Macromol. Symp. ***132****, 127-141 (1998)*

SOME STILL UNSOLVED PROBLEMS IN CARBOCATIONIC POLYMERIZATION

Pierre Sigwalt

Laboratoire de Chimie Macromoléculaire
Université Pierre et Marie Curie, 4, place Jussieu, Paris, France

Abstract : Some controversial problems in both "conventional" and "living" carbocationic polymerizations are discussed : direct initiation, apparently negative activation energies, effect of hindered bases and of other electron donors.

INTRODUCTION

In 1973 was organized in Rouen what we called the "First International Symposium on Cationic Polymerization" in which the present author gave the opening lecture on "Persistent problems and recent progress in the field of cationic polymerization". The analogy with the title of the present lecture is obvious, but this one is less ambitious since cationic ring-opening polymerizations will not be discussed and only a few problems examined. We shall see however that they are often closely related to those discussed 23 years ago (ref.1). Important progress have been made since then, the main ones being the discovery and the development of "living" carbocationic systems (ref.2,3), which led to a much better control of polymerization reactions and of polymer structure (ref.4-7).

Among the various problems discussed in 1973 about the mechanisms of initiation, propagation, transfer and termination reactions, a few have been partly solved but other remain and new ones have arised.

First, I am planning to discuss a controversial problem which has been partly solved recently, that of the occurrence of direct initiation by Friedel Crafts acids. What is still unknown is the extent of a possible contribution of direct initiation, particularly in reactions in which protonic initiation has been suppressed. Then, I shall examine the explanations proposed for the apparently negative activation energies observed in various carbocationic polymerizations, the role of hindered bases (and of other electron donors) on initiation and on the stability of the active sites, (either paired or unpaired ions).

There are many aspects of initiation of carbocationic polymerizations which are not well understood. This is the case for initiation of usual monomers (isobutylene, styrene...) with weak as well as with strong protonic acids (even if there is a better understanding for some model compounds), and this explains in part why these initiators are not used generally in the recent controlled or "living" polymerizations. In this case, the best control of initiation has been obtained by ionization of a cationating reagent (halide, ether or ester) by a Friedel Crafts acid.(F.C acid). However, this one may lead to competitive initiation by reacting directly with the monomer ("direct initiation") or with a proton donor present in the medium ("cocatalyzed initiation"). For a long time, this last type of initiation was the only one considered in the

CCC 1022-1360/98/$ 17.50

absence of a cationating reagent added on purpose, while direct initiation was considered with strong scepticism. The mechanism of cocatalyzed initiation by proton donors (such as traces of water always present) is still not well understood, but its occurrence has been proven in many cases, particularly with weak protonic acids such as $SnCl_4$ and BCl_3.

DIRECT INITIATION OF CARBOCATIONIC POLYMERIZATIONS BY FRIEDEL-CRAFTS ACIDS (F.C ACIDS)

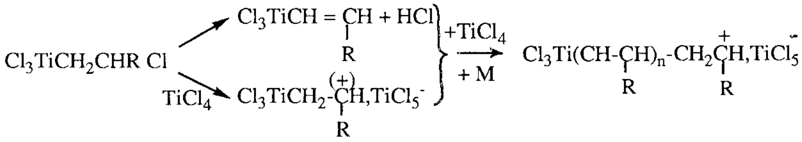
The possible occurrence of direct initiation by F-C acids of isobutylene and of arylsubstituted ethylenes (styrene, indene, 1,1-diphenylethylene) as well as the mechanisms proposed have been discussed in detail (ref.8). The conclusion of a recent complete review (ref.9) was that the most likely mechanism was halometalation of the double bond (perhaps via zwitterion formation) followed by an ionization of the halide formed by excess F-C acid.

The earlier proposal of a direct reaction between isobutylene and aluminium trichloride had been made in 1933 by W.H. Hunter and R.V. Yohe, and written as a reaction between a polarized complex $IB \rightarrow AlCl_3$ and monomer(ref.10). No charges were written, but the complex could also be represented as a zwitterion

$Cl_3\overset{(-)}{Al}CH_2\text{-}\overset{+}{C}(CH_3)_2$ with further growth between $C^{(+)}$ and $Al^{(-)}$ (ref.8)

Following our discovery of polymerization by condensation of isobutylene with $TiCl_4$ occurring in high purity conditions (ref.11) we investigated the reaction of Friedel Crafts acids with model compounds. For initiation with $TiCl_4$, I made in the Rouen meeting in 1973 the first detailed proposal (ref.1) of initiation occurring through halometalation, followed by an activation of the halide formed by a second $TiCl_4$ molecule. Another possibility considered was the transitory formation of HCl acting as protogen.

$$TiCl_4 + CH_2 = CHR \rightarrow \left[Cl_4\overset{(-)}{Ti}CH_2\overset{(+)}{CH}\,R\right] \rightarrow Cl_3TiCH_2CHRCl(\text{or higher oligomers}) \quad (1)$$



$$Cl_3TiCH_2CHR\,Cl \begin{cases} \nearrow Cl_3TiCH = \underset{R}{C}H + HCl \\ \xrightarrow{TiCl_4} Cl_3TiCH_2\text{-}\underset{R}{\overset{(+)}{C}}H,TiCl_5^- \end{cases} \xrightarrow[+M]{+TiCl_4} Cl_3Ti(CH\text{-}\underset{R}{C}H)_n\text{-}CH_2\underset{R}{\overset{+}{C}}H,\overset{-}{TiCl_5} \quad (2)$$

A similar mechanism was proposed in the same meeting by G.A. Olah for polymerization of e.g. isobutylene by SbF_5 or by $AlBr_3$, by analogy with the hydro alanation of alkenes (ref.12) The main difficulty to prove this type of carbocationic initiation is to distinguish it clearly from those involving protonic impurities (H_2O or HCl), and this necessitates to measure the yield in carbocations and to compare it with the concentration of metal halides and proton donors.

The determination of the yield of carbocationic species was not possible with isobutylene and styrene, and could be made only with sufficiently stable carbocations.

This was the reason for the use of 1,1- diphenylethylene (DPE) as a model. But with $TiCl_4$, in high purity conditions at -30°C the yields of C^+ based on $TiCl_4$ were only between 1 and 10% (ref.13,14). Even if they were much higher than could be expected from the concentration of protonic impurities (water, HCl) in these experiments made in sealed apparatus in conditions of high purity, these results could not be considered completely conclusive. A reason of the low yield in carbocations formed through halometalation could be the instability of the organotitanic intermediates giving eventually inactive compounds.

But when $AlCl_3$ in CH_2Cl_2 was used for the direct initiation of DPE at - 30 and -50°C, the yields in carbocations were equal to 50% (ref.15) which was in agreement with the metalation hypothesis

$$AlCl_3 + CH_2 = CPh_2 \rightarrow Cl_2Al\,CH_2\,CPh_2Cl \qquad (3)$$

$$AlCl_3 + Cl_2AlCH_2CPh_2Cl \rightarrow Cl_2AlCH_2\overset{+}{C}Ph_2,AlCl_4^- \qquad (4)$$

A comparative study was made with the addition of water as cocatalyst, and initiation was much more rapid in that case (ref.16). This explains why direct initiation can generally be shown only in the absence of protonic initiation and is generally kinetically negligible when the reagents are not highly purified and in the absence of proton traps.

Another hypothesis for the direct initiation mechanism of isobutylene was that of P.H. Plesch who proposed that it resulted from the autoionization of $AlBr_3$ or $TiCl_4$ (ref.17)

$$2\,AlBr_3 \rightleftarrows \overset{+}{AlBr_2} + AlBr_4- \qquad (5)$$

$$2\,TiCl_4 \rightleftarrows TiCl_3^+ + TiCl_5^- \qquad (6)$$

Addition of $AlBr_2^+$ or $TiCl_3^+$ to the monomer would give the same final product as halometalation.

Autoionization of $AlBr_3$ explaining the initiation of isobutylene in heptane solution had been proposed earlier by Marek et al. (ref.18). They also found that while $TiCl_4$ alone was inactive, the addition of $AlBr_3$ led to rapid polymerization, attributed to the higher ionization resulting from the presence of two Lewis acids of different strengths. But in a non polar solvent, halometalation seems more likely than autoionization , and this is also the case for polymerization by condensation of isobutylene (ref.11) (and later of other monomers) observed by Chéradame and myself.

The demonstration of the occurrence of direct initiation has been made by R. Faust for the polymerization of isobutylene initiated by BCl_3, (ref.19,20) and more recently for that of α-methylstyrene initated with BI_3 or BBr_3 (ref.21).This was made possible by the addition of 2,6-di-*tert*-butylpyridine (DBP) acting as a proton trap.

With BCl_3, large concentrations had to be used (e.g. $[BCl_3]= 0{,}51$ for $[IB] = 0{,}95$ and $[DBP] = 5.10^{-3}\ mol{\cdot}l^{-1}$) for reactions at -35°C in CH_2Cl_2, in CH_3Cl or in CH_2ClCH_2Cl.With the solvent mixture CH_2Cl_2/hexane (60/40 by vol) the polymer was not formed, showing the importance of the solvent polarity. Polymerization is slow and shows auto acceleration, in agreement with a regular increase of active sites concentration. The rate increases with BCl_3 concentration but the $\overline{Mn}$ are similar at similar conversion and remain low (~3 000- 4 000) for complete conversion. From a comparison of the two schemes, autoionization and haloboration followed by BCl_3 coinitiation, it was concluded that the second one only is in agreement with the effect of $[BCl_3]$ on the rate (ref.20).

The haloboration rate (as well as the global polymerization rate) was found much slower in CH_3Cl than in CH_2Cl_2. This is similar to the observation of Masure (ref.22) for the reaction of DPE with $AlCl_3$ (which gave however the same final yields in carbocations : $1C^+$ for $2AlCl_3$) and may be attributed to a stronger solvation of BCl_3 and $AlCl_3$ by CH_3Cl.

Due to the relatively low mol.wts of the polyisobutylene, the presence of-$C(CH_3)_2Cl$ end groups could be determined by ^1H NMR and the concentration of $-B(OCH_3)_2$ end-groups (after methanolysis of BCl_2) by ^{11}B NMR and by elemental analysis.

It may be mentioned that direct initiation of DPE by BCl_3 attempted earlier (ref.22) was not successful because the concentrations of BCl_3 used ($3{,}6.10^{-3} mol{\cdot}l^{-1}$ for [DPE] : $3{,}8.10^{-2} mol{\cdot}l^{-1}$) were too low : only a very small amount of carbocations were formed, not distinguishable from possible cocatalysis by water. However, using a larger concentration of BCl_3 ($0{,}13 mol{\cdot}l^{-1}$) and working in high purity conditions, Bui et al. (ref.23) had concluded that direct initiation of isobutylene did occur.

Recently, evidence for initiation by haloboration has been given by Faust in the case of α-methylstyrene in CH_2Cl_2 initiated by BBr_3 and BI_3(ref.21) with much lower concentrations than with BCl_3. With BI_3 ($5.10^{-3} mol{\cdot}l^{-1}$) and α-methylstyrene ($0{,}35 mol\ l^{-1}$) in the presence of DBP ($3.10^{-3} mol{\cdot}l^{-1}$) at - 80°C, complete conversion and $\overline{Mw}/\overline{Mn} \sim 1{,}1$ were obtained in 4 mn, and the $\overline{Mn} \sim 25\ 000$ was in agreement with the theoretical value (20 300), as well as with the boron content (also for lower mol. wts). At higher temperature (-60 and -40°C) the yields were much lower resulting from termination reactions. With BBr_3 in CH_3Cl at-80°C,initiation was slower and higher mol wts were obtained.

Direct halometalation of the double bond (as in equation 3) is probably not the only possible mechanism for direct initiation by Friedel Crafts acids. In chlorinated solvents, self-ionization might occur particularly when the equilibrium of ionization (equations 5 or 6) is established before monomer addition . In heptane, direct initiation of DPE was not observed with $AlBr_3$ + $TiCl_4$, and the acceleration of IB polymerization with the two initiators was better explained by protonic initiation and an increase in the propagation rate (ref.9,24). However, coinitiation involving $FeCl_3$ (together with BCl_3 or $TiCl_4$) might proceed as suggested by Marek et al (ref.25) by electron transfer to $FeCl_2^+$ giving a monomeric cation radical.

One problem for which very little information is available is that of the relative importance of direct initiation and of initiation involving conventional organic cationogens (halides, etc...) or proton donors. In the case of DPE with $AlCl_3$ in CH_2Cl_2 (at - 30° and -50°C) initiation by water was much more rapid than direct initiation (ref.15) and HCl was not an initiator (ref.16).Similar conclusions about these two initiators were reached by Kennedy et al.(ref.26) for polymerizations of IB coinitiated by BCl_3 in CH_2Cl_2. H_2O was an initiator, and HCl addition did not increase the yields (of only a few % at - 50°C) and increased them only slightly at - 78°C. It may be understood why the proofs for direct initiation were more easily obtained with $AlCl_3$ and BCl_3 because cocatalysis by HCl is inefficient while with e.g. $SnCl_4$ or $TiCl_4$, it is generally a good initiator (ref.9). From the data observed with BCl_3, it may be concluded that a possible contribution of direct initiation is strongly dependent on the Lewis acid concentration. But more reactive F-C acids (BI_3, $AlCl_3$, $TiCl_4$, $SbCl_5$) may be efficient at much lower concentration than BCl_3 and no comparative data with known concentration of e.g.water are available.

APPARENTLY NEGATIVE ACTIVATION ENERGIES (ANAE)

The observation of a strong increase in polymerization rate with a lowering of temperature has been made in many examples of carbocationic polymerization as may be seen on the next Table Contrarily to the few examples known in anionic polymerization, apparently negative activation energies were observed in a range of temperatures as large as 60°C.

In a first series of experiments, all with $TiCl_4$ as coinitiator, ANAE were based on the variation of the initial apparent rate constant k_1 = Rpo/[M]o with 1/T and were of the order of -8 kcal · mol^{-1} for styrene type monomers and - 2,5 for isobutylene (ref.27-30).

In the second series of experiments, propagation rate constants kp could be determined by measuring simultaneously the polymerization rate (by calorimetry) and the initiation rate (by UV spectrophotometry, for cyclopentadiene and p-methoxystyrene)(ref.31,32). The activation energy for initiation was high and positive, and that for termination was very low.

The third series of experiments is relative to <u>living carbocationic polymerizations</u> which were initiated by cumyl derivatives and $TiCl_4$, sometimes with addition of an electron donor (ref.34-37).

For the first series of experiments, two main schemes were considered as an explanation for the ANAE of the global polymerization rate constant.

One was the establishment of a quasi stationary state for the active species with rapid unimolecular termination (ref.29). This leads to a global apparent rate constant $kg=\frac{kikp}{kt}$ and to Eg = Ei +Ep - Et. Eg could be negative if Et > Ei+Ep, but it is now known that Et is very small and much lower than Ei...

The other explanation was a shift in the equilibrium between paired and unpaired ions favouring the much more reactive unpaired ones when temperature is lowered (ref.28,31). But it is now known that their difference in reactivity is small and this explanation is also not acceptable.

For the second series of ANAE corresponding to apparent propagation rate constants kpapp, the dissociation equilibrium was also considered, but when it was found that for p-MeOstyrene kp+/kp$\pm$ = 4 only, another suggestion was the occurrence of a solvation equilibrium with the monomer before its incorporation (ref.32)

$$M_n^+ + M \overset{Ks}{\rightleftharpoons} M_n^+,M \xrightarrow{kp} M_{n+1}^+$$

This may lead to kpapp ~kp Ks and to $E_{papp} = Ep^+ + \Delta Hs$ = -6 kcal mol^{-1}. Ep^+in CH_2Cl_2 is known to be very small (near zero) (ref.38) and this would be compatible with $\Delta Hs \sim$-6kcal·mol^{-1}.

APPARENTLY NEGATIVE ACTIVATION ENERGIES (ANAE) IN CARBOCATIONIC POLYMERIZATIONS a)

Monomer	Initiator	ANAE (kcal·mol^{-1})	Temperature range (°C)	Authors
Styrene*	$TiCl_4$ + ?	-8,5	-30 to + 10	Plesch (1953)
Isobutylene	$TiCl_4 + H_2O$	-2,5	-60 to - 30	Biddulph et al(1965)
Indene	$TiCl_4$ + ?	-8.3	-50 to + 10	Nguyen et al (1973)
α-methylstyrene	$TiCl_4$ + ?	-9	-40 to + 10	Bourne-Branchu et al (1976)

Monomer	Initiator	ANAE (kcal·mol^{-1}	Temperature range (°C)	Authors
Cyclopentadiene	$Ph_3C^+,SbCl^-_6$	-8	- 50 to + 10	Sauvet et al (1974)
p-methoxystyrene	$Ph_3C^+,SbCl^-_6$	-6	- 15 to + 25	Cotrel et al (1976)
α-methylstyrene	$TiCl_3OBu+H_2O$	-7	- 70 to - 30	Villesange et al (1977)

Monomer	Initiator	Polar additive	ANAE (kcal·mol^{-1})	Temperature range (°C)	Authors
Isobutylene**	bis-cumyl chloride + $TiCl_4$	pyridine	-8,5	- 80 to -50	Storey et al (1992)
Isobutylene**	bis-cumyl chloride+ $TiCl_4$	2,4-dimethyl pyridine	-8,2	- 80 to -30	Storey et al (1995)
Indene	cumyl methylether +$TiCl_4$	-	-3,3	- 60 to 0	Thomas et al (1992)
Indene	cumylchloride +$TiCl_4$	DMSO	-4,3	- 40 to-20	Thomas et al (1995)

a) Solvent, CH_2Cl_2 except for*: CH_2ClCH_2Cl and** : CH_3Cl/hexane (40/60 by vol)

The main difficulties in the interpretation of these two first series of ANAE were either that there was no evidence (e.g. in the first series) that the yield in carbocations was the same at various temperatures, or that initiation was known to be slow (and incomplete). This last situation occurred for the two polymerizations initiated by $Ph_3C^+,SbCl_6^-$, and various objections about the assumptions made in order to calculate the apparent kp have been made by P.H. Plesch (ref.39) and by M. Szwarc (ref.40) and I think some of them are probably valid. I have not the time to discuss them here, but my provisional conclusion is that no complete and satisfactory explanation has been given yet, and this is true also for those we proposed at that time. For example, the explanation based on solvation of carbocations by p-MeOstyrene does not seem satisfactory since more recent data obtained using CF_3SO_3H as initiator have led to a positive global activation energy (Eg = +2 kcal·mol^{-1}). To be compatible with the solvation hypothesis, the Ep with this initiator should be much higher (~+8kcal·mol^{-1}).

The possibilities of determining reliable kp app are in principle much better since the discovery of various "living" carbocationic polymerizations by the groups of T. Higashimura and J.P. Kennedy (ref.2,3,4). Kinetic studies have been limited, but 1st order in [M] after the initiation period was generally verified, showing that a constant number of active sites is present, equally distributed on all macromolecules (the number of which is equal to $[I]_o$).

Even if the exact nature of active species is still under discussion, it is now generally agreed that they are ionic species in equilibrium (constant Ki) with inactive terminal end-groups (such as halides) through a reversible ionization ("reversible termination"), the ion-pairs being dissociated in polar solvents (dissociation constant K_D)

$$RM_nX + M_tX_n \underset{I}{\overset{Ki}{\rightleftharpoons}} RM_n^+,M_tX_{n+1}^- \underset{II}{\overset{K_D}{\rightleftharpoons}} RM_n^+ + M_tX_{n+1}^- \qquad (7)$$

After initiation is completed, the constant number of active species is determined by Ki and K_D, and this eliminates the possibility that the ANAE would result from an effect of temperature on the initiation yield or from the activation energy of a definitive termination. It may be seen however in Table 1 that ANAE were observed in the 4 last examples given.

With isobutylene in the solvent mixture (60 hexane/40 CH_2Cl_2) initiated by a cumyl chloride activated by $TiCl_4$, the ANAE is equal to -8,5 kcal·mol^{-1} in the presence of pyridine ([Py]=[RCl]) (ref.34) and-8,2 kcal·mol^{-1} with dimethyl pyridine (ref.35).

With indene in CH_2Cl_2, with cumyl chloride and $TiCl_4$ in the presence of DMSO , Eg is equal to -4,3 kcal·mol^{-1}. With cumylmethyl ether as initiator, the addition of an electron donor was not necessary in order to observe complete initiation between -60 and 0°C, and Eg = -3,2kcal·mol^{-1} (ref.36,37). The explanation proposed was that the apparently negative activation energy is resulting from the increased ionization at lower temperature of the inactive covalent species into ionic species.

General discussion of the apparently negative activation energies.

We have seen that for conventional systems the hypothesis of the establishment of a quasi stationary state was not satisfactory. It is still less so in the case of polymerization with reversible termination. Solvation of carbocations by monomer for all propagation steps, which did not seem satisfactory for p-methoxystyrene, is still less likely with monomers without donor groups.

The displacement of the dissociation equilibrium of ion-pairs towards free ions may eventually be a contribution to ANAE since dissociation is exothermic, but the values of ΔH_D for known systems are only between -1 and -2kcal·mol^{-1}and too low to explain the ANAE (ref.41). Moreover, the difference in reactivity between paired and unpaired ions is too small.

But a similar origin for the ANAE may be considered in both conventional and living systems as long as initiation is completed rapidly in both cases, and if both equilibrium I(between inactive end-groups and ion-pairs) and equilibrium II (between ion-pairs and unpaired ions) in equation (7) are established rapidly.

We may consider two limit cases. If the ion-pairs contribution is predominant

$$k_{papp} = k_{p^{\pm}} \cdot K_i.$$

and the global activation energy for propagation

$$Eg = Ep^{\pm} + \Delta H_i$$

If unpaired ions contribution is predominant (this is the case for very low ionization : the low concentration of ion-pairs formed is then completely dissociated ; BIE of P.H. Plesch) (ref.42)

$$k_{papp} = k_{p^{+}} K_i K_D$$

$$\text{and } Eg = Ep^{+} + \Delta H_i + \Delta H_D$$

The observation of an ANAE may result in the first case from the negative value of ΔH_i if $|\Delta H_i|>|Ep^{\pm}|$and in the second case from those of ΔH_i and ΔH_D if $|\Delta H_i|+|\Delta H_D|>|Ep^{+}|$.

Ep^{+} have been estimated to be very low (between 0 and 2kcal·mol^{-1}) for various radiation-induced carbocationic polymerizations (cyclopentadiene, IB, styrene, α-methylstyrene...) and for the polymerization of styrene in CH_2Cl_2 initiated by $HClO_4$ (Ep^{+}~1kcal·mol^{-1} ; $Ep^{\pm}$~3kcal·mol^{-1}(ref.39)). But unfortunately, the Ep^{+} and $Ep^{\pm}$ in CH_2Cl_2 (or other halides) are not known for most polymerization systems.

Are the known values of ΔH_i compatible with the observed ANAE values (see table1) between -3 and -9kcal·mol^{-1} ?

For model p-substituted diphenylmethyl chlorides ionized by BCl_3 in CH_2Cl_2, ΔH_i obtained by calorimetry varied from -7,8 for the CH_3 to -11,8kcal·mol^{-1} for the OCH_3 substituent (ref.43).

These values are compatible with those obtained for the same compounds by direct measurement of carbocations concentrations by UV absorption, for the bi-ionogenic equilibrium giving unpaired ions, e.g.

$$\Delta H_i + \Delta H_D = -10.8\text{kcal·mol}^{-1} \text{ for } (CH_3Ph)_2\ CHCl \text{ with } BCl_3 \text{ (ref.42)}$$

There are unfortunately much less data for the formation of more localized carbocations similar to propagating species of IB or styrene. However, ΔH_i =-3,7kcal·mol^{-1} for tert-butylchloride and -4,5 kcal mol^{-1}for cumyl chloride, both ionized by SbF_5 in CH_2Cl_2 at -55°C (ref.44). It seems then that known values of ΔH_i and ΔH_D may be compatible with ANAE values up to -8kcal·mol^{-1} if the activation energies Ep^{+} and $Ep^{\pm}$ for the propagation steps are low.

What is not obvious and is not easily explained are the differences in ANAE with the same monomer (e.g. indene) and the same coinitiator ($TiCl_4$) for conventional polymerizations (with $TiCl_4$"alone") and for the living ones. This might result in the first case from a decrease in the initiation yield at higher temperatures resulting from a rapid termination competitive with initiation, or from different values of Ki with the different type of counterion formed when H_2O is the initiator.

Another large difference in ANAE was observed for a similar initiation (by $TiCl_4$ and presumably H_2O) with a change in monomer : -2,5 for IB ; ~ -8kcal·mol^{-1} for styrene (S), α-methyl styrene (αMS) and indene.

This may result from differences in both Ep^+ and ΔH_i. The latter is expected to be more negative for the more delocalized S^+ cation than for the IB^+ one, while Ep^+ may be larger with IB^+ if it is more strongly solvated by CH_2Cl_2 than S^+. If $Ep^+ \sim +2$kcal·mol^{-1} for S and + 5 for IB, with $\Delta H_i + \Delta H_D \sim -10$kcal·mol^{-1} for S and -7 for IB, this may lead to the observed values of Eg : -2 for IB and -8kcal·mol^{-1} for S.

For polymerizations in which Lewis bases were added (pyridine, 2,4-di Me pyridine, DMSO) the interpretation of the values of the ANAE is more difficult since equilibria I and II in equation (7) are modified, as they may complex with both the F-C. acid (displacing them towards the left) and with the dissociated carbocations (displacing them to the right).

In conclusion, it seems that an ionization equilibrium favoured at low temperatures may explain the occurrence of apparently negative activation energies in both "living" and conventional carbocationic polymerizations, for reactions in which initiation is completed rapidly and ionization and dissociation equilibria rapidly established. But a complete explanation of this effect will need more data about ΔH_i (based if possible on direct observation of carbocations concentration) and of the activation energies for propagation on paired and unpaired ions in simple real polymerization systems.

ROLE OF HINDERED PYRIDINES AND OF OTHER ELECTRON DONORS

There are both analogies and differences in the effect of the addition in carbocationic polymerizations of hindered bases (proton traps such as di-tert-butylpyridine, DBP, or its methyl derivative DBMP), or of other polar additives ("electron donors" ED such as pyridines, DMA,DMSO, esters...).

In conventional polymerization such as that of α-methyl styrene (α-MS), initiated by addition of F-C acids "alone" in CH_2Cl_2 at - 30°C and below, the presence of DBP (or of DBMP)led to a decrease in the yield and to a narrowing of the mol.wt distribution resulting from the suppression of a lower mol.wt fraction. This was observed for initiation by BCl_3 (ref.45) or by $TiCl_4$ (ref.46) or $SnCl_4$ (ref.47) alone, but the interpretation of the two groups were different, even if they both admitted an absence of interaction of these crowded bases with the F-C acids and with carbocationic species. Kennedy et al.(ref.45) concluded that DBP acted as a proton-trap for protons resulting from transfer of zero order in [M] ("spontaneous transfer"), while Chéradame and Gandini (ref.46) considered that the base only inhibited "cocatalyzed" initiation (by water) but did not interfere with direct initiation.

The observations we made at the same time (ref.48,49) for the chain dimerization of 1,1-diphenylethylene (DPE) initiated by $AlCl_3$ alone or by $AlCl_3 + H_2O$ led to different conclusions, based on the quantitative measurement of carbocations C^+ by UV spectrophotometry and on NMR data. DBMP gives complexes with $AlCl_3$ (with Ke = 10^3 at -30°C, while those with $TiCl_4$ were not detected) (ref.49) and when DBMP was present beforehand in the $AlCl_3$ solution

([DBMP]/[Al]=0,25) cocatalyzed initiation by H_2O was not inhibited. But when direct initiation was completed (complete consumption of $AlCl_3$), DBMP addition led to the immediate destruction of the corresponding amount of C^+. However, when excess $AlCl_3$ was still present, the destruction of C^+ was much slower showing that the complexed base is much less reactive than the free base. A much better stability of carbocations resulting from initiation with water was also observed, which was attributed to the difference in the types of counter-ions. These data led to a different interpretation of the results of the former authors (ref.9, 49) which it would be too long to reproduce here.

A difficulty in reaching a simple conclusion is that the described results involved different Friedel-Crafts acids, but the possibility of direct initiation in the various cases may be discussed. It may seem unlikely with $SnCl_4$ and BCl_3 at the concentrations used, but direct initiation of α-methylstyrene by $TiCl_4$ at -70°C might look possible. However, since the suppressed polymer had a much <u>lower</u> mol.wt than the remaining one it is difficult to believe that it was resulting from cocatalyzed initiation and it seems more likely that it was formed by spontaneous transfer, suppressed by DBP as suggested by Kennedy et al.(ref.50). This would lead to the conclusion that a certain type of initiation involving water is not inhibited by the proton trap and may result from a concerted mechanism .

It would be too long to discuss the many results obtained for polymerizations of IB in the presence of DBP, mainly observed with BCl_3+CumCl or with $AlCl_3$ "alone". There was a strong decrease in both the yields and the $\overline{Mn}$ for increasing DBP concentration, which are better explained by a progressive suppression of initiation by proton donors than by proton entrapment after transfer of zero order in [M]. But the residual conversions still observed for the highest DBP concentration (ref.50) might also result from concerted initiation involving H_2O and giving more stable active species.

"Living" carbocationic polymerizations of isobutylene, styrene, and substituted styrenes were decribed by R. Faust and J.P. Kennedy (ref.3,4) and demonstrated by the linear increase at-30°C of $\overline{Mn}$ versus the amount of polymer formed ($\overline{Mn}$ lin) up to e.g. 10^4 for IB and 2.10^4 forp-Me styrene, with $\overline{Mw}/\overline{Mn}\sim 2$. No polar additive was present, but in the absence of the added initiator (tertiary esters, BCl_3 being the coinitiator) much higher mol. wts and low yields were obtained, attributed to non living polymerization resulting from protic initiation. A narrowing of the mol. wt distribution could be obtained either by using less polar solvent mixtures (hexane and CH_2Cl_2 or CH_3Cl) or by adding electron pair donors such as ethylacetate, DMSO or DMA.

In all these systems, the linearity of the $\overline{Mn}$ with conversion as well as the mol wt narrowing were assumed to result from a stabilization of the reactive cationic species leading to the suppression of transfer and termination reactions. (ref.51) This was explained by the formation of stabilized active species (ion pairs ?) such as

$$-CH_2C(CH_3)_2^+ \ldots [DMSO,nBCl_3] \ldots BCl_4^-$$

In the absence of added donor, with e.g CumOMe and $TiCl_4$, stabilization would involve an "internal" electron donor formed in situ (CH_3OTiCl_3 or $CH_3CO_2TiCl_3$) (ref. 52). But if propagation and transfer occur on the same species, a reduction of the relative amount of transfer (of k_{trM}/k_p and k_{tr}/k_p) for the same yield is not easily explained.

The explanation of $\overline{Mn}$ lin and of the assumed absence of transfer and termination reactions either by a propagation on non-ionic species or by a stabilization of the ionic propagating species has been challenged(ref.53). It was pointed out that there was no evidence for a reduction of the transfer reactions in these "apparently living" systems. In fact, the mol wts (with similar coinitiator) in "non living" systems have been generally much higher, which may result from the lower initiator concentration. The best way to decrease transfer is still a lowering of the temperature . The two main characteristics of these living systems were considered to be a favourable Ri/Rp ratio permitting a complete initiation (and the obtention of theoretical mol. wts) and the absence of definitive termination, with reversible deactivation of the ionic active sites which permit a narrowing of the mol. wt distribution if the exchange is fast enough.

We have shown later that in the polymerization of indene at -40°C in CH_2Cl_2, $\overline{Mn}$ lin was observed up to 4.10^4 using as initiator either CumOMe/$TiCl_4$ (ref.36) or CumCl/$TiCl_4$/DMSO (ref.37). The values of k_{trM}/k_p were similar and did not change significantly when DMSO was absent . However, the addition of DMSO ([DMSO]o/[I]o = 0,55) with CumCl led to a (moderate) decrease of the propagation rate and to an increase of the initiation rate, permitting complete initiation in about 1 sec.

The situation with IB is not as clear since no attempts have been made at the determination of transfer constants (k_{trM}/k_p and k_{tr}/k_p) in "living" systems in which pyridine derivatives were added. It was shown however by Kennedy et al.(ref.54) that the addition of DBP or that of various ED (pyridine, *tert* -amines, DMA...) to IB polymerization initiated by TMPCl/$TiCl_4$ at -40°C had very similar effects on the narrowing of mol wt distributions and it was concluded that this resulted from proton trapping by the $TiCl_4$-ED complexes or by DBP. DBP and most ED (except the trialkylamines) gave insoluble complexes with $TiCl_4$. $\overline{Mn}$ lin was observed (with [pyridine]/[$TiCl_4$]=1) even with the IMA technique, but pyridine in excess stopped the polymerization. Faust et al reached similar conclusions for the effect of DBP when initiator was TMPOAc/BCl_3.

There is now little doubt that DBP and some ED may inhibit at least part of the initiation by proton donors. But some initiation involving H_2O in a concerted process still cannot be excluded, as well as terminative proton entrapment by DBP(following the transfer of zero order in [M]). The latter may explain the results of Gyor et al (ref.55) for IB polymerization initiated by bis-cumylmethylethers and $TiCl_4$ in CH_3Cl/hexane at -80°C.The observations made for IMA experiments were a strong deviation from $\overline{Mn}$lin above 3.10^4 in the absence of DBP, linearity up to 9.10^4 in the presence of 10^{-3} mol·l^{-1} of DBP ($TiCl_4$: $3,6.10^{-2}$ mol·l^{-1})but not for [DBP] = 5.10^4 mol·l^{-1}. This might have resulted from a trapping of the eliminated proton before initiation of a new polymer chain. Similar results ($\overline{Mn}$ lin→9.10^4 for AMI with DBP addition) were obtained with a dicumylchloride initiator at -80°C. The authors concluded that the living nature of the reaction was not due to carbocation stabilization since the rates with both types of initiators did not change with the addition of increasing amounts of DBP.

The same conclusions were reached in the case of styrene initiated by TMPCl or dicumylmethylether with $TiCl_4$ at -80°C, since the rate did not change significantly for a large increase in [DBP] (ref 56). Its presence however suppressed initiation by proton donors since in the absence of added initiator (only $TiCl_4$ present : $3{,}6.10^{-2}$ mol·l $^{-1}$), DBP addition led to a strong decrease of the rate. But a slower polymerization still subsisted for DBP $\geq 4.10^{-3}$ mol·l^{-1} which was attributed to direct initiation.

Since the theoretical $\overline{Mn}$ and small values of $\overline{Mw}/\overline{Mn}$ were observed as well when the initiator was an ether or an halide (they were even better in this last case) the beneficial effect of an " in situ formed ED" (i.e.$TiCl_3OBu$) was disputed. The apparent decrease of the transfer reactions in the presence of DBP was attributed to the suppression of an "induced chain transfer" resulting from the presence of e.g.HCl in its absence.

This interpretation by Gyor et al (ref.55) of the $\overline{Mn}$lin observed in presence of DBP has been challenged by Ivan et al (ref.57) who considered that the stability of polymer end-groups which they observed at-78°C after complete monomer consumption could not be explained if the active chain ends were in equilibrium with "classical" ion-pairs or with free cations, because proton expulsion was expected. In fact, this happened with the more basic DBP but not with pyridine and DMA (ref.57). Ivan (ref.58) has also pointed out that if the $\overline{Mn}$lin observed in the presence of pyridines resulted only from the trapping of protons-formed by spontaneous transfer- a decrease in the carbocations concentration and in the rate should have been observed, which was not the case for initiation by ethers. But with the cumylchlorides a decrease in the rate of 20-30% was in fact observed after 20 mn when DBP was added.

It should be acknowledged that the similar effects of the addition of e.g. pyridine (Py) and hindered pyridine (DBP) have not received yet a completely satisfactory explanation.

If their complexation with the carbocations leads to their stabilization, the reduction in the acidity of the β–hydrogens responsible for transfer may be compensated by a corresponding decrease in kp, without modification of transfer for the same yield. A satisfactory explanation for the narrowing of the mol wts. and for an eventual decrease of transfer would be the suppression of one type of active species, if the remaining one exchanges very rapidly with the dormant species. For example, it has been suggested that the suppression of unpaired ions could result from the formation with the scavenged proton donors (in relatively large amount in these experiments) of pyridinium salts of complex anions (e.g. $M_tX_nOH^-$ or $M_{t2}X_{2(n-1)}O^-$) which would displace equilibrium II (equation 7) towards the left. Moreover, it is well known that k_{trM}/k_p values vary widely with the type of counter ion (ref.53). The independence of kpapp on initiator concentration when pyridine was present (ref.34) has been given as an argument for a propagation involving a single type of active species, namely ion pairs. But there is no evidence that $k_{trM}{}^{+}/k_p{}^{+}$ is larger than $k_{trM}{}^{\pm}/k_p{}^{\pm}$. On the contrary, it is known that the highest mol wts for polyisobutylene have been obtained for γ rays initiated polymerization in bulk which occurs on unpaired ions (ref.59). But there are no comparative data for reactions in chlorinated solvents.

An alternative explanation could be that propagation is occurring only on unpaired ions. Since the concentration of active ionic species is extremely low with IB in these systems, the complete dissociation of ion-pairs is quite likely.

$$RM_nCl + TiCl_4 \xrightleftharpoons{K_iK_D} RM_n^+ + Ti_2Cl_9^- + Py \xrightleftharpoons{K_{Py}} RM_nPy^+ + Ti_2Cl_9^-$$

The equilibria are not completely displaced towards $RMnPy^+$ because $[Py] << [TiCl_4]$, and moreover, the latter also gives a complex with Py. Propagation might occur only on a small amount of uncomplexed ions RMn^+. This would be similar to what was shown for the polymerisation of vinyl ethers in the presence of less nucleophilic Lewis bases in large excess (ref.7).

In conclusion, the question which should be answered first is that of the real occurrence (or not) of a decrease of transfer in these systems on the addition of the Lewis bases.

Direct determinaion of k_{trM}/k_p is possible by working at higher temperatures for which a deviation of linearity of $\overline{M}n$ lin is observed (ref.36,37).It is known that for e.g IB, transfer is negligible at -80°C in conventional systems (ref.53) (e.g. with $TiCl_4$ "alone", a value of $k_{trM}/k_p = 3.10^{-5}$ has been found at -48°C, and it should be $<10^{-5}$ at -80°C (ref.28), but there are no reliable data on k_{tr}/k_p).

If the decrease is real, this may result from the absence of ion-pairs if $k_{tr}^+/k_p^+ < k_{tr}^\pm/k_p^\pm$, as proposed above for Py addition. In the case of DBP addition, the existence of a strong complex with carbocations may a priori look unlikely. However, Dembinski et al. (ref. 60) showed a rapid deactivation of photochemically produced unpaired vinyl carbocations (sterically hindered...) with DBP and DBMP, which might result from the formation of a complex.

If there is no significant decrease in the tranfer constants, the general and simple explanation (ref.5) for the narrowing of the mol wt distribution would be a salt effect leading to a propagation on only ion-pairs.

REFERENCES

1) P. Sigwalt, Introductory lecture to the 1st International Symposium on Cationic Polymerization, Rouen (1973) ; *Makromol. Chem.* **175,** 1017 (1974)
2) T. Higashimura,M. Miyamoto, M. Sawamoto, *Macromolecules* **17,** 265 ; ibid **17**, 2228 (1984)
3) R. Faust, J.P. Kennedy, *Polym. Bull.* **15**, 317 (1986)
4) J.P. Kennedy, B. Ivan, *Designed Polymers by Carbocationic Macromolecular Engineering*, Hanser, München (1992)
5) K. Matyjaszewski, P. Sigwalt, *Polym. Int.* **35**,1 (1994)
6) P. Sigwalt, "*Carbocationic polymerization*" in *Encyclopedia of Advanced Materials*, Pergamon (1994), p. 328.

7) *Cationic Polymerizations*, ed by K. Matyjaszewski, Marcel Dekker (1996)

8) J.P. Kennedy, E. Maréchal, *J. Polym. Sci., Macromol. Rev.* **16**,123 (1981)

9) G. Sauvet, P. Sigwalt, *Comprehensive Polymer Science*, Pergamon Press (1989)Vol III, chapter 39 p. 579

10) W.H. Hunter, R.V. Yohe, *J. Am. Chem. Soc.* **55**,1248 (1933)

11) H. Chéradame, P. Sigwalt, *Bull. Soc. Chim. Fr.* 843 (1970)

12) G. A. Olah, *Makromol. Chem..* **175**, 1039 (1974)

13) G. Sauvet, J.P. Vairon, P. Sigwalt, *J. Polym. Sci., Polym. Symp.* N° **52**, 173 (1973)

14) G. Sauvet, J.P. Vairon, P. Sigwalt, *J. Polym. Sci., Polym. Chem. Ed.* **16**, 3047 (1978)

15) M. Masure, G. Sauvet, P. Sigwalt, *J. Polym. Sci., Polym. Chem.* Ed. **16**, 3065 (1978)

16) M. Masure, G. Sauvet, P. Sigwalt, *Polym. Bull.* **2**, 699 (1980)

17) P. Plesch, *Makromol. Chem.* **175**, 1065 (1974)

18) M. Marek, M. Chmelir, *J. Polym. Sci., Part C* **23**, 223 (1968)

19) L. Balogh, L. Wang, R. Faust, *Macromolecules* **27**, 3453 (1994)

20) L. Balogh, Z. Fodor, T. Kelen, R. Faust, *Macromolecules* **27**, 4648 (1994)

21) B. Koroskenyi, L. Wang, R. Faust, to be published.

22) M. Masure, P. Sigwalt, unpublished data, see also ref.9

23) C. Bui, H.A. Nguyen, E. Maréchal, *Polym. Bull.* **17**, 157 (1987)

24) M. Masure, Nguyen A.H., G. Sauvet, P. Sigwalt, *Makromol. Chem.* **182**, 2695 (1981)

25) M. Marek, J. Pesch, V. Halaska, *Makromol. Chem., Macromol. Symp.* **13-14**, 443 (1988)

26) J.P. Kennedy, F.J.Y. Chen, *Polym. Bull.* **15**, 201 (1986)

27) P.H. Plesch, *J. Chem. Soc.* 1653 (1953)

28) R.H.Biddulph, P.H. Plesch and P.P. Rutherford, *J. Chem. Soc.* 275 (1965)

29) Nguyen Anh Hung, H. Cheradame, P. Sigwalt, *Eur. Polym. J.* **9**, 385 (1973)

30) R. Bourne-Branchu, Nguyen A.H.H. Chéradame, *Bull. Soc. Chim. Fr.* 1349 (1976)

31) G. Sauvet, J.P. Vairon, P. Sigwalt, *Eur. Polym. J.* **10**, 501 (1974),

32) R. Cotrel, G. Sauvet, J.P. Vairon, P. Sigwalt, *Macromolecules* **9**, 931 (1976)

33) M. Villesange, G. Sauvet, J.P. Vairon, P. Sigwalt, *J. Macromol. Sci. - Chem.* **A11**, 391 (1977)

34) R.F. Storey, B.J. Chisholm, L.B. Buster, *Macromolecules* **28**, 4055 (1995)

35) R.F. Storey, K.M. Choate, *Polym.Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **35** [2], 506 (1994)

36) L. Thomas, A. Polton, M. Tardi, P. Sigwalt, *Macromolecules* **25**, 5886 (1992)

37) L. Thomas, A. Polton, M. Tardi, P. Sigwalt, *Macromolecules* **26**, 4075 (1993) ; **28**, 2105 (1995)

38) A. Deffieux, D. R. Squire and V. Stannett, *Polym. Bull.* **2**, 469 (1980)

39) P.H. Plesch, *Prog. React. Kinet.* **18**, 1 (1993)

40) M. Szwarc, *Ionic Polymerization Fundamentals,* Hanser, Munich (1996)

41) K. Matyjaszewski, C. Pugh, Ch 3 in *Cationic Polymerizations* (see table 12) p. 184

42) R. Schneider, H. Mayr, P.H. Plesch, *Ber. Bunsenges. Phys. Chem.* **91**, 1369, (1987)

43) C. Schade, H. Mayr, E.M. Arnett, *J. Am. Chem. Soc.* **110**, 567 (1988)

44) E.M. Arnett, C. Petro, *J. Am. Chem. Soc.* **100,** 5408 (1978)

45) J.P. Kennedy, R.T. Chou, *J. Macromol. Sci.- Chem.* **A 18**, 17 ; ibid **A 18**, 47 (1982)

46) J.M. Moulis, J. Collomb, A. Gandini, H. Chéradame, *Polym. Bull.*3, 197 (1980)

47) A. Gandini, A. Martinez, *Makromol. Chem., Macromol. Symp.* **13/14**, 211 (1988)

48) M. Masure, G. Sauvet, P. Sigwalt, *Polym. Bull.* **2**, 699 (1980)

49) M. Masure, P. Sigwalt, G. Sauvet, *Macromol. Chem., Rapid Commun.* **4**, 269 (1983)

50) S.C. Couhaniyogi, J.P. Kennedy, W.M. Ferry, *J. Macromol. Sci.-Chem.* **A 18,** 25 (1982)

51 G. Kaszas, J. Puskas, J.P. Kennedy, C.C. Chen, *J. Macromol. Sci.-Chem.* **A 26,** 1099 (1989)

52) G. Kaszas, J.E. Puskas, C. Chen; J.P. Kennedy, *Macromolecules* **23**, 3909 (1990)

53) P. Sigwalt, Lecture at the Internation.Symposium on Cationic Polymerization (Paris 1990) ; *Makromol. Chem., Macromol. Symp.* **47**, 179 (1991)

54) J.P. Kennedy, A. Hayashi, *J. Macromol. Sci.-Chem.* **A 28,** 197 (1991)

55) H. Gyor, H.C. Wang, R. Faust, *J. Macromol.Sci.-Chem.* **A 20**, 639 (1992)

56) Z. Fodor, M. Gyor, H.C. Wang, R. Faust, *J. Macromol. Sci.-Chem.* **A 30**, 349, (1993)

57) D. Held, B. Ivan, A.H.E. Müller, F. de Jong, T. Guafland, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **37** [1] 333 (1996)

58) B. Ivan Lecture to the present Symposium

59) J.P. Kennedy, *Cationic Polymerization of Olefins : a Critical Inventory,* I. Wiley (1975)

60) A. Dembinski, Y. Yagci, W. Schnabel, *Polymer* **34**, 3738 (1993).