J. E. Johnson for the proposition explaining the BF_3 -5-methoxyindene system, and to Professor K. Harmon for directing his attention to publications indicating that the principle of carbenium ion generation by direct hydride abstraction by boron halides is well documented in small molecule organic chemistry.

Support of this work from NSF Grant GP-26147 and Petroleum Research Fund, administered by the American Chemical Society (Grant 5362-AC1) is gratefully acknowledged.

REFERENCES

- [1] M. Chmelir, M. Marek, and O. Wichterle, J. Polym. Sci., Part C, 16, 833 (1967).
- [2] J. M. Solich, M. Chmelir, and M. Marek, Collect. Czech. Chem. Commun., 34, 2611 (1969).
- [3] M. Marek and M. Chmelir, J. Polym. Sci., Part C, 23, 223 (1968).
- [4] M. Chmelir and M. Marek, J. Polym. Sci., Part C, 22, 177 (1968).
- [5] P. Lopour and M. Marek, Makromol. Chem., 134, 23 (1970).
- [6] M. Chmelir and M. Marek, Collect. Czechoslov. Chem. Commun., 32, 3047 (1967).

- [7] H. Cheradame and P. Sigwalt, Bull. Soc. Chim. Fr., 3, 843 (1970).
- [8] H. Cheradame and P. Sigwalt, C. R. Acad. Sci., Paris, 260, 159 (1965).
- [9] H. Cheradame and P. Sigwalt, C. R. Acad. Sci., Paris, 259, 4273 (1964).
- [10] R. G. W. Norrish and K. E. Russel, Trans. Faraday Soc., 48, 91 (1952).
- [11] I. Kössler, M. Stolka, and K. Mach, J. Polym. Sci., Part C, 4, 977 (1963).
- [12] M. Matyska, M. Svestka, and K. Mach, Collect. Czech. Chem. Commun., 31, 659 (1966).
- [13] N. G. Gaylord, B. Matyska, K. Mach, and J. Vodehnal, J. Polymer Sci., Part A-1, 4, 2493 (1966).
- [14] M. Matyska, K. Mach, J. Vodehnal, and I. Kössler, Collect. Czech. Chem. Commun., 30, 2569 (1965).
- [15] H. Cheradame, N. A. Hung, and P. Sigwalt, C. R. Acad. Sci., Paris, 268, 476 (1969).
- [16] A. Polton and P. Sigwalt, Bull. Soc. Chim. Fr. 1, 131 (1970).
- [17] A. Polton and P. Sigwalt, C. R. Acad. Sci., Paris, 268, 1214 (1969).
- [18] R. B. Branchu, H. Cheradame, and P. Sigwalt, C. R. Acad. Sci., Paris, 268, 1292 (1969).
- [19] F. S. Dainton and R. H. Tomlinson, J. Chem. Soc., 1951, 151.
- [20] J. P. Kennedy, Unpublished Results.
- [21] J. Vairon and P. Sigwalt, Bull. Soc. Chim. Fr., 1971, 559.
- [22] J. Vairon and P. Sigwalt, Bull. Soc. Chim. Fr., 1971, 569.
- [23] J. P. Totrai, M. Mayen, and E. Marechal, (1971), I.U.P.A.C., Boston, July, 1971, Macromol. Preprints, p. 172, and Personal Communication.
- [24] T. Szell and A. M. Eastham, J. Chem. Soc., B, 1966, 30.
- [25] V. C. Armstrong, Z. Katovic, and A. M. Eastham, Can. J. Chem., 49, 2119 (1971).
- [26] R. A. Woolhouse and A. M. Eastham, J. Chem. Soc., B, 1966, 33, and nine previous papers.
- [27] J. M. Clayton and A. M. Eastham, J. Amer. Chem. Soc., 79, 5368 (1957).
- [28] P. H. Plesch, Progr. High Polym., 2, 137 (1968).
- [29] H. Cheradame and P. Sigwalt, Bull. Soc. Chim. Fr., 3, 843 (1970).
- [30] H. Cheradame and P. Sigwalt, C. R. Acad. Sci., Paris, 260, 159 (1965).
- [31] H. Cheradame and P. Sigwalt, C. R. Acad. Sci., Paris, 259, 4273 (1964).
- [32] R. B. Branchu, H. Cheradame, and P. Sigwalt, C. R. Acad. Sci., Paris, 268, 1292 (1969).

- [33] Z. Zlamal, (1969) Kinetics and Mechanisms of Polymerization, Vol. 1 (G. E. Ham, ed.), Dekker, New York, 1969, p. 231.
- [34] A. G. Evans and M. Polanyi, J. Chem. Soc., 1947, 252; J. Polym. Sci., 4, 359 (1949).
- [35] P. H. Plesch, ed., The Chemistry of Cationic Polymerization, Macmillan, New York, 1963.
- [36] D. Pepper, in Friedel-Crafts and Related Reactions, Vol. 2 (G. A. Olah, ed.), Wiley (Interscience), 1964, p. 1293.
- [37] G. Sauvet, J. P. Vario, and P. Sigwalt, Bull. Soc. Chim. Fr., 11, 4031 (1970).
- [38] B. Elliott, A. G. Evans, and E. D. Owens, J. Chem. Soc., 1962, 689, and ten previous papers.
- [39] J. M. Clayton and A. M. Eastham, Can. J. Chem., 39, 138 (1961).
- [40] J. M. Roberts, J. Chem. Soc., 1965, 310.
- [41] J. M. Roberts, J. Chem. Soc., 1965, 1761.
- [42] M. C. Fontana and G. A. Kidder, J. Amer. Chem. Soc., 70, 3745 (1948).
- [43] H. P. Leftin, in Carbonium Ions, Vol. 1 (G. A. Olah and P. R. Schleyer, eds.), Wiley (Interscience), New York, 1968, p. 393.
- [44] G. A. Olah, B. R. Clifford, Y. Halpern, and R. G. Johnson, J. Amer. Chem. Soc., 93, 4219 (1971).
- [45] J. Goubean and R. Bergman, Z. Anorg. Allg. Chem., 263, 69 (1950).
- [46] D. Clark, in Cationic Polymerization and Related Complexes (P. H. Plesch, ed.), Heffer, Cambridge, 1953, p. 99.
- [47] D. O. Jordan and F. E. Treolar, J. Chem. Soc., 1961, 737.
- [48] G. J. Schmitt and C. Schuerch, J. Polym. Sci., 49, 287 (1961).
- [49] K. M. Harmon and A. B. Harmon, J. Amer. Chem. Soc., 83, 865 (1961).
- [50] K. M. Harmon, A. B. Harmon, and F. E. Cummings, J. Amer. Chem. Soc., 83, 3912 (1961).
- [51] K. M. Harmon and F. E. Cummings, J. Amer. Chem. Soc., 84, 1751 (1962).
- [52] K. M. Harmon, A. B. Harmon, and F. E. Cummings, J. Amer. Chem. Soc., 86, 5511 (1964).
- [53] Z. N. Parnes, M. I. Kalinkin, and D. M. Kursanov, Dokl. Akad. Nauk SSSR., 165, 1093 (1965).
- [54] J. Holmes and R. Pettit, J. Org. Chem., 28, 1695 (1963).

Accepted by editor August 17, 1971

Received for publication October 28, 1971