NATURE AND CONCENTRATION OF ACTIVE SPECIES IN CATIONIC POLYMERIZATION OF VINYL ETHERS: A KINETIC INVESTIGATION

HENRI CRAMAIL AND ALAIN DEFFIEUX*

Laboratoire de Chimie des Polymères Organiques, ENSCPB, Université Bordeaux 1, CNRS, Avenue Pey-Berland, BP108, 33405 Talence Cédex, France

The Kinetics of the polymerization of isopropyl vinyl ether, isobutyl vinyl ether (IBVE) and chloroethyl vinyl ether initiated by HI in CH_2Cl_2, in the presence and in the absence of tetrabutylammonium iodide as common anion salt, were investigated. The polymerizations proceed directly through the carbon–iodide termini without any necessary electrophilic activator. As previously observed with cyclohexyl vinyl ether, it was found that the addition of small amounts of salt, (0·5–10% with respect to initial [HI], depending on the monomer) drastically reduces the polymerization rate and leads to living-type polymerizations. Higher amounts of salt have no influence on the polymerization rate which remains constant over a broad range of $[NBu_4I]/[HI]$ ratios. This general behaviour, observed for the all vinyl ethers, suggests a common ion salt effect and therefore an ionic polymerization mechanism involving ion pairs and free ions. In the absence of salt, both ion pairs and free ions of higher reactivity participate in the propagation, whereas only ion pairs contribute to the propagation in the presence of a common ion salt. According to this scheme, the living character of the polymerization is assumed to result from a propagation reaction governed by undissociated ionic species. The validity and the implications of this reaction scheme, in terms of active centre concentrations, are also discussed.
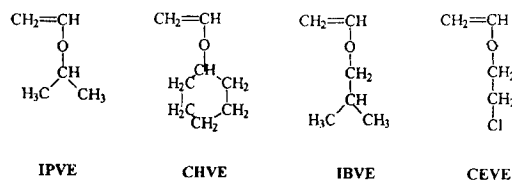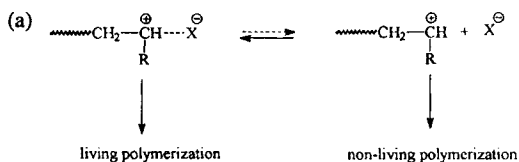
1. INTRODUCTION

The cationic polymerization of vinyl-type monomers emerged as a potentially interesting synthetic tool in the early 1980s, when it was shown that 'living' or 'quasi-living' polymerization processes could be induced by a new generation of initiating systems. The first examples of such living-type carbocationic polymerizations were reported by Miyamoto et al.[1] in the case of alkyl vinyl ethers and by Faust and Kennedy[2] for isobutylene. Before that time, carbocationic polymerizations were traditionally known as uncontrollable and irreproducible reactions. These peculiarities may now be attributed to the very high reactivity of fully ionized carbocationic species, such as free or loosely bound ion pairs, which prevail in conventional cationic systems. Incomplete initiation resulting from extremely fast propagation, and also side-reactions such as isomerization, chain transfer and uncontrolled termination, generally occur and lead to the formation of ill-defined oligomers. New-generation cationic polymerization systems[3,4] involve less active species of adjusted reactivity. This allows undesirable reactions to be suppressed but also the kinetics of initiation, propagation and termination steps
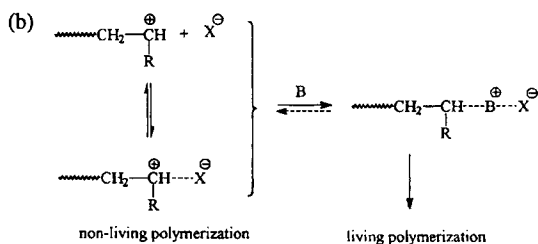
to be distinguished and therefore precise control of the dimensions, structure and functionality of the polymer chains.

Different routes have been explored in order to lower the reactivity of carbocationic species, but all are based on decreasing their ionicity. In the case of vinyl ethers, for example, this can be achieved either by associating the carbocationic ends with counterions of high nucleophilicity, to prevent the formation of free cationic species [Scheme 1(a)], or, for dissociated systems involving counterions of too weak nucleophilicity, by the addition of electron donor molecules (B) (Lewis bases, nucleophiles) which can complex with the carbocationic species to form, reversibly, more stable onium ions [(Scheme 1(b)]. Among the various initiating systems checked for the living polymerization of vinyl ethers, α-halo ethers, obtained by quantitative addition of Brönsted acids (HX) to vinyl ethers, have been widely investigated. Usually, in non-polar solvents (e.g. toluene) and at low temperature, these species cannot directly propagate the vinyl ether polymerization and a catalyst must be added to trigger the reaction. Iodine, mild Lewis acids (e.g. ZnX_2, SnX_2) or ammonium salts (e.g. NBu_4ClO_4) are typical activators. Polymerizations generally proceed in two distinct steps (Scheme 2): (a) formation of a vinyl ether adduct
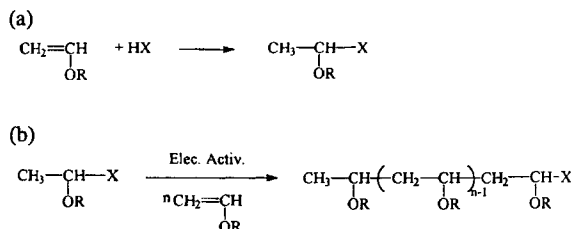
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* Author to whom correspondence should be addressed.

(a) living polymerization / non-living polymerization

(b) non-living polymerization / living polymerization

Scheme 1

(a)
$$CH_2=CH + HX \longrightarrow CH_3-CH-X$$
$$\quad\quad OR \quad\quad\quad\quad\quad\quad OR$$

(b)
$$CH_3-CH-X \xrightarrow[nCH_2=CH]{Elec.\ Activ.} CH_3-CH(CH_2-CH)_{n-1}CH_2-CH-X$$
$$\quad OR \quad\quad\quad\quad\quad OR \quad\quad OR \quad\quad OR$$

Scheme 2

IPVE   CHVE   IBVE   CEVE

Scheme 3

and (b) start of the polymerization by addition of an electrophilic activator.

Discussion continues concerning the accurate nature, covalent or ionic, of the active species involved in these polymerization systems. In particular, the quasi-absence of side-reactions and any detectable ionic species has led some workers[5] to consider a covalent insertion mechanism involving the formation of a six-member transition state between the carbon–halogeno termini, the Lewis acid and the monomer. Nevertheless, an alternative ionic mechanism dealing with the transient formation of ions in dynamic equilibrium with dormant covalent species has also been proposed and is now recognized by most workers.[6]

We have recently shown that fast polymerization of cyclohexyl vinyl ether (CHVE) can be initiated by hydrogen iodide without the necessary contribution of an activating agent, although the polymerization is not living under these conditions.[7] Surprisingly, it was found that a low concentration of tetrabutyl ammonium iodide (ca 1% with respect to α–iodo ether polymer ends) drastically reduces the polymerization rate and leads to polymers of predicted molar masses and narrow distribution. Kinetics[8] were interpreted by a mechanism

governed by ionic species of different nature, present in extremely low concentration.

This paper reports on a broader kinetic investigation of the polymerization of different vinyl ethers (Scheme 3), initiated by hydrogen iodide (HI) in the presence and in the absence of tetrabutylammonium iodide as common anion salt. The propagation kinetics of isopropyl vinyl ether (IPVE), isobutyl vinyl ether (IBVE) and chloroethyl vinyl ether, (CEVE) and those previously obtained for CHVE[8] are examined and discussed in terms of the polymerization mechanism.

RESULTS AND DISCUSSION

Polymerization of vinyl ethers initiated by HI in the presence or in the absence of tetrabutylammonium iodide

Polymerizations of vinyl ethers were carried out at $-30\,^{\circ}C$, in methylene dichloride (CH_2Cl_2). The HI–monomer adduct was directly prepared, in situ, by adding HI to a monomer solution in CH_2Cl_2, or containing both the monomer and NBu_4I for experiments performed in the presence of added salt. Polymerizations started immediately on adding HI and monomer conversions versus time were followed by dilatometry.

Conversion curves of the various vinyl ethers, including CHVE,[8] obtained in the absence and in the presence of 1 equiv of NBu_4I with respect to HI, are shown in Figure 1. It can be seen that for all the vinyl ethers investigated, a polymerization takes place despite the absence of any added electrophilic activator. Fast polymerizations are observed with IPVE and CHVE, whereas much longer reaction times are required for the other two monomers. A similar 'sluggish' IBVE polymerization was noted by Higashimura and co-workers[9] under very similar conditions (CH_2Cl_2, HI alone). Nevertheless, in these systems, traces of iodine, either (a) formed by a side process during the polymerization or (b) present in the initial HI solution, could be suspected of acting as the electrophilic activator. In the case of assumption (a), an acceleration of the polymerization rate, corresponding to an increase in the iodine concentration with time, should be observed: the rectilinear variations of $\ln[M]_0/[M]$ versus time, up to very high monomer conversions (Figure 2), allow us to reject this assumption. It is more
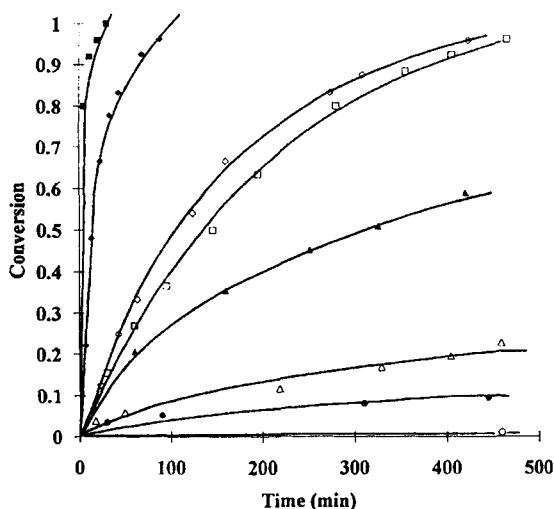
Figure 1. Variation of monomer conversion with time for the polymerization of various vinyl ethers initiated by HI in the presence and absence of NBu_4I, in CH_2Cl_2 at $-30\,°C$.
($\blacksquare$) [IPVE] = 1·67 M [HI] = 0·0152 M [NBu_4I] = 0;
($\square$) [IPVE] = 1·67 M, [HI] = [NBu_4I] = 0·0152 M;
($\blacklozenge$) [CHVE] = 1·46 M [HI] = 0·0154 M [NBu_4I] = 0;
($\lozenge$) [CHVE] = 1·46 M, [HI] = [NBu_4I] = 0·0154 M;
($\blacktriangle$) [IBVE] = 1·43 M [HI] = 0·0120 M, [NBu_4I] = 0;
($\triangle$) [IBVE] = 1·43 M, [HI] = [NBu_4I] = 0·0120 M;
($\bullet$) [CEVE] = 2·00 M, [HI] = 0·0120 M, [NBu_4I] = 0;
($\circ$) [CEVE] = 1·43 M, [HI] = [NBu_4I] = 0·0120 M

difficult to definitely eliminate the possibility (b). However, it was checked that both fresh and aged HI solutions gave identical polymerization kinetics. In addition, it has been shown[10] that the addition of an ammonium salt to $HI-I_2$-mediated vinyl ether polymerizations leads to rapid inhibition of the reaction, owing to the complexation of iodine with NBu_4I. As will be seen further, in the present systems the polymerization rate first decreases on adding a small amount of NBu_4I, then rapidly reaches a plateau corresponding to a constant rate, independent of further amounts of added salt. These findings support that traces of iodine, if present, do not have a significant influence on the kinetics and, consequently, that monomer insertion can proceed directly into α-iodo ether species in CH_2Cl_2.

Therefore, considering a fast initiation, the propagation rate, R_{p0} can be satisfactorily expressed by

$$R_{p0} = k_p \text{ (app) } [M]_0[RI]$$

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

$$R_{p0} = k_p \text{ (app) } [M]_0[HI]_0$$

and an apparent initial propagation rate constant, k_p(app), can be calculated. Results are given in Tables 1 and 2 for the various monomers.

(a)

(b)

Figure 2. (a) Variation of semi-logarithmic monomer concentration with time for the polymerization of IPVE initiated by HI in the presence of various amounts of NBu_4I in CH_2Cl_2 at $-30\,°C$. [IPVE] = 1·67 M, [HI] = 0·0152 M. ($\blacksquare$) [NBu_4I] = 0; ($\square$) [NBu_4I]/[HI] = 0·0089; ($\blacklozenge$) [NBu_4I]/[HI] = 0·085; ($\lozenge$) [NBu_4I]/[HI] = 0·21; ($\blacktriangle$) [NBu_4I]/[HI] = 1; ($\triangle$) [NBu_4I]/[HI] = 9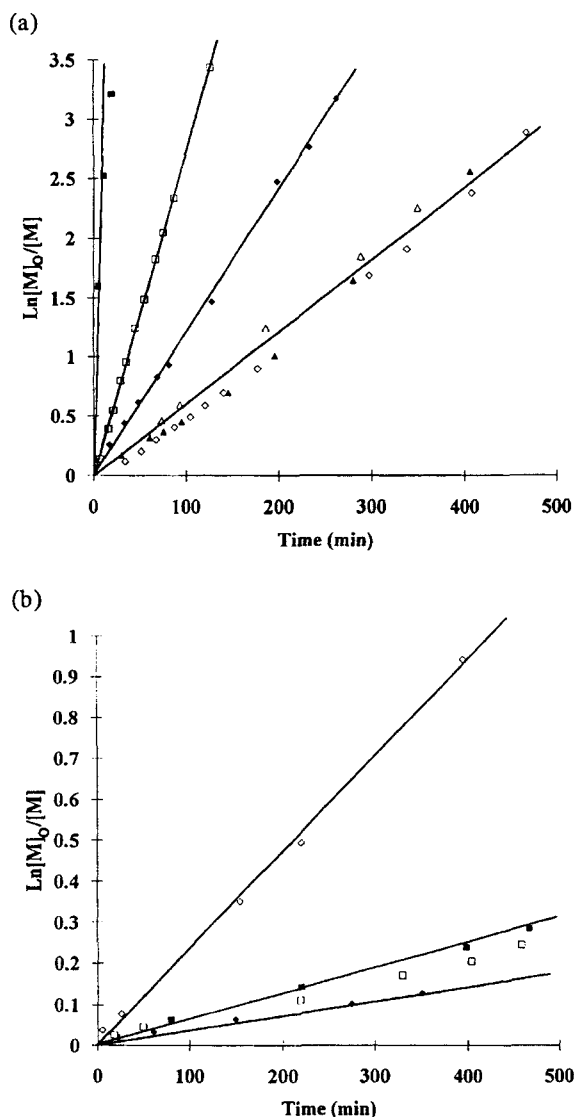. (b) Variation of semi-logarithmic monomer concentration with time for the polymerization of IBVE initiated by HI in the presence of various amounts of [NBu_4I] in CH_2Cl_2 at $-30\,°C$. [IBVE] = 1·43 M, [HI] = 0·0120 M. ($\lozenge$) [NBu_4I] = 0; ($\blacksquare$) [NBu_4I]/[HI] = 0·0037; ($\square$) [NBu_4I]/[HI] = 0·0067; ($\blacklozenge$) [NBu_4I]/[HI] = 1

Table 1. Polymerization of vinyl ethers initiated by HI alone or in the presence of 1 equiv. of NBu_4I at $-30\,^\circ C$ in CH_2Cl_2

Monomer M	[M] (mol l^{-1})	[HI] $\times 10^2$ (mol l^{-1})	$[NBu_4I]/[HI]$	$t_{50\%}$ (min)	$10^2\, k_p(app)$ (l $mol^{-1}s^{-1}$)	$\bar{M}_n(th.)^a$ (g mol^{-1})	$\bar{M}_n(exp.)^b$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
IPVE	1·67	1·52	0	2	27	9560	5910	1·23
	1·67	1·52	1	140	0·60	9560	10500	1·10
CHVE	1·46	1·54	0	14	5·20	12120	9940	1·47
	1·46	1·54	1	100	0·80	12120	12150	1·15
IBVE	1·43	1·20	0	310	0·30	12050	11200	1·17
	1·43	1·20	1	1740^c	0·04	1800^d	1900^d	1·08
CEVE	2·00	1·20	0	9630^c	0·01	2700^d	2630^d	1·52
	2·00	1·20	1	^{c}	–	17900	–	–

^{a}Calculated from the equation $\bar{M}_n(th.) = ([M]_0/[HI]_0)M_{monomer} \times \%$ conv. $+ M_{end\ groups}$.
^{b}Determinted by SEC at the end of the polymerization after complete monomer conversion.
^{c}Estimated from $k_p(app)$; $t_{50\%}$ (min) $= \ln 2/k_p(app) \times [HI]_0 \times 60$.
^{d}Determined by SEC after 15% conversion.

Table 2. Influence of $[NBu_4I]/[HI]$ ratio on IPVE and IBVE polymerizations at $-30\,^\circ C$ in CH_2Cl_2

Monomer M	[M] (mol l^{-1})	[HI] $\times 10^2$ (mol l^{-1})	$[NBu_4I]/[HI]$	$t_{50\%}$ (min)	$10^2\, k_p(app)$ (l $mol^{-1}s^{-1}$)	$\bar{M}_n(th.)^a$ (g mol^{-1})	$\bar{M}_n(exp.)^b$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
IPVE	1·67	1·52	0	2	27	9560	5910	1·23
	1·67	1·52	0·0089	25	2·90	9560	8900	1·09
	1·67	1·52	0·085	60	1·40	9560	9750	1·06
	1·67	1·52	0·21	140	0·59	9560	9200	1·13
	1·67	1·52	1	140	0·60	9560	10500	1·10
	1·67	1·52	9	130	0·62	9560	10150	1·08
IBVE	1·43	1·20	0	310	0·30	12050	11200	1·17
	1·43	1·20	0·0037	1375	0·07	12050	11000	1·05
	1·43	1·20	0·0067	1925^c	0·05	12050	11840	1·09
	1·43	1·20	1	2405^c	0·04	1800	1900^d	1·08

^{a}Calculated from the equation $\bar{M}_n(th.) = ([M]_0/[HI]_0)M_{monomer} \times \%$ conv. $+ M_{end\ groups}$.
^{b}Determinted by SEC at the end of the polymerization after complete monomer conversion.
^{c}Estimated from $k_p(app)$; $t_{50\%}$ (min) $= \ln 2/k_p(app) \times [HI]_0 \times 60$.
^{d}Determined by SEC after 15% conversion.

In the absence of NBu_4I, the polymerization reactivity order, CEVE ≪ IBVE < CHVE < IPVE, follows the order of increasing donor character of the vinyl ether substituent, as observed in conventional cationic polymerization.

As can be seen in Figure 1 and Table 1, the addition of tetrabutylammonium iodide ($[NBu_4I]/[HI] = 1$) reduces drastically the vinyl ether polymerization rates. A much more pronounced effect is observed for IPVE [$k_p(app)$ reduced by a factor of 45] compared with other vinyl ethers (factor of 6–8). This leads to a reversed reactivity order for IPVE and CHVE in the presence of salt. It is interesting that the $k_p(app)$ value obtained for IBVE in the presence of NBu_4I is in good agreement with those reported by Nuyken and Kröner.[11] However, our results with IBVE show that NBu_4I does not act as an activator, in contrast to other tetrabutylammonium salts (e.g. perchlorate).

The polymer molar masses and polymer molar mass distributions (MMDs), given in Table 1, show that polymerizations performed in the absence of salt are not living, except possibly for IBVE. The experimental molar masses are much lower than the theoretical values calculated assuming one polymer chain per HI molecule. Moreover, relatively broad poly(vinyl ether) MMDs are also observed. Since we may assume a constant active centre concentration during the polymerization from the rectilinear variation of $\ln[M]_0/[M]$ with time, (Figures 2) the non-living character of the polymerization in the absence of salt can be mainly attributed to chain-transfer reactions.

In the case of polymerizations performed in presence of NBu_4I, in contrast, the experimental $\bar{M}_n$ remain very close to the theoretical values and the polymer MMDs are ≤ 1·15, in agreement with the occurence of a
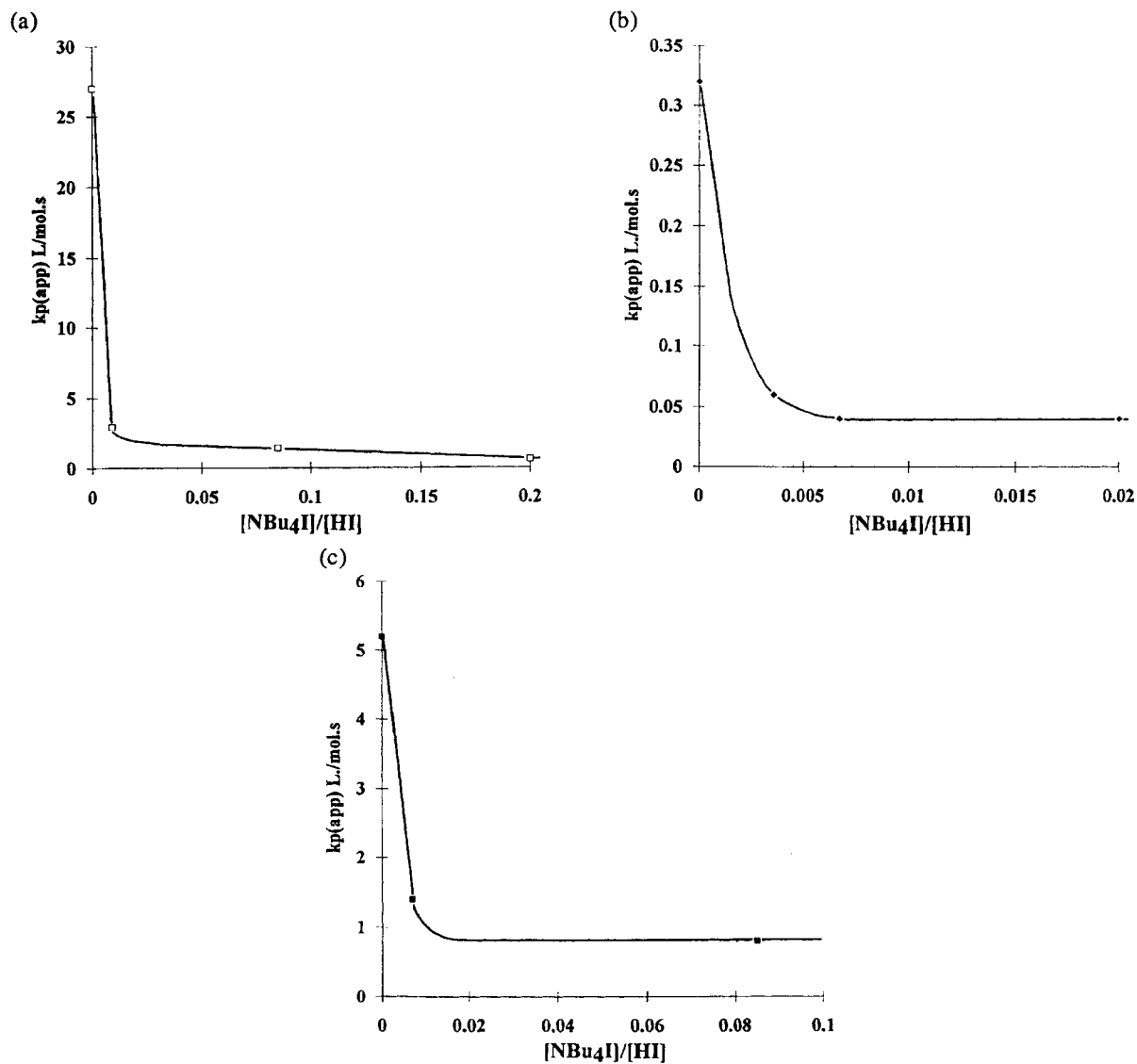
living-type polymerization process for the all vinyl ethers.

As already pointed out for CHVE,[8] the kinetic data are consistent with a conventional common ion salt effect, and suggest a propagation reaction under the control of ionized species of different nature. In the absence of salt, both ion pairs and free ions of higher reactivity would participate to the propagation, whereas only ion pairs would contribute to the propagation in the presence of a common ion salt. According to this scheme, the living character of the polymerization might result from a propagation reaction governed by undissociated ionic species (Scheme 4).

Influence of NBu₄I concentration on kinetics of vinyl ether polymerizations

In order to confirm the hypothesis of an ionic polymerization mechanism, the influence and the role of NBu₄I on the propagation reaction of vinyl ethers initiated by HI in CH₂Cl₂ were further investigated. A series of polymerizations were conducted with both IPVE and IBVE in the presence of various amounts of NBu₄I. The reactivity of the CEVE system was too low to permit an accurate investigation.

The variations of $\ln[M]_0/[M]$ with time for different [NBu₄I]/[HI] ratios ranging from 10^{-3} to $\geqslant 1$ are shown in Figure 2(a) and (b) for IPVE and IBVE, respectively. A linear dependence is observed up to very high monomer conversions. As it may be seen in Table 2, for both IBVE and IPVE, the polymerization rates decrease drastically on adding extremely small amounts of NBu₄I and then reach a plateau corresponding, for each system, to a constant k_p(app), independent of higher amounts of added salt. The variations of the propagation rate constant k_p(app) with ([NBu₄I]/[HI]) are plotted in Figure 3(a) and (b). As can be seen, the amount of NBu₄I necessary to reach the plateau depends strongly on the vinyl ether structure. 0·5% of added salt [NBu₄I]/[HI] = 0·005) is sufficient to drive the apparent propagation rate constant of IBVE to the plateau, whereas 10% (20 times more) is necessary in the case of IPVE. As already reported for CHVE, the plateau is reached with about 1% of added salt, [see Figure 3(c)].

Moreover, as can be seen in Table 2, the presence of minute amounts of salt gives access to living-type polymerizations. These results confirm that the behaviour first observed for CHVE may be generalized to

other vinyl ethers of various reactivity. A similar salt effect has also been used to induce the living polymerization of N-vinyl carbazole initiated by HI in CH₂Cl₂.[12]

These data can be interpreted by the occurrence of a conventional ionic mechanism involving free carbocations in equilibrium with ion pairs.

Although already discussed in the case of CHVE,[8] the fact that extremely small amounts of ammonium salt are sufficient to shift the ionic equilibrium completely towards associated ions requires further comment. In these vinyl ether polymerization systems, it is generally accepted that most of the α-iodo ether polymer ends are covalent species. It has been proposed that the latter are inactive ('dormant') towards vinyl ether polymerization but can temporarily and reversibly ionize (Scheme 5), to lead to active carbocationic species.

In this scheme, the ionic polymer ends concentration C^* will depend mainly on the overall α-iodo ether concentration C (reasonably assumed to be equal to [HI]₀) and on the ionization equilibrium constant value (K_i). Taking account of the constant value of k_p(app) at the plateau, over a broad range of NBu₄I concentrations (see Figure 3), f)r a polymerization system and a given C value, C^* may be assumed to be constant. A tendency for higher ionization of α-iodo ether species (higher K_i) may be expected with an increase in the donor effect of the OR vicinal substituent of the α-iodo ether group.

Further, the relative proportion of ionic species, i.e. free ions and ion pairs, will depend on the K_D and C^* values, and also on the concentration of the added common ion salt: the higher is [NBu₄I], the smaller is the fraction of free ions.

Subira et al.[13] have reported a K_D value of 3×10^{-5} mol l⁻¹ for the system CH₂CH(OEt)⁺SbCl₆⁻, but no value is available in the literature for α-iodo ether species. The effects of a series of hypothetical K_D and C^* values on the fraction of free ions, in the presence of increasing proportions of NBu₄I as common salt [$K = 8 \times 10^{-5}$ mol l⁻¹ (Ref. 14)], have been examined. The variations of α/α_0, where α and α_0 are the ionic dissociation coefficient of α-iodo ether ends in the presence and in the absence of NBu₄I, respectively, with [NBu₄I]/[HI] are plotted in Figures 4 and 5. It can be seen that it is necessary to consider both low K_D and low C^* values to explain the salt effect (suppression of free ions) for very low [NBu₄I]/[HI] ratios, as is suggested by the kinetic

non-living polymerization   living polymerization

Scheme 4

Scheme 5

(a)

(b)

(c)

Figure 3a. Variation of the apparent propagating rate constant, k_p(app), of (a) IPVE, (b) IBVE and (c) CHVE with the [NBu$_4$I]/[HI] ratio

results. For a K_D value in the range 10^{-5}–10^{-6} M, consistent with the value reported by Subira et al.,[13] C^* should correspond to 10^{-5}[HI] and 10^{-4}[HI], respectively, to be in agreement with the kinetic data. These C^* values signify that at time t, for one chain end ionized and active, 10^4–10^5 are dormant covalent ones. Since each HI molecule introduced gives rise to a poly(vinyl ether) chain and that, as shown by the narrow MMD, all chains grow at the

same rate, very fast interconversions should proceed between the covalent and the ionic forms of polymer ends.

Since the overall propagation rate constant k_p is linked to k_p(app) by the relationship

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

and assuming that k_p represents the relative and unique contribution of ion pairs and free ions to the
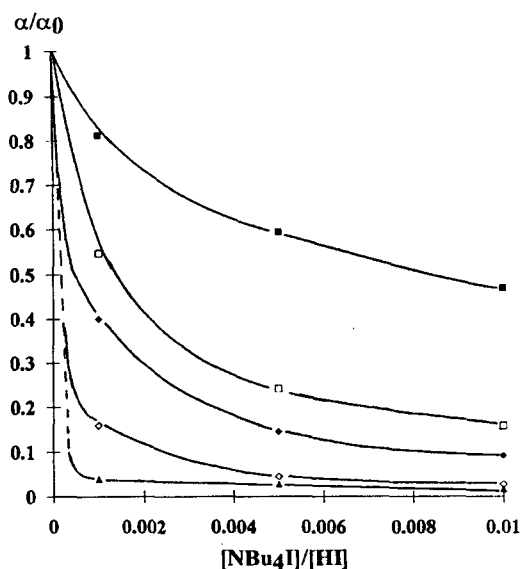
Figure 4. Variation of α/α_0 with [NBu$_4$I]/[HI] ratio for different hypothetical K_D values assuming $C^* = 10^{-4}$[HI] M; $K_{NBu4I} = 8 \times 10^{-5}$ M;[14] [HI] $= 0{\cdot}01$ M. $K_D =$ (■) 5×10^{-5}; (□) 1×10^{-5}; (♦) 10^{-6}; (◊) 1×10^{-6}; (▲) 5×10^{-7}

Figure 5. Variation of α/α_0 with [NBu$_4$I]/[HI] ratio for different hypothetical C^* values assuming $K_D = 10^{-6}$ M; $K_{NBU4I} = 8 \times 10^{-5}$ M;[14] [HI] $= 0{\cdot}01$ M. $C^* =$ (■) 10^{-1} [HI]$_0$; (□) 10^{-2} [HI]$_0$; (▲) 10^{-3} [HI]$_0$; (◊) 10^{-4} [HI]$_0$; (▲) 10^{-5} [HI]$_0$

polymerization,

$$k_p = \alpha k^+_p + (1 - \alpha)k^\pm_p$$

then

$$k_p(\text{app}) = [\alpha k_p^+ + (1 - \alpha)k_p^\pm]C^*/[\text{HI}]_0$$

Since [HI]$_0$ was kept constant in the kinetic studies, C^* may be assumed to be constant for a given polymerization system. Therefore, for a given vinyl ether, changed in kinetic data mainly result from the variation in the fraction of free ions.

In the case of various vinyl ethers, however, the k^+_p, $k^\pm_p$ and C^* terms will also vary. A comparison is therefore difficult between the kinetic data for different vinyl ethers, in particular regarding the variance in the [NBu$_4$I]/[HI] ratio necessary to reach the k_p(app) plateau. Indeed, the observed variations in polymerization rate will also depend very much on the difference between the propagation rate constants of free cations and of ion pairs, k^+_p and $k^\pm_p$. This might explain in part the specific behaviour of IPVE.

In conclusion, the kinetics of vinyl ether polymerizations initiated by HI in CH$_2$Cl$_2$ strongly suggest a reaction mechanism involving ionic species of different natures, namely ion pairs and free ions, present in extremely small concentration. These are formed by reversible ionization of covalent α-iodo ether species which are inactive for vinyl ether polymerization. The reactivity of free ions is much higher than that of ion
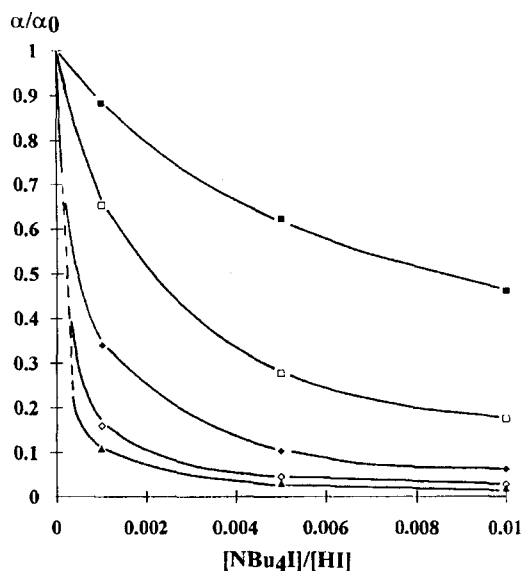
pairs and the dissociated species govern the polymerization in the absence of a common ion salt to lead to a non-living polymerization. However, because of the very low concentration of active ionic species, minute amounts of a common ion salt, such as tetrabutylammonium iodide, are sufficient to shift completely the ionic dissociation equilibrium towards ion pairs of lower reactivity. The latter are able to give a living-type polymerization.

Apart from the monomer reactivity effect, the differences observed in the kinetic behaviour of the various vinyl ethers on adding increasing amounts of salt can be interpreted by the capacity of the corresponding α-iodo ether ends, probably related to the donor character of the OR substituent, both to ionize and to form free ions. In addition, the absolute reactivities of ion pairs and free ions will also strongly influence the polymerization kinetics on varying the dissociation coefficient α.

The relative contributions of these different parameters to kinetics are under investigation using a more refined mathematical treatment and detailed copolymerization experiments.

EXPERIMENTAL

Materials. CH$_2$Cl$_2$ (from Aldrich), IBVE (from Aldrich) and CHVE (from BASF) were stored in glass flasks over CaH$_2$ and cryo-distilled just before use. nBu$_4$NI (from Aldrich) was dried over CaH$_2$ in CH$_2$Cl$_2$

solution; after 24 h, the solution was filtered with a cannula and CH_2Cl_2 was pumped off to recover the dried ammonium salt. The latter was stored under vacuum in a dry atmosphere (P_2O_5).

Synthesis of isopropyl vinyl ether.[15] Mercury(II) acetate (6·5 g, 0·020 mol) was dissolved in a mixture of dry isobutyl vinyl ether (81 ml, 0·623 mol) and dry propan-2-ol (62 ml, 0·809 mol). The resulting solution was placed in a large distillation column fitted with a total condensation partial take-off head. The distillation was first maintained at total reflux until the vapour temperature settled at 55–56 °C and the rate of distillation was thereafter adjusted so as to keep the boiling point within this range. The recovered product was distilled again over NaH to give 21·5 ml of IPVE (30% yield).

Polymerization procedure (see Ref. 8). Although no promoting effect of light on vinyl ether polymerization initiated by HI could be detected, for safety the kinetic studies vere performed in systems protected from light.

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

REFERENCES

1. M. Miyamoto, M. Sawamoto and T. Higashimura, *Macromolecules* 17, 265 (1984); M. Sawamoto and T. Higashimura, *Makromol. Chem., Macromol. Symp.* 3, 83 (1986).
2. R. Faust and J. P. Kennedy, *Polym. Bull.* 15, 317 (1986); R. Faust and J. P. Kennedy, *J. Polym. Sci., Polym. Chem. Ed.* 25, 1847 (1987).
3. M. Sawamoto, *Prog Polym. Sci.* 16, 111–172 (1991).
4. J. P. Kennedy and B. Ivan, *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practise.* Hanser Publishers, New-York (1991).
5. T. Higashimura, M. Miyamoto and M. Sawamoto, *Macromolecules* 18, 611 (1985); K. Kojima, M. Sawamoto and T. Higashimura, *Macromolecules* 24, 1552 (1989); P. H. Plesh, *Makromol. Chem., Macromol. Symp.* 32, 299 (1990); K. Matyjaszewski, *J. Polym. Sci., Part A, Polym. Chem.* 25, 765 (1987).
6 K. Matyaszewski, *Makromol. Chem., Macromol. Symp.* 13/14, 433 (1988); P. Sigwalt, *Makromol. Chem., Macromol. Symp.* 47, 179 (1991); M. Schappacher and A. Deffieux, *Macromolecules* 24, 4221 (1991); H. Cramail, A. Deffieux and O. Nuyken, *Makromol. Chem., Rapid Commun.* 14, 17 (1993); M. Kamigaito, Y. Maeda, M. Sawamoto and T. Higashimura, *Macromolecules* 26, 1643 (1993).
7. H. Cramail and A. Deffieux, *Macromol. Chem. Phys.* 195, 217 (1994).
8. H. Cramail and A. Deffieux, *Macromolecules* 27, 1401–1406 (1994).
9. T. Enoki, M. Sawamoto and T. Higashimura, *J. Polym. Sci., Part A, Polym. Chem. Ed.* 24, 2261 (1986); M. Sawamoto, C. Okamoto and T. Higashimura, *Macromolecules* 20, 2693 (1987).
10. T. Ohtori, Y. Hirokawa and T. Higashimura, *Polym. J.* 11, 471, (1979).
11. O. Nuyken and H. Kröner, *Makromol. Chem.* 191, 1 (1990).
12. M. Sawamoto, J. Fujimori and T. Higashimura, *Macromolecules* 20, 916 (1987).
13. F. Subira, J. P. Vairon and P. Sigwalt, *Macromolecules* 21, 2339 (1988).
14. I. Svorstol, H. Hoiland and J. Songstad, *Acta Chem. Scand., Ser. B* 38, 885 (1984); I. Svorstol and J. Songstad, *Acta Chem. Scand., Ser. B* 39, 639 (1985).
15. W. H. Watanabe and L. B. Coulon, *J. Am. Chem. Soc.* 79, 2828 (1957).