A study of the cationic copolymerization of ethyl and isopropyl vinyl ethers induced by radiation

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The radiation-induced cationic copolymerization of ethyl and isopropyl vinyl ethers has been studied in bulk with varying compositions of the monomer feed. The copolymer compositions have been determined. The results show that incorporation rates of IPVE and EVE differ only by about 5 times, leading us to conclude that the large difference previously observed in the bulk homopolymerization rates comes mainly from the relative reactivity of the growing ends. The overall rate of consumption of the comonomers varies drastically with the composition of the feed and a deactivating effect of EVE on the homoaddition rate of IPVE has been observed. This was attributed to an intrasolvation of the growing ~~~IPVE⁺ ends by the last EVE units incorporated in the copolymer chain.

INTRODUCTION

The radiation-induced cationic polymerization of ethyl and isopropyl vinyl ethers in bulk and in various solvents ranging from hydrocarbons to nitromethane have been reported in the previous articles in this series[1-4].

It was shown that the experimental rates of polymerization fitted the theoretical Hayashi–Williams equation[5,6]. The kinetics have been interpreted by a predominant effect on the reactivity of the solvation state of the unpaired* propagating cations. In the polymerization of ethyl vinyl ether (EVE) in solvents of low polarity[1,3], solvation of the poly EVE growing ends was assumed to be largely dominated by an intrasolvation of the active centres by the polymer chains themselves. With the isopropyl vinyl ether (IPVE) much higher reactivity was observed and attributed to a drastic reduction of the polymer intrasolvation of the growing chain ends, due to the bulkiness of the isopropyl side groups[4].

In polar solvents the reactivities of both monomers are strongly affected by the nature of the solvent. The polymerization rates decrease drastically with such solvents compared with those of low polarity. Moreover the rates with both monomers tend to approach each other suggesting a similar state of solvation of the growing cations. It was postulated that in these media solvation occurred mainly by the solvent molecules. The activation parameters of the reactions $\Delta G\neq$, $\Delta H\neq$ and $\Delta S\neq$ supported these interpretations.

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* As they are generally solvated 'free' cations will be qualified as 'unpaired' in the text.

The propagation rate constants for the unpaired ion polymerization process, k_p, have been determined in these different media using the simplified Hayashi–Williams equation:

$$R_p = \frac{k_p[M]R_{im}^{1/2}}{k_{tm}^{1/2}} \tag{5}$$

where R_p, k_p, R_{im} and k_{tm} are the rates of polymerization the propation rate constants the rates of initiation and the rates of termination, respectively in the given medium.

Some typical results are collected in *Table 1*. Determination of the rate constants imply the calculation of the stationary unpaired propagating cation concentrations, $[C^+]$, which depends on the nature and on the relative amount of monomer and solvent. As discussed previously[1-3] the calculation is based on the estimation of the 'free' ion yields of mixtures, G_{im}, by the theory developed by Allen[7,8] and on the determination of the rate constant of ion recombination, k_{tm}, from the simplified Debye equation[6]

$$|C^+| = \left|\frac{10IG_{im}}{Nk_{tm}}\right|^{1/2} = \frac{R_{im}^{1/2}}{k_{tm}^{1/2}} \tag{2}$$

Rate measurements, combined with electrical conductivity measurements in the radiation field have also been used to obtain an estimate of the termination rate constant[5,6]. In the case of isobutyl vinyl ether all the parameters have been determined[5,9]. A good correlation in k_{tm} values calculated by both methods was observed[6],

Table 1 Rate constants of polymerization in the radiation-induced cationic polymerization of EVE and IPVE in bulk and in solution at 30°C

Solvent	EVE $k_p \times 10^{-2}$ ($l\,mol^{-1}\,s^{-1}$)	IPVE $k_p \times 10^{-2}$ ($l\,mol^{-1}\,s^{-1}$)
Bulk	600	13000
Benzene	360	5700
Diethylether	260	3400
Diglyme	480	–
Methylene dichloride	34	150
Nitromethane	1	2

$[IVE]_0 = 5.4$ mol l^{-1}
$[IPVE]_0 = 4.4$ mol l^{-1}

giving us some confidence in using the Debye equation.

However, in all these calculations the bulk dielectric constants have been used. These could largely differ from the effective microdielectric constants around the ions which would be more valid but unfortunately are not accessible. The discrepancy should be particularly important in polymerization in solvents of high dielectric constant, but also with the different solvation processes that we have already postulated. These could strongly affect the rates of formation and the rates of recombination of unpaired ions and in consequence the stationary concentration of unpaired ions. These could account, at least in part for the large differences in the rate constants of propagation observed in the homopolymerization of EVE and IPVE in solvents of low polarity[1,4].

In order to minimize these effects in the determination of the relative reactivity of vinyl ethers, the kinetic behaviour of ethyl and isopropyl vinyl ethers have been directly compared in copolymerization experiments.

The results are reported and discussed in this paper.

EXPERIMENTAL

Materials

EVE (Aldrich Co) and IPVE (Pfaltz and Bauer) were purified as previously described[1-4].

Polymerization

The techniques used have already been described in detail[1-4]. The polymerization tubes were degassed under high vacuum at 450°C for 24 h, filled with suitable amounts of EVE and IPVE, measured in calibrated tubes and sealed under high vacuum.

Irradiations were carried out in a ^{60}Co γ-ray source

under controlled temperature. After the appropriate irradiation time the tubes were opened and the unreacted monomers evaporated. The overall conversions were obtained by gravimetry.

The composition of the copolymers were determined on a Brücker 250 MHz proton n.m.r. apparatus.

The molecular weight distributions of the copolymers were determined with a G.P.C. (Water Associates), fitted up with 6μ-styragel columns of 10^5, 10^4, 10^3, 500 and 2×100 Å. Toluene was used as the eluent.

RESULTS AND DISCUSSION

Copolymerizations have been performed in bulk at +1°C with varying relative amounts of EVE and IPVE in the feed. The composition of the copolymers have been determined by proton n.m.r. analysis. Typical experimental results are given in *Table 2* where good reproducibility was found. The variation of the percentage of IPVE incorporated in the copolymer *versus* the percent of IPVE monomer in the feed is plotted in *Figure 1*.

The unimodal distribution of the molecular weights was verified by g.p.c. No significant variation in the $\bar{M}_w$ was observed with the monomer composition, indicating significant transfer reactions and at the same time that the
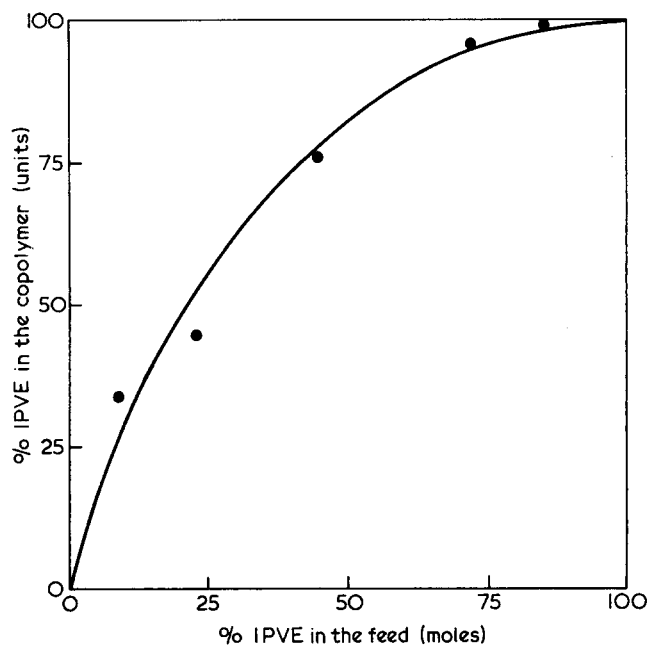

Figure 1 Copolymer compositions with different compositions of the monomer feed ($T = +1°C$, dose rate: 71 rad s^{-1})

Table 2 Radiation-induced cationic copolymerization of EVE and IPVE in bulk ($T = 1°C$, dose rate 71 rad s^{-1})

Composition of the feed			Irradiation time (h)	% Conversion	Copolymer composition % IPVE units
$[EVE]_0$ mol l^{-1}	$[IPVE]_0$ mol l^{-1}	% IPVE (mol)			
10.5	0	0	32.85	10.7	0
9.5	0.9	9	13.33	6.8	34
7.9	2.2	22	9.66	18.6	45
5.3	4.4	45	3.75	33.2	76
2.7	6.5	71	0.66	17.1	96
1.4	7.7	85	0.3	13.5	>99
0	8.7	100	0.66	39.6	100

ratio of the constants $k_p/k_{transfer}$ were similar for both monomers.

The copolymer compositions confirm the higher rate of incorporation of the IPVE in the copolymer, in agreement with the overall order of reactivity previously established in bulk homopolymerization. The ratio of the incorporation rates of both monomers was found to be close to 5 within the experimental error. This value is much lower than the ratio of the homopolymerization rate, more than 100 at 0°C.
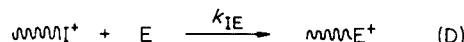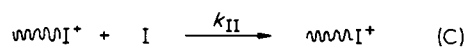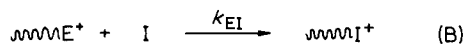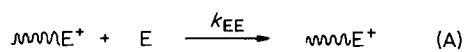
In the copolymerization the incorporation ratios reflect the differences in the reactivity of each monomer towards the same active centres. A very similar value was obtained by Subira et al.[10,11] in their study of the initiation reaction of the cationic polymerization of EVE and IPVE with trityl hexachloroantimonate. They found a ratio of addition rates of EVE and IPVE on Ph_3C^+ of 6.5 at 0°C, in CH_2Cl_2.

The incorporation ratio clearly show that the monomer reactivities are not responsible for the large difference in reactivity observed in the radiation-induced homopolymerization of ethyl and isopropyl vinyl ethers in the bulk.

In spite of the very similar structure of both ethers a strong variation in the active centre concentration, due to side phenomena, linked for example to the solvation of growing cations could be postulated. However, such processes would lead to an increase in the unpaired ion concentration with the increase in charge stabilization, similar to what is observed with an increase in the dielectric constant[2,3,7] and are not in agreement with the trend observed, i.e., the more active (IPVE) is the less solvated. It appears therefore that the main contribution to the reactivity observed in the radiation-induced polymerization of ethyl and isopropyl vinyl ethers in the bulk could only come from the relative reactivity of the poly EVE and the poly IPVE growing ends.

The overall rates of consumption of the monomer mixtures have been determined in the copolymerization experiments using gravimetric and n.m.r. techniques. The results are collected in *Table 3*. A drastic decrease of the rate is observed when the proportion of EVE in the feed increases.

According to the kinetic scheme of the copolymerization reaction:

$$\text{\it mmmE}^+ + E \xrightarrow{\ k_{EE}\ } \text{\it mmmE}^+ \qquad (A)$$

$$\text{\it mmmE}^+ + I \xrightarrow{\ k_{EI}\ } \text{\it mmmI}^+ \qquad (B)$$

$$\text{\it mmmI}^+ + I \xrightarrow{\ k_{II}\ } \text{\it mmmI}^+ \qquad (C)$$

$$\text{\it mmmI}^+ + E \xrightarrow{\ k_{IE}\ } \text{\it mmmE}^+ \qquad (D)$$

where E and I are the EVE and IPVE monomers respectively, E^+ and I^+ the corresponding propagating centres and k_{EE}, k_{II}, k_{EI} and k_{IE} the rate constants of homo and cross addition.

The overall rate of consumption of both monomers, R_C, can be expressed by the kinetic equation:
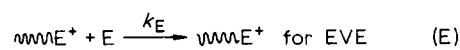
$$R_C = k_{EE}|E^+||E| + k_{EI}|E^+||I| + k_{II}|I^+||I| + k_{IE}|I^+||E| \quad (3)$$

$$R_C = |E^+|[k_{EE}|E| + k_{EI}|I|] + |I^+|[k_{II}|I| + k_{IE}|E|] \quad (3a)$$

Table 3 Experimental and calculated overall rate of incorporation of monomers in the radiation-induced copolymerization of EVE and IPVE, in bulk at +1°C
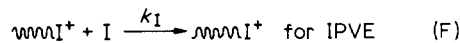
Initial monomer Composition in the feed mol l^{-1}		Experimental R_C mol l^{-1} s^{-1}	Calculated R_C minimal mol l^{-1} s^{-1}	$\dfrac{R_C \text{ minimal}}{R_C \text{ exp.}}$
$[EVE]_0$	$[IPVE]_0$			
0	8.7	1.4×10^{-3}	1.4×10^{-3}	–
1.4	7.7	1×10^{-3}	1.2×10^{-3}	1.2
2.7	6.5	6.5×10^{-4}	1×10^{-3}	1.5
5.3	4.4	2.4×10^{-4}	4.7×10^{-4}	2.0
7.9	2.2	5.4×10^{-5}	1.6×10^{-4}	3.0
9.5	0.9	1.5×10^{-5}	5.5×10^{-5}	3.7
10.5	0	9.5×10^{-6}	9.5×10^{-6}	–

while, in bulk homopolymerization experiments the kinetic scheme is reduced to only

$$\text{\it mmmE}^+ + E \xrightarrow{\ k_E\ } \text{\it mmmE}^+ \quad \text{for EVE} \qquad (E)$$

$$\text{with } R_{P_E} = k_E, \quad |E^+|, \quad |E| \qquad (4)$$

and

$$\text{\it mmmI}^+ + I \xrightarrow{\ k_I\ } \text{\it mmmI}^+ \quad \text{for IPVE} \qquad (F)$$

$$\text{with } R_{P_I} = k_I, \quad |I^+|, \quad |I| \qquad (5)$$

In copolymerization, if we assume in a first approximation that the reactivity of the growing ends is only governed by the nature of the last incorporated unit, rate constants of equations (A) and (C) can be identified to the rate constants of the corresponding homopolymerization (E) and (F)

$$k_{EE} \simeq k_E = \frac{R_{PE}}{|E^+||E|} \qquad (4a)$$

$$k_{II} \simeq k_I = \frac{R_{PI}}{|I^+||I|} \qquad (5a)$$

In the case of low conversion experiments, the stationary concentration of unpaired ions generated in the systems by radiation, $|C^+|$, has been determined according to Allen theory[7] from the 'free' ion yields of the pure monomers and from their relative amounts in the feed.

Alternatively, the ratio of the active centre concentrations $|I^+|/|E^+|$ formed during the copolymerization reaction was deduced from the relative proportion of IPVE and EVE units incorporated in the copolymer

$$|C^+| = |I^+| + |E^+| \qquad (6)$$

$$|I^+|/|E^+| = \text{units IPVE/units EVE in the copolymer} \quad (7)$$

finally the consumption of the comonomers is expressed by:

$$R_C = |E^+|\left[\frac{R_{PE}|E|}{|E^+||E|} + k_{EI}|I|\right] + |I^+|\left[\frac{R_{PI}|I|}{|I^+||I|} + k_{IE}|E|\right] \qquad (8)$$

k_{EI} and k_{IE}, the rate constants of cross addition are not accessible, thus a theoretical *minimal* value of R_C was calculated by neglecting the contribution of the cross reactions in the propagation.

$$R_{C_{minimal}} = |E^+| \frac{R_{PE}|E|}{|E^+||E|} + |I^+| \frac{R_{PI}|I|}{|I^+||I|} \qquad (9)$$

The results are collected in *Table 3* with the relevant experimental rates. In the monomer mixtures examined the contribution of the EVE rate term, remains less than 10% of the overall rate.

The theoretical minimal rates obtained in the calculation are far higher than the corresponding experimental values. Moreover discrepancy between theoretical and experimental values tend to increase with the proportion of EVE in the feed. These results lead to the conclusion that the rate constant of homoaddition of IPVE, k_{II}, which is used in the calculation of the theoretical rate of copolymerization has been highly overevaluated. In fact $k_{II} \ll k_I$ (from pure bulk experiments).

This signifies that $\sim\!\sim$ IPVE$^+$ propagating cations are less reactive in the conditions of a copolymerization than they are in bulk homopolymerization.

The decrease in the reactivity of the IPVE growing ends in the presence of a comonomer could be attributed to an interaction between either the EVE monomer or the EVE units incorporated in the copolymer chains. We have already shown, in EVE homopolymerization[1], that solvation by the monomer was much weaker than the intrasolvation of the active cations $\sim\!\sim$ EVE$^+$ by the last oxygens of their own chain. In the case of IPVE polymerization this process was drastically reduced due to the bulkiness of the isopropyl side groups.

It appears from the copolymerization results that substituting some IPVE units by EVE units in the growing chains make possible the intrasolvation process to occur, leading to a strong deactivation of the IPVE growing cations.

One of the more favoured type of interaction is represented in the following scheme.

R= Ethyl or/and isopropyl
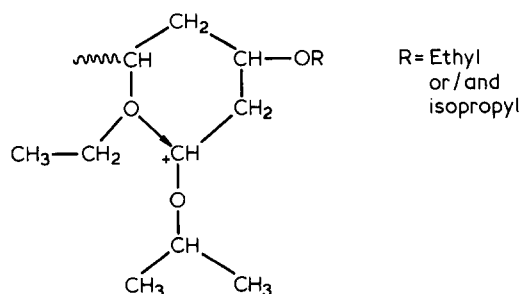
In conclusion, the radiation induced copolymerization of EVE and IPVE monomers has been studied in order to compare more directly their reactivity. Analysis of the copolymer composition has shown that reactivities of both monomers towards same active centres differ only of a factor of 5. This is much less than the difference observed in bulk homopolymerization, and indicates that most of the large difference in reactivity comes mainly from the actual reactivity of the growing cations IPVE$^+$ and EVE$^+$.

The overall rate of consumption of the comonomers has been measured and compared with a theoretical value obtained from the homopolymerization rate constants. It appears that the presence of EVE units in the copolymer chains lead to a deactivation of the $\sim\!\sim$ IPVE$^+$ cations. This was attributed to an intrasolvation process between the IPVE$^+$ chain ends and some of the last EVE units incorporated in the chain. These results show, again, the powerful role of solvation processes on the reactivity of active centres in cationic polymerization and confirm that rate constant of polymerization of IPVE and EVE in low polar solvents are governed by this process.

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