Reaction Mechanisms

Reply to "Criticism Hypotheses by Gandini and Cheradame Regarding the Initiation of Carbocationic Polymerization" (Pol. Bull. *10*, 141 1983)

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Summary
The mechanism of grafting and blocking in cationic polymerisa-
tions initiated by the system $RCl-Et_2AlCl$ is discussed. The
criticism by Kennedy and Wondraczek of the proposal of a
grafting-<u>onto</u> (and blocking-<u>onto</u>) mechanism given in our book
is refuted point by point and new arguments are put forward to
corroborate our original hypothesis.

Introduction
    It is essential to start this reply with a point of order.
Both in the abstract and in paragraph 2 of the second page of
their paper (1) Kennedy and Wondraczek (K & W) grossly mis-
represent the stand we took in our book (2) on the subject of
the mechanisms operating in the grafting and blocking promoted
by the initiating system $RCl-Et_2AlCl$ (or Et_3Al, Me_3Al), RCl
being a polymeric chloride. First of all we did not "argue
without experimental evidence", but substantiated our alterna-
tive proposals with specific references to experimental work
both from Kennedy's laboratory (to show the weaknesses of the
arguments in favour of grafting and blocking <u>from</u>) and from
Sigwalt's laboratory (to show that grafting <u>onto</u> is indeed
operational in some systems). A careful reading of pp 169-188
and 241-242 of our book (2) should set this point straight.
Secondly, our discussion was aimed at underlining that the
<u>from</u> mechanism is by no means proved or the <u>sole</u> possible route
to grafting and blocking by the initiating systems specified
above: the contribution of the <u>onto</u> mechanism, ignored by
Kennedy's school, must be taken into account as an important
one. The second half of p.241 and the conclusion on p.183 of
our book for example summarise our position without ambiguities
(2).
    It must be remembered that at the start of the present
divergence of views is our proposal that the large body of evi-
dence accumulated on the cationic polymerisations initiated by
$RCl-Et_2AlCl$ (or Et_3Al, Me_3Al), with R= alkyl, arylalkyl or
polymeric, can readily be rationalised by a mechanism alterna-
tive to that put forward by Kennedy's school and given in p.1
of the "Criticism" (1); our mechanism is based on the <u>in situ</u>
production of the highly acidic species$EtAlCl_2$ and $AlCl_3$ by
exchange reactions between the two entities making up the ini-
tiator, e.g.:

$$RCl + Et_2AlCl \longrightarrow REt + EtAlCl_2 \quad \text{and}$$
$$RCl + EtAlCl_2 \longrightarrow REt + AlCl_3.$$
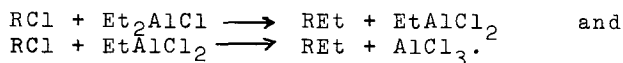
Direct initiation by these species would then follow. The
reader will find this point treated in detail in pp. 169-186 of
our book (2). Clearly, if our alternative mode of initiation
predominates, the growing polymer chain will form graft or
block copolymers by reacting onto specific sites of the added
macromolecules (may they be halogenated or not), e.g. unsatur-
ations or aromatic rings, through classical electrophilic alkyl-
ation.

This reply is layed-out in the same way as the "criticism"
that spurred it (1). We wish however to point out that we will
maintain the classical terminology which calls catalyst (or
initiator) the Lewis acid and cocatalyst (or coinitiator)the
species being activated (in terms of its acidity) by the catal-
yst, e.g. H_2O with BF_3. We see no reasons to adopt Kennedy's
proposal (3) for a reverse terminology because it contains two
intrinsic flaws: (i) when direct initiation is operative
Kennedy's "coinitiator" (the Lewis acid) is the only species
needed for the electrophilic attack onto the monomer, and con-
versely (ii) the term "initiator" for, say, water is misleading
since this compound alone does not display any catalytic acti-
vity.

Our Arguments in Favour of a Grafting-Onto Mechanism

Concerning ref. 615 in our book (1,2), we consider it
absolutely normal to quote a "personal communication", a
standard practice for yet unpublished work discussed with the
author. K. & W. have decided it is "obscure" and "not to be
taken seriously", yet this work is now in press (4) and corro-
borates the arguments we put forward when we originally quoted
it (ref. 2,p.175). Indeed when indene is polymerised by
$Et_2AlCl-(CH_3)_3CCl$ in the presence of an ethene-propene copoly-
mer devoid in principle of unsaturations, grafting is observed
in a polymer-copolymer reaction which the authors (4) attribute
to the formation of carbocations on the aliphatic copolymer
induced by the initiating system, but which could also be vis-
ualised as the grafting of polyindene active chains onto acci-
dental unsaturations present in the copolymer. Previous work
on a similar system had escaped our search when writing the
book. Carrick (5) showed in fact that the cationic polymeri-
sation of styrene by $BF_3.Et_2O$ in the presence of high-pressure
polyethene results in the grafting of the latter (about 3% of
aromatic rings in the graft). Since neither grafting nor deg-
radation of either polymer were observed when the polyethene
was mixed with preformed polystyrene in the presence of
$BF_3.Et_2O$, we take this as evidence that growing polystyrene
carbocations can graft onto a polymer (probably containing some
trace unsaturations) in the absence of labile carbon-halogen
bonds. When Carrick used $AlCl_3$ as catalyst, the same polymer
mixture interacted to give rapid grafting followed by degrada-
tion. Again, in the absence of labile C-Cl bonds, one can
achieve, through a complex mechanism, both grafting of a polymer
onto another and chain scission through $AlCl_3$ catalysis.

If we now turn from non-chlorinated and apparently satur-
ated (but probably slightly unsaturated) substrates to non-
chlorinated but polyunsaturated ones, the following important
observations can be made from work carried out in Sigwalt's
laboratory. In a first paper (6), several commercial

elastomers ranging from butyl rubber to polybutadiene were used in a study of the grafting ability of growing polyindene chains onto unsaturations, the initiating system being Et_2AlCl - $(CH_3)_3CCl$. Grafting efficiencies were high in all instances and reached about 90% in some cases. When EPDM rubbers were employed crosslinking was occasionally observed. Blank experiments involving EPDM and the initiating system in the absence of indene showed that crosslinking readily took place, indicating that a polyunsaturated polymer without any labile C-Cl bond can be activated by Et_2AlCl-$(CH_3)_3CCl$ and made to react onto an unsaturation belonging to another chain. More recently (4) this work was extended and different modes of grafting observed including grafting through, demonstrated by the use of the system indene-2-hexene (the latter comonomer being a model compound of the unsaturations in certain terpolymers used in this study).

Before turning to grafting with chlorine-containing polymers, it is important to emphasize that grafting onto and crosslinking readily occur by the reaction of the growing chain, not only with polymer unsaturations, but also by functionalisation of saturated polymer molecules, the latter mechanism being in need of further elucidation. These reactions seem quite common and obviously do not involve the mechanism invoked by K. & W.

As for the grafting with chlorine-bearing polymers, two situations are encountered:
(i) Polymers not containing any unsaturations. Again Sigwalt and coworkers (6) showed that grafting of indene in the presence of chlorinated ethene-propene copolymers with Et_2AlCl can lead to crosslinking if the chlorine content of the copolymer is high. The grafting onto contribution in these systems was seen to have originated from dehydrochlorination of the substrate copolymer catalysed by the Lewis acid, followed by the alkylation of the resulting double bond by a growing polyindene chain. We share of course this interpretation, but are inclined to consider it as the dominant mechanism rather than a secondary one.
(ii) Polymers containing unsaturations. Chlorinated butyl rubber (CBR) has been used as a substrate for grafting in two studies by Sigwalt's group. In the first (6) it was pointed out that when the CBR concentration was low with respect to the indene concentration, large amounts of homopolyindene were formed. This observation argues in favour of a mechanism of grafting onto. Indeed, since the catalyst used, Et_2AlCl, was unable to initiate the polymerisation of indene in the absence of CBR, two possibilities can be envisaged: according to Kennedy's mechanism, upon addition of a low concentration of CBR, grafting from should occur and there is no reason to expect indene to homopolymerise; if on the other hand initiation arises from Cl-Et exchange between the Lewis acid and the CBR, and the concentration of the latter is low, the growing homopolyindene chains will have little kinetic chance to graft onto before transfer or termination reactions neutralise them. Thus these results can be rationalised by our interpretation. When the CBR concentration is raised, grafting is successful because the growing indene macromolecules alkylate onto the unsaturations. Crosslinking was also observed under specific conditions of relative reagents' concentration: gel formation probably

arose from grafting <u>through</u> reactions, i.e. postalkylation mech-
anisms reinitiating the indene polymerisation or attacking a dou-
ble bond of another chain. In the second paper (7) more details
were reported. In particular, it was shown that under the cond-
itions in which cocatalysis is absent, but transfer is relativ-
ely important, the grafting efficiency is very high (up to 93%).
This apparent contradiction can only be rationalised by the pre-
dominance of a grafting-<u>onto</u> mechanism, in which the frequency
of this reaction overweighs the frequency of transfer. A graft-
ing-<u>from</u> mechanism could not have reduced the importance of tra-
nsfer and would have resulted in a large percentage of homo-
polyindene.

The only argument K& W bring forward in their general dis-
cussion against our interpretation has to do with high polymer
conversions, and the fact that grafting <u>onto</u> "can be forced to
occur at very high monomer conversions". First we must make our-
selves clear: when we speak of grafting <u>onto</u> we obviously do not
mean only grafting onto the side chains containing aromatic
moieties, but essentially an electrophilic attack of the growing
polymer chains onto the <u>substrate polymer</u>. On this basis we
fail to understand why the reactivity of the growing chains
should change with monomer conversion, since the two kinetic
entities determining the rate of grafting <u>onto</u> are the concentr-
ation of active species and that of available sites on the poly-
mer to be grafted. Since K & W seem to admit that grafting <u>onto</u>
does take place at high monomer conversion, the real question
has to do with the relative importance of this mechanism with
respect to grafting <u>from</u>. The fact that gellation is not comm-
only observed in the systems under discussion (i.e. with chlor-
inated polymers) implies that an important contribution from
both mechanisms is impossible. Indeed if the average number of
grafts is higher than two, one of the two mechanisms must pre-
dominate at the expense of the other, otherwise crosslinking
would be a common <u>early</u> feature of all these reactions. To us,
the evidence discussed above favours grafting <u>onto</u> and we see
no important argument against it, least of all that based on
monomer conversion. We have shown that grafting <u>onto</u> is the
only reasonable mechanism in the absence of C-Cl bonds in
the substrate polymer. It seems logical to extend this observ-
ation to chlorine-containing polymers with unsaturations from
the start or as a result of Lewis-acid catalysed dehydrochlori-
nation, particularly because the formation of $EtAlCl_2$ and
$AlCl_3$ upon mixing these polymers with Et_2AlCl promotes the
direct initiation of the monomer. It is up to K & W to prove
the occurence of grafting <u>from</u> unambiguously. They try to do
that in the second section of their paper through a series of
"facts", the reply to which is given below.

<u>Examination of "Facts" Supposedly "Proving Blocking or Grafting</u>
<u>From and Refuting the Hypothesis of Blocking or Grafting Onto"</u>
1) <u>The Effect of Conversion on Grafting Efficiencies</u>. The cont-
ention that grafting <u>from</u> should give 100% GE at low monomer
conversion is only valid if monomer transfer is absent. On the
other hand grafting <u>onto</u> will give high GE even when transfer
reactions are relatively important because the grafting react-
ion is in this case competing with them. We have pointed out
above that this consideration is the only valid rationalisation

of some results obtained in Sigwalt's laboratory (7). K & W find
it "very difficult to conceive a grafting onto scenario that
would give high GE at low monomer conversions", but we see no
logical barrier in envisaging growing macromolecules, generated
by direct initiation and possessing a carbocationic active end,
reacting efficiently with unsaturations on a substrate polymer
via electrophilic addition, and this irrespective of monomer
conversion, or, if the unsaturations are not frequent, with a
rate which would be maximum at the <u>beginning</u> and would decrease
with the decreasing concentration of available unsaturations.
2) <u>Carbocationic Grafting Onto Saturated Aliphatic Polymers is
Virtually Impossible</u>. Strictly speaking this assertion is corr-
ect, but, as we have amply illustrated in the general discussion
above, grafting <u>onto</u> does take place, simply because residual
unsaturation (polymer defaults) in the case of non-chlorinated
polymers (which obviously would never produce grafting <u>from</u>) or
unsaturations formed <u>in situ</u> by acid-catalysed dehydrochlorina-
tion in the chlorinated polymers, do exist, even if in moderate
concentrations.
3) <u>Carbocationic Grafting Onto PVC Impossible</u>. This statement
is surprising. The dehydrochlorination of such an unstable pol-
ymer as PVC must be one of the most studied reactions ever! It
is well known that solutions of low molecular-weight PVC are
highly unstable towards dehydrochlorination. In the presence of
a Lewis acid the process is moreover accelerated so that it is
perfectly normal to us to envisage that, in the conditions of
the experiments we are discussing, the PVC will contain <u>from</u>
<u>the start</u> some unsaturations which are likely to increase in
number when the polymer is dissolved in an acidic solution. As
to the "incompatibility" between PVC and PIB, this physical
phenomenon will not prevent in any way the chemical interaction
of the two macromolecules. The number of reactions reported in
the literature between polymers which display physical incompat-
ibility is too large and too well known to deserve a more det-
ailed reply.
4) <u>High Efficiency Grafting From Occurs Only with Et_2AlCl, Et_3Al
or Me_3Al but not with $AlCl_3$ or $EtAlCl_2$</u>. The argument in this
section can readily be turned around since we could ask why the
proposed grafting <u>from</u> is not very efficient with $AlCl_3, EtAlCl_2$
and $MeAlCl_2$. Indeed, nothing in Kennedy's general mechanism
provides an answer to this diminished activity. We have pointed
out over and over again in our book (ref.2, pp.169-186) that
<u>in situ</u> formation of $EtAlCl_2$ and $AlCl_3$ provides most probably a
much moreefficient catalytic mixture than the use of either of
these compounds as purified commercial samples added to the
reaction medium. Suffice it to remember that $AlCl_3$ is only
sparingly soluble in the latter conditions but will operate
in solution when continuously generated in conjunction with
$EtAlCl_2$ by Et-Cl exchange reactions.
5) <u>Formation of PIB-b-PSt</u>. We have carefully read the paper
quoted by K & W to support their present argument (8) and found
some evidence in favour of our mechanism. For the two experim-
ents conducted at -40°C with a high concentration of Et_2AlCl
(samples 1 and 2, Table IB) the styrene conversion was 11 and
40% respectively, and the amount of homopolystyrene in the
product was 21 and about 45% respectively. This result goes

against the blocking from hypothesis since according to that
mechanism the relative importance of initiation and transfer
should not vary,but it obviously did in these experiments. Ano-
ther observation which is not compatible with the blocking-from
scheme, but is instead in tune with that of blocking onto is
the decrease in % conversion with increasing Et_2AlCl initial
concentration (Table IB, samples 1 through 4). Oddly enough,
this apparent anomaly was not discussed by the authors (8).
Unfortunately the PIB concentration in step 2 was not given,
but it seems clear to us that as the Et_2AlCl is decreased the
excess of C-Cl groups in the PIB will increase and favour mul-
tiple Et-Cl exchanges towards a greater proportion of $AlCl_3$.
The latter is a much more efficient catalyst than $EtAlCl_2$ and
gave therefore the higher yields observed when the Et_2AlCl con-
centration was reduced by a factor of 10 or even 100. We fail
to see how this could be rationalised on the basis of a block-
ing-from mechanism. Concerning the actual mode of blocking, we
envisage it as taking place mostly onto terminal unsaturations
produced on the PIB by transfer or dehydrochlorination of C-Cl
endgroups. Once again we wish to emphasize that the evidence in
favour of blocking from is by no means conclusive and that our
alternative mechanism becomes more likely when the experimental
evidence is carefully scrutinised.
6) Preferential Grafting of St from Chlorobutyl over Bromobutyl.
The different reactivities of C-Cl and C-Br bonds towards
Et_2AlCl explain equally well the lower GE encountered with bro-
minated butyl rubber, whether one considers the onto or the
from mechanism. Indeed the products of Et-halogen exchange
invoked in our interpretation are less efficient initiators
with C-Br bonds. Moreover, a proper discussion of this point
would require specific quantitative data concerning the indi-
vidual steps, given the complexity of such a "mixed" system.
7) Surface Grafting. Once more we reiterate that PVC and chlo-
rinated polypropene can contain, or develop by dehydrochlori-
nation, sufficient unsaturations on their surface to justify
grafting onto. The case of silica bearing $-Si(CH_3)_2-CH_2-CH_2-$
$-C_6H_4-CH_2Cl$ groups must be discussed apart. A careful inspec-
tion of the work quoted by K & W (9) shows an interesting fea-
ture concerning the initiation mechanism: grafting becomes re-
latively important only when the ratio of Et_2AlCl to C-Cl
groups attached to the silica is 20, higher values of this
ratio being much less favorable to grafting. Since the silica
concentration remained constant in the series of runs (ref.9,
Table I), this implies that GE's were the higher the lower the
initial Et_2AlCl concentration, a situation similar to that
discussed under point 5 and related to ref.8. Here again the
authors refrained from commenting these peculiar results which
are in kinetic contradiction with the grafting-from mechanism.
From our point of view it seems normal that a decrease in
Et_2AlCl concentration relative to C-Cl will favour multiple
Et-Cl exchanges over a single one,thus leading to higher pro-
portions of $AlCl_3$ with respect to $EtAlCl_2$, the former being a
more efficient initiator. As for the actual mode of grafting,
we think that the aromatic nuclei on the groups attached to the
silica were excellent targets for alkylation by growing PIB
chains. K & W restate the problem of incompatibility to which

we already answered under point 3.

8) <u>The Synthesis of PαMeSt-b-PIB-b-PαMeSt Triblocks from Chlo-</u>
<u>rine-Telechelic PIB Only Conceivable by a From Mechanism</u>. We
disagree with this statement. Again, a careful reading of the
paper quoted by K & W is enlightening. The contention that the-
re is no homopolymer contamination in the triblock is not cle-
arly verified. Looking at the extraction given in Scheme I for
TB-C (10) we find 35% of a <u>n</u>-pentane-soluble fraction (B) con-
taining 88% PIB. We feel that had this fraction been precipit-
ated in acetone, important quantities of homoPIB would have
been isolated. The final fraction (H), representing 33% of the
total product, contained 87% PαMeSt; together with fraction G
(not analysed, 7%),they probably contained important proport-
ions of homoPαMeSt. As for our disagreement with the point
statement, we can readily conceive some dehydrochlorination of
Cl-PIB-Cl taking place during the blocking stage, catalysed by
the acidic catalysts. Direct initiation of αMeSt promoted by
EtAlCl$_2$ and AlCl$_3$ formed <u>in situ</u> , followed by grafting <u>onto</u>
the unsaturations produced on the telechelic PIB could equally
well explain the results obtained.

9) <u>The Synthesis of Polyisobutenylstyrene Macromer Only Conce-</u>
<u>ivable by a From Mechanism</u>. The reference given to support this
argument (11) does not provide either experimental details or
analytical data sufficient for a proper appraisal. The reader
is asked to believe that "according to subsequent kinetic and
spectroscopic analysis (sic)these conditions led to controlled
initiation,i.e., headgroup control by well defined initiation,
and transferless propagation". To our knowlegde these "subseq-
uent " data have not been published yet. Given the remarkable
control claimed, it seems more than natural that the specific
tests carried out to prove it should be available in print. We
were puzzled by the fact that the styryl group would remain
untouched during the cationic polymerisation to prepare the IB
macromer, i.e. that its double bond would not enter copolymeri-
sation with isobutene to give branched products. A subsequent
publication from Kennedy's laboratory (12), not quoted by K &
W, confirmed our doubts in that the "danger" of the styryl
group being lost during the synthesis of the macromer was reco-
gnised and a different starting reagent, not containing unsa-
turations, was used for the isobutene polymerisation. Given the
lack of specific information we cannot comment on the validity
of this point, but look forward to the data announced in both
refs. 11 and 12.

10) <u>Direct Spectroscopic Observation of the Blocking and Graf-</u>
<u>ting Sites</u>. K & W inverted their last two references since the
first deals in fact with blocking PIB <u>from</u> polyindene (13) and
the second with grafting the same polymers (14). We regret to
have to say once again that neither work contains the ^{1}HNMR ev-
idence announced by K & W. We carefully read both papers look-
ing for such information, and only came across the use of ^{1}HNMR
for the determination of the IB content of the copolymers, with
no spectra given, nor any mention of structural characterisation.
Yet K & W assert that "the <u>structure</u> of these grafts analysed
by ^{1}H NMR spectroscopy"(our underlining); they probably possess
this information, but it was certainly not in the papers they
quoted. The only spectroscopic observation supposedly relevant
to the graft-copolymer structure is a portion of IR spectrum

(14, Fig.2-C) which,the authors claim, shows the lack of tris-
ubstituted aromatic rings in a fraction of their graft copoly-
mer. We think that K & W will agree with us that a low-resolut-
ion IR spectrum such as that cannot possibly be used as eviden-
ce or discriminating feature for the presence or absence of
small amounts of trisubstituted structures in a "bath" of disu-
bstituted ones. Despite their conclusions, particularly in the
second one, these two papers (13,14) do not offer,to our view,
any specific evidence in favour of blocking and grafting from,
just as they do not provide, despite claims to the contrary,
any proof refuting our alternative onto pathways.

Conclusions
        We are ready to accept, as we clearly did in our book, that
the mechanism of grafting (and blocking) from catalysed by
Et_2AlCl in conjunction with a C-Cl bond is operative, but our
contention is that this contribution to the overall process is
a minor one in most systems studied. We have shown that grafti-
ng (and blocking) onto, following direct initiation by mixtures
of $EtAlCl_2$ and $AlCl_3$ (formed by Et-Cl exchanges between the
catalyst and the C-Cl bonds on the substrate polymer) is a
common and widespread feature with a large variety of systems.
We think that this mechanism predominates over that of grafting
(or blocking) from, when both can occur. We feel that all the
points raised by K & W can readily be answered, at least when
the specific systems they quoted are sufficiently well chara-
cterised by experimental details and analytical data for a ser-
ious appraisal.

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