Contributions to the Mechanism of Isobutene Polymerization. I. Theory of Allylic Termination and Kinetic Considerations

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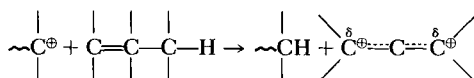
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Contributions to the Mechanism of Isobutene Polymerization. I. Theory of Allylic Termination and Kinetic Considerations

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Summary

Theories dealing with the problem of termination in ionic polymerizations by hydride transfer coupled with allylic stabilization have been examined and extended. It is postulated that cationic polymerizations in general terminate with the irreversible destruction of growing ions by the following mechanism:

$$\sim\!\!C^{\oplus} + \underset{|}{\overset{|}{C}}\!\!=\!\!\underset{|}{\overset{|}{C}}\!\!-\!\!\underset{|}{\overset{|}{C}}\!\!-\!\!H \rightarrow \sim\!\!CH + \overset{\delta}{C^{\oplus}}\cdots C\cdots\overset{\delta}{C^{\oplus}}$$

A kinetic model is developed and used to define an empirical poison coefficient (P.C.) and transfer coefficient (T.C.), characterizing a material as to its effectiveness in kinetic chain termination and chain breaking, respectively.

Experiments indicate that allylic self-termination in unhibited polymerizations of isobutene with $AlCl_3$ catalyst, although undoubtedly present, is not an important molecular weight determining event.

INTRODUCTION

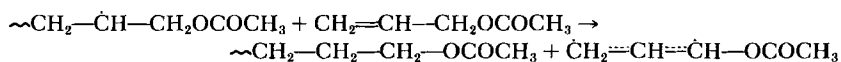The mechanism of kinetic chain termination, e.g., the complete destruction of the propagating species in ionic, particularly in cationic, polymerization systems is still a controversial and largely unsolved problem. Various theories have been advanced to explain termination in specific systems, but the simple question "Why do

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cationic polymerizations stop?" cannot be answered in a general way and no over-all termination theory has yet been formulated.

According to Meyer (1), colored tars which are obtained in various carbonium ion reactions are due to resonance-stabilized allylic carbonium ions. Schmerling (2) proposed that hydride transfer and allylic carbonium ions are involved in the polymerization of ethylene with AlCl$_3$ and HCl and attributed the formation of low molecular weight paraffinic products to these reactions. Broad molecular weight distributions and low molecular weight products in cationic propene and 1-butene polymerizations were explained by assuming hydride transfer and the formation of allyl carbonium ions (3). Significantly, Kramer et al. (4) found that the isomerization of n-hexane by AlBr$_3$ was inhibited by 1-hexene and postulated that inhibition was due to allylic hydride transfer from 1-hexene to the chain-carrying ion.

In the field of free-radical polymerizations, Bartlett and Altschul (5) found that the rate of polymerization of allyl acetate and the degree of polymerization of polyallyl acetate were abnormally low. Propagation was visualized to occur via the unstable $\sim$CH$_2$—$\dot{C}$H—CH$_2$—O—COCH$_3$ radical. Significantly, it was suggested that this aggressive radical is able to abstract an allylic hydrogen from the monomer itself:

$$\sim\text{CH}_2\text{—}\dot{\text{C}}\text{H—CH}_2\text{OCOCH}_3 + \text{CH}_2\text{==CH—CH}_2\text{OCOCH}_3 \rightarrow$$
$$\sim\text{CH}_2\text{—CH}_2\text{—CH}_2\text{—OCOCH}_3 + \dot{\text{C}}\text{H}_2\text{==CH==}\dot{\text{C}}\text{H—OCOCH}_3$$

and that the new resonance-stabilized radical was too stable to sustain propagation. Consequently, in this reaction, which Bartlett and Altschul call "degradative chain transfer," the monomer can be regarded as the terminating agent.

These observations and conclusions led us in our fundamental studies on the low-temperature cationic polymerization of isobutene with AlCl$_3$ catalyst, to develop and test a theory which might explain why polymerization stops in this and conceivably in similar olefin systems. This theory turned out to be extremely helpful in explaining in simple terms a large amount of until now unexplained observations and facts.

It should be emphasized that kinetic termination of a chain means the complete and irreversible destruction of the propagating species (6). Proton expulsion (a) or reactions between the gegenion

and the growing center (b), processes which sometimes were called "termination," are, in reality, chain-transfer or chain-breaking processes, because the active species is not destroyed but merely modified:

$$
\sim CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{}^{\oplus} \; MeX^{\ominus}_{n+1}
\begin{array}{c}
\overset{(a)}{\diagup} \\[2mm]
\underset{(b)}{\diagdown}
\end{array}
$$

$$
\sim CH_2-\overset{\overset{\displaystyle CH_2}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} \quad or \quad \sim CH=\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} \; + H^{\oplus}MeX^{\ominus}_{n+1}
$$

$$
\sim CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-X + MeX_n
$$
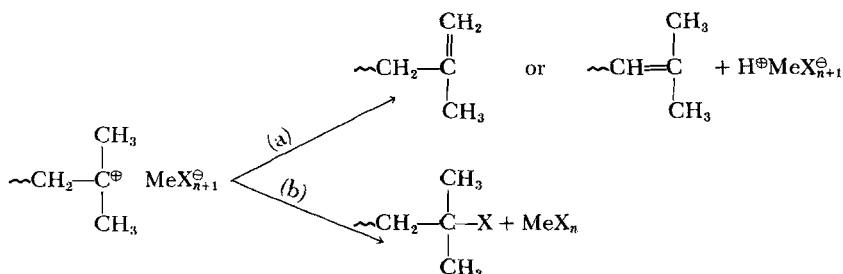
These chain-transfer steps do not stop the kinetic chain but merely decrease the molecular weight.

The cationic polymerization of isobutene with $AlCl_3$ catalyst is peculiar inasmuch as the polymerization does not go to completion when a small amount of $AlCl_3$ (say in methyl chloride diluent) catalyst is added to a certain amount of monomer (7,8). The polymerization is extremely rapid; it starts without an induction period immediately after catalyst introduction, but it very rapidly stops at low conversions, and repeated or continuous catalyst additions are necessary to increase the yield. Significantly, equal catalyst increments introduced produce equal increments of polymers. In other words,when the cumulative conversion is plotted against the amount of catalyst introduced, a straight ascending line is obtained (7). Evidently catalyst is somehow consumed during polymerization. It has been suggested that in instances when the conversion stops at low levels, the cocatalyst supply (water or other cocatalytic impurity) has been exhausted (6). This theory was apparently true in the isobutene–$TiCl_4$–trichloroacetic acid or water systems in hexane (9). However, in the polymerization under investigation, this cannot be the case, because small amounts of moisture and HCl introduced in a "dead" system did not reinitiate propagation and did not increase conversion (see below).
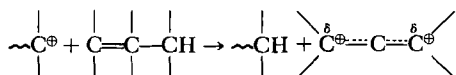
It is also pertinent that the lifetime of a kinetic chain is extremly short (7,10) and that the molecular weight does not change after the introduction of the catalyst. This is characteristic for a chain reaction.

It is important to note in this context that irradiation polymeriza-
tion of isobutene proceeds only when under the influence of irradi-
ation, and polymerization stops abruptly when the source is re-
moved (*11*).

A theory which might shed some light on these facts and might
provide a possible answer to the question of why and how kinetic
chain termination could occur in carbonium ion polymerizations is
now presented.

CONCEPT OF ALLYLIC TERMINATION

The following over-all equation summarizes the concept of termi-
nation by intermolecular hydride transfer and allylic stabilization
in carbonium ion polymerizations:

$$\sim\overset{|}{C}{}^{\oplus} + \overset{|}{C}{=}\overset{|}{C}{-}\overset{|}{C}H \rightarrow \sim\overset{|}{C}H + \overset{\delta}{C}{}^{\oplus}\cdots C\cdots \overset{\delta}{C}{}^{\oplus}$$

i.e., termination in cationic polymerizations may involve the irre-
versible destruction of growing (free or associated) ions by intra-
molecular hydride abstraction from a suitable olefin in the system
with the simultaneous formation of a resonance-stabilized allyl
carbonium species. The substituted allyl cation is resonance-stabi-
lized, and its propagating ability is much reduced as compared to
less stable aliphatic carbonium ions. The driving force of this re-
action is provided by the formation of a covalent C—H bond and
a resonance-stabilized substituted allyl carbonium ion from an un-
saturated molecule and a comparatively less stable carbonium ion.
According to this theory, unsaturated molecules carrying allylic hy-
drogen atoms are potential terminators. Thus monomers may func-
tion as their own terminating agents ("suicide polymerizations").

It is very difficult to directly prove this theory with today's experi-
mental techniques. A direct experimental demonstration would be
to show spectroscopically the transformation of the propagating ion
into some, most likely substituted, allylic ion. However, the identi-
fication of these ions by UV or NMR spectra is at the present a con-
troversial art and we did not carry out systematic research in this
direction.

Strong but admittedly indirect evidence for the correctness of
the proposed theory was obtained by the following reasoning and
experiment. According to the present theory, if allylic termination

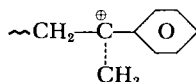takes place in a cationically polymerized isobutene system, methallyl carbonium ions,

$$\overset{\delta\oplus}{C}H_2\text{---}\underset{\underset{CH_3}{|}}{C}\text{---}\overset{\delta\oplus}{C}H_2$$
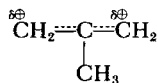
might be formed. Since this ion is less stable than the styril

$$\sim\!CH_2\text{---}\overset{\oplus}{C}H\text{---}\!\!\left\langle\,O\,\right\rangle$$

α-methyl styril

$$\sim\!CH_2\text{---}\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}\text{---}\!\!\left\langle\,O\,\right\rangle$$
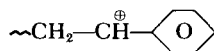
or cyclopentadienyl

cation it is conceivable that by introducing styrene, α-methyl styrene, or cyclopentadiene into "dormant" isobutene polymerization mixtures, polymerization of these subsequently added monomers will ensue. Thus we polymerized isobutene (7.1 g) with AlCl₃ catalyst to substantially less than 100% conversion, and, after having ascertained that polymerization had stopped, we introduced to these "dormant" systems (7 g) styrene, α-methyl styrene, and cyclopentadiene, respectively, in three independent runs. Subsequently, the

TABLE 1

Demonstration of the Existence of Initiating Species in
Quiescent Isobutene Polymerization Systems

System	Wt. polymer formed, g	Wt. increase, g
Isobutene control	3.848 (53.5%)	0
Isobutene + styrene	4.485	0.737
Isobutene + α-methyl styrene	4.218	0.370
Isobutene + cyclopentadiene	4.025	0.177

reactions were quenched with methanol. In all three cases additional polymerization occurred which was evidenced by substantial weight increases. Table I gives the data.

These experiments indicate qualitatively that "dormant" polyisobutene mixtures still might contain some active species, perhaps carbonium ions, which are able to initiate the polymerization of the second monomer. Since the conversion of isobutene was incomplete, it is quite unlikely that unreacted catalyst remained in the system and was responsible for polymerization resumption. Conceivably methallyl cations which might have formed in the system could have initiated subsequent polymerizations proceeding via the more stable styril, α-methyl styril, or cyclopentadienyl carbonium ions.
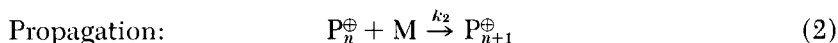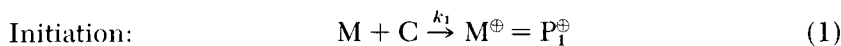
It should also be noted that the weight increase in these experiments is largest with styrene and increasingly diminishes with α-methyl styrene and cyclopentadiene. The products formed in the second part of these experiments are most likely copolymers of isobutene and the second monomer introduced. The analysis of these systems is obviously very difficult. However, styrene having no allylic hydrogens would be expected to yield the largest amount of product and α-methyl styrene and cyclopentadiene, which, in line with the present theory, are increasingly efficient self-terminators would give less product.

Further evidence for the general validity of the basic postulate will be presented in subsequent publications. Numerous experiments have been designed and carried out to test the above theory in detail. These involved isobutene polymerizations in the presence of a great variety of unsaturated molecules and other compounds and the quantitative determination of the compound's effect on polymer yield and product molecular weights. Since a large amount of experimental material can be readily explained by a simple concept, the same becomes quite useful, although it has not been proved directly and the evidence for it remains circumstantial.
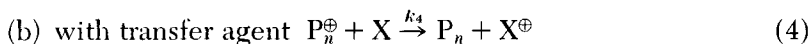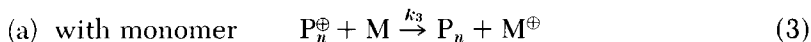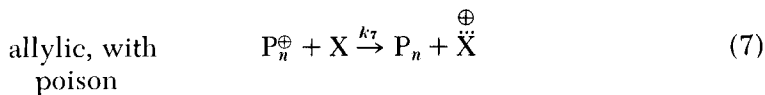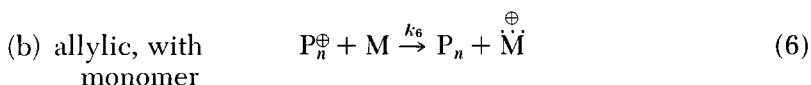
KINETIC MECHANISM

The Model

The following kinetic model will be employed in our subsequent analysis:

Initiation:
$$M + C \xrightarrow{k_1} M^{\oplus} = P_1^{\oplus} \tag{1}$$

Propagation:
$$P_n^{\oplus} + M \xrightarrow{k_2} P_{n+1}^{\oplus} \tag{2}$$

Transfer:

  (a) with monomer
$$P_n^{\oplus} + M \xrightarrow{k_3} P_n + M^{\oplus} \tag{3}$$

  (b) with transfer agent
$$P_n^{\oplus} + X \xrightarrow{k_4} P_n + X^{\oplus} \tag{4}$$

Termination:

  (a) spontaneous
$$P_n^{\oplus} \xrightarrow{k_5} P_n \tag{5}$$

  (b) allylic, with monomer
$$P_n^{\oplus} + M \xrightarrow{k_6} P_n + \overset{\oplus}{\overset{\displaystyle\cdot\cdot}{M}} \tag{6}$$

     allylic, with poison
$$P_n^{\oplus} + X \xrightarrow{k_7} P_n + \overset{\oplus}{\overset{\displaystyle\cdot\cdot}{X}} \tag{7}$$
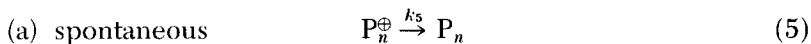
where M = monomer, C = catalyst, X = poison and/or transfer agents, $P_n^{\oplus}$ = growing polymer of n monomer units, P_n = "dead" polymer, $\overset{\oplus}{\overset{\displaystyle\cdot}{M}}$ = resonance-stabilized allyl cation from monomer ("suicide" step), and $\overset{\oplus}{\overset{\displaystyle\cdot\cdot}{X}}$ = resonance-stabilized allyl cation from terminating agent ("poisoning"), in line with the postulate of allylic termination.

Initiation. The molecular details of initiation in the isobutene–methyl chloride–aluminum chloride system under investigation are still obscure. Most disturbing is the fact that the "true" catalyst concentration is for some reason much less than what one would expect from the measured catalyst concentration. The number of kinetic chains produced from 1 mole of $AlCl_3$ is much less than one. The physical chemistry of $AlCl_3$ catalyst solutions is still a mystery on the molecular level.

Although it is assumed that initiation of isobutene polymerization with $AlCl_3$ catalyst can occur only in the presence of cocatalyst

no direct evidence supports this assumption. Chmelir et al.'s finding (12) that cocatalyst is not necessary for the polymerization of isobutene with $AlBr_3$ catalyst has little bearing on the present problem, considering the significant differences between $AlBr_3$ and $AlCl_3$ catalysts. Thus with $AlCl_3$ it is still possible that H_2O, HCl, or RX might be cocatalysts, and unless a direct experiment is carried out in high vacuum under extreme precautions this problem remains unanswered. It is useless to speculate on the exact catalytic species in our system at this time.

For our treatment, however, it is safe and sufficient to assume that initiation [Eq. (1)] is much faster than any other kinetic step. Thus the catalyst immediately reacts to form a "pool" of active initiating complexes whose concentration, which is initially equal to the "catalyst" concentration, decreases as the complexes are consumed by the termination reaction. Thus the concentration of active complexes is changing with time and no steady state concentration is attained. If the original catalyst concentration is small, the termination process may use up the active complexes before the propagation reaction has time to consume all the monomers, resulting in low conversions. A similar nonsteady state polymerization scheme has been proposed by Burton and Pepper (13) to explain the polymerization of styrene by sulfuric acid.

Propagation [Eq. (2)] is visualized as a carbonium ion attack on the olefinic double bond with the simultaneous regeneration of propagating species $\sim C^{\oplus} + C{=}C \rightarrow \sim C{-}C{-}C^{\oplus}$. Since all experimental work was carried out under essentially identical conditions, the influence of solvation, gegenion, dielectric milieu, temperature, etc., can be ignored in our treatment.

Transfer can occur either with the monomer or with "X" present in the system [Eqs. (3) and (4)]. These processes do not interfere with the kinetic chain in the first approximation; however, they strongly affect the molecular weight of the product. The basic mechanism of chain transfer probably involves proton expulsion-reprotonation: $\sim C^{\oplus} \rightarrow \sim C^= + H^{\oplus}$ followed by $H^{\oplus} + C{=}C \rightarrow HC{-}C^{\oplus}$, where $C{=}C$ can be the monomer or transfer agent in general. The reaction is probably a concerted one (i.e., $\sim C^{\oplus} + C{=}C \rightarrow \sim C^= + C{-}C^{\oplus}$), and no protons, not even in the solvated state, have appreciable physical lifetimes.

Termination is the complete and irreversible destruction of propagating ability and the annihilation of kinetic chain. Termina-

tion governs the extent of conversion and should not affect molecular weight in an unhibited system. Termination, we postulate, can occur by a spontaneous, unimolecular process [Eq. (5)] or by "allylic termination," a bimolecular process which may involve the monomer [Eq. (6)] or the poison [Eq. (7)]. Spontaneous termination is visualized as a reaction between the growing cation and the corresponding gegenion. Since the ion/gegenion pair is kinetically one unit, spontaneous termination is a unimolecular process: $\sim C^{\oplus} AlCl_4^{\ominus} \rightarrow \sim CCl + $ "$AlCl_3$." It is important to keep in mind, however, that the actual structure of the gegenion is unknown and $AlCl_4^{\ominus}$ should be regarded only as a symbol. Also, the "$AlCl_3$" is not identical to the original initiating species and the presence or availability of catalyst in the system is not sufficient to activate this species. Indeed, we visualize this reformed "$AlCl_3$" as a species most likely unable to reinitiate a new kinetic chain. We have demonstrated in independent and repeated experiments that cocatalyst depletion is not the reason for lack of reinitiation. Thus we introduced traces of potential cocatalyst, i.e., water and HCl, to systems polymerized to low conversions but in no case did we experience progression of polymerization on cocatalyst introduction and the system remained "dead."

Following this kinetic scheme, we will henceforth use the term "poison" to designate a material which decreases the over-all polymer yield or conversion but does not necessarily affect molecular weight, whereas we will use the term "transfer agent" to define a molecule involved in transfer reactions and thereby reducing product molecular weight. According to this terminology, monomer can act in both ways; as "poison" leading to suicide termination, as discussed earlier, or as "transfer agent," depressing its own molecular weight by chain transfer to the monomer. A pure poison would control conversions without interfering with product molecular weight, whereas a pure transfer agent would control molecular weights without affecting conversions. A large number of materials can act in both capacities.

Polymerization Rate and Poison Coefficient

The rate of monomer disappearance is given by

$$\frac{-d\mathrm{M}}{dt} = (k_2 + k_3 + k_6)\mathrm{M}\mathrm{P}^{\oplus} \tag{8}$$

For the sake of clarity, the conventional square brackets indicating concentrations will be omitted, e.g., M and $P^{\oplus}$ refer to monomer and growing polymer concentrations, respectively. To solve Eq. (8) for M, we must know $P^{\oplus}$ as a function of time. Thus

$$\frac{-d P^{\oplus}}{dt} = k_5 P^{\oplus} + k_6 P^{\oplus} M + k_7 P^{\oplus} X \tag{9}$$

Note that Eqs. (2), (3), and (4), while influencing the molecular weight of the product, do not affect $P^{\oplus}$ and thus are not represented in Eq. (9). Since, at low conversions, M is approximately constant, Eq. (9) may be integrated to give

$$P^{\oplus} = P_i^{\oplus} \exp\left[(-k_5 - k_6 M - k_7 X)t\right] \tag{10}$$

where $P_i^{\oplus}$ is the initial growing site concentration. Combining Eqs. (8) and (10) gives

$$\frac{-dM}{dt} = (k_2 + k_3 + k_6) M P_i^{\oplus} \exp\left[(-k_5 - k_6 M - k_7 X)t\right] \tag{11}$$

Equation (11) may be integrated between $t = 0$ and $t = \infty$, assuming constant M and $P_i^{\oplus}$, to give

$$\frac{W_p}{MW_m V} = M_i - M_f = \frac{(k_2 + k_3 + k_6) M_i P_i^{\oplus}}{k_5 + k_6 M_i + k_7 X} \tag{12}$$

where W_P is the weight of polymer obtained in the presence of X, MW_m is the molecular weight of the monomer, and V is the system volume. M_i and M_f refer to initial and final monomer concentrations, respectively. Since M_i was assumed constant in the derivation of Eq. (12), it follows that $M_i - M_f \ll M_i$. Since the molecular weight of the resulting polymer is high, i.e., 10^4 to 10^6, the assumption $k_2 \gg k_3$ or k_6 is justified. Equation (12) then becomes

$$W_p = \frac{k_2 M_i P_i^{\oplus}(MW_m V)}{k_5 + k_6 M_i + k_7 X} \tag{13}$$

If no X is present, Eq. (13) may be rearranged to give

$$\frac{1}{W_0} = \frac{k_5}{k_2 M_i P_i^{\oplus}(MW_m V)} + \frac{k_6}{k_2 P_i^{\oplus}(MW_m V)} \tag{14}$$
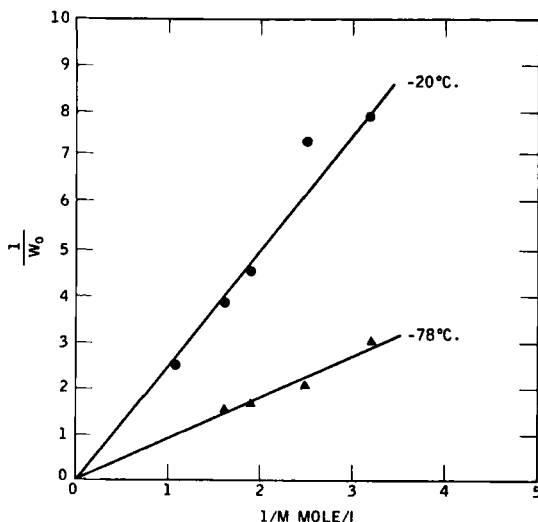
FIG. 1. Effect of monomer concentrations on polyisobutene yield.

where W_0 is the yield in the absence of X. Thus a plot of $1/W_0$ vs. $1/M_i$ should result in a straight line of slope $k_5/k_2P_i^{\oplus}(MW_mV)$ and intercept $k_6/k_2P_i^{\oplus}(MW_mV)$. Figure 1 shows experimental results obtained with the isobutene–AlCl$_3$ system at -20 and $-78°C$. Since both lines extrapolate to the origin, $k_6 \approx 0$. Thus the effect of "suicide" termination, in which isobutene monomer itself functions as a chain terminator, is much smaller than the effect of spontaneous termination. If $k_6 \ll k_5$, Eq. (13) may be rearranged to give

$$\frac{1}{W_p} = \frac{k_5}{k_2 M_i P_i^{\oplus}(MW_m V)} + \frac{k_7 X}{k_2 M_i P_i^{\oplus}(MW_m V)} \tag{15}$$

in the presence of X and

$$\frac{1}{W_0} = \frac{k_5}{k_2 M_i P_i^{\oplus}(MW_m V)} \tag{16}$$

in the absence of X.

The ratio of the rate of termination due to X to the rate due to spontaneous termination (i.e., k_7/k_5) is useful in comparing the rate inhibiting properties of various X's.

This ratio k_7/k_5, i.e., the ratio or rate constants for allylic termina-

tion with X and spontaneous termination conceivably involving the gegenion, will be designated as the poison coefficient, P.C. The P.C. may be calculated directly by dividing Eq. (15) by (16) to give

$$\frac{W_0}{W_p} = 1 + \frac{k_7}{k_5} X \qquad (17)$$

Thus P.C. is the slope of the plot of W_0/W_p vs. X. Owing to the experimental variations, it is advisable to plot $1/W_p$ vs. X and extrapolate to $X = 0$ to determine the "best" experimental value of W_0. Once this plot is constructed, however, it is no longer necessary to plot the data in the form of Eq. (17), since P.C. may be immediately determined by dividing the slope of the $1/W_p$ vs. X plot by the corresponding intercept [Eq. (15)]. Numerous such curves will be examined in subsequent publications.

Molecular Weight and Transfer Coefficient

To calculate molecular weights* it is necessary to take into account the change of M as well as $P^{\oplus}$ with time (13,14). In the case of low conversion, however, M will not vary appreciably with time and the average molecular weight corresponds to the instantaneous molecular weight corresponding to M_i. In this case

$$\frac{1}{MW_p} = \frac{k_3 M_i P^{\oplus} + k_4 X P^{\oplus} + k_5 P^{\oplus} + k_7 X P^{\oplus}}{k_2 M_i P^{\oplus} (MW)_m} \qquad (18)$$

or

$$\frac{1}{MW_p} = \frac{k_3 M_i + k_5}{k_2 M_i (MW)_m} + \frac{k_4 + k_7}{k_2 M_i (MW)_m} X \qquad (19)$$

where MW_p is the molecular weight of the polymer produced in the presence of X and $(MW)_m$ is the molecular weight of monomer. In the absence of X,

$$\frac{1}{MW_0} = \frac{k_3 M_i + k_5}{k_2 M_i (MW)_m} \qquad (20)$$

---

* It can be shown that this derivation is valid for both number- and weight average molecular weights if the degree of polymerization is $\geqslant 1$ and conversions are low.

where MW_0 is the molecular weight in the absence of X. Dividing Eq. (19) by (20) we obtain:

$$\frac{MW_0}{MW_p} = 1 + \frac{k_4 + k_7}{k_3 M_i + k_5} X \tag{21}$$

The quantity $(k_4 + k_7)/(k_3 M_i + k_5)$ we will define as the empirical transfer coefficient, T.C. It must be pointed out, however, that T.C. reflects the influence of allylic termination (k_7) as well as transfer (k_4) on molecular weight. To separate unambiguously the effect of k_4 and k_7 on molecular weight, the ratio k_3/k_5 must be known. Unfortunately, the value of this ratio is obscured because of an undefined impurity in the solvent (see the Appendix).

The transfer coefficient is most conveniently calculated from Eq. (19). Thus a plot of $1/MW_p$ vs. X should result in a straight line of slope $(k_4 + k_7)/k_2 M_i$ and intercept $(k_3 M_i + k_5)/k_2 M_i$. As in the case of the poison coefficient, the experimental variability makes it advisable to calculate $1/MW_0$ i.e., reciprocal product molecular weight in the absence of X, by extrapolating this plot to X = 0, rather than using the average $1/MW_0$ obtained in different runs. Dividing the slope of this plot by the intercept gives the transfer coefficient:

$$\frac{slope}{intercept} = \frac{(k_4 + k_7)/k_2 M_i}{(k_3 M_i + k_5)/k_2 M_i} = \frac{k_4 + k_7}{k_3 M_i + k_5} \equiv T.C.$$

Number of Moles of Polymer Formed

Once the effect of a chemical, X, on both termination and transfer has been determined, the relationship between chemical concentration and the relative number of moles of polymer formed in the presence of this chemical is easily obtained. The number of moles of polymer in the control system is given by $W_0/MW_p = n_p$, where W and MW stand for product weight and molecular weight, respectively, and the subscripts 0 and p indicate the absence and presence of X. Thus n_p/n_0, the relative change in the number of moles of polymer due to the addition of X, may be derived in terms of the poison coefficient and transfer coefficient:

$$\frac{n_p}{n_0} = \frac{W_p}{W_0} \frac{MW_0}{MW_p} = \frac{1 + (T.C.)X}{1 + (P.C.)X} \tag{23}$$

A plot of n_p/n_0 vs. X indicates the effect of the chemical, X, on the relative number of polymer molecules formed. According to Eq. (23), for n_p/n_0 to be constant and unaffected by the concentration of X, T.C. must equal P.C. Thus

$$\frac{\text{T.C.}}{\text{P.C.}} = 1 = \frac{(k_4 + k_7)/(k_5 + k_3 M_i)}{k_7/k_5} = \frac{1 + k_4/k_7}{1 + k_3/k_5 M_i} \qquad (24)$$

Therefore, when $n_p/n_0 = 1$,

$$k_4/k_7 = (k_3/k_5) M_i \qquad (25)$$

The number of moles formed in the presence of a chemical X reveals important clues as to the poisoning or transfer activity of this particular material. For example, when the transfer coefficient of a material is larger than its poison coefficient, the number of moles of polyisobutene produced in the presence of this agent is larger than in the corresponding uninhibited or control experiment. This can be construed as strong indication that the investigated material is a transfer agent. The possibilities are summarized in Table 2.

TABLE 2

Possible Transfer Agents

Relative moles	Coefficients	Kinetic constants
$n_p/n_0 > 1$	T.C. > P.C.	$k_7/k_5 < k_4/k_3 M_i$
$n_p/n_0 = 1$	T.C. = P.C.	$k_7/k_5 = k_4/k_3 M_i$
$n_p/n_0 < 1$	T.C. < P.C.	$k_7/k_5 > k_4/k_3 M_i$

Since

$$\frac{d}{dX} \left[\frac{1 + (\text{T.C.})X}{1 + (\text{P.C.})X} \right] = \frac{\text{T.C.} - \text{P.C.}}{[1 + (\text{P.C.})X]^2}$$

the slope of the n_p/n_0 vs. X curve can only be zero if T.C. = P.C. or if $X \to \infty$. Therefore, no maximum or minimum would be expected. In addition, it is easily shown that the limiting value of n_p/n_0 as $X \to \infty$ is (T.C./P.C.) and the slope of the curve as $X \to 0$ is (T.C. − P.C.).

To give some insight into the effect of chain transfer and termination on yield and molecular weight, let us first consider the case of pure termination and pure chain transfer.
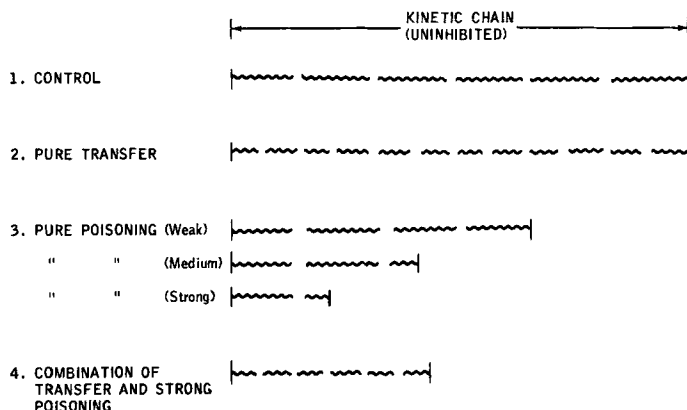
FIG. 2. Visualization of the effect of termination and chain transfer on transfer on number of moles of polymer.

Figure 2 helps to visualize the situation: The control represents an uninhibited polymerization, in the absence of X. As a rule in cationic polymerizations, molecular weights are determined by transfer to the monomer and the kinetic chain by, probably, spontaneous termination. A pure chain-transfer agent affects only the number of molecules, leaving the polymer yield, i.e., the length of the kinetic chain, unchanged. A pure rate poison, however, reduces the yield of polymer and may also reduce the number of molecules by lowering the lifetime of the growing chain. By definition, the molecular weight should remain unaffected by a pure rate poison. Molecular weight depression by poisons can be visualized, however, if the last mole of polymer in the kinetic chain is terminated by the poison and not by chain transfer. This is shown in row 3 of Fig. 2. This "end effect" must be averaged in all molecules present in determining its effect on molecular weight. Thus the effect of a rate poison on molecular weight should increase as the yield decreases, and consequently an extremely strong rate poison could drastically reduce the molecular weight without being a chain-transfer agent.

Also a particular compound may cause both transfer and termination. In such a case, the number of moles may rise or fall depending on the relative strength of termination and transfer. In the particular case shown in row 4 of Fig. 2, these processes balance each other, causing the number of molecules to be the same as in

the case of the control. Although such a material might strongly influence both rate and molecular weight, its n_p/n_0 vs. X plot could not be distinguished from that of an inert solvent. In this case, the experimentally obtained molecular weights should be examined; if they are strongly depressed, this is indication for simultaneous termination and transfer, and the material is a strong poison as well as a transfer agent.

Experimental

Unless otherwise indicated, all experiments were performed in a stainless-steel dry box (15) at −78°C under N_2 atmosphere. Moisture content was ∼50 ppm.

The origin and purity of isobutene monomer, together with catalyst preparation, has been described. All the other chemicals used were commercially available materials (16). They were distilled before use and their purity was established by gas chromatography.

Control experiments were carried out with every series using 7.0 ml, i.e., 4.9 g of isobutene dissolved in 21 ml of n-pentane. The total volume of this mixture was 28 ml at −78°C, giving a 3.14 M monomer solution. In experiments with terminators or transfer agents, the n-pentane was replaced by the appropriate amount of chemical, keeping the total volume of the mixture at 28 ml. Four concentrations were used: 0.001, 0.01, 0.05, and 0.1 mole X/l. The systems were thermoequilibriated at −78°C, and subsequently 0.2 ml of catalyst solution (9.40 × 10⁻³ mole/liter of $AlCl_3$ in methyl chloride) was added dropwise to the agitated mixture. Polymerizations were homogeneous, but initiation was apparent by a distinct schlieren effect. Reactions were terminated 5 min after catalyst introduction with 1 ml of cold methanol. The reaction mixtures were poured into tared weighing dishes and evaporated on a steam bath. Subsequently the polymer products were dried for 48 hr in a vacuum oven at 60°C and weighed. No effort was made to remove catalyst residues from the samples, because identical amounts of catalyst solutions were used in every experiment and the total amount of catalyst residue in the samples was ∼0.00025 g, corresponding to ∼0.07% error.

The catalyst concentration [$AlCl_3$] in our experiments was purposely kept low (1.8 × 10⁻⁶ mole/liter), so that conversion was

< 10%. Typical values of M and X were 3.14 moles/liter and 10^{-3} to 10^{-1} mole/liter, respectively. Under these conditions M and X remain approximately constant during the polymerization, allowing a simplified mathematical treatment of the kinetic equations.

Control experiments were also carried out to determine and correct for the potential self-polymerization of olefins used in conjunction with isobutene. In these runs the catalyst solution was added to the olefins in the n-pentane in the absence of isobutene. Conditions under which the self-polymerization of terminators was neglibible were worked out in advance. Thus in our experiments the self-polymerization of olefins on $AlCl_3$ catalyst addition was negligible, and either no corrections were necessary or they were of little consequence (< 1%). Apparently the extremely small amount of catalyst employed sufficed to polymerize the isobutene but was insufficient to yield appreciable amounts of products with other olefins.

It should be pointed out that our molecular weights are not number-average values but viscosity averages and were obtained from single point determinations (14). Also in our discussion we assumed that the molecular-weight distributions of individual samples were similar and comparable. Thus our molecular weights cannot be used for exact quantitative calculation and are only indicators of trends.

APPENDIX. TESTING THE VALIDITY OF THE MODEL

Monomer Concentration Effects

A series of runs were performed with constant monomer/solvent (M/S) ratios and various volumes of solutions using constant amounts of catalyst. It was found that the volume of solution had no effect on the over-all yield. This implies that either the solvent contained negligible amounts of impurities (since increasing the ratio of total grams of solvent present to grams of catalyst added had no effect on the yield) or that the reaction occurred so rapidly that only impurities in the "reaction zone" could affect the reaction. In the latter case, the "effective" concentration of solvent (and therefore impurities) in the reaction zone and not over-all concentrations would be rate-controlling.
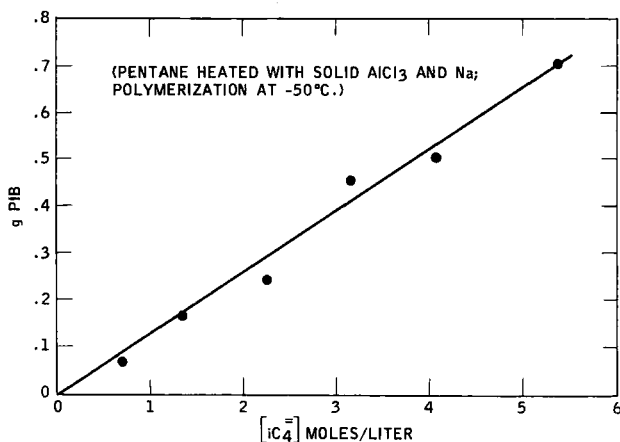
FIG. 3. Yield vs. initial monomer concentration.

This ambiguity was resolved in experiments designed to test the purity of the n-pentane solvent used in these investigations. A series of polymerizations were performed at $-50°C$, with constant monomer concentrations (3.14 moles/liter) with varying amounts of S_1 and S_2, where S_1 and S_2 are n-pentane solvents with differfng degrees of purification. The S_1 n-pentane solution was purified by contact with 5A powdered molecular sieves, whereas the S_2 n-pentane solution was purified by refluxing reagent-grade n-pentane and distilling over solid $AlCl_3$ and storing over Na. Polymerizations were performed using 0, 33.3, 66.6, and 100% S. The results indicated that the molecular sieves treated solvent contained an unidentified impurity of extremely low concentration, certainly below that of gas chromatographic detectability, which affected the course of polymerization. The linearity of the $1/W_p$ vs. M_0 curves obtained in these experiments indicates that this solvent impurity is a "catalyst poison," reducing the original catalyst concentration, rather than a "rate poison," which would have attacked the growing polymer molecule, resulting in a quadratic nonlinear relationship between $1/W_p$ and M_i. That such "catalyst poison" would have no effect on T.C. or P.C. is discussed below.

The monomer dependency of yield was then investigated using highly purified ($AlCl_3$ and Na-treated) n-pentane solvent. Figure 3 shows the resulting linear dependency with zero intercept. This

linear dependency is a strong argument that spontaneous termination is much more important than allylic or "suicide" termination (i.e., $k_6 \ll k_5$, as was indicated earlier), since, if this were not the case, the polymer yield would be expected to obey the relation $W_p = (k_2/k_6)P^\oplus$ and thus be independent of M in the region under study.

It should be pointed out, however, that k_5/k_2 cannot be determined from the slope of this line, since this slope is a function of $P_i^\oplus$ [see Eq. (16)]. Since the exact role of $AlCl_3$ in forming the "catalyst" in this system is obscure, it is impossible to calculate, a priori, the initial catalyst concentration, $P_i^\oplus$. By careful control of experimental conditions, however, it is possible to achieve reproducibility, which implies that $P_i^\oplus$, while unknown, is constant for a given set of experiments. A change in solvent impurities, however, would affect the value of this unknown constant.

Thus we assume that the amount of $AlCl_3$ added is proportional, but not equal, to $P_i^\oplus$. Calculated estimates of $P_i^\oplus$ will be discussed subsequently.

The effect of initial monomer concentration (M_i) on the over-all yield in the presence of poisons (W_p) was also investigated in experiments using higher catalyst concentrations. The assumption of constant M_i (on which the previous derivations are based) should not hold in this case. Burton and Pepper (*13*) have shown that, if M varies appreciably with time, the dependency of yield on monomer concentration is given by

$$\ln(M_i/M) = k_2/k_5 P_i^\oplus \tag{26}$$

At low conversions $\ln(M_i/M_f) = (M_i - M_f)/M_i$ and Eq. (26) becomes

$$\frac{M_i - M_f}{M_i} = \frac{k_2}{k_5} P_i^\oplus \tag{27}$$

which may be rearranged to give

$$W_0 = (k_2/k_5) M_i P_i^\oplus (MW_m V) \tag{28}$$

which is identical with Eq. (26).

Figure 4 is a plot of $\ln(M_i/M_f)$ vs. "catalyst concentration" [Eq. (26)] for initial monomer concentrations of 0.209 and 0.696 mole/liter, respectively. The expected linear relationship is well obeyed
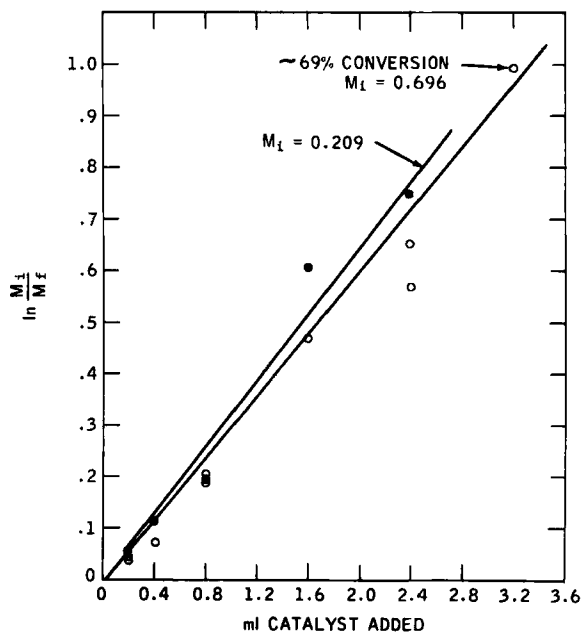
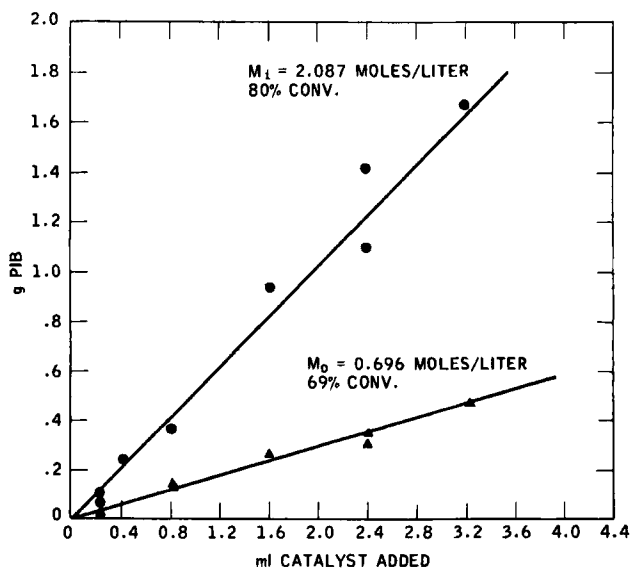**FIG. 4.** Effect of amount of catalyst on conversion as predicted by Eq. (29).

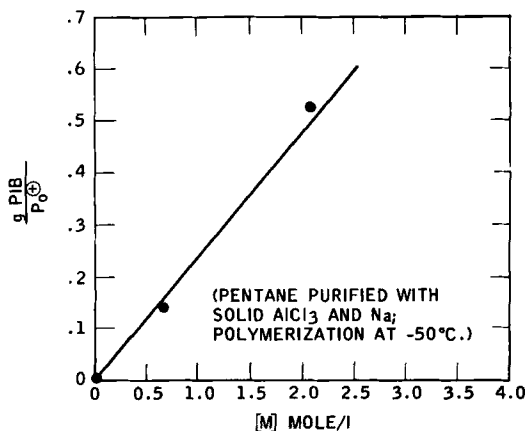**FIG. 5.** Effect of catalyst on conversion as predicted by Eq. (30).

FIG. 6. Effect of monomer concentration on the yield/catalyst ratio.

at low to medium conversions. Deviations from linearities are seen at highest conversions for $M_i = 0.209$ and 0.696 mole/liter, respectively. Burton and Pepper (*13*) point out that such deviations at high conversions might be expected if spontaneous transfer reactions occur. Although such reactions are certainly possible, we have not included them in our kinetic model. The effect of such chain-transfer reactions, if appreciable, would be included in the $1/MW_0$ term of Eqs. (19) and (20) and would become part of the kinetic constants in the empirical transfer coefficient.

It is interesting to replot the same data, in the form of Eq. (28). Although this equation should theoretically be obeyed only at low conversion, Fig. 5 indicates the surprisingly good fit of this now empirical relationship, at conversions as high as 80%. In Fig. 6, the excellent agreement of the $W_0/P_i^{\oplus}$ vs. M_i relationship, predicted by Eq. (28), is demonstrated.

Effect of Catalyst Concentration

Equation (16) predicts that W_0 should be directly proportional to $P_i^{\oplus}$. This effect has already been demonstrated in Fig. 5. It is even more significant, however, that Eq. (17) predicts that the poison coefficient should be independent of catalyst concentration. This effect was examined in a series of runs in which the catalyst concentrations were varied by a factor of 4. The data from these runs are shown in Figs. 7 and 8. Figure 7 once again shows the linear
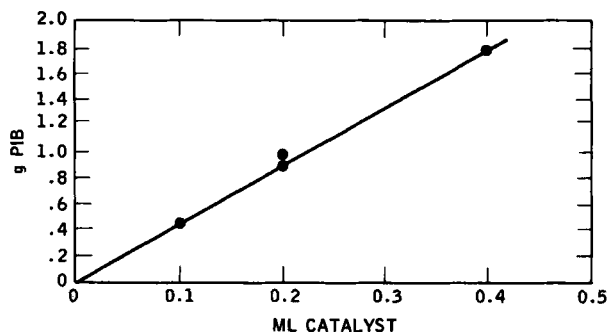
FIG. 7. Effect of amount of catalyst on polymer yield.

dependence of W_0 on catalyst concentration. The independence of the poison coefficient on catalyst concentration is shown in Fig. 8. Thus the poison coefficients of runs made with a fourfold variation in catalyst concentration agree within the expected experimental variation.
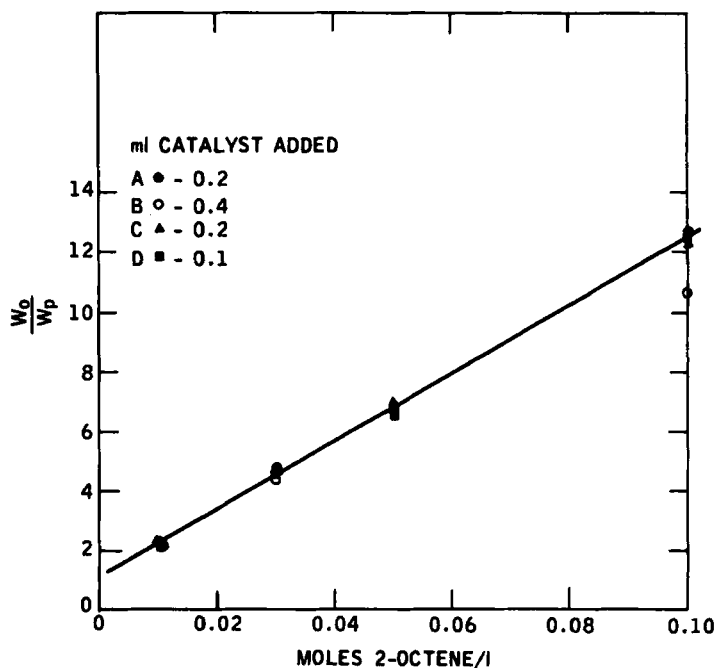
FIG. 8. Effect of catalyst concentration on dependence of W_0/W_p at various poison (2-octene) concentrations.

Unfortunately, owing to the large experimental variation in the corresponding molecular weight data for these runs, no definite conclusion can be drawn for this data concerning the dependency of T.C. on catalyst concentration. We will assume that the independency of MW on $P_i^{\oplus}$ predicted by Eq. (18) is correct, owing to the large amount of data supporting the other effects predicted by the proposed mechanism.

Catalyst Efficiency

An estimate may be made of the catalyst efficiency by comparing the calculated number of molecules of product with the number of moles of $AlCl_3$ introduced. Thus 1.88×10^{-6} mole of $AlCl_3$ catalyst at $-78°C$ results in ~ 0.33 g. of polyisobutene with a MW of $\sim 10^6$ g/mole. Thus $n_0 = W_0/MW = 0.33 = 10^{-6}$ moles of polymer. If no chain transfer occurs, the resulting catalyst efficiency is 0.175. If, however, as is likely the case, appreciable chain transfer does occur, true catalyst efficiency could be much less than this estimate indicates.

The upper limit of catalyst efficiency may also be estimated from the proposed kinetic model. Thus, from Eq. (19), the slope of the $1/MW_p$ vs. X curve (which we shall designate S_{MW}) is given by

$$S_{MW} = \frac{k_4 + k_7}{k_2 M_i (MW)_m}$$

Equation (15) indicates that the slope of the $1/W_p$ vs. X curve, S_{W_p}, is given by

$$S_{W_p} = \frac{k_7}{P_i^{\oplus} k_2 M_i (MW_m V)}$$

Thus

$$\frac{S_{MW_p}}{S_{W_p}} = P_i^{\oplus}(V) \frac{k_4 + k_7}{k_7}$$

$$P_i^{\oplus}(V) = \text{initial moles catalyst} = \frac{S_{MW_p}}{S_{W_p}} \frac{k_7}{k_4 + k_7}$$

Since $k_7/(k_4 + k_7) \leq 1$, an upper limit for $P_i^{\oplus}(V)$ may be estimated if we assume that $k_4 \ll k_7$. If such a calculation is made for all the materials investigated, a series of estimates of $P_i^{\oplus}$ max results. The lowest $P_i^{\oplus}$ could then be used to estimate the catalyst efficiency.

Thus 2,3-dimethyl-2,4-butadiene gave the lowest $P_i^{\oplus}$ max ($P_i^{\oplus}$ max = 0.015 × 10⁻⁶ mole). The resulting catalyst efficiency is therefore (0.015 × 10⁻⁶)/(1.88 × 10⁻⁶) = 0.008.

The accuracy of such estimates is difficult to determine. There is little doubt, however, that the true catalyst species represents only a small fraction of the number of moles of $AlCl_3$ present.

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Zusammenfassung

Die mit dem Problem des Kettenabbruchs bei ionischen Polymerisationen durch Hydridübertragung und gekoppelter Allylstabilisierung in Zusammenhang stehenden Theorien wurden untersucht und erweitert. Es wird vorgeschlagen, dass kationische Polymerisationen ganz allgemein dadurch zum Stillstand kommen, dass die wachsenden Ionen irreversibel nach folgendem Mechanismus vernichtet werden:
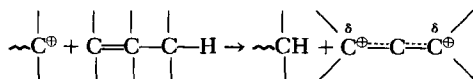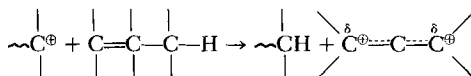
Ein kinetisches Modell wurde entwickelt und dazu benutzt, um empirische Vergiftungskoeffizienten (P.C.) und Übertragungskoeffizienten (T.C.) zu definieren, welch beide eine Substanz in Bezug auf ihre Wirksamkeit in kinetischen Kettenabbruch- und Kettenabschlussreaktionen charakterisieren.

Experimente zeigen, dass allylische Selbstabbruchreaktion in nicht-inhibierten Isobutenpolymerisationen mit AlCl₃ als Katalysator ohne Zweifel vor sich gehen, aber keinen nennenswerten, molekulargewichtsbestimmenden Einfluss haben.

Résumé

On a étudié et élargi les théories concernant le problème de la terminaison de polymérisation ionique par transfert hybride, associée avec une stabilisation allylique. On a stipulé que les polymérisations cationiques en genéral, se terminent par la destruction irréversible des ions croissants, suivant le mécanisme:

$$\sim\!\overset{|}{\underset{|}{C}}{}^{\oplus} + \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H \rightarrow \sim\!\overset{|}{\underset{|}{C}}H + \overset{\backslash}{\underset{/}{C}}{}^{\oplus}\!\cdots\!\overset{|}{C}\!\cdots\!\overset{/}{\underset{\backslash}{C}}{}^{\oplus}$$

On a developpé et utilisé un modèle cinétique pour la définition du coëfficient empirique d'empoisonnement (P.C.) et du coëfficient de transfert (C.T.), qui caractérisent un matériel du point de vue de son efficacité dans la terminaison cinétique des chaînes et rupture des chaînes, respectivement. Les éssais indiquent, que la self-terminaison allylique dans les polymérisations non-inhibées d'isobutène, avec l'AlCl₃ comme catalyseur, n'est pas le fait important, déterminant la masse moléculaire, bien que sans doute présente.