lactone) obtained, at total conversion, in benzene at 30 °C with the $ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$ compound ([M]/[C] = 60) is 0.94 dl/g, while after hydrolysis its value falls to 0.53 dl/g.

The coordination of the monomer takes place before every insertion and is probably the rate determining step in the polymerization.

The flip–flop mechanism proposed here explains all of the basic facts described in this study and will also be useful to explain the main characteristics of oxiranes polymerization as described elsewhere.[4,5,11] The implication of two available and vicinal metal atoms in the chain growing process can account for the effect of the association degree of the catalytic coordination aggregates on the polymerization characteristics. Since the catalyst association can be controlled by specific conditions, new ways are opened to control homopolymerization and, as discussed in another paper,[19] block copolymerization processes.

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Kinetic Study of the Cationic Polymerization of p-Methoxystyrene Initiated by Trityl Hexachloroantimonate

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ABSTRACT: The cationic polymerization of *p*-methoxystyrene has been studied between +25 and −15 °C in dichloromethane solution, using a technique allowing the rapid consumption of monomer by calorimetry and initiator (Ph_3C^+, $SbCl_6^-$) concentration by spectrophotometry to be followed simultaneously. First orders with respect to monomer and to initiator were observed for the initiation reaction. An overall second order with respect to monomer was found for polymerization which leads to a first order for the propagation step. A kinetic scheme is proposed and rate constants of the different steps were computed assuming unimolecular termination and transfer to monomer. At +10 °C, values of initiation, propagation, transfer, and termination constants are respectively $k_i = 0.28 \pm 0.05$ M^{-1} s^{-1}, $k_p = 2.8 \pm 0.5\ 10^4$ M^{-1} s^{-1}, $k_{trm} = 53 \pm 16$ M^{-1} s^{-1}, $k_t = 0.08 \pm 0.05$ s^{-1}. Corresponding apparent activation energies were found to be $E_i = 13.3 \pm 0.6$ kcal mol^{-1}, $E_p = -6 \pm 1$ kcal mol^{-1}, $E_{trm} = 5.9 \pm 0.5$ kcal mol^{-1}. No significant variation with temperature was found for the observed low values of k_t, and apparent E_t is probably close to zero, though it was not possible to specify whether it is negative or positive. Negative E_p value may be explained by a shift of the dissociation equilibrium of propagating ion pairs into free ions, accompanied by an exothermic solvation process. An alternative explanation might be the existence of a solvation equilibrium between active species and monomer prior to the propagation step.

In most cases for cationic polymerization of ethylenic monomers the concentration of active centers remains unknown, and it is generally difficult to propose valid kinetic schemes and to determine the rate constants for the different steps of the reaction. This explains the increasing interest for initiation by stable carbocations such as triphenyl methyl carbenium ions for which a simple electrophilic addition on ethylenic double bonds is generally assumed. In addition, the concentration of trityl salts can be followed spectrophotometrically during the course of the polymerization. Kinetic schemes and propagation rate constants have been proposed for the polymerization of some ethylenic monomers, initiated in CH_2Cl_2 by stable carbocations, i.e., *N*-vinylcarbazole (NVC),[1] alkyl vinyl ethers (VE),[2-4] and cyclopentadiene (CPD).[5] In the first two cases (NVC and VE), initiation by tropylium or trityl salts is reported to be complete and rapid, leading to relatively stable active centers which are assumed to be mainly free ions. Thus propagation rate constants, obtained from a rather simple kinetic treatment,[2] are relative to free ions and the corresponding activation energies are positive.

In the case of the polymerization of cyclopentadiene, initiation by trityl salt is slower, important termination processes occur, and a nonstationary state is observed for active centers concentration. The dissociation equilibrium of propagating ends is shifted toward ion pairs on account of the strong salt effect of remaining initiator and a negative apparent activation energy is observed for propagation.

We previously reported preliminary results on the kinetics of *p*-methoxystyrene polymerization initiated by trityl hexachloroantimonate (Ph_3C^+, $SbCl_6^-$) in dichloromethane solution.[6] With the concentrations needed for monomer (10^{-2} to 10^{-1} M) and initiator (2 to 11.10^{-5} M) and the temperature range (−15 to +25 °C), observed polymerization rates were high and monomer consumption was followed by adiabatic

Table I
Initiation, Propagation, and Termination Rate Constants for *p*-Methoxystyrene Polymerization Initiated by $Ph_3C^+SbCl_6^-$ in CH_2Cl_2

T, °C	$\|M\|_0 \times 10^2$, M	$\|I\|_0 \times 10^5$, M	k_i, $M^{-1}\,s^{-1}$	$(k_p + k_{trm})_0 \times 10^{-3}$, $M^{-1}\,s^{-1}$[a]	$(k_p + k_{trm}) \times 10^{-3}$, $M^{-1}\,s^{-1}$[b]	k_t, s^{-1}
+25	4.0	8.6	0.89	12	16	0.08
+10	1.5 to 8	2.5 to 11	0.28 ± 0.05[c]	24 ± 5[c]	28 ± 5[c]	0.08 ± 0.05[c]
−2	4.1	7.2	0.10	30	39	0.07
−15	4.2	6.5	0.03	75	74	0.25

[a] "External" value from eq 4. [b] "Internal" value from eq 5. [c] Mean value for five experiments.

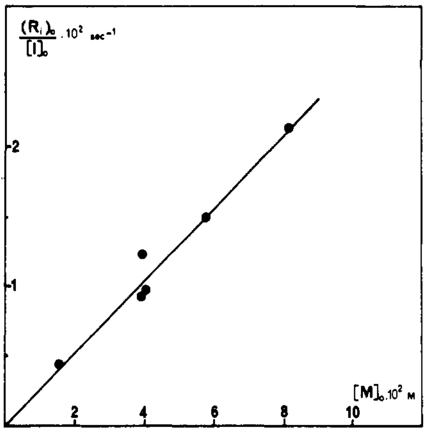


Figure 1. First order with respect to monomer for initiation reaction $|I|_0$ = 2.5 to 11 × 10^{-5} M, T = +10 °C.

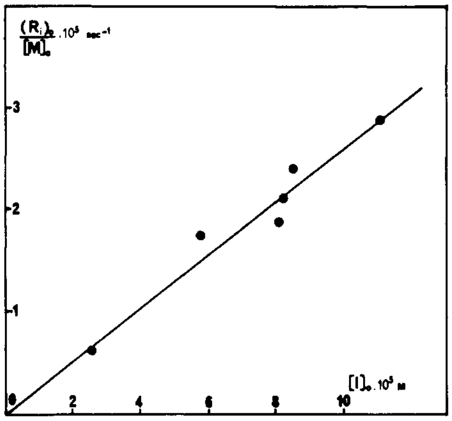


Figure 2. First order with respect to initiator for initiation reaction $|M|_0$ = 1.5 to 8 × 10^{-2} M, T = +10 °C.

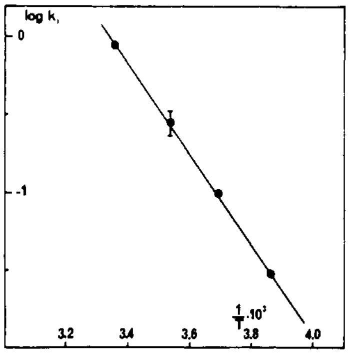


Figure 3. Arrhenius plot for initiation rate constant.

calorimetry whereas remaining initiator concentration was simultaneously measured through the 410 nm absorption of trityl cation. For the proposed kinetic scheme, the knowledge of initiation and propagation rates allows the determination of all contributing rate constants and we intend to present here the complete data.

A kinetic study was undertaken by Sherrington et al. with the same monomer and tropylium hexachloroantimonate as initiator. Their results were very recently published,[7] but reported rate constants and kinetic analyses are somewhat conflicting with ours and we shall develop a critical comparison in the discussion of this paper.

Experimental Section

Materials. *p*-Methoxystyrene was prepared from anisaldehyde through a Grignard synthesis.[8] Thermal dehydration of the corresponding alcohol leads to a monomer of chromatographic purity better than 99.5% (bp = 100 °C (23 mm), n^{24}D 1.5592). Residual water and alcohol were removed, under vacuum, with calcium hydride and successive sodium films. Appearance of living carbanions was the evidence of ultimate dehydration of the monomer.

Triphenylmethyl hexachloroantimonate was prepared as described in the literature[9] from Ph_3CCl and $SbCl_5$. Trityl chloride was obtained by reaction of triphenylmethanol with acetyl chloride and then recrystallized several times in benzene and petroleum ether. Salt synthesis was followed by several dissolutions and crystallizations in anhydrous methylene chloride and hexane. Initiator phials (4-ml bulbs) were prepared under vacuum and stored in darkness.

Methylene chloride was treated with oleum, washed, dried over $CaCl_2$, and carefully distilled. Ultimate dehydration was performed over P_2O_5 and sodium films.[10] Solvent was then distributed in storage ampules equipped with suitable breakseals.

Polymerization. An adiabatic Biddulph-Plesch type calorimeter based on our early design[11] and provided with an uv cell has been recently worked out[12] and used for this study. It can be fitted in the sample compartment of a CARY 14 spectrophotometer. Polymerization is started by crushing the initiator phial at the desired initial temperature. The decay of the 410-nm absorption of the trityl cation is followed simultaneously with the heat evolution in the solution. Monomer consumption is obtained from the thermogram (compensated 100 Ω platinum wire, Bertin electronic bridge type D 554, Sefram Servorac recorder, overall response time 0.6 s). Polymerizations were always quantitative. Polymerization enthalpy was found equal to ΔH_p = −15.2 ± 1.5 kcal mol^{-1} at +10 °C. Number average molecular weights were measured with a Mechrolab automatic osmometer in toluene solution at 37 °C.

Results

Initiation. Initial rate of the initiation reaction $(R_i)_0 = -d|I|_0/dt$ is obtained from the initial slope of the uv recorder trace. Variations of $(R_i)_0/|I|_0$ against $|M|_0$ (Figure 1) and $(R_i)_0/|M|_0$ against $|I|_0$ (Figure 2) are linear, showing first orders with respect to monomer and initiator for the initiation reaction. Corresponding rate constants k_i were obtained at −15, −2, +10, and +25 °C (Table I). The activation energy for initiation step was found to be (Figure 3) E_i = 13.3 ± 0.6 kcal mol^{-1}.

Initiation results from a bimolecular reaction between reagents and the simplest process should be, as in cyclopentadiene polymerization,[13] a direct addition of the trityl cation on monomer double bond. NMR spectroscopy gave evidence for trityl fixation on *p*-methoxystyrene oligomers prepared

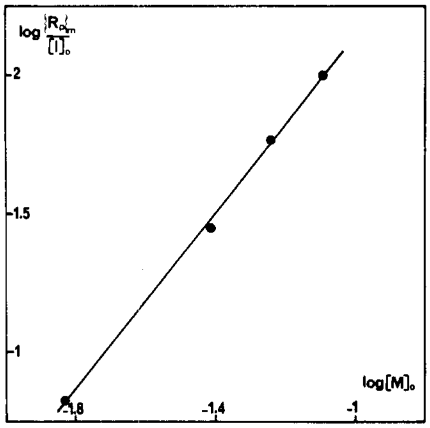


Figure 4. Overall external second order with respect to monomer at +10 °C ($\{R_p\}_m$ = maximal rate at inflexion point; see text).

Table II
Determination of (k_p/k_{trm}) Ratios at Different Temperatures

T, °C	$\overline{DP}_n$	$\|M\|_0/\|I\|_c$	k_p/k_{trm}	k_{trm}, M^{-1} s^{-1}
25	183	1.125	218	73
10	231 to 496		530 ± 70^a	53 ± 16^a
−2	1.240	5.615	1.591	25
−15	2.960	9.460	4.390	17

^{a} Mean value for six experiments.

at 25 °C using high initiator concentration and low monomer concentration. But the importance of transfer processes in this system, much higher than in CPD polymerization, and the difficulty to separate oligomers from the excess initiator residues limits the accuracy of quantitative determinations. Nevertheless we found one trityl group for a mean of 7.5 chains which fits with what could be expected from $\overline{DP}_n$ and experimental monomer transfer rate constant at 25 °C (see Table II).

Propagation and Termination. Monomer polymerization curve $|M| = f(t)$ is "S" shaped showing that initiation is still occurring during most of the reaction. This fact is confirmed by the very incomplete consumption of initiator (less than 15% of $|I|_0$ at +10 °C at the end of the polymerization). Inflexion on the curve is close to the starting time, when only a small quantity of monomer is consumed and we used the corresponding maximum rate $(R_p)_m$ for the external determination of the overall order with respect to monomer. A straight line of slope close to two (Figure 4) is obtained by plotting log $(R_p)_m/|I|_0$ against log $|M|_0$. This would indicate an overall second order with respect to monomer and thus the expected first order for propagation. Taking into account a probable monomer transfer reaction and assuming termination to be unimolecular, polymerization rate is expressed by

$$R_p = -\frac{dM}{dt} = (k_p + k_{trm})MM^* \tag{1}$$

brackets are omitted, for simplicity. The rate of formation of active centers is the difference between initiation and termination rates.

$$\frac{dM^*}{dt} = R_i - R_t = k_i MI - k_t M^* \tag{2}$$

This leads to

$$\frac{d}{dt}\left(\frac{R_p}{M}\right) = -\frac{d^2 \ln M}{dt^2} = (k_p + k_{trm})\frac{dM^*}{dt}$$
$$= (k_p + k_{trm})(R_i - R_t) \tag{3}$$

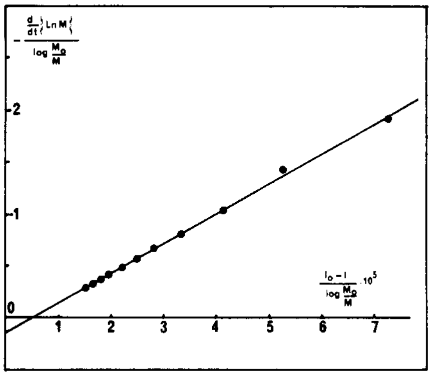


Figure 5. Example of determination of the $(k_p + k_{trm})$ and k_t values: T = +10 °C, $|M|_0 = 4.0 \times 10^{-2}$ M; $|I|_0 = 5.8 \times 10^{-5}$ M.

At the beginning of the polymerization $R_t = 0$ and it comes:

$$\left\{\frac{d}{dt}\left(\frac{R_p}{M}\right)\right\}_0 = (k_p + k_{trm})(R_i)_0 \tag{4}$$

For each experiment, the value of $(R_i)_0$ is experimentally known from initiator consumption curve, that of $\{(d/dt)\cdot(R_p/M)\}_0$ is derived from the thermogram, and an "external" value $(k_p + k_{trm})_0$ is obtained (see Table I). Combination of (2) and (3) leads to:

$$-\frac{d^2 \ln M}{dt^2} = (k_p + k_{trm})\left(-\frac{dI}{dt}\right) - k_t\left(-\frac{d \ln M}{dt}\right)$$

which gives on integration:

$$-\frac{d \ln M}{dt} = (k_p + k_{trm})(I_0 - I) - k_t \ln\left(\frac{M_0}{M}\right) \tag{5}$$

If assumptions concerning unimolecular termination and monomer first order for propagation are valid, a straight line should be obtained by plotting

$$\left\{\frac{-d \ln M/dt}{\ln (M_0/M)}\right\} \text{ against } \left\{\frac{(I_0 - I)}{\ln (M_0/M)}\right\}$$

leading to "internal" values of propagation and termination rate constants. Experimental values of $|I|$ and $|M|$ are known at any time and those of $(-d \ln M/dt)$ are easily deduced. Such plots were drawn for each experiment and linearity was observed accurately (Figure 5). Values of $(k_p + k_{trm})$ determined by the two methods are compared in Table I.

The observed low values of termination rate constants, in agreement with the continuous increase of active centers concentration during the course of the polymerization (Figure 6), are determined with a large error and no significant activation energy can be deduced from temperature variation.

Monomer Transfer. Monomer conversion is always complete and, in absence of transfer, the number average degree of polymerization should be equal to

$$\frac{\int_0^\infty R_p\, dt}{\int_0^\infty R_i\, dt} = \frac{|M|_0}{|I|_c}$$

where $|I|_c$ = consumed initiator. If transfer to monomer occurs, the observed $\overline{DP}_n$ is given by

$$\overline{DP}_n = \frac{\int_0^\infty R_p\, dt}{\int_0^\infty R_i\, dt + \int_0^\infty R_{trm}\, dt}$$

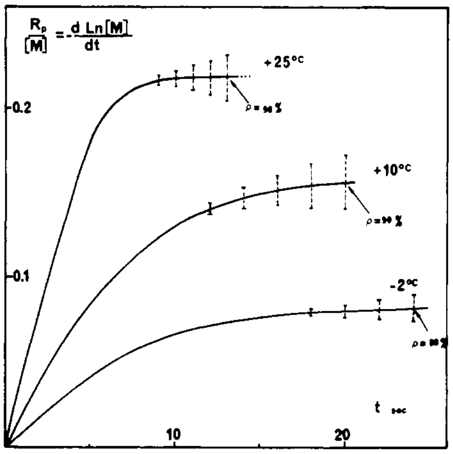


Figure 6. Variation of active centers concentration during the polymerization, at different temperatures (ρ = monomer conversion at the last significant point of each plot).

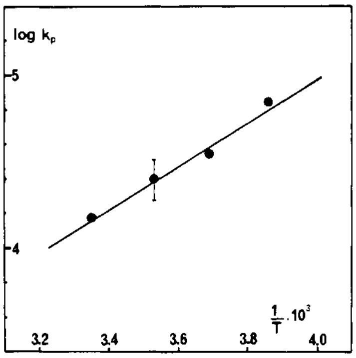


Figure 7. Arrhenius plot for propagation rate constant.

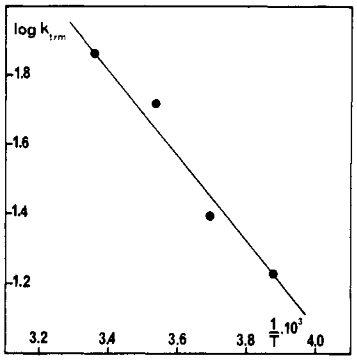


Figure 8. Arrhenius plot for monomer transfer rate constant.

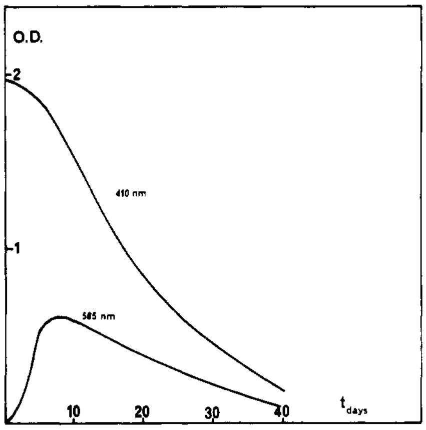


Figure 9. Reaction between initiator and polymer; slow decrease of the initiator 410-nm peak and evolution of the 585-nm secondary peak.

which leads to

$$\frac{1}{\overline{DP}_n} = \frac{|I|_c}{|M|_0} + \frac{k_{trm}}{k_p}$$

and

$$k_p/k_{trm} = \frac{(|M|_0/|I|_c)\overline{DP}_n}{|M|_0/|I|_c - \overline{DP}_n}$$

$\overline{DP}_n$ was measured and $|M|_0/|I|_c$ ratios were calculated for each experiment. Values of (k_p/k_{trm}) at different temperatures are listed in Table II. It may be seen from Tables I and II that k_{trm} is always much smaller than k_p and the values of propagation rate constants are quite similar to those of $(k_p + k_{trm})$.

Activation Energies for Propagation and Monomer Transfer Reactions. Plots of ln k_p (Figure 7) and of ln k_{trm} (Figure 8) against $1/T$ give the corresponding E_p and E_{trm} values. A highly negative apparent activation energy is found for the propagation step,

$$(E_p)_{app} = -6 \pm 1 \text{ kcal mol}^{-1}$$

Whereas a positive one is found for transfer to monomer

$$E_{trm} = 5.9 \pm 0.5 \text{ kcal mol}^{-1}$$

Secondary Reactions at the End of the Polymerization. A slow consumption of initiator was observed after completion of the polymerization but the rate of this reaction remained negligible compared to initiation rate. Simultaneously new absorption maxima began to build up in the visible spectrum: the first one at 505 nm, which increases to a constant and low value of optical density has already been observed by Higashimura[14] with the system p-MeOSt/BF$_3$, Et$_2$O/1,2-dichloroethane; the second one at 585 nm goes slowly through a maximum intensity and then decreases. In order to confirm the most probable hypothesis of a reaction between the polymer and the remaining salt, we followed the spectral behavior of a mixture of $Ph_3C^+SbCl_6^-$ and poly(p-methoxystyrene) in CH_2Cl_2. A solution of dead polymer in anhydrous CH_2Cl_2 was freed from remaining traces of methanol by successive bulb-to-bulb distillations of solvent on sodium mirrors and then a known quantity of trityl salt was added under vacuum. Absorption at 585 nm slowly reached a maximum value after several days and then decreased whereas the 410-nm peak of the salt was continuously decreasing (Figure 9).

Molecular weight determinations on the polymer sample before ($\overline{M}_n$ = 92 500) and after experiment ($\overline{M}_n$ = 90 000) showed no significant variation and chain breaking is not involved in this secondary reaction. We cannot yet propose a definite explanation of the reaction which could be an electrophilic attack of Ph_3C^+ cation on the p-methoxy phenyl ring or on the terminal double bonds of the chains, but nevertheless these secondary reactions are very much slower than polymerization and we may assert that they cannot significantly affect the kinetic parameters we determined.

Discussion

Polymerization of p-methoxystyrene initiated by $Ph_3C^+SbCl_6^-$ in CH_2Cl_2 solution is always quantitative. Initiation is much slower than the rapid propagation observed (completion in 10–30 s) and gives relatively stable active centers. The kinetic treatment of experimental results agrees with a unimolecular termination process although it was not possible to decide between a true first order (spontaneous termination) or a pseudo-first-order (termination agent). Whatever that may be, the observed termination rate constant

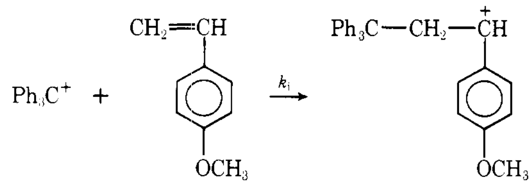
Table III
Values of k_i for the Polymerization of Styrene and Analogues Initiated by Trityl Salts in Chlorinated Solvents, at 30 °C

Monomer (solvent)	Salt and (concn range)	$k_i \times 10^2$ at 30 °C, $M^{-1}\,s^{-1}$	E_i, kcal mol^{-1}	Ref
Styrene ($ClCH_2$–CH_2Cl)	$Ph_3C^+\ ^-HgCl_3$	0.006		16
	$Ph_3C^+\ ^-SnCl_5$ (4 to 9 × 10^{-5} M)	0.088	6.7	17
Indene (CH_2Cl_2)	$Ph_3C^+\ ^-SnCl_5$ (5 × 10^{-4} M)	0.197[a]	18	18
α-Methylstyrene ($ClCH_2$–CH_2Cl)	$Ph_3C^+\ ^-SnCl_5$ (5 × 10^{-5} M)	1.3	5	19 and 17
p-Methoxystyrene ($ClCH_2$-CH_2-Cl)	$Ph_3C^+\ ^-SnCl_5$ (10^{-5} M)	102		19
(CH_2Cl_2)	$Ph_3C^+\ ^-SbCl_6$ (2 to 11 × 10^{-5} M)	137[a]	13.3	This work

[a] Extrapolated.

is small and therefore determined with a large error. Evidence is also provided for important monomer transfer processes.

As we found trityl groups incorporated in oligomeric chains, the most probable mechanism of initiation is the bimolecular addition on the monomer double bond,



In the range of concentrations used (10^{-4} to 10^{-5} M), the salt is highly dissociated (≥80% at 0 °C[15]) and initiation process should mainly occur on free trityl cation, which agrees with the simple order observed with respect to catalyst. Values of initiation rate constants, which are already reported for the polymerization of styrene and analogues by trityl salts at +30 °C, are collected in Table III. Even if the data are not directly comparable (solvents, counterions, concentration ranges of the salt are sometimes different) these values agree with the order of reactivity toward the same cation, which could be expected for the monomers.

For p-methoxystyrene polymerization, it may be noted that, within the same range of initiator concentrations, values of k_i observed with $Ph_3C^+SbCl_6^-$ and $Ph_3C^+SnCl_5^-$ are in good agreement. Kinetics of initiation by $C_7H_7^+\ SbCl_6^-$ were not followed, but Sherrington[7] reported a surprisingly rapid consumption of catalyst (assumed to be complete before 15% monomer conversion). No termination was observed, leading thus to an assumed steady state of the second kind ($|P_n^+| = |I|_0$). With the same experimental conditions, we observed a very incomplete consumption of triphenylmethyl salt (less than 15% of $|I|_0$ at +10 °C), and, even if steric hindrance could make trityl cation less efficient than tropylium cation, it cannot reasonably explain so large a difference in reactivities. In fact, no experimental evidence was provided for a rapid reaction between $C_7H_7^+SbCl_6^-$ and p-methoxystyrene and, on the contrary, the linear dependence of the reported "k_p" with $|M|_0$ would agree with a slow initiation analogue to that we observed with trityl salt. This rate constant, obtained through the kinetic treatment precedingly applied by the same author in the case of IBVE polymerization,[2] is valid only when $|P_n^+| = |I|_0$ and must obviously be independant of $|M|_0$. Then a slow and bimolecular initiation by $C_7H_7^+SbCl_6^-$ followed by slow termination processes might easily explain the factor of ~5 observed at 0 °C between the k_p reported by Sherrington and our values. In addition, the discrepancy should increase at lower temperatures as the difference between initiator initial concentration and true active centers concentration becomes much larger. This may explain why Sherrington observed a positive apparent activation energy for propagation whereas we found a negative energy.

It remains to account for this apparent negative E_p observed for our experiments. A simple explanation might be, as for cyclopentadiene polymerization,[5] to assume a substantial shift of the dissociation equilibrium of active centers toward free ions with a decrease of temperature. This dissociation would occur with a strong solvation of the active centers. Another satisfactory and more generalizable explanation could be the existence of a prior solvation equilibrium between active centers and monomer followed by the propagation step itself:[21,22]

$$\sim\!\!\sim P_n^+ + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \sim\!\!\sim P_n^+, M \xrightarrow{k_p} \sim\!\!\sim P_{n+1}^+$$

$$(K_S = k_1/k_{-1})$$

If $k_1 \gg k_p$, the mass action law may be applied, and the propagation rate is expressed by

$$R_p = \frac{k_p K_S}{1 + K_S M} P^* M$$

(P^* = overall active species concentration) where $K_S M \ll 1$, as a first order with respect to monomer was observed for the propagation step. Thus the apparent propagation rate constant is reduced to

$$(k_p)_{app} \sim k_p K_S$$

and

$$(E_p)_{app} \sim E_p + \Delta H_S \text{ with } (E_p)_{app} = -6 \text{ kcal mol}^{-1}$$

The E_p value is unknown, but we may consider that the monomer solvated carbocation involved in our scheme is most probably a free ion. Thus the process is quite similar to that occurring in radiation-induced polymerization in bulk. Unfortunately values of E_p for p-methoxystyrene polymerization by radiation are not available in the literature. We may only compare with styrene itself for which a value of 2 kcal mol^{-1} is reported.[20] Assuming for p-methoxystyrene a value between 0 and 4 kcal, ΔH_S would lay in the range of −6 to −10 kcal.

This order of magnitude may be compared with the enthalpies of −8 to −11 kcal mol^{-1} found by Penczcek et al.[23] for the solvation equilibria of trityl cation by several acetals.

We reported recently[24] a value of ca. −5 kcal mol^{-1} for the enthalpy of the equilibrium

$$CH_3CPh_2^+ + CH_2{=}CPh_2 \rightleftharpoons CH_3CPh_2^+, CH_2{=}CPh_2$$

which is formally very close to that we are assuming in the case of p-methoxystyrene.

A similar solvation process should obviously occur for the initiation:

$$Ph_3C^+ + M \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ph_3C^+, M \xrightarrow{k_i} M_1^+$$

But, in this case, it is necessary to assume $k_2 \ll k_i$ to account for the highly positive activation energy $(E_i)_{app}$ which is observed (~13 kcal mol^{-1}). This means that the above equilibrium is never reached and that the concentration of the solvated intermediate Ph_3C^+, M remains very low during the initiation. The apparent rate constant $(k_i)_{app}$ is then equal to k_2, which leads to a positive activation energy.

We could not decide between these two possible explanations but the effect of common ion salts is now being studied and might give us more information about the dissociation equilibrium of propagating species.

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Reactivity of Vinylferrocene and Vinylcymantrene in Radical Initiated Solution Copolymerizations

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ABSTRACT: Vinylferrocene (M_1) has been classified within the *Q–e* scheme as an exceptionally electron rich vinyl monomer from copolymerization studies with 12 vinyl organic monomers. In copolymerizations with vinylcymantrene, *N*-vinylcarbazole, *p-N,N*-dimethylaminostyrene, 1,3-butadiene, *N*-vinyl-2-pyrrolidone, and styrene, the value of *e* for vinylferrocene was consistently in the range of −2.0 to −2.6 and the *Q–e* scheme was applicable. The *Q–e* scheme failed when electron deficient comonomers such as methyl methacrylate, methyl acrylate, acrylonitrile, diethyl fumarate, fumaronitrile, and maleic anhydride were employed, presumably due to competition of the charge transfer model with the terminal model. Vinylcymantrene exhibited the same copolymerization behavior and its value of *e* was about −2 when using electron-rich comonomers where the *Q–e* scheme held. The reactivity ratios, from which values of *e* were calculated, were obtained using the integrated form of the copolymer equation and the proper nonlinear least-squares fitting technique. The importance of this method, especially with regard to past classification of vinylferrocene by the *Q–e* scheme, is discussed.

Vinylferrocene, **1**, was first copolymerized with styrene, methyl acrylate, and chloroprene by Arimoto and Haven.[1] More recently, quantitative vinylferrocene copolymerization studies[2–8] have been carried in order to determine reactivity ratios and the values of *Q* and *e*[9] for this monomer. Similarly, quantitative copolymerization studies of vinylcymantrene, **2**, have recently been reported.[8,10] These studies are of fundamental interest in order to understand how organometallic functions effect vinyl polymerization behavior. This knowledge is needed to help design copolymers of vinyl organometallic monomers with classic organic monomers and also to provide a framework in which the electronic effects, that organometallic functions impart in radical initiated copolymerizations, may be viewed.

Reports of the value of *e* for vinylferrocene seem to be in disagreement in the literature. Using cationic initiation, a value of $e = -1.3$ was reported in styrene copolymerizations while values of about −2.1 and +0.47 have also been observed.[4,8,10,11] In this paper we report a careful classification of both vinylferrocene and vinylcymantrene according to the *Q–e* scheme. It is demonstrated that both monomers are exceptionally electron rich as indicated by their large negative values of *e*.

Results and Discussion

To evaluate the values of *Q* and *e*, the equation $r_1r_2 = \exp[-(e_1 - e_2)^2]$ is employed.[9] The values of r_1 and r_2 are first obtained by fitting experimental composition–conversion data to the copolymer equation.[9,12] The process of fitting this data should be performed by a *nonlinear* least-squares method.[12,13]

$$\frac{d[M_1]}{d[M_2]} = \left[\frac{[M_1{}^0]}{[M_2{}^0]}\right]\left[\frac{r_1[M_1{}^0] + [M_2{}^0]}{r_2[M_2{}^0] + [M_1{}^0]}\right]$$

Linear methods, such as the frequently used Fineman Ross technique,[14] are mathematically incorrect and in some cases lead to large errors.[13] Furthermore, the *integrated form* of the copolymer equation must be employed to account for monomer drift even when polymerizations to low conversions have been used.

Computer programs for routine application of the nonlinear least-squares fitting of the integrated form of the copolymer