Chemically-initiated solution polymerizations and radiation-initiated bulk polymerizations of isopropyl vinyl ether

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The unusually high rates of polymerization of isopropyl vinyl ether initiated in bulk by high energy radiation, compared with other vinyl ethers, reported previously have been confirmed. The rates, molecular weights and heats of polymerization initiated by triphenylmethyl hexachlorantimonate have now been measured in methylene dichloride solution. Both methods of initiation are believed to involve essentially free ions. The chemically initiated polymerization rates however were similar to those found with the other vinyl ethers. The conflicting results are explained in terms of solvation effects rather than to differences in the methods of initiation. Qualitatively these results have been interpreted in terms of the Eyring theory of reaction rates between an unpaired ion and a neutral molecule.

INTRODUCTION

Previous publications have presented determinations of relative reactivities for a series of vinyl ethers made in these laboratories under conditions for favouring propagation by essentially unpaired carbenium ions. Radiation-induced bulk polymerizations were conducted in highly purified systems with exhaustively dried monomers[1]. Ethyl vinyl ether (EVE) and isobutyl vinyl ether (IBVE) were also polymerized in methylene dichloride solutions by means of the stable carbocation salt initiator, triphenylmethyl hexachloroantimonate[2]. The estimated rate constants of propagation (k_p) for EVE and IBVE polymerized by radiation in bulk were found to be about twice the corresponding k_p values for polymerizations in methylene dichloride solutions initiated chemically. This ratio is smaller than would be predicted by theoretical reaction rate calculations based on the dielectric constants of vinyl ethers and methylene dichloride. In such calculations the assumption is made that the overall composition of the reaction medium is representative of the composition of the solvent shell surrounding the propagating carbenium ion. However, the lack of gross variations in rate constants with respect to overall dielectric constant may indicate preferential solvation of the propagating cations by vinyl ether monomer. If such solvation is the cause of the similarity in rate constants in different reaction media, then the phenomenon should be observed for similar polymerizations of other vinyl ethers.

A preliminary study[1] demonstrated that the calculated rate constant of propagation for radiation-induced polymerizations of isopropyl vinyl ether (IPVE) was extremely high in comparison with those of other vinyl ethers. Consequently the present work was undertaken to determine whether the high reactivity of IPVE in radiation-induced bulk polymerizations could be observed also in chemically-initiated polymerizations in methylene dichloride solutions.

EXPERIMENTAL

Materials

Methylene dichloride and IPVE (Pfaltz and Bauer) were purified as described previously[1,2]. The preparation of triphenylmethyl hexachloroantimonate was also outlined in a previous publication[2].

Procedures

An adiabatic calorimeter described earlier[2] was used to monitor the progress of chemically-initiated polymerizations. The radiation-induced polymerizations were conduced in a γ-ray source described in detail in a previous publication[1]. Monomer conversions were determined gravimetrically and polymer number-average molecular weights measured on a Hewlett–Packard Model 302 vapour pressure osmometer in toluene at 37°C.

RESULTS

Chemically-initiated polymerizations

Calorimetric traces for polymerizations of IPVE initiated by triphenylmethyl hexachloroantimonate in methylene dichloride showed induction periods and the monomer conversions were somewhat less than quantitative. At initiator concentrations less than 1.8×10^{-4} M the yellow colour of the initiator was seen to disappear before the end of the reaction. These observations indicated that initiation was relatively slow though complete under certain circumstances and that termination processes were kinetically significant in this system.

Semilogarithmic plots of monomer concentration as a function of time for typical reactions are presented in *Figure 1.* These plots display an increase in the absolute magnitude

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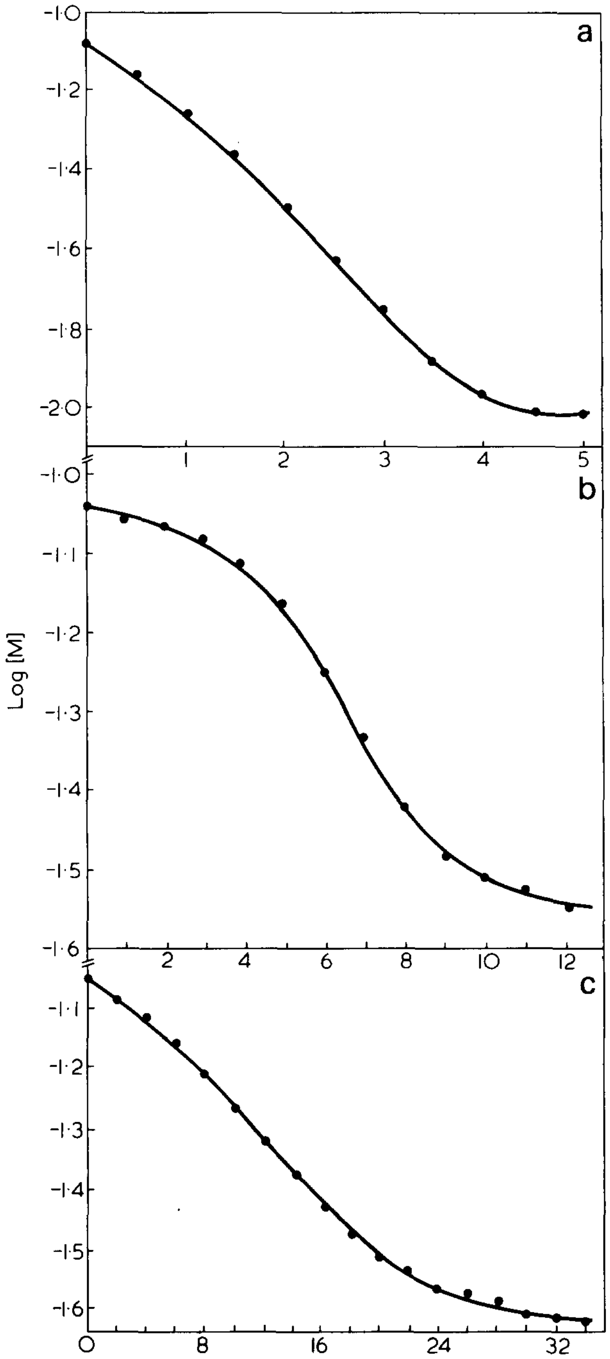

Figure 1 Semilogarithmic plots of monomer concentration as a function of time for IPVE polymerizations initiated by triphenylmethyl hexachloroantimonate in methylene dichloride at (a) 15°C, $[I]_0 = 1.8 \times 10^{-4}$ M, $[M]_0 = 9.1 \times 10^{-2}$ M; (b) 0°C, $[I]_0 = 1.1 \times 10^{-4}$ M; $[M]_0 = 8.9 \times 10^{-2}$ M; (c) –25°C, $[I]_0 = 1.8 \times 10^{-4}$M, $[M]_0 = 9.0 \times 10^{-2}$ M

of the slope followed by a decrease which suggests that the concentration of active centres passes through a maximum value, $(M^+)_{max}$, during polymerization. Similar behaviour has been noted and interpreted for the polymerization of IBVE by Subira *et al.*[3]. In the present work, values of k_p were calculated according to the method of Bawn *et al.*[4] and are listed in *Table 1*. This method of calculation is open to criticism on the grounds that it implies an $(M^+)_{max}$ equivalent to the original concentration of initiator, $(I)_0$. The difference between the actual and calculated k_p values will be determined by the extent to which $(M^+)_{max}$ deviates from $(I)_0$. When this deviation is significant, the calculated k_p values exhibit a strong direct dependence on the initial monomer concentration, $(M)_0$[3]. The k_p values listed in *Table 1* show a slight inverse dependence on $(M)_0$, and it may be inferred that the difference between actual and calculated k_p values is smaller for the IPVE system than the difference found for the IPVE system than the difference found for the IBVE system[3].

However, some deviation in $(M)_{max}$ from $(I)_0$ does occur and is probably reflected in the dependence of the calculated k_p values on $(I)_0$ shown in *Table 1*. As $(I)_0$ is increased initiator consumption should become less efficient, the dispersity between $(M^+)_{max}$ and $(I)_0$ should increase and calculated k_p values should be lower than the actual k_p values. An alternative explanation of the decrease in k_p with increasing $(I)_0$ involves the hypothesis of an equilibrium between paired and unpaired propagating carbeniums ions. As $(I)_0$ is increased, the total concentration of ions in the system is increased and the equilibrium is shifted in favour of the presumably less reactive paired carbenium ions. Such an effect has been observed in cationic polymerizations of *p*-methoxystyrene[5] and *N*-vinyl carbazole[6]. Ionic equilibria in cationic polymerizations may also influence the molecular weights of polymeric products, since paired counterions tend to hinder propagation slightly more than chain transfer reactions[7]. In the present work the molecular weights of polyIPVE do show a slight dependence on $(I)_0$, indicating that a shift in the ionic equilibrium between paired and unpaired carbenium ions may be occurring. However, it is unlikely that this shift accounts fully for the observed influence of $(I)_0$ on the experimental k_p values. Recently, the dissociation constant, K_d, of a model compound representative of a propagating poly(alkyl vinyl ether) chain end was estimated as 1×10^{-5} M[8] using this value of K_d, the fraction (α) of propagating centres dissociated into unpaired ions can be calculated, assuming $(M^+) = (I)_0$. If the observed propagation rate constant (k_p obs) is considered to be the sum of weighted contributions from paired ($k_p^{\pm}$) and unpaired (k_p^{+}) ions, and if $k_p^{\pm}$ is assumed to be negligible in comparison with k_p^{+}, then the formula:

Table 1 Rate constants of propagation molecular weights and heats of polymerization for the system IPVE–Ph_3CSbCl_6

Temperature (°C)	(I) x 10^4 (mol/l)	(M) x 10^2 (mol/l)	Conversion (%)	K_p x 10^{-2} (l/mol sec)	M_n	ΔH_p (kcal/mol)
15	1.8	9.1	68.7	10.0	1997	26.2
0	0.3	9.1	68.2	15.7	2832	20.3
0	0.6	8.9	76.8	16.1	2750	22.3
0	1.1	8.9	85.0	8.4	2611	19.8
0	1.1	13.4	75.5	7.5	2621	25.5
0	1.1	18.2	77.1	7.0	3117	21.7
0	1.8	8.4	63.8	4.2	2616	27.2
0	10.0	9.5	58.5	–	2369	–
–25	1.8	9.0	72.9	3.2	3468	25.3

Table 2 Degree of dissociation and rate constants of propagation for the system IPVE – Ph_3CSbCl_6 at 0°C

(I) × 10^4 (mol $/l^{-1}$)	α*	$k_p \times 10^{-2}$ (l/mol^{-1} sec^{-1})
0.3	0.43	15.7
0.6	0.33	16.1
1.1	0.26	8.4
1.8	0.21	4.2

* α was calculated using $K_d = 1 \times 10^{-5}$ M [8]

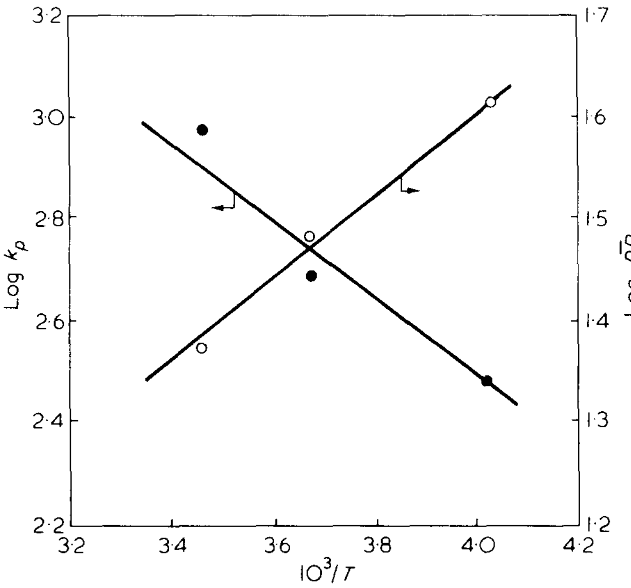

Figure 2 Arrhenius plots of the rate constant of propagation and degree of polymerization for IPVE polymerizations initiated by triphenylmethyl hexachloroantimonate in methylene dichloride

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

can be approximated by

$$k_p \text{ obs} = \alpha k_p^{+}$$

and the k_p values listed in *Table 1* should be directly proportional to α. As the data in *Table 2* indicate, the variation in k_p, with respect to (I) is too large to be attributed solely to the influence of ionic equilibria in the IPVE system.

The temperature dependence of the calculated k_p values, depicted in *Figure 2*, reflects a relatively low activation energy for propagation of approximately 4 kcal/mol. Number-average degrees of polymerization ($\overline{DP}_n$) were always well below the ratio $\Delta M/I_0$, indicating that chain transfer reactions governed polyIPVE molecular weights. Analysis of the Arrhenius plot of $\overline{DP}_n$ shown in *Figure 2* yielded an activation energy for chain transfer of 7.0 kcal/mol. The exact nature of the chain transfer reactions is unclear. However, recent work[8] has suggested that transfer to both monomer and solvent occurs with polymerizations of vinyl ethers in methylene dichloride solutions.

Radiation-induced polymerizations

In *Figure 3* monomer conversion curves for radiation-induced polymerizations of IPVE are presented as functions of time. Rates of polymerization derived from these curves were dependent on the dose rate raised to a power of 0.57. Under conditions where no termination with adventitious impurities occurs, the dose rate-dependence should be 0.50[9]. Values of k_p were estimated for these IPVE polymerizations by applying the kinetic model derived by Williams *et al.*[9] for the IBVE system and assuming that rates of radiation-induced initiation and diffusion-controlled termination are similar for IPVE and IBVE. By this means a k_p value of 3.9×10^5 l M^{-1} sec^{-1} was estimated for bulk IPVE polymerization at 0°C. A previous study[1] estimated k_p for these conditions a 9.0×10^5 l M^{-1} sec^{-1}. In that study a dose rate dependence of 0.52 was observed, indicating a higher degree of system purity. The difference in impurity levels probably accounts for the discrepancy between k_p values. However, the present results confirm the finding that the k_p values for radiation-induced bulk polymerizations of IPVE is more than ten times greater than the values reported for polymerizations of EVE and IBVE under similar conditions.

DISCUSSION

Despite the experimental errors inherent in the determination of the k_p values, certain conclusions can be drawn from the data presented above:

(1) The rate constant for IPVE propagation in triphenyl methyl hexachlorantimonate polymerizations in methylene in dichloride solution is of the order of 10^3 l m^{-1} sec^{-1} at 0°C.

(2) The rate constant for IPVE propagation in radiation-induced bulk polymerizations is on the order of 10^5 l m^{-1} sec^{-1} at 0°C.

(3) The rate constant for IPVE propagation appears to exhibit a much greater dependence on the nature of the polymerization medium than do the k_p values for IBVE and EVE.

According to reaction rate theory based on the hypothesis of activated complexes[10], the natural logarithms of the rate constant for a reaction between an unpaired ion and

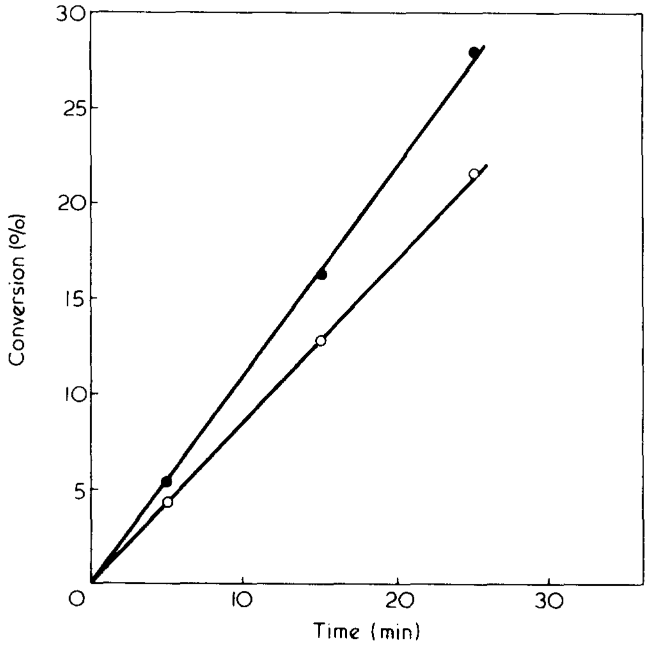

Figure 3 Monomer conversion curves for radiation-induced bulk polymerization of IPVE at 30°C. Dose rate (rad/sec); ○, 70.6; ●, 49.4

a neutral molecule is inversely proportional to the dielectric constant (D) of the reaction medium:

$$\frac{\mathrm{d}(\ln k_p)}{\mathrm{d}(1/D)} = \frac{\epsilon^2 Z^2}{2kt}\left(\frac{1}{r} - \frac{1}{r_\ddagger}\right)$$

where Z is the ion charge, ϵ is the unit charge and k is the Boltzman constant. Assuming that the ionic radius of the activated complex, $r_\ddagger$, exceeds the ionic radius of the propagating cation, r, by about 10^{-8} cm, the k_p value for polymerization in a pure vinyl ether ($D \sim 3$) would be expected to be several orders of magnitude higher than the k_p value in methylene chloride ($D \sim 9$). However, if the propagating cations were preferentially solvated by vinyl ether molecules in methylene dichloride solutions, the dielectric constant of the immediate environment of the cations would be similar to that of bulk vinyl ethers, and the observed effect of solvent type on k_p would be diminished. Specific solvation of cations by vinyl ethers in methylene dichloride solutions is plausible since the electron donor activity[11] of vinyl ethers exceeds that of methylene dichloride[12].

In theory the k_p values for the homologous series of alkyl vinyl ethers should be influenced similarly by changes in the nature of the solvating medium. However, while the k_p values for IBVE and EVE show only small differences between bulk and solution polymerizations, the present study indicates that the k_p of IPVE varies dramatically with the nature of the solvent. A further indication that solvation plays a greater role in polymerization of IBVE and EVE than in polymerizations of IPVE arises from a consideration of activation energies of propagation (E_p). Both radiation-induced and chemically-initiated polymerizations of EVE showed E_p values of about 10 kcal/mol[13], and the corresponding values for IBVE polymerizations are about 7–8 kcal/mol[1,14]. These values are higher than would be anticipated for propagation of unpaired, unsolvated carbenium ions, and the usual magnitudes have been attributed in part to the effects of solvation by monomer[14]. In the present work an E_p of about 4 kcal/mol was determined for chemically-initiated polymerizations of IPVE in methylene dichloride, and a previous study reported a somewhat lower E_p value for radiation-induced polymerizations of IPVE, 1.8 kcal/mol. The observed values of E_p for IPVE polymerizations are more compatible with the expected temperature dependence of processes involving unpaired, unsolvated carbenium ions.

The reasons for the differences in polymerization rate behaviour between IPVE and the other vinyl ethers are unclear. Two lines of experimentation are necessary in elucidating this problem: (1) evaluation of the rates of initiation and lifetimes of charge carriers in radiation-induced polymerizations of each vinyl ether, and (2) studies of chemically-initiated polymerizations of vinyl ethers in solvents of various dielectric constants. It is hoped to carry out these experiments in the near future.

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