

# Radiation-induced cationic polymerization of vinyl ethers in solution:

## 4. Polymerization of isopropyl vinyl ether in bulk and in various solvents

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The influences of the polymerization media, the monomer and solvent concentrations and the temperature on the radiation-induced polymerization of isopropyl vinyl ether (IPVE) have been studied in detail under super-dry conditions. Rates of polymerization were measured and estimates of the rate constants of polymerization were calculated according to the simplified Hayashi-Williams equation. A comparison of the results with those previously reported for ethyl vinyl ether (EVE) is made. The much higher reactivity of IPVE in low polar solvents is interpreted by a drastic reduction of the polymer intramolecular solvation of the growing chain ends. This is ascribed to the bulkiness of the isopropyl side-chain groups. The radiation-induced polymerization of IPVE in bulk and in various solvents with different physical and solvating properties was studied. This was to obtain further information on the kinetics and the mechanisms involved with this monomer and also the role of the polymerization media. The influence of the monomer and solvent concentrations and of the polymerization temperature on the rate of polymerization have also been investigated.

**Keywords** Cationic polymerization; monomer; radiation; isopropyl vinyl ether; solvation; polymer chain ends

### INTRODUCTION

In the previous articles of this series<sup>1-3</sup> the radiation-induced polymerization of ethyl vinyl ether (EVE) in bulk and in different solvents has been reported. The experimental rates of polymerization were found to follow the theoretical Hayashi-Williams<sup>4,5</sup> equation. In low polar solvents<sup>1,3</sup> the kinetic results were interpreted by a predominant solvation of the free propagating cations by the polymer chain, whereas in methylene dichloride<sup>2</sup> and in nitromethane the growing chain ends appeared to be solvated by the solvent molecules.

Some preliminary results on the radiation-induced polymerization of isopropyl vinyl ether (IPVE) in bulk and in solution with monomer concentrations kept constant at 50% by volume have also been reported<sup>6-8</sup>. Very high reactivities of IPVE compared to the corresponding ones of EVE were observed, particularly in low polar media. Moreover, in bulk, large differences in the activation energies of the two monomers were also found. These results led us to examine the radiation-induced polymerization of IPVE in more detail.

### EXPERIMENTAL

#### Materials

IPVE (Pfaltz and Bauer Inc. and Polysciences Inc.), benzene, diethyl ether, methylene dichloride and nitromethane were purified as previously described<sup>2,3,7</sup>.

#### Polymerization

The polymerization tubes were degassed under high vacuum at 450°C for 24 h and filled as reported previously<sup>1</sup>. Irradiations were carried out in a <sup>60</sup>Co source under controlled temperature and the polymer yield determined gravimetrically.

### RESULTS AND DISCUSSION

All IPVE polymerizations were carried out successfully under super-dry conditions, i.e. half-power dose rate dependence of the polymerization rate was observed for all the bulk and solution polymerizations studied as reported in a previous paper<sup>7</sup>. This allowed us to neglect, in the propagation rate calculations, the influence of the termination of the polymerization by protonic impurities.

#### Polymerization in bulk and low dielectric constant solvents

The kinetics of the radiation-induced cationic polymerization of IPVE were first studied in bulk and in benzene and diethyl ether solutions. Typical plots of the monomer conversion *versus* irradiation time and the corresponding plots of the variation  $\log([M]_0/[M])$  with irradiation time are given in *Figures 1* and *2* for bulk and benzene solutions. A first-order dependence of the polymerization rate on the monomer concentration was observed, at least up to 45% conversion.

The influence of the initial monomer concentration

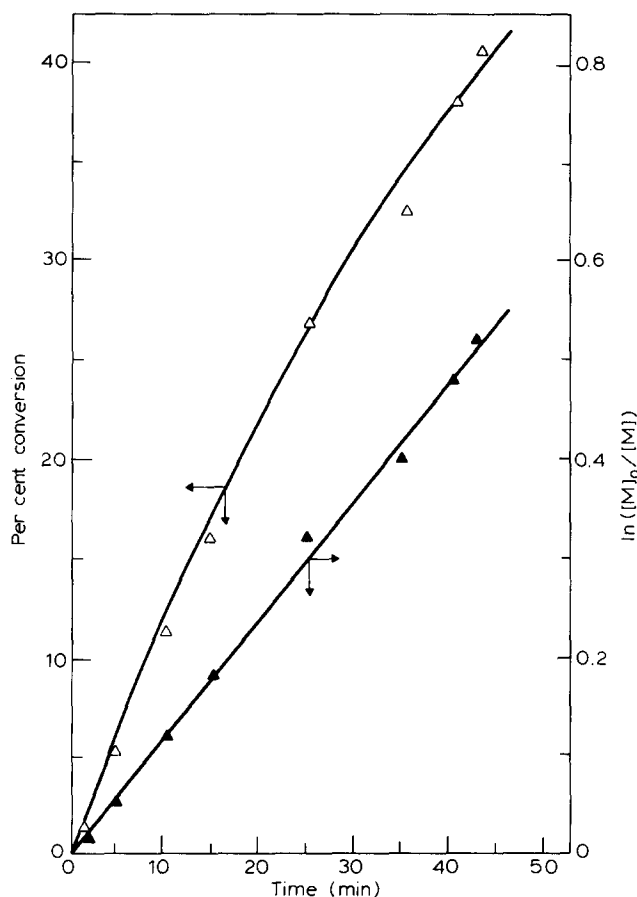


Figure 1 Per cent conversion and  $\ln([M]_0/[M])$  versus time for IPVE in bulk at 26°C; dose rate = 71 rad s<sup>-1</sup>

$[M]_0$  on the rate of polymerization was also examined in benzene solution over monomer concentrations ranging from 0.6 mol l<sup>-1</sup> to 8.72 mol l<sup>-1</sup> (bulk). The values of the polymerization rates are given in Table 1 and the logarithms of the polymerization rates are plotted against the yield of the monomer concentrations in Figure 3. As previously reported for EVE polymerization<sup>1</sup>, the rates of polymerization are proportional to an order 1.5 with respect to monomer in the main concentration range examined. For the higher monomer concentrations the rates increase more sharply. Calculations were made to estimate the variations of the stationary free propagating

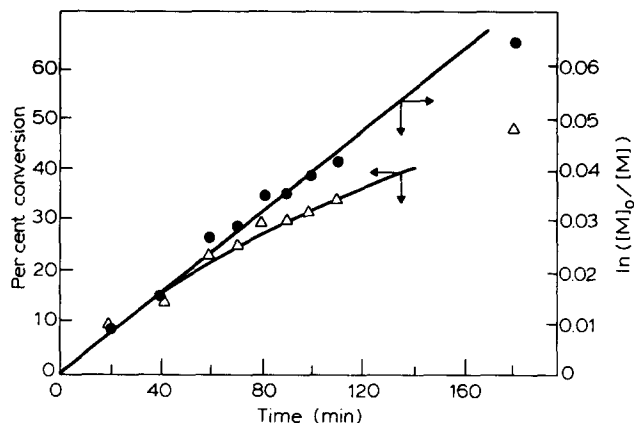


Figure 2 Per cent conversion and  $\ln([M]_0/[M])$  versus time for IPVE in benzene at 30°C;  $[M]_0 = 4.4$  mol l<sup>-1</sup>; dose rate = 71 rad s<sup>-1</sup>

cations  $[C^+]$  with the different amounts of monomer and solvent. Details of the procedure have been reported previously<sup>1,9</sup>. Estimates of  $[C^+]$  are given in Table 1. The logarithmic variation of  $R_p[C^+]$  is plotted against the logarithm of the monomer concentration in Figure 4. An order of 1.3 with respect to monomer for the propagation reaction was found. A similar monomer dependence was reported for the radiation-induced polymerization of EVE<sup>1,8</sup>. The small difference between the value obtained and a first-order dependence could come from the assumptions made in the calculations of  $[C^+]$ . The rate constants of polymerization, however, were calculated assuming an order of unity with respect to monomer in the different solvents studied.

The values are given in Table 2, together with the relevant rate constants previously obtained for EVE. The results confirm the trend observed in the preliminary studies, i.e. the much higher reactivity of IPVE compared to EVE.

The apparent activation energies of the reaction were determined over a temperature range of at least 40°C in bulk and in benzene. As already pointed out, this value represents approximately that of the activation energy of the propagation reaction<sup>9,13</sup>. The logarithmic variations of  $R_p$  are plotted versus the reciprocal of  $T$  in Figure 5. On the basis of  $k_p$  (at 30°C) and the  $E_p$  values, the frequency factors were also calculated. The values are collected in Table 3.

Table 1 Kinetic parameters and concentrations of the propagating cations<sup>a</sup> at various monomer concentrations for IPVE polymerization in benzene at 26°C

[IPVE] (mol l <sup>-1</sup> )	$R_p \times 10^6$ (mol l <sup>-1</sup> s <sup>-1</sup> )	$G_{im}^b$ (free ions per 100 eV)	$R_i \times 10^9$ (mol l <sup>-1</sup> s <sup>-1</sup> )	$k_t \times 10^{-11}$ (l mol <sup>-1</sup> s <sup>-1</sup> )	$[C^+] \times 10^{10}$ (mol l <sup>-1</sup> )
8.72	1600	0.14	7.74	3.56	1.48
8.13	480	0.13	7.51	3.62	1.44
6.80	510	0.12	6.96	3.75	1.36
5.81	250	0.11	6.19	3.93	1.26
4.36	240	0.10	5.83	4.03	1.20
3.85	200	0.09	5.56	4.09	1.17
2.56	84	0.08	4.89	4.25	1.07
2.12	48	0.07	4.64	4.32	1.04
1.45	20	0.07	4.25	4.41	0.98
1.28	18	0.07	4.18	4.45	0.97
0.64	9.4	0.06	3.68	4.54	0.90

<sup>a</sup> For details of calculation, see refs 1 and 9

<sup>b</sup> Determined by Allen method<sup>10,11</sup> with  $G_i$  (IPVE) = 0.14 (ref 7), and  $G_i$  (benzene) = 0.053 (ref 12)

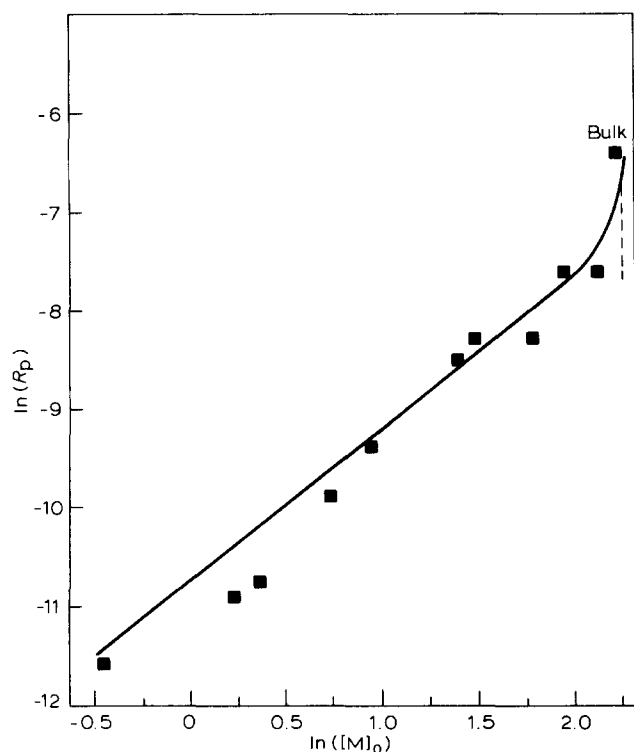


Figure 3  $\ln R_p$  versus  $\ln ([M]_0)$  for IPVE in benzene at 26°C; dose rate = 71 rad s<sup>-1</sup>; slope = 1.5

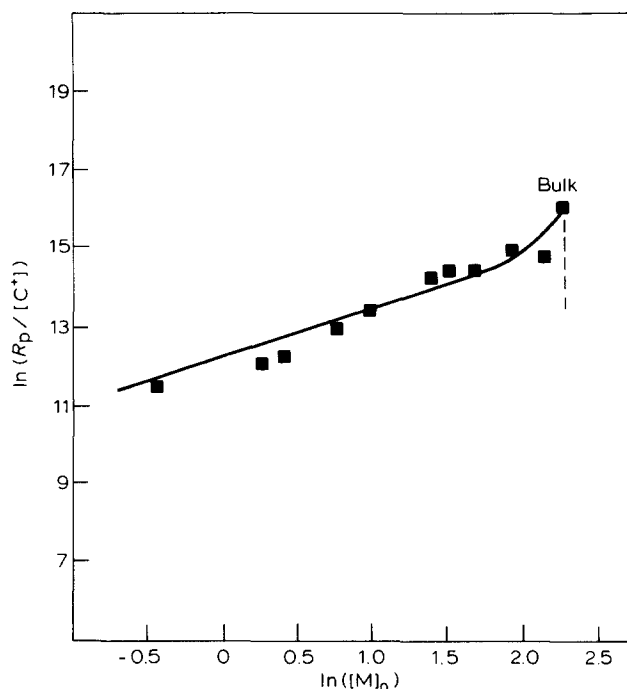


Figure 4  $\ln(R_p/[C^+])$  versus  $\ln([M]_0)$  for IPVE in benzene at 26°C; dose rate = 71 rad s<sup>-1</sup>; slope = 1.3

Table 2 Kinetic rate constants and concentrations of propagating cations for IPVE and EVE polymerizations at 30°C

Polymerization medium	IPVE <sup>b</sup>					EVE $k_p \times 10^{-4}$ (l mol <sup>-1</sup> s <sup>-1</sup> )
	$\epsilon^a$	$G_{im}$ (free ions per 100 eV)	$[C^+] \times 10^{-10}$ (mol l <sup>-1</sup> )	$R_p \times 10^6$ (mol l <sup>-1</sup> s <sup>-1</sup> )	$k_p \times 10^{-4}$ (l mol <sup>-1</sup> s <sup>-1</sup> )	
Benzene	2.7	0.09	1.2	300	57	3.6
Bulk	3.0	0.14	1.5	1700	130	6.0
Diethyl ether	3.7	0.23	2.1	310	34	2.6
Methylene chloride	6.0	0.34	3.9	26	1.5	0.34
Nitromethane	19.5	0.21	0.5	0.43	0.02	0.01

<sup>a</sup> The apparent dielectric constant of the medium is calculated by  $\epsilon = \epsilon_m V_m + \epsilon_s V_s$  where  $\epsilon$  and  $V$  denote the dielectric constant and the volume fraction in the mixture, and the subscripts m and s correspond to the monomer and the solvent, respectively

<sup>b</sup>  $[IPVE]_0 = 4.4 \text{ mol l}^{-1}$

#### Polymerization in polar solvents

Polymerization experiments were performed in methylene dichloride and nitromethane. As shown in Figure 6 a first-order dependence of the polymerization conversion also applies for methylene dichloride solution. The polymerization rate constants were calculated assuming an order of unity for monomer. The kinetic parameters and rate constants are summarized in Table 2. The activation energies and the estimated frequency factors for these polymerizations including methylene chloride are given in Table 3.

As can be seen, no important changes were observed in the activation energy values on changing the solvent, and the large decrease in reactivity appears to be due mainly to the frequency factor of the reaction. Considering<sup>14</sup> that the frequency factor could be regarded as the desolvation entropy of the propagating cation from the ground state to the transition state, the kinetic results would imply a large increase in solvation in the polar solvents.

As previously observed for EVE, the kinetics of the

radiation-induced polymerization of IPVE follow the simplified Hayashi-Williams equation. However, large differences in the kinetic behaviour of these monomers are observed. The much higher reactivity found with IPVE compared to EVE is one of the most intriguing results. For example, at 0°C the estimated  $k_p$  value for IPVE in bulk is 65 times that of EVE. Because of the different activation energies, which change in low polar media from about 13 kcal mol<sup>-1</sup> for EVE to 5.5 kcal mol<sup>-1</sup> for IPVE, the differences in reactivity diminish at higher temperatures, being only a factor of about 20 at 30°C. Similarly, as can be seen in Table 2, in high dielectric constant solvents the differences in the rates are reduced. This last observation could explain why only a small difference in the rate was found for the chemically induced cationic polymerization of these ethers, which are generally conducted in methylene chloride solutions<sup>7,15,16</sup>.

A possible influence of the greater inductive donor effect of the isopropyl group on the reactivity of IPVE is

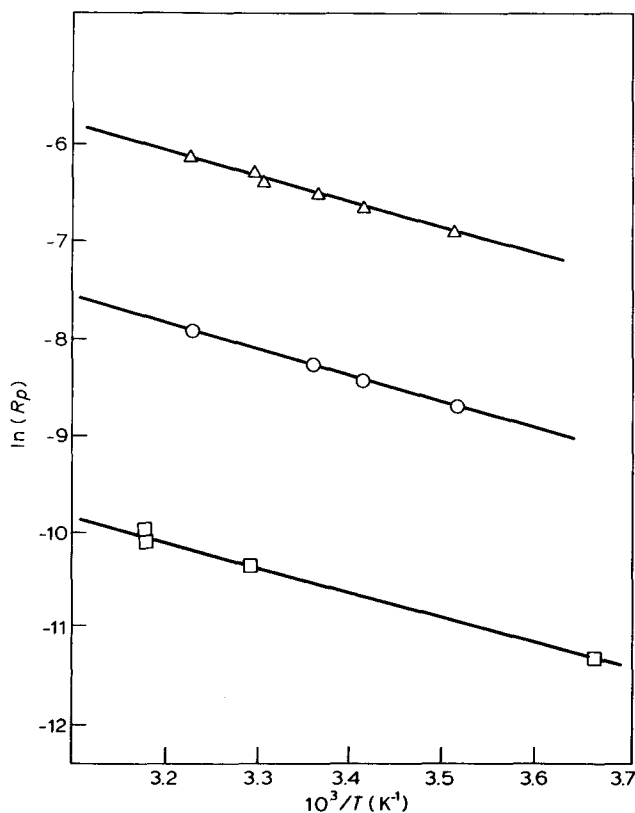


Figure 5 Arrhenius plots for IPVE in bulk ( $\Delta$ ), in benzene,  $4.4 \text{ mol l}^{-1}$  ( $\circ$ ) and in methylene chloride,  $4.4 \text{ mol l}^{-1}$  ( $\square$ ); dose rate =  $71 \text{ rad s}^{-1}$

Table 3 The activation energies and frequency factor values for the radiation-induced polymerization of IPVE

Solvent	$E_a$ ( $\text{kcal mol}^{-1}$ )	$A$ ( $30^\circ\text{C}$ ) ( $\text{mol}^{-1} \text{s}^{-1}$ )
Bulk	5.3	$8.2 \times 10^9$
Benzene	5.4	$4.2 \times 10^9$
Methylene chloride	4.9	$6.8 \times 10^7$

not sufficient to explain satisfactorily the very large differences found in the rates as well as the trends observed with the temperature and the increasing dielectric constant of the solvents.

In low polar solvents<sup>1,3</sup> solvation of the poly-EVE growing ends was reported to be largely dominated by an intrasolvation of the active centres by the polymer chains. Rate constants were almost equal in all these solvents and the Laidler-Eyring equation does not apply satisfactorily in these media. The rates for IPVE appear to be more sensitive to the polymerizing medium than for EVE and the much higher reactivity observed would suggest that the more bulky isopropyl groups make such solvation by the chain much weaker, leaving the propagating ions more accessible. Molecular models strongly support this suggestion. With polar solvents, however, the solvation of the growing cations tends to occur mainly with the solvent molecules<sup>2</sup>. Reactivity would then become very similar for both monomers and the rates tend to approach each other. Similarly, at higher temperatures, the chain solvation of the growing ends would start to diminish and,

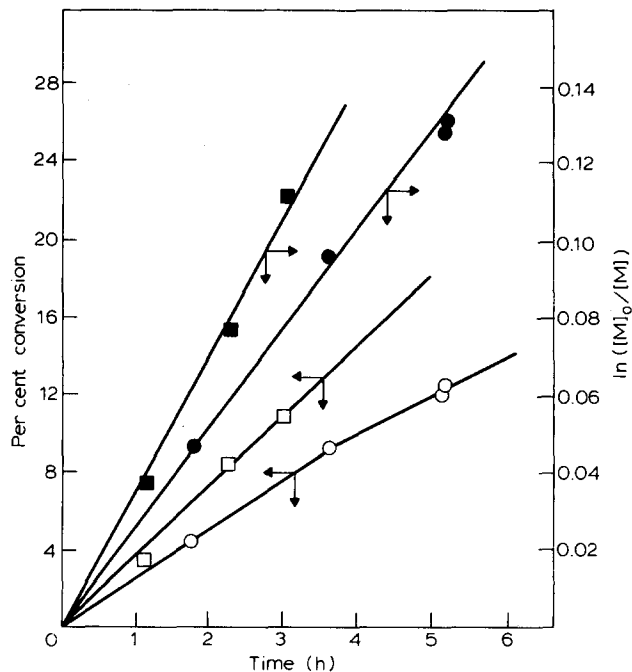


Figure 6 Per cent conversion and  $\ln([M]_0/[M])$  versus time for IPVE in methylene chloride at  $30.5^\circ\text{C}$  ( $\circ$ ,  $\bullet$ ) and at  $41.5^\circ\text{C}$  ( $\square$ ,  $\blacksquare$ ); dose rate =  $71 \text{ rad s}^{-1}$

again, the rates of polymerization of EVE and IPVE would tend to become similar. All these effects are actually observed and therefore support our general interpretation of reactivity through a solvation process.

Further evidence for these processes is now being determined through <sup>13</sup>C n.m.r. studies on the microstructure of the polymers and in the analysis of the reactivity ratios in IPVE and EVE radiation-induced copolymerizations. The results will be reported later.

#### NOTE

In part 1 of this series<sup>1</sup>, solvation of the free cation chain ends by the polymer chain or by the formation of a six-membered ring with the oxygen atom of the last-but-three monomer units was suggested. It has been pointed out to us that a similar solvation, but including the gegen ion, was postulated by Bawn and Ledwith with chemically initiated vinyl ether polymerizations<sup>17</sup>.

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