REACTION MECHANISM IN CATIONIC AND PSEUDOCATIONIC POLYMERIZATIONs

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INTRODUCTION

The polymerizations of olefinic and cyclic compounds catalysed by conventional acids and by syncatalytic systems comprising a metal halide and a co-catalyst have been reviewed from several points of view1–6. These reactions are unusual in that the ideas used in their interpretation have changed frequently and the theoretical position is still somewhat confused. I shall examine here some of the reasons for this situation and attempt to clarify the picture by an historical approach. I will also give an account of some recent work leading to a revival of the old “ester” theory and indicate some of its implications and connections.

CO-CATALYSIS

Since the 1930s it has been recognized that polymerizations catalysed by metal halides are in many essential respects different from those induced by radicals, and it was generally agreed by the early 1940s that the chain-carriers, or active species, are highly polar and, possibly, cationic. The discovery in the late 1940s of co-catalysis in isomerizations, alkylations, and polymerizations catalysed by metal halides appeared to bring some uniformity to the subject, because many of the syncatalysts (metal halide and co-catalyst) could plausibly be considered to act in the same way as conventional acids. Thus the reactions catalysed by them were open to interpretation by the Whitmore carbonium ion mechanism.

Whilst this view was widely accepted as explaining many of the observations, a few workers retained for some time a modified version of Hunter and Yohé’s “direct” initiation mechanism to explain a limited range of phenomena. The point at issue is whether the polymerization of an olefinic hydrocarbon can be initiated by a metal halide alone, without the participation of a co-catalyst, which might be water, a hydroxylic impurity, or a solvent alkyl halide. This whole problem is extremely difficult and complicated, and it has been analysed in some detail2,6.

It is difficult because the definitive answers must come from quantitative experiments with extremely pure materials under the most rigorous conditions, and such are very rare. It is complicated because of the great diversity of behaviour which is shown by different metal halides and monomers, and because we are still very ignorant of the chemistry of metal halides.

The interpretation of reactions catalysed by metal halides was complicated and confused further by the formation of π-complexes between these catalysts and olefins, and the unfortunate fact that many of these complexes formed
from aromatic olefins have a colour which to the unaided eye is indistinguishable from that of the triphenylmethyl and related cations. There is no evidence that these complexes are catalytic, and quite a lot that they are not.

Recent work has shown that in some systems in which polymerization was believed to occur without co-catalyst, a co-catalyst is in fact required\textsuperscript{7, 8-11}. But it has also been shown that in others\textsuperscript{12, 13} the addition of water has no effect on the rate and, therefore, there is evidently no need for a co-catalyst of this type. Since "direct" initiation by metal halide alone seemed very unlikely, an explanation in terms of co-catalysis by the solvent was suggested for lack of any more plausible theory\textsuperscript{12}. Whilst "direct" initiation by the Hunter–Yohé mechanism remains implausible\textsuperscript{6}, a different form of "direct" initiation has been suggested and must be considered; it is analogous to initiation of anionic polymerization by sodium naphthyl, and involves formation of a cation-radical by oxidation. This reaction is limited to reducible catalysts and its details (if it occurs at all!) remain to be explored. Scott, Miller and Labes\textsuperscript{14} have suggested such a reaction for the initiation of N-vinylcarbazole polymerization by organic catalysts with marked electron-acceptor character; Bawn, Fitzsimmons and Ledwith\textsuperscript{15} suggested it for initiation by the tripylum ion; Chi-Hua Wang\textsuperscript{15a} put forward the idea with respect to initiation by reducible metal ions, but emphasized the radical reaction which might ensue therefrom; and Bawn, Ledwith and Yang Shih-lin\textsuperscript{15b} reported polymerization of N-vinylcarbazole by sodium chloroaurate involving reduction of the Au(III). I would like to suggest here that the mechanism could be generalized to metal halide catalyst. One might represent it as involving the metal halide molecule, or the cation formed from this by the self-dissociation of metal halides in suitable solvents\textsuperscript{16}:

\[
2\text{TiCl}_4 + \text{RCH} : \text{CH}_2 \rightarrow \text{TiCl}_3 + \text{TiCl}_5 + \text{RCH} \cdot \text{CH}_2^+ \\
\text{TiCl}_3^+ + \text{TiCl}_5^- + \text{RCH} : \text{CH}_2
\]

The formation of the easily identifiable lower halides should facilitate diagnosis of this type of reaction.

**INFLUENCE OF VIEWS DERIVED FROM RADICAL CHEMISTRY**

The mode of action of catalysts and the mechanism of initiation are inseparable from the problems concerning the nature of the chain-carriers. From the discovery of co-catalysis it was generally believed that the chain-carriers are ions, but we can now see that this theory was neither firmly based, nor thoroughly worked out in its consequences. It has been shown that there was, until recently, extraordinarily little evidence for ions being the reactive species\textsuperscript{6}. Seeking the reasons for this, one can now see that in the 1940s and 1950s workers refrained from conductivity measurements, or ignored negative or equivocal results of such studies, probably for two reasons: the electrochemistry of non-aqueous solutions, especially those of metal
halides, was still largely unexplored and beset by great experimental difficulties; and, perhaps more important, most workers still looked upon all addition polymerizations from the point of view of radical reactions, which implied that the concentration of chain-carriers is too small to be measured directly.

The "radical" point of view had several other consequences which retarded the development of an adequate conceptual framework for the acid and metal halide catalysed reactions. Among these was the practice of studying only initial rates and ignoring the complete reaction curves as important evidence concerning the nature of the reactions; the prejudice that these reactions could all be treated in terms of a steady state of the First Kind; and the (usually implicit) assumptions that for all systems the chain-carrier is fundamentally the same (i.e. a carbonium ion) and that in any one system there is only one kind of active species. The electrochemically and thermodynamically obvious implication of any ionic theory, that the presence of ions implies necessarily the simultaneous existence of ion-pairs and free ions, was largely ignored, or circumvented by guesswork. A detailed analysis of this problem has only been given very recently.6,17

The somewhat wayward development of the theory of acid and metal halide catalysed polymerizations is in great measure due to the slowness with which ideas taken over from radical chemistry were re-examined and, when found inappropriate, discarded. During the last fifteen years an adequate theory has grown up—but it is still far from complete.

In the light of our present knowledge, the logical steps in the elucidation of reaction mechanism must include these:

(i) To decide whether the propagation is a first or second order process it is necessary to construct a First Mayo Plot for polymer formed at low conversion. If $1/DP$ against $1/m$ gives a straight line, $V_p = kpnm^*$ ($m = $ monomer concentration, $m^* = $ concentration of active centres); if $1/DP$ against $m$ gives a straight line, $V_p = k'pn^*$. (For a detailed discussion see Ref. 6).

(ii) Kinetic analysis of whole reaction curves. If the order of reaction is constant, $m^* = $ constant (except for the unlikely situation in which $dm^*/dt = -dm/|dt|$), and the reaction is stationary—at least over that part for which the order is constant.

(iii) Whether stationary reactions are of the First Kind ($V_1 = V_1 
eq 0$) or of the Second Kind ($V_1 = V_1 = 0$) cannot be decided by any generally applicable procedure. The only unambiguous method is to determine (e.g. spectroscopically or conductimetrically) the concentration of growing chains, and its relation to initial catalyst concentration.

(iv) Identification of chain-breaking reactions by end-group analysis and Mayo plots.

DISCOVERY OF PSEUDOCATIONIC POLYMERIZATION

The chemical and kinetic complexity of systems involving metal halides led to a search for simple catalysts, such as conventional acids. However, since these were generally believed to give much lower D.P.'s than syndiotactic catalysts (and with aliphatic monomers, especially, gave not even oligomers under many conditions) they were eschewed by polymer chemists who were
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more interested in making high polymers with any catalytic system that
would serve, than in the elucidation of reaction mechanism. Moreover, such
attempts as were made in this direction seemed to show that "simple"
catalysts gave reactions which were hardly less complex than those catalysed
by syncatalysts\textsuperscript{18-27}.

The first to succeed in devising a truly simple system in which oligomers
higher than dimer are formed, were Pepper and Reilly\textsuperscript{28}. They found that
the polymerization of styrene by anhydrous perchloric acid in ethylene
dichloride obeyed very simple kinetics over a reasonable range of tempera-
ture and they interpreted these in terms of a very fast initiation with com-
plete consumption of catalyst, leading to a stationary system of the Second
Kind, so that the second order rate constant is $k_p$. In conformity with then
current ideas they considered the initiation to consist of protonation of the
styrene, and the propagating species to be the polystyryl ion. Although
there are at least three features of the results which seem hard to reconcile
with this interpretation, any other theory would have seemed quixotic at
that time. These features are the high activation energy for propagation,
$E_p \text{ ca. } 10 \text{ kcal mole}^{-1}$; that water, even in ten-fold excess over the acid,
does not affect $k_p$; and the fact that over a wide range of concentrations and
temperatures the plots of the first-order rate constant against the concentra-
tion of perchloric acid gave accurately straight lines; this has the unlikely
implication\textsuperscript{6} that the $k_p$ for free ions and ion-pairs are equal to within a factor
of 10 or less.

Pepper and Reilly's views on the mechanism of this polymerization implied
that with the concentrations of perchloric acid used by them, it should be
possible to estimate the concentration of polystyryl ions spectrophotometri-
cally and so to test whether initiation did indeed give carbonium ions in
concentration equal to that of the acid. When Gandini and Plesch\textsuperscript{5, 29-31}
carried out the appropriate measurements, they found from spectroscopic,
conductimetric and kinetic studies that \textit{no} ions were present \textit{during} the
polymerizations, but that they were formed once the styrene concentration
had been reduced by polymerization to less than four times the concentra-
tion of acid. Addition of more styrene instantly removed the ions, which re-
appeared once again when polymerization had reduced the styrene con-
centration sufficiently. This formation of ions \textit{after} polymerization had mis-
led some workers into concluding that they were also present \textit{during} that
reaction.

Detailed studies led Gandini and Plesch to formulate the concept of
\textit{pseudocationic} polymerizations. These are reactions which show many of the
characteristics of cationic polymerizations, but do not involve ions. Since
they could see no other alternative compatible with general chemical know-
ledge, they formulated the reactive species as an ester, and they were able
to support this view by direct experiments (formation of the ester in the
styrene solution by metathesis). The evidence indicates that in the
system styrene, perchloric acid, methylene dichloride, the poly(styryl
perchlorate) ester requires four molecules of styrene for its stabilization.
When these are no longer available, the ester ionizes, and the residual styrene
is consumed by a very fast, truly cationic polymerization; ionization of
the ester is a complicated reaction which has been only partly elucidated.
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The initiation and propagation of the pseudocationic polymerization can be represented thus:

$$\frac{1}{4}(\text{HClO}_4) + 5 \text{C}_8\text{H}_8 \rightarrow (\text{CH}_3\text{CHPh} \cdot \text{O} \cdot \text{ClO}_3)_{4\text{C}_8\text{H}_8}$$

The formation of the ester is very fast and the propagation is rate-determining. The chain-breaking reactions (which do not include a termination) are essentially those characterized by Pepper and Reilly.\textsuperscript{32}

The (very few) systems in which the character of the reaction has been definitely established as cationic or pseudocationic have been listed\textsuperscript{5}; one of the most urgent current tasks is to extend this list by exploring a range of monomers, catalysts, solvents and temperatures so that the type-determining factors may be quantified.

ESTERS AS CHAIN-PROPAGATING SPECIES

It is now opportune to examine the status and implications of the ester theory. Historically, esters are the oldest of the "active species" which have been adduced to account for the reactions of olefins in the presence of acids. A most perspicacious comparison of theories concerning interaction of olefins and acids has been given by Schmerling and Ipatieff in which they include various forms of ester theory\textsuperscript{33}. They found that whilst there was then little experimental evidence for preferring one theory to another for the (conventional) acid catalysed reactions of olefins, the carbonium ion theory provided greater insight into the detailed processes. Since that time all forms of "ester theory" have lost popularity, but it now seems that the pendulum of fashion has swung too far in favour of carbonium ions; this is in no small measure due to the increasing amount of information concerning the properties of carbonium ions which has become available\textsuperscript{34}–\textsuperscript{36}.

When we now reconsider the ester theory we can do no better than to start by quoting Whitmore\textsuperscript{37}:

"Esters are often assumed as intermediates in various processes of the types in which we are interested. It should be noted, however, that any use of a pure neutral ester is naturally ineffective since the ester by itself probably has no more tendency to give ions than does water by itself or hydrogen chloride by itself. On the other hand, the ester in the presence of a suitable donor of protons can form carbonium ions."

and Schmerling and Ipatieff\textsuperscript{38}:

"It should be remembered, of course, that in the carbonium theory the word "ion" has a different connotation than it does in inorganic chemistry; the degree to which the ester is dissociated may actually lie somewhere between the undissociated ester as in the ester mechanism and the free ions as usually written (although actually believed to be very short-lived) in the carbonium ion mechanism."

Whilst today we can no longer accept either of these statements as literally and universally valid, they contain two very important and closely related ideas which have been proved useful. The first of these is that a normal,
stable ester may become activated by interaction with another species; a
natural corollary of this is that esters can also be deactivated, or stabilized,
by such interaction. The other idea is that in a series of esters gradations of
polarity may be found, or that the polarity of any one ester, in particular
the reactivity of the bond linking the potentially anionic and cationic
moieties, may change according to the environment in which the ester finds
itself. The two ideas are thus closely linked. One serious point in which I
find myself in disagreement with Schmerling and Ipatieff and some con-
temporary writers is that, with respect to identifiable reaction intermediates,
I consider there to be a sharp distinction between the most polar form of a
molecule and its ionically dissociated form. The reason for this is empirical:
An ion is defined as a species carrying a charge equal to an integral multiple
of the electronic charge, and this definition implies that it will have a
characteristic predictable electronic spectrum and, under suitable condi-
tions, mobility in an electric field. There is so far no evidence which would
compel one to abandon this definition, and I think it is important to distin-
guish clearly in this context between reaction intermediates (chain carriers,
active species) of finite life-time, and transition states.

Whilst the kinetics, and probably the mechanism of pseudocationic poly-
ermerizations are simple, those of the reactions following polymerization are
not. Since generalizations are dangerous in this field, I will confine the
discussion here to the system which we have explored and hope that others
will find useful analogies in systems well known to them. Our findings on
the ionogenic reaction which follows polymerization in the system styrene,
perchloric acid, methylene dichloride and other related evidence can be
summarized tentatively by the following scheme:31:

\[
\begin{align*}
(I) & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ Quad
because a new species (IV) is formed and its formation shifts all the equilibria.

We can say that the ester (I) is stabilized by being specifically solvated by four molecules of styrene (it is not known yet whether other compounds can fulfill this function); in other words, the specific solvation reduces the polarity of the C—O bond and gives the ester a stability which the pure ester does not possess: attempts to prepare it at room temperature result in a mixture containing species (II), (III) and others.

The reactivity of the ions (in terms of rate constants) is at least two orders of magnitude greater than that of the stabilized ester, but it can only show itself under special conditions: when a high concentration of acid is formed locally in a solution, especially at low temperatures, or when ions such as (II) are introduced into a styrene solution, or at the end of a "normal" ester polymerization when the remaining four molecules of styrene per acid molecule are polymerized with great speed. Under the first two of these conditions the exceedingly fast ionic polymerizations can consume all the monomer before the ions are removed through the reactions (II) → (I) → (IV). Under the same conditions which with styrene give pseudocationic polymerization (perchloric acid, methylene dichloride), the much more basic p-methoxystyrene does give a cationic polymerization, but with the weaker trifluoroacetic acid it polymerizes pseudocationically.

The opposite of the stabilization of an ester is its activation. If we include in the concept ester the alkyl halides, their Friedel-Crafts reactions provide familiar examples of this phenomenon. An unusual example especially relevant to our present considerations is provided by some results made available to me in advance of publication by Giusti and Andruzza. Their results on the polymerization of styrene by iodine and hydrogen iodide can be interpreted in terms of an organic iodide derived from styrene, probably 1-phenylethyl iodide, being activated by the co-ordination of one or two molecules of iodine. This process appears to polarize the C—I bond to such an extent that the normally stable ester becomes activated to a chain-propagating species and induces a pseudocationic polymerization:

\[ \text{CH}_3\text{CHPhI} \cdot (\text{I}_2)_n + \text{C}_8\text{H}_8 \rightarrow \text{CH}_3\text{CHPhCH}_2\text{CHPhI} \cdot (\text{I}_2)_n \]

\[ n = 1 \text{ or } 2 \]

**CONCLUSION**

It now remains to place the concept of an ester as an active species into a wider chemical context, with special reference to polymerization catalysts. Sinn and Patat\(^\dagger\) have emphasized the distinction between monofunctional and bifunctional catalytic systems\(^\dagger\) and this distinction is obviously and necessarily related to the idea, explained above, that there is a difference in kind between polarized molecules and the ions which can be formed from them. Whereas the carbonium and other cations as reactive species are monofunctional, the esters evidently belong to the class of bifunctional catalysts; their mode of action—the addition of their constituent parts across a double bond—is, in modern terminology, an insertion reaction. In this context, we

\(^\dagger\) The term "bifunctional" as used by these authors is not to be confused with its use by Keulemans and Schuit who give it a quite different meaning\(^40\).
must note the important role of labile esters (e.g. 1-alkoxyvinyl esters) in synthetic organic chemistry, and that of enzyme-activated esters in biochemical processes.

Many authors have noted that one could find in the vast range of more or less complex polymerization catalysts evidence that changing composition was accompanied by a change in type of catalytic activity—from pure cationic to pure anionic—and that certain catalysts could show cationic or anionic characteristics according to the type of monomer offered to them. Whilst such speculations are always attractive to the scientist searching for unifying principles, and whilst they were well founded at the anionic end in the metal alkyls, no cationically acting species was known which, whilst bifunctional, is a well-defined chemical species. Our discovery of the pseudo-cationic reactions catalysed by esters has now completed the range; by analogy we would call the polymerisations catalysed by covalent metal alkyls pseudoanionic. Moreover, it seems to me that the complementary ideas of activation and stabilization of a potentially reactive species may be useful in thinking about the modes of action of many complex catalytic systems.

References

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34. Ref. 2, Chapters I and 2.
38. P. Giusti and F. Andruzz. This Symposium, Paper A275.
41. See e.g. M. Roha. Adv. Polymer Sci. 4, 353 (1965); and references therein.