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Kinetic Study of the "Living" Cationic Polymerization of Cyclohexyl Vinyl Ether Initiated by Hydrogen Iodide in the Presence of Ammonium Salts

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ABSTRACT: Kinetics of the cyclohexyl vinyl ether (CHVE) cationic polymerization, initiated by HI in the presence of ammonium salts (nBu_4NX, with X = Cl, Br, I), have been investigated. It has been shown that the presence of minute amounts of added salt ($[nBu_4NX]/[HI] \leq 1\%$) are sufficient to induce a "living" process. In the same time, the polymerization rate drastically decreases, suggesting a common ion salt effect and therefore an ionic-type polymerization mechanism. For a $[nBu_4NI]/[HI]$ ratio higher than 1%, the apparent polymerization rate constant remains invariable, up to a very high amount of salt, in agreement with the only contribution of ion pairs. An estimate of the ionic dissociation constant of active species and of their concentration in the polymerization medium, as well as an evaluation of k_p^+ and $k_p^\pm$ values, accounting for kinetic data, has been made. With nBu_4NCl as added salt, a halide exchange is observed with polymer ends, in addition to the common ion salt effect. These two processes result in a continuous decrease of the polymerization rate with an increase of the tetrabutylammonium chloride amount. The main reaction mechanisms involved in these polymerization systems are discussed.

Introduction

Although the first report on the "living" cationic polymerization of vinyl ethers, involving the controlled activation of α-halogeno ether species, is already 10 years old,[1] the nature of the active centers and the operating polymerization mechanism are not completely elucidated. The question still remains on the ionic or covalent character of the polymer ends during the monomer insertion process leading to the living polymerization.

Usually, vinyl ethers cannot directly add onto α-halogeno ether termini and a catalyst must be added to trigger the polymerization. Mild Lewis acids (ZnX_2, SnX_2,...) or ammonium salts (NBu_4ClO_4,...) are typical examples of activating agents which, in appropriate conditions, can induce "living" cationic polymerizations. The specific characteristics of these polymerization systems, in particular the very low contribution of transfer and termination reactions and the absence of any detectable amount of ionic species in the polymerization media, strongly contrast with conventional cationic polymerizations. These criteria have led several authors[2,3] to sustain first the hypothesis of a concerted insertion mechanism through formation of a six-member transition state[4] involving simultaneously the carbon-halogen termini, the Lewis acid, and the monomer.

An alternative mechanism, assuming the possibility for α-halogeno ether termini to be ionized, was later proposed.[5,6] In this scheme, the covalent α-halogeno ether polymer ends, which are those experimentally observed, are assumed to be inactive for the polymerization. However, they can be partially ionized, usually with the assistance of an electrophilic activator and ensure the cationic propagation. Very fast reactions of interconversion between ionic and covalent forms of the polymer ends have been postulated.

An ionic mechanism has also been suggested by Nuyken for the living polymerization of isobutyl vinyl ether (IBVE) initiated by HI/tetrabutylammonium salt systems.[7] Reversible exchanges between iodide anions of α-iodo ether ends and ClO_4^- anions of tetrabutylammonium perchlorate have been proposed as the key reaction of the polymerization mechanism. Nevertheless, again with these systems, ionic species could not be experimentally detected.

To gain experimental results supporting one of these polymerization mechanisms, several studies have dealt with the characterization of the nature of active and inactive α-halogeno ether species and of their interconversion processes.

Using systems constituted of mixed α-halogeno ethers $(RI + RCl)/ZnX_2$ as initiators, Deffieux et al.[8] have shown that rapid reversible halide exchanges actually take place between polymer ends during the living polymerization of chloroethyl vinyl ether. Similar exchange processes have also been recently noticed during the IBVE polymerization initiated with $(RI + RCl)/NBu_4ClO_4$.[9] These halide exchanges strongly suggest a temporary ionization of α-halogeno ether species. However, it can be argued that these reactions might also proceed by a concerted way and a polymerization mechanism involving covalent species could not be definitely ruled out.

Fast halide exchanges as well as the presence of ionic species were further confirmed by Higashimura et al. in the case of isobutyl vinyl ether[10] and styrene[11] polymerizations initiated by monomer-HCl adduct/$SnCl_4$ systems, in the presence of ammonium salts. It was shown in NMR studies that the polymerizations are not living when free ions are present and that the living character of the polymerizations may be obtained by adding ammonium salts.

We have reported recently that the cationic polymerization of cyclohexyl vinyl ether (CHVE) can be directly initiated by hydrogen iodide without any necessary nucleophilic activator.[12] Though the polymerization was not living in these conditions, it has been shown that the addition of an ammonium salt (NBu_4I) led to a living-type polymerization, indicating that the added salt is able to stabilize the active species. The relative simplicity of this polymerization system—no need of electrophilic activator—prompted us to investigate the nature of the active α-iodo ether species involved in the living and nonliving CHVE polymerizations.

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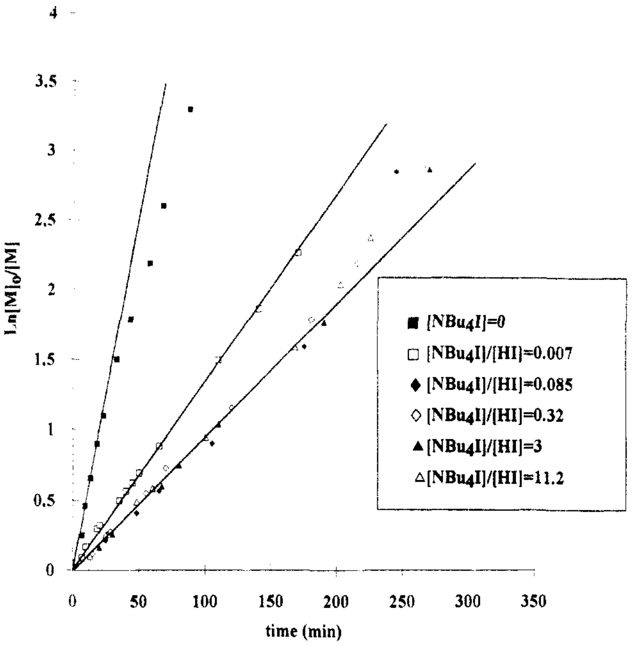


Figure 1. Variation of semilogarithmic monomer concentration with time, for the polymerization of CHVE, initiated by HI–CHVE adduct, in the presence of various amounts of NBu_4I, in CH_2Cl_2 at -30 °C. [CHVE] = 1.46 M. [HI] = 1.54×10^{-2} M.

The present paper reports on the kinetic study of CHVE polymerization, initiated by HI, in the presence of various ammonium salts and discusses the polymerization mechanism operating in these systems.

Results and Discussion

Kinetic Study of the CHVE Polymerization Initiated by HI/NBu_4X (X = Cl, Br, I). Polymerizations of CHVE were carried out at -30 °C in CH_2Cl_2. The HI–CHVE adduct was prepared, in situ, by adding HI onto a monomer solution in CH_2Cl_2, or containing both the monomer and the ammonium derivative, in experiments performed in presence of a salt. Polymerizations started immediately on adding HI (zero polymerization time), and monomer conversions versus time were followed by dilatometry.

In absence of any ammonium salt, the CHVE polymerization, initiated by HI alone, proceeds very rapidly ($t_{1/2} < 15$ min at -30 °C) and goes up to completion. However, as already reported,[12] the experimental polymer molar masses are lower than the theoretical values calculated assuming the formation of one polymer chain per HI molecule. Moreover, the molar masses distributions are quite broad (~1.5). Since the semilogarithmic variation of $[M]_0/[M]$ versus time, plotted in Figure 1, remains rectilinear up to high monomer conversion (>80%), in agreement with a first monomer order dependence of the reaction and a constant active centers concentration along the polymerization, the nonliving character of the polymerization may be attributed mainly to the occurrence of chain-transfer reactions.

Assuming that the CHVE initial propagation rate, R_{p0}, can be satisfactorily expressed by

$$R_{p0} = k_p(\mathrm{app})[\mathrm{CHVE}]_0[\mathrm{RI}] \qquad (1)$$

and that the concentration of active and dormant polymer chains [RI] is equal to $[HI]_0$,

$$R_{p0} = k_p(\mathrm{app})[\mathrm{CHVE}]_0[\mathrm{HI}]_0 \qquad (2)$$

an apparent initial propagation rate constant k_p(app) can be calculated. It is given in Table 1. This value will be used as a reference in the kinetic studies of CHVE polymerization in the presence of various ammonium salts.

Table 1. Polymerization of CHVE Initiated by HI–CHVE Adduct in the Presence of NBu_4I (solvent = CH_2Cl_2, T = -30 °C, [CHVE] = 1.46 M, [HI] = 1.54×10^{-2} M, $\bar{M}_n$(theor)[a] = 12120 g mol^{-1})

$[NBu_4I] \times 10^2$	$[NBu_4I]/[HI]$	$t_{50\%}$, min	$10^2 k_p$(app) $M^{-1}\ s^{-1}$	$\bar{M}_n$ (exp)[b]	$\bar{M}_w/\bar{M}_n$
0	0	14	5.2	9940	1.47
0.010	0.007	50	1.4	11360	1.30
0.015	0.01	90	0.8	10870	1.22
0.131	0.085	90	0.8	14050	1.18
0.493	0.32	75	0.9	11500	1.11
1.540	1	100	0.7	12150	1.15
2.800	1.8	90	0.8	11500	1.10
4.620	3	75	0.8	12060	1.14
17.300	11.2	80	0.8	11860	1.18

[a] Calculated from the equation $\bar{M}_n(\mathrm{theor}) = ([\mathrm{CHVE}]_0/[\mathrm{HI}]_0)M_{\mathrm{CHVE}} \times \%\ \mathrm{conv} + M_{\mathrm{end\ groups}}$. [b] Determined by SEC at the end of the polymerizations after complete monomer conversion.

(1) Polymerization of CHVE in Presence of NBu_4I. A first series of experiments was performed in the presence of various NBu_4I concentrations, ranging from 1×10^{-4} to 1.7×10^{-1} M and corresponding to ratio $[NBu_4I]$/[HI-adduct] between 0.007 to 11, whereas the HI-adduct and monomer initial concentrations were kept constant. The variations of $\ln([M]_0/[M])$ versus time for increasing amounts of NBu_4I are presented in Figure 1. In the whole NBu_4I concentration range examined, a linear dependence of the $\ln([M]_0/[M])$ with respect to time is observed up to very high monomer conversions.

As it may be seen in Figure 1, the CHVE polymerization rate strongly decreases on adding extremely small amounts of NBu_4I. Less than 1% of added salt, with respect to the HI-adduct concentration, is enough to reduce the apparent propagation rate constant, calculated using eq 2, by more than 6 times (see Table 1). Then, after this low value has been reached with a $[NBu_4I]$/[HI-adduct] ratio of about 0.01, no further decrease of the polymerization activity is induced by the presence of higher salt concentrations. This shows that the rate decrease cannot be attributed to impurities present in NBu_4I. The apparent propagation rate constants values are collected in Table 1: within the experimental error, $k_p$app remains unchanged for a $[NBu_4I]$/[HI-adduct] ratio ranging from 0.01 to 11. The overall variation of k_p(app) versus the $[NBu_4I]/[HI]$ ratio is plotted in Figures 2a,b.

The experimental molar masses and the MWD of the poly(CHVE), obtained in the presence of various amounts of NBu_4I are given in Table 1. As it may be seen, experimental $\bar{M}_n$ are in good agreement with theoretical $\bar{M}_n$ calculated assuming the growth of one polymer chain per HI molecule introduced, even for polymerizations performed with a very small amount of salt, such as 1% molar with respect to the total number of chains formed. The influence of NBu_4I on the MWD is however less pronounced and higher proportions of salt are required to get distributions narrower than 1.2.

These results are consistent with a conventional common ion salt effect and therefore suggest the contribution of ionized α-iodo ether species to the propagation reaction. In absence of ammonium salt, both dissociated ions of very high reactivity and ion pairs likely participate in the polymerization, whereas, in the presence of an added common ion salt, only ion pairs would significantly contribute to the propagation process. The living character of the polymerization might then result into a propagation reaction governed exclusively by undissociated ionic

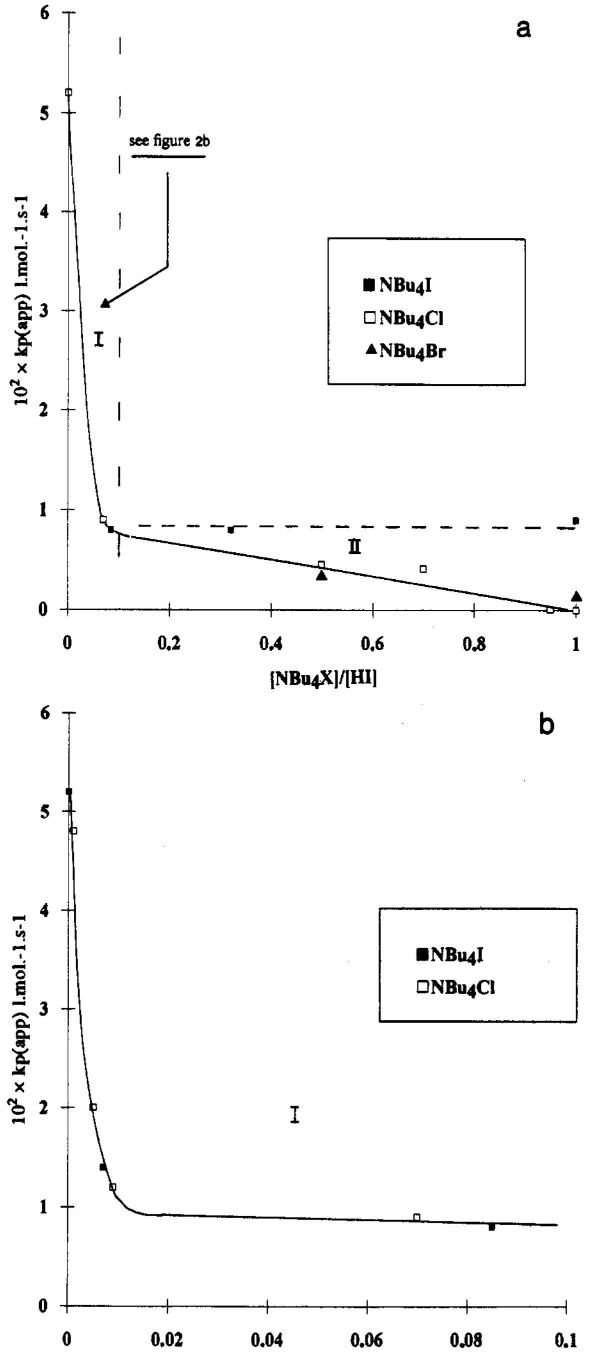
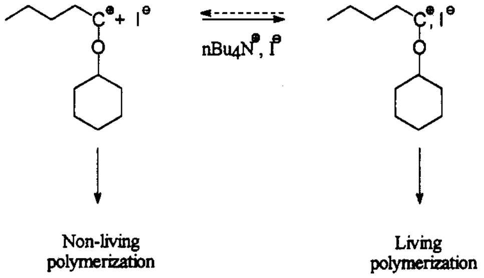


Figure 2. Variation of the apparent propagating rate constant, k_p(app), with the ratio $[NBu_4X]/[HI]$.

Scheme 1



species, see Scheme 1. The consistency of a common ion salt effect, with respect both to the equilibrium dissociation constants of α-iodo ether ends and NBu_4I and to their relative concentrations in the polymerization media, will be examined and discussed in a further section.

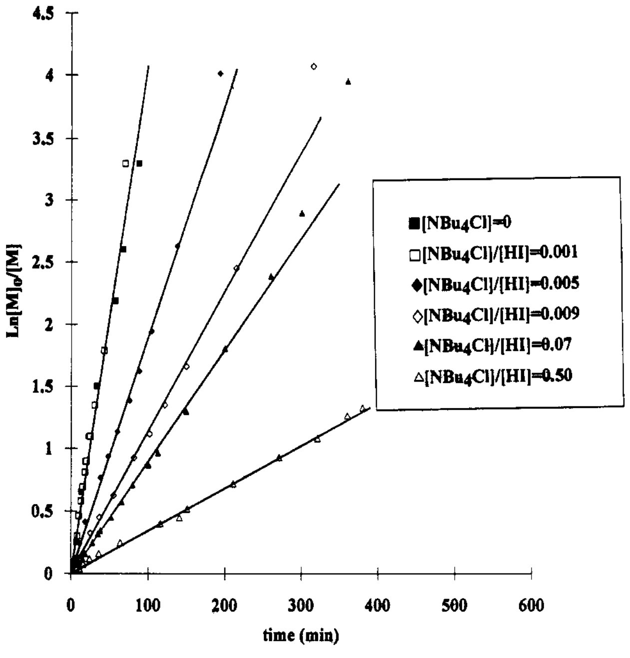


Figure 3. Variation of semilogarithmic monomer concentration with time, for the polymerization of CHVE, initiated by HI–CHVE adduct, in the presence of various amounts of NBu_4Cl, in CH_2Cl_2 at −30 °C. [CHVE] = 1.46 M. [HI] = 1.54×10^{-2} M.

(2) Polymerization of CHVE Initiated by HI/NBu_4Cl. A second set of polymerizations was performed in the presence of various initial concentrations of tetrabutylammonium chloride as added salt. With this chloride derivative, no common anion I^- is initially introduced to the polymerization system. This has allowed us to investigate some other aspects of these polymerizations.

NBu_4Cl concentrations were varied from 1.5×10^{-5} to 2×10^{-2} M which correspond to a $[NBu_4Cl]/[HI]$ ratio ranging from 0.001 to 1.35, whereas other reaction parameters were kept identical to those used for experiments with NBu_4I.

The variations of $\ln([M]_0/[M])$ versus time are shown in Figure 3. A first monomer order dependence of the polymerization, up to a very high monomer conversions (≈90%), is again observed with these systems.

A strong reduction of the polymerization activity is also observed in the presence of NBu_4Cl. Again, we can notice the drastic effect of minute amounts of salt on the polymerization rate. The latter is approximately reduced by a factor of 6 in the presence of less than 1% of NBu_4Cl with respect to HI. However, the general behavior of NBu_4Cl-containing systems is rather different than with NBu_4I. Polymerization rates decrease continuously with increasing NBu_4Cl initial concentration and, finally, for $[NBu_4Cl]/[HI]$ molar ratio higher than one, the CHVE polymerization completely stops. The apparent polymerization rate constants, calculated from eq 2, are collected in Table 2. Variation of k_p(app) with an increasing $[NBu_4Cl]/[HI]$ ratio is plotted in Figure 2a,b.

As it may be seen also in Table 2, a good agreement between experimental and theoretical $\bar{M}_n$, calculated assuming the growth of one polymer chain per HI molecule, is observed in the presence of NBu_4Cl. The MWD of the poly(CHVE) becomes narrow for a $[NBu_4Cl]/[HI]$ ratio equal or higher than 0.01. This supports again that the ammonium salt is able to bring about the living character of the polymerization.

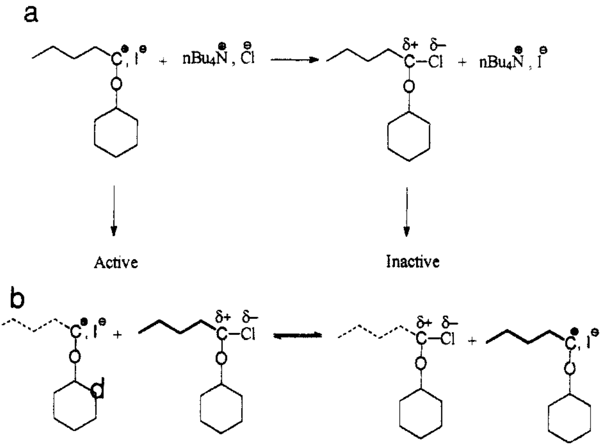
In the light of the kinetic data obtained with NBu_4I, the influence of NBu_4Cl on the CHVE polymerization suggests a more complex role of the chloride salt. It has been shown in a previous paper that, at low temperature (<0 °C), the

Table 2. Polymerization of CHVE Initiated by HI–CHVE Adduct in the Presence of NBu_4Cl (solvent = CH_2Cl_2, T = −30 °C, [CHVE] = 1.46 M, [HI] = 1.54×10^{-2} M, $\bar{M}_n$(theor)[a] = 12120 g mol^{-1})

$[NBu_4Cl] \times 10^2$	$[NBu_4Cl]/[HI]$	$t_{50\%}$, min	$10^2 k_p$(app) $M^{-1}\,s^{-1}$	$\bar{M}_n$ (exp)[b]	$\bar{M}_w/\bar{M}_n$
0	0	14	5.2	9940	1.47
0.0015	0.001	15	4.9	10360	1.40
0.0077	0.005	35	2.0	11500	1.18
0.0138	0.009	62	1.2	11980	1.15
0.103	0.067	75	0.9	11750	1.17
0.770	0.500	200	0.4	12360	1.18
1.078	0.700	220	0.4	12270	1.17
1.463	0.950	21600	0.003	1430[c]	1.17
2.079	1.350	–	0	–	–

[a] Calculated from the equation $\bar{M}_n(\text{theor}) = ([\text{CHVE}]_0/[\text{HI}]_0)M_{\text{CHVE}} \times \%\ \text{conv} + M_{\text{end}}$ groups. [b] Determined by SEC at the end of the polymerizations after complete monomer conversion. [c] Determined by SEC after 12% conversion.

Scheme 2



HCl-adduct of CHVE is inactive per se for CHVE polymerization;[12] the addition of $ZnCl_2$ is necessary to trigger the polymerization, indicating that the C–Cl bond of CH(O-cyclohexyl)–Cl termini is not able to sufficiently ionize per se and behaves like a covalent species. Therefore, the continuous decrease of the polymerization rate, down to complete inhibition of the reaction, observed with increasing the NBu_4Cl/HI molar ratio, strongly suggests a halide exchange between NBu_4Cl and α-iodo ether ends. Moreover, the inertness observed for the ratio [Cl]/[I] > 1 indicates that all the α-iodo ether termini have been completely converted into covalent-like α-chloro ether ones, unable to induce the polymerization of CHVE, as shown in Scheme 2a. The driving forces of this process are, on one hand, the pronounced nucleofugic character of the iodide, which allows the transient formation of carbocationic species and, on the other hand, the predominant nucleophilic character, in an aprotic solvent as CH_2Cl_2, of the chloride anions which leads to the formation of covalent-like C–Cl ends, species thermodynamically more stable than the corresponding iodo ones.

Despite this situation, a good agreement is found, for $[NBu_4Cl]/[HI] < 1$, between the poly(CHVE) experimental $\bar{M}_n$ and theoretical ones calculated on the basis of one chain formed per initial HI molecule, independent of the amount of NBu_4Cl introduced. This finding clearly indicates the contribution of both chlorine and iodine chain termini to the polymer growth. Besides, the narrow MWD of the poly(CHVE) suggests that rapid and reversible halide exchanges take place between chains, as depicted in Scheme 2b. Unlike the reaction involving NBu_4Cl and α-iodo ethers (Scheme 2a), the reversibility of the halide exchange between chloro- and iodo-chain termini can be explained by the high electrophilic character of active carbocationic polymer-ends, associated to I^-, which makes them capable to abstract the chlorine atom of covalent-like C–Cl polymer ends. This reaction corresponds to a reversible chain transfer (Scheme 2b). A very similar situation has already been found for the polymerization of IBVE initiated by mixed α-halogeno ethers (RI + RCl), activated by NBu_4ClO_4.[9]

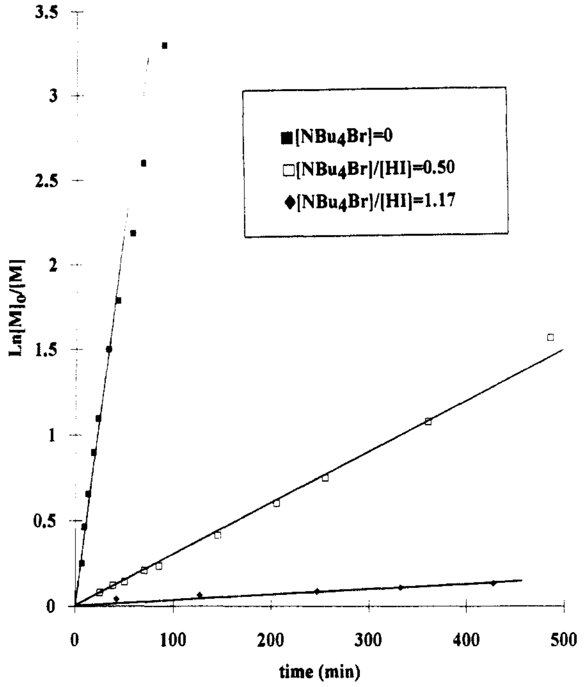


Figure 4. Variation of semilogarithmic monomer concentration with time, for the polymerization of CHVE, initiated by HI–CHVE adduct, in the presence of various amounts of NBu_4Br, in CH_2Cl_2 at −30 °C. [CHVE] = 1.46 M. [HI] = 1.54×10^{-2} M.

Indeed, the presence of a very small amount of α-iodo ether termini is necessary, but sufficient, to activate, through this exchange procedure, the polymer chains with chloro ether ends. Consequently, the overall polymerization rate will then vary with the proportion of iodo termini in the system, as observed in the kinetic study, see Figure 2a (part II). Besides, NBu_4I, generated in these halide exchanges, brings into the system iodide anions which act as common anions toward ionized α-iodo ether species and suppress the ionic dissociation. This is illustrated by the drastic decrease of the polymerization rate observed on adding minute amounts of NBu_4Cl to the polymerization system, as shown in Figure 2a (part II) and Figure 2b. It also explains the shift of the polymerization character from nonliving to living. The close fitting of the kinetic curves, observed in the presence of low amounts of NBu_4Cl or NBu_4I, (for a $[NBu_4X]/[HI]$ ratio < 0.01), indicates that the kinetic effect of the substitution of active α-iodo ether ends by inactive α-chloro ether ones remains negligible. On the contrary, for a $[NBu_4X]/[HI]$ ratio higher than 0.1, this last process becomes dominant in the case of NBu_4Cl-containing systems, and consequently, the polymerization kinetics of the two systems diverge.

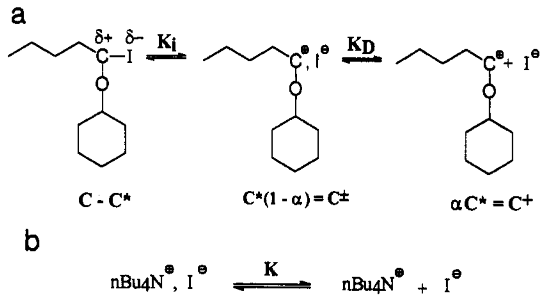
(3) Polymerization of CHVE Initiated by HI/NBu_4Br. A similar kinetic investigation was performed in the presence of NBu_4Br. The semilogarithmic variations of $[M]_0/[M]$ versus time are plotted in Figure 4. The influence of increasing amounts of NBu_4Br in the polymerization system is very close to what is observed with NBu_4Cl, see Figure 2a; the higher the concentration of the ammonium salt, the lower the polymerization rate. How-

Table 3. Polymerization of CHVE Initiated by HI–CHVE Adduct in the Presence of NBu_4Br (solvent = CH_2Cl_2, T = –30 °C, [CHVE] = 1.46 M, [HI] = 1.54×10^{-2} M, $\bar{M}_n$(theor)[a] = 12120 g mol^{-1})

$[NBu_4Br] \times 10^2$	$[NBu_4Br]/[HI]$	$t_{50\%}$, min	10^2k_p(app) $M^{-1}\,s^{-1}$	$\bar{M}_n$ (exp)[b]	$\bar{M}_w/\bar{M}_n$
0	0	14	5.2	9940	1.47
0.739	0.50	235	0.3	12770	1.20
1.80	1.17	2760	0.026	3080	1.88
1.97	1.28	2700	0.026	3430	1.84

[a] Calculated from the equation $\bar{M}_n(\text{theor}) = ([\text{CHVE}]_0/[\text{HI}]_0)M_{\text{CHVE}} \times \%\ \text{conv} + M_{\text{end}}$ group. [b] Determined by SEC at the end of the polymerizations after complete monomer conversion.

Scheme 3



ever, a small polymerization activity is still observed for $[NBu_4Br]/[HI]$ ratios higher than 1, unlike the case of NBu_4Cl, suggesting either a small activity of α-bromo ethers termini or that the halide exchange between α-iodo ethers and NBu_4Br is not complete in these conditions.

The apparent polymerization rate constants, calculated according to eq 2 from data of Figure 4, are collected in Table 3.

Though a tendency to get an apparently living polymerization in the presence of added salt ($[NBu_4Br]/[HI]$ = 0.50) is first observed, a larger amount of NBu_4Br induces the formation of polymers with experimental $\bar{M}_n$ much lower than the predicted ones and with MWD as high as 1.8. Attempts to better purify the ammonium salt do not lead to better results and these systems were not examined further.

Discussion

The results reported in the present paper are fully consistent with recent publications concerning the living polymerization of styrene,[11,13] α-methylstyrene,[14] and isobutyl vinyl ether[10] initiated by $RX/SnCl_4$ systems, in the presence of ammonium salts. However, in the case of CHVE, the presence of a strong Lewis acid is not required to "activate" the polymerization; propagation directly proceeds from α-iodo ether ends. As for systems mentioned above, the addition of an ammonium salt is required to get a "living" polymerization.

Kinetic data clearly show that ammonium salts are involved in different reaction processes, the main one corresponding to a conventional common ion salt effect. Therefore, this implies that the active propagating centers involved behave as ionic species, i.e., free and associated ions, coexisting in equilibrium. The extremely small amount of ammonium salt required to completely shift the equilibrium toward associated ions, deduced from the variation of k_p(app), is at first very surprising. In fact, it has to be taken into account that, in such systems, most of the α-iodo ether ends are assumed to be covalent species which only serve as reservoir to active ionic species,[13,14] as shown in Scheme 3a: α is the dissociation coefficient, C the total concentration of α-iodo ether, and C^* the concentration of ionized α-iodo ethers ($C^* = C^+ + C^{\pm}$).

On the basis of this polymerization pathway, we have tried to estimate which hypothetical K_D and C^* values best fit with kinetic data, considering that:

$$k_p = \alpha k_p^{+} + (1-\alpha)k_p^{\pm}$$

where k_p^+ and $k_p^\pm$ are, respectively, the propagating rate constants of free cations and of ion pairs, and k_p, the overall rate propagation constant, equals

$$k_p = k_p(\text{app})([\text{HI}]_0/C^*)$$

Accounting for the constant k_p(app) value over a large NBu_4I concentration range, it can be postulated that the ionization equilibrium (characterized by K_i) is independent of the ammonium salt concentration. Therefore, we may assume that C^* is constant for a given C and the classical mathematical treatment of ionic systems in the presence of a common ion salt has been applied.

The dissociation constant, K, of the ammonium salt (Scheme 3b) may be expressed by

$$K = \frac{[\text{NBu}_4^+][\text{I}^-]}{[\text{NBu}_4^+,\text{I}^-]}$$

whereas, the ionic dissociation constant of α-iodo ether ends, K_D, in the presence of NBu_4I, is expressed by

$$K_D = \frac{\alpha[\text{I}^-]}{1-\alpha}$$

where α is the dissociation coefficient. Besides, the electrical neutrality of the solution allows one to write

$$[\text{I}^-] = C^+ + [\text{NBu}_4^+]$$

Therefore, for $[NBu_4I] = C_0$, $C_0 = [NBu_4^+,I^-] + [NBu_4^+]$, and

$$K = \frac{[\text{NBu}_4^+][\text{I}^-]}{C_0 - [\text{NBu}_4^+]}$$

then

$$[\text{NBu}_4^+] = \frac{KC_0}{[\text{I}^-] + K}$$

From the classical treatment, we get the following expression of K_D:

$$K_D = \left([\text{I}^-] - \frac{KC_0}{[\text{I}^-] + K}\right)\frac{[\text{I}^-]}{C^*}$$

which leads to

$$[\text{I}^-]^3 + K[\text{I}^-]^2 - (KC_0 + K_DC^*)[\text{I}^-] - KK_DC^* = 0 \quad (3)$$

An ionic dissociation constant, $K = 8 \times 10^{-5}$ mol L^{-1}, for the ammonium salt, extrapolated from value of ref 15, was used in the calculations. Besides, a K_D value of 3×10^{-5} mol L^{-1} has been reported by Subira et al.[16] for the system $CH_2CH(OEt)^+SbCl_6^-$, but no K_D value is available in the literature, neither for α-iodo CHVE termini nor for others α-iodo ether ends. Therefore, a series of hypothetical K_D, recalculated from the K_D value of ref 16, and C^* values have been introduced in eq 3 in order to determine α, as well as the corresponding k_p^+, $k_p^\pm$, and k_p. Calculations were performed with $[NBu_4I] = C_0 = 1.54 \times 10^{-4}$ M,

Table 4. Variation of α and CHVE Propagation Rate Constants k_p, k_p^+, and $k_p^{\pm}$ for Different Hypothetical K_D and C^* Values ($[HI]_0 = 1.54 \times 10^{-2}$ M)

C^*,[a] mol L^{-1}	K_D, mol L^{-1}	α_1[b]	α_2,[c] with NBu_4I	$k_p^{\pm}$,[d] L mol^{-1} s^{-1}	k_p^+,[e] L mol^{-1} s^{-1}	k_p,[f] L mol^{-1} s^{-1}	$k_p/k_p^{\pm}$	$k_p^+/k_p^{\pm}$
$10^{-2}[HI]_0$	5×10^{-7}	0.055	0.006	0.8	108	1.5	1.85	135
$5 \times 10^{-3}[HI]_0$	10^{-6}	0.107	0.012	1.6	84	2.6	1.64	52
	5×10^{-7}	0.077	0.006	1.6	115	2.3	1.45	72
$10^{-3}[HI]_0$	10^{-6}	0.224	0.012	8	204	10.5	1.30	25
	5×10^{-7}	0.164	0.006	8	275	9.7	1.21	34
$10^{-4}[HI]_0$	5×10^{-6}	0.802	0.060	80	630	113	1.41	8
	10^{-6}	0.544	0.012	80	890	90	1.12	11
$10^{-5}[HI]_0$	10^{-5}	0.985	0.113	800	5270	1310	1.63	6.5
	5×10^{-6}	0.971	0.060	800	5340	1070	1.34	6.6
$10^{-6}[HI]_0$	10^{-5}	0.998	0.113	8000	52090	12980	1.62	6.5
	5×10^{-6}	0.996	0.060	8000	52170	10650	1.33	6.5

[a] $C^* = C^+ + C^{\pm}$ (see Scheme 3a). [b] Without ammonium salt, $\alpha_1 = [-K_D + (K_D^2 + 4C^*K_D)^{1/2}]/2C^*$. [c] With NBu_4I ($K = 8 \times 10^{-5}$ at −30 °C and $[NBu_4I] = [HI]_0/100 = 1.54 \times 10^{-4}$ M); $\alpha_2 = K_D/K_D + [I^-]$ with $[I^-]$ calculated from eq 3. [d] $k_p^{\pm} = k_p(\mathrm{app})[HI]_0/C^{\pm}$ L mol^{-1} s^{-1} ($k_p(\mathrm{app}) = 0.8 \times 10^{-2}$ L mol^{-1} s^{-1}, see Figure 3 and Table 1). [e] $k_p^+ = [(5.2 \times 10^{-2}) - 0.8 \times 10^{-2}(1 - \alpha_1)]/\alpha_1)([HI]_0/C^*)$ (see Figure 3 and Table 1. [f] $k_p = (1 - \alpha_2)k_p^{\pm} + \alpha_2 k_p^+$.

corresponding to 1% of $[HI]_0$, for which we may assume that $k_p \approx k_p^{\pm}$ (see Figures 3a,b). Values giving the best fitting with kinetic data are collected in Table 4.

With 1% of ionized α-iodo ether ends, corresponding to $C^* = 1.54 \times 10^{-4}$ M, even with a K_D value as low as 5×10^{-7} mol L^{-1}, the presence of NBu_4I ($C_0 = 1.54 \times 10^{-4}$ M) is not sufficient to completely suppress the contribution of free ions on k_p ($k_p/k_p^{\pm} = 1.85$).

It is necessary to take C^* lower than 1.54×10^{-6} M, i.e. $[HI]_0 \times 10^{-4}$, with appropriate K_D values ranging from 10^{-6} to 10^{-5} mol L^{-1}, to get k_p values close to $k_p^{\pm}$ ($k_p/k_p^{\pm} \leq 1.35$) for $[NBu_4I] = [HI]_0/100$ in satisfactory agreement with experimental results. These findings are consistent with an extremely low concentration of ions, as already postulated for such polymerization systems.[13,14]

It is now interesting to examine the k_p^+ and $k_p^{\pm}$ values, which may be determined from such low active species concentrations, and compare them with the propagation rate constants of conventional vinyl ether cationic polymerization. No k_p value is directly available for CHVE, but, in a first approach, we have used, as reference, kinetic data of isopropyl vinyl ether (IPVE), a monomer with a structure close to CHVE.[12] From Subira et al.,[16] a k_p of 5500 L mol^{-1} s^{-1}, at −30 °C, may be estimated for the IPVE polymerization initiated by $(Ph)_3C^+SbCl_6^-$ in CH_2Cl_2. In this system, the free ions' contribution is assumed to largely predominate,[16] therefore k_p^+ and k_p may be considered of the same order of magnitude ($k_p < k_p^+ < 2k_p$).

As indicated in Table 4, the concentration of active ionic species must be extremely low, close to 1.5×10^{-7} M, to obtain k_p^+ values in the same range of magnitude for CHVE and IPVE. This hypothetical C^* value would lead to $k_p^+ \approx 5000$ L mol^{-1} s^{-1}, assuming $K_D \approx 5 \times 10^{-6}$ mol L^{-1}.

Since going down again in C^* by a factor 10 (last line, Table 4) results in much higher rate constants for CHVE than reported for IPVE, which is unlikely, we may estimate the instantaneous concentration of active α-iodo ether ends to be in the 10^{-7} M range. This would correspond to about 1 active polymer end per 10^5 α-iodo ether chain termini.

In conclusion, this kinetic study, performed on the CHVE polymerization, initiated by hydrogen iodide, strongly suggests that the propagation reaction proceeds by an ionic mechanism involving both free ions and ion pairs. The addition of a minute amount of ammonium salts induces a common ion salt effect and leads to a "living" polymerization exclusively governed by ion pairs.

Experimental Section

Materials. CH_2Cl_2 (from Aldrich) and CHVE (from B.A.S.F. Co.) were stored in glass flasks over CaH_2 and cryodistilled just before use. nBu_4NCl, nBu_4NBr, and nBu_4NI (from Aldrich) were dried on CaH_2 in a CH_2Cl_2 solution; after 24 h, the solution was filtered with a cannula, and then CH_2Cl_2 was pumped off to recover the dried ammonium salt. The ammonium salts were stored under vacuum in a dry atmosphere (P_2O_5).

Polymerization Procedures. Polymerizations were carried out under dry nitrogen in a dilatometer at −30 °C. Successively introduced were 1 mL of HI (1.7×10^{-4} mol from a 0.17 M solution in toluene), nBu_4NX in a CH_2Cl_2 solution, and then 2.3 mL of CHVE (1.62×10^{-2} mol) in 6.5 mL of CH_2Cl_2. Kinetics were followed by measuring the level decrease of the solution in the dilatometer. The polymerization was quenched by tranferring the solution, through a cannula, to a chilled solution of $MeOH/NH_3$.

Polymer Characterization. Size exclusion chromatography (SEC) measurements were performed on a Varian apparatus fitted with 5TSK columns calibrated with polystyrene standards.

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