Radiation-induced cationic polymerization of vinyl ethers in solution: 1. Influence of monomer and solvent concentration on the rate of polymerization of ethyl vinyl ether in benzene

A. Deffieux, W. C. Hsieh, D. R. Squire and V. Stannett

Chemical Engineering Department, North Carolina State University, Raleigh, NC 27650, USA
(Received 7 May 1981)

The influence of the monomer concentration on the radiation-induced polymerization of ethyl vinyl ether has been studied in detail in benzene solution under super-dry conditions. Estimations of the rate of initiation and of the rate of termination have shown that the variations in the observed rates of polymerization represent mainly variations in the kinetic parameters of the propagation process. The experimental results, which are in good agreement with the theoretical Hayashi–Williams equation over most of the monomer concentration range are explained by a solvation of the propagating species of the polymer chain. Little or no solvation by the monomer was observed.

INTRODUCTION

Earlier studies concerning the radiation-induced ionic polymerization of liquid vinyl monomer have mainly been conducted in bulk. In the absence of protonic impurities, usually achieved by rigorous drying techniques under high vacuum, the kinetics in bulk are simple and follow the Hayashi–Williams equation[1,2]:

$$R_p = k_p[M]\left(\frac{R_i}{k_t}\right)^{1/2} \qquad (1)$$

where R_p is the rate of polymerization, [M] the bulk monomer concentration, and k_p and k_t the rate constants for propagation and termination by charge neutralization, respectively. R_i is the rate of initiation and is equal to:

$$6.24 \times 10^{14} \times \frac{G(i)dI}{N}$$

where $G(i)$ is the number of free initiating cations per 100 eV of absorbed radiation, d the density of the medium, N is the Avogadro number and I the dose rate in rad s^{-1}. The rate constants, rate and monomer concentrations are in units of moles, litres, seconds.

It is only recently, mainly because of the experimental difficulties and greater complexity of the systems, that the radiation-induced polymerization of vinyl monomers has been examined in any detail in solution. In these laboratories studies were first performed in different solvents with the monomer concentration kept constant at 50% by volume[3-5]. A drastic reduction in the rate with increases in the overall dielectric constant was found. For example, the rate constants of polymerization, calculated

assuming the validity of equation (1) for solutions, were found to decrease more than 100 times from bulk to high dielectric constant solutions.

To obtain further information on the kinetics and mechanism of these solution radiation-induced polymerizations, the polymerization of ethyl vinyl ether (EVE) has been examined in further detail in bulk and in benzene solution. The influence of monomer concentration and polymerization temperature on the rate of polymerization has also been investigated.

EXPERIMENTAL

Materials

EVE (Aldrich Co.) was purified and dried by the techniques previously described[9].

Benzene was refluxed for 24 h over concentrated sulphuric acid, washed several times with water, dried over potassium hydroxide, distilled and stored under vacuum over calcium hydride.

The final drying of the monomer and the solvent was carried out under high vacuum over several sodium mirrors until the sodium remained unattacked and bright. Generally, 4 to 5 mirrors were needed. The purity of the products was finally confirmed by the half-dose rate dependence of the rate of polymerization.

Polymerization

The manifold of polymerization tubes was previously degassed under high vacuum at 450°C for 24 h. Suitable amounts of monomer and solvent were then measured in a calibrated tube, transferred through breakseals and Rotaflow stopcocks into the reacting vessel, and sealed. Irradiations were carried out in a ^{60}Co γ-ray source under controlled temperature. After the appropriate irradiation
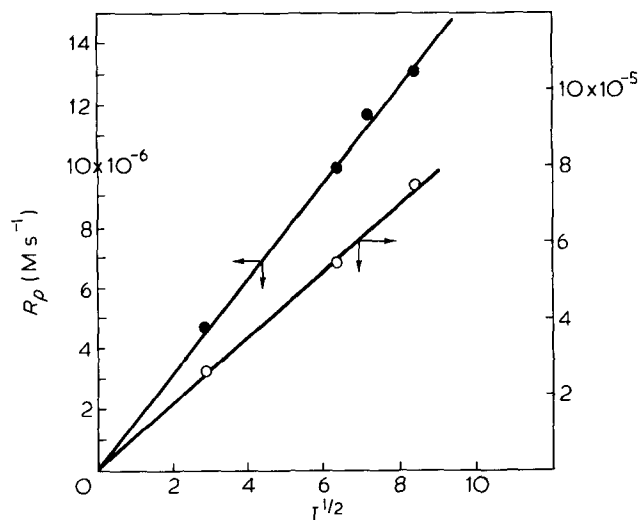
Figure 1 Dose rate dependence of the rate of polymerization of EVE: $\bigcirc$, in bulk at 26°C; $\bullet$, 5.4 molar in benzene at 24°C

Table 1 Variation of the polymer conversion and the rate of polymerization of EVE in bulk with the time of irradiation. $T = 20°C$; dose rate, 71 rad s^{-1}

Time (h)	Conversion (%)	$R_p \times 10^5$ M l^{-1} s^{-1}
1.5	2.7	5.3
3.0	5.6	5.4
4.0	6.9	5.1
6.0	11.1	5.4
9.0	16.0	5.2
12.0	21.0	5.1
18.0	29.0	4.7
21.0	32.0	4.5
25.0	36.5	4.3
41.0	49.5	3.5
50.0	55.5	3.2

Table 2 Variation of the polymer conversion and the rate of polymerization of EVE in benzene, with the time of irradiation. $T = 30°C$; [EVE]$_0$ = 3.1 M; dose-rate, 71 rad s^{-1}

Time (h)	Conversion (%)	$R_p \times 10^5$ M l^{-1} s^{-1}
3.15	4.6	4.2
8.0	9.5	3.5
19.5	18.6	2.7
45.0	32.3	2.1
70.0	41.6	1.7
91.0	45.7	1.5

time the tubes were opened and the unreacted monomer and the solvent were evaporated. Polymer yields were determined gravimetrically.

RESULTS AND DISCUSSION

The dose rate dependence of the rate of polymerization of EVE, in bulk and in benzene solution, is presented in *Figure 1*. A value very close to 0.5 is seen, indicating that polymerizations without termination by impurities were occurring.

The polymer yields obtained for different irradiation times are given in *Tables 1* and *2* and the corresponding

conversion time curves are plotted in *Figure 2*. The logarithmic variations of $[M]_0/[M]$ *versus* the time of irradiation are plotted in *Figure 3* where $[M_0]$ is the initial monomer concentration. For the bulk polymerization the internal order of the reaction with respect to monomer is equal to one, the small deviation observed at high monomer conversions probably coming mainly from the important increase in the viscosity of the medium. In benzene solution the deviations from a theoretically similar monomer dependence is much more important and, referring to bulk, cannot be explained by the viscosity increase alone.

In order to minimize these side phenomena the rates of polymerization were determined from low (5 to 10%) conversion polymerization experiments. The influence of the initial monomer concentration on the rate of polymerization of EVE was studied in benzene solution over concentrations ranging from 0.54 M l^{-1} to 10.54 M l^{-1} (bulk). The values of the polymerization rates are given in *Table 3*. In *Figure 4*, the logarithm of the rates of polymerization are plotted against the logarithm of the
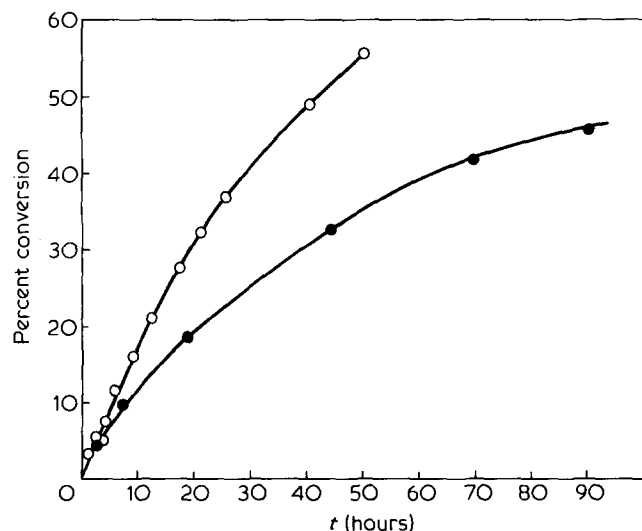

Figure 2 Conversion curves for EVE: $\bigcirc$, in bulk at 20°C; $\bullet$, 3.1 molar in benzene at 30°C. Dose rate, 71 rad s^{-1}
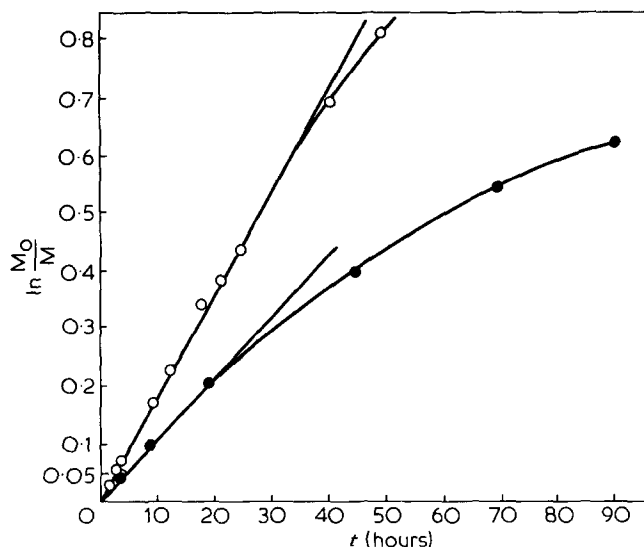

Figure 3 First order plots in monomer for EVE: $\bigcirc$, in bulk at 20°C; $\bullet$, 3.1 molar at 30°C. Dose rate, 71 rad s^{-1}

Table 3 Rate of polymerization, estimated rate constant of termination, free ion yields, stationary free propagating species concentration and kinetic parameters in the radiation-induced polymerization of EVE in benzene. $T = 20°C$; dose rate, 71 rad s⁻¹

[EVE]₀ M l⁻¹	$R_p \times 10^6$ M l⁻¹ s⁻¹	$k_{tm} \times 10^{-11}$ l M⁻¹ s⁻¹	G_{im} (free ions) / 100 eV		$[C^+]^c \times 10^{10}$ M l⁻¹	$\dfrac{R_p \times 10^{-4} \text{ s}^{-1}}{[C^+]}$	$k_p^d \times 10^4$ l M⁻¹ s⁻¹
			a	b			
10.54 bulk	52.7	3.61	0.140	0.140	1.71	31.0	2.94
10.17	45.2	3.63	0.136	0.131	1.62	27.9	2.74
9.42	38.2	3.70	0.129	0.129	1.59	29.0	2.55
8.63	26.3	3.75	0.122	0.119	1.58	16.6	1.92
8.46	28.9	3.79	0.121	0.116	1.49	19.4	2.29
7.64	23.1	3.88	0.113	0.108	1.42	16.3	2.14
7.27	19.5	3.89	0.110	0.105	1.40	13.9	1.91
7.20	19.9	3.92	0.109	0.103	1.38	14.4	2.0
5.44	8.6	4.07	0.095	0.089	1.31	6.6	1.21
5.37	8.3	4.11	0.094	0.084	1.22	6.8	12.7
4.11	6.0	4.26	0.084	0.082	1.18	5.1	1.24
4.04	5.1	4.26	0.083	0.073	1.12	4.6	1.48
3.10	3.6	4.33	0.076	0.069	1.07	3.4	1.10
3.04	3.6	4.38	0.075	0.068	1.05	3.4	1.12
2.07	1.6	4.45	0.068	0.060	1.02	1.5	0.77
1.51	1.5	4.55	0.064	0.056	0.98	1.5	0.99
1.32	1.1	4.55	0.063	0.056	0.94	1.2	0.91
0.54	0.3	4.66	0.057	0.054	0.91	0.3	0.55
Benzene pure	—	4.73	0.053	0.053	0.90	—	—

[a] Determined by the simple additivity method
[b] Determined by Allen method (6, 7)
[c] $[C^+] = (R_{im}/k_{tm})^{1/2}$
[d] Determined from equation 1 (assuming first order with monomer)
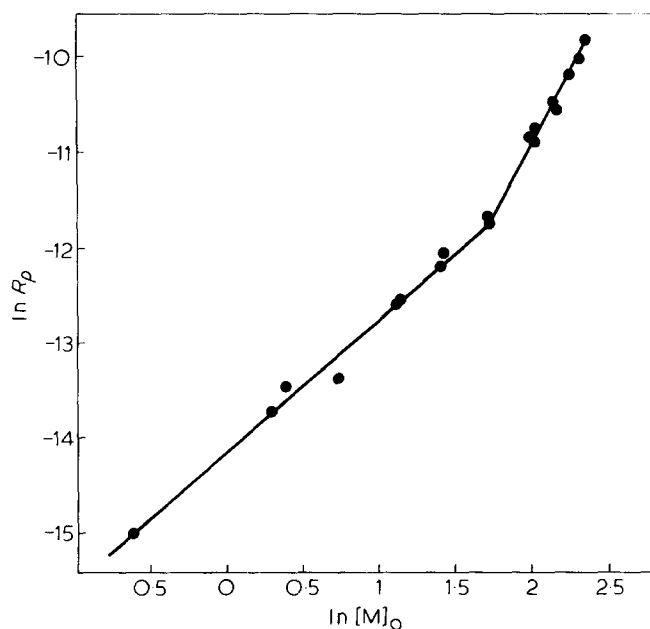
Figure 4 Monomer concentration dependence of the initial rates, EVE in benzene at 20°C including bulk value. Dose rate, 71 rad s⁻¹

monomer concentration. After an initial fast decrease of the rate of polymerization on decreasing the EVE concentration, the order of the reaction becomes equal to 1.4 with respect to the monomer. However, as shown from the expression for R_p (equation 1), this observed order is not a direct and single representation of the propagation reaction dependence. Several other parameters of the reaction such as the rate constant of termination in the mixture k_{tm} and the rate of initiation, R_{im} are also affected by the changes in the composition of the mixture. A closer analysis of the kinetics and the mechanism of the

propagation yields at least an estimate of these parameters.

The values of the rate constant k_{tm} can be estimated from the simplified Debye equation, i.e.[2]:

$$k_{tm} = \frac{4\pi e^2}{\varepsilon kT} D \tag{2}$$

where ε is the dielectric constant of the mixture and D is the total diffusion constant of the reacting species. A constant value of 2.5×10^{-5} cm² s⁻¹ was assumed for D in all the mixtures. The k_{tm} values are given in *Table 3*. It should be emphasized that bulk dielectric constants were used and these could differ from the effective, micro-dielectric constants, which would be more valid. Rate measurements combined with electrical conductivity measurements in the radiation field can also be used to give an estimate of the termination rate constant[1,2]. The specific conductivity σ is rigorously related to the average life time of the charge carriers thus:

$$\tau = \varepsilon/4\pi\sigma$$

Also from simple kinetics[1]:

$$k_t = \tau^{-2} R_i^{-1}$$

In the case of isobutyl vinyl ether all the parameters have been determined[1,6]. This gives an opportunity to compare the k_t values, in bulk, calculated by both methods. The simple Debye equation gives a value of 3.14×10^{11} l M⁻¹ s⁻¹ compared with 3.40×10^{11} from the experimental conductivity and other measurements[1,6]. Since k_t enters into the rate expression (equation 1) as a square root, the difference is only about 4% in calculating the k_p values in this particular case. This gives us some confidence in using
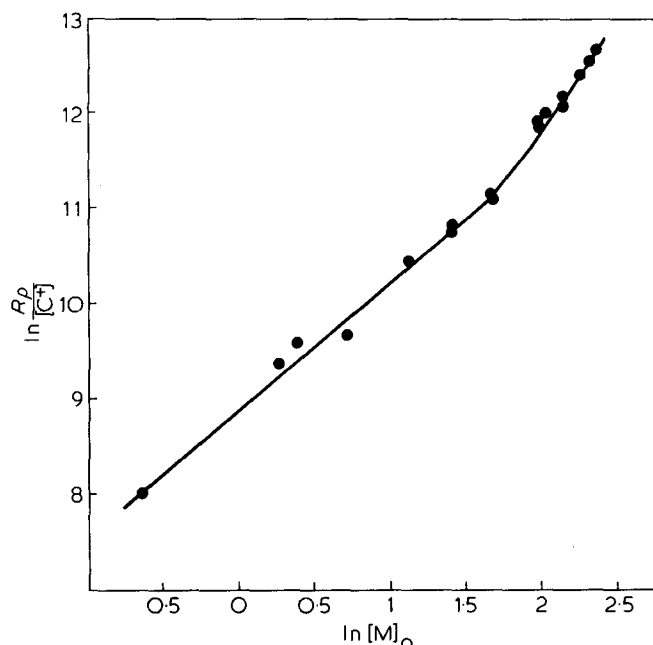
Figure 5 Monomer concentration dependence of $R_p/[C^+]$, EVE in benzene at 20°C. Dose rate, 71 rad s^{-1}

the simplified Debye equation in this work. Two methods can be used to estimate R_{im}. The first, previously applied to the polymerization of EVE in n-pentane and neopentane[3] assumed the additivity of the free-ion yields of the two components, i.e.:

$$G_{im} = G_{IM}X + G_{IS}(1 - X)$$

where G_{IM} and G_{IS} are the free ion yields of the monomer and the solvent, and X and $(1 - X)$ their respective volume fractions. Unfortunately this simple relation has been reported to be quite often in poor agreement with the corresponding experimental G_{im}, especially for polar mixtures.

Allen and coworkers[7,8] have developed a more satisfactory method in which the free ion yield of a liquid can be calculated from the product of the escape probability of an electron formed (according to Onsager) and the Gaussian distribution of the intra-pair separation distances. Probably because of the rather similar bulk dielectric constants of the two components of the mixtures, the estimated G_{im} obtained by both methods are similar. The values are given in *Table 3*.

The stationary concentration of free propagating species $[C^+]$, equal to the ratio $(R_{im}/k_{tm})^{1/2}$, as previously shown by Hayashi and Williams[1], was then calculated (*Table 3*). $[C^+]$ was found to decrease by less than a factor of 2 from bulk to the pure benzene, confirming that the important variations of R_p are mainly due to the propagation parameters of the reaction, $k_p.[M]^x$, which are equal to

$$\frac{R_p k_{tm}^{1/2}}{R_{im}^{1/2}} = R_p[C^+]$$

The values of this expression for different monomer concentrations are given in *Table 3*. For most of the concentration range, the variation of the logarithm of $R_p/[C^+]$ versus the logarithm of [M] (*Figure 5*) leads, for the propagation reaction, to an external order of 1.25 with respect to the monomer.

The apparent activation energies of the polymerization were measured in bulk and at two different monomer concentrations in benzene over a temperature range of $-5°$ to $+40°C$. The corresponding Arrhenius plots are presented in *Figure 6*. These lead to an apparent activation energy of 13.5 ± 0.5 kcal mol^{-1} for all three systems. This is somewhat higher than the previously reported values of 10–11 kcal mol^{-1} obtained in bulk[9,10]. These were not obtained with a vigorous half-power dose rate dependence, however. If there is some termination by impurities this would lower the observed activation energy by a few kcal mol^{-1}, which could account for the differences.

The first order rate dependence on the monomer concentration, generally assumed for such reactions, leads to a propagation rate constant for EVE in benzene equal to 7.0×10^3 l M^{-1} s^{-1} at 20°C. However, at higher monomer concentrations, ranging from bulk to about 6 l M^{-1}, an order of 2.2 with respect to the monomer concentration was observed. The simplest explanation would be to assume that some solvation of the active species by the monomer occurs leading to a new species with a higher reactivity, the amount of which increases with the monomer concentration. However, the fact that the internal monomer order in bulk is close to unity and that the activation energies in bulk and in benzene are quite similar indicates that such a process is not significant.

Note that in the chemically-induced polymerization of cyclic ethers Penczek et al.[11-13] reported a solvation of the propagating cations by the monomer molecules. However, as recently pointed out by Szwarc[14], the internal order of one with respect to the monomer observed for the polymerization rate is not in agreement with this single process and involves at least a similar solvating ability of the polymer chain.

In the vinyl ether polymerization, the solvation of the free cations by the polyether-type polymer chain can also occur. This process, which will lead to a first order of the rate on the monomer concentration, is supported further by the higher solvating ability of the polymer unit compared with the monomer and by a possible chelation
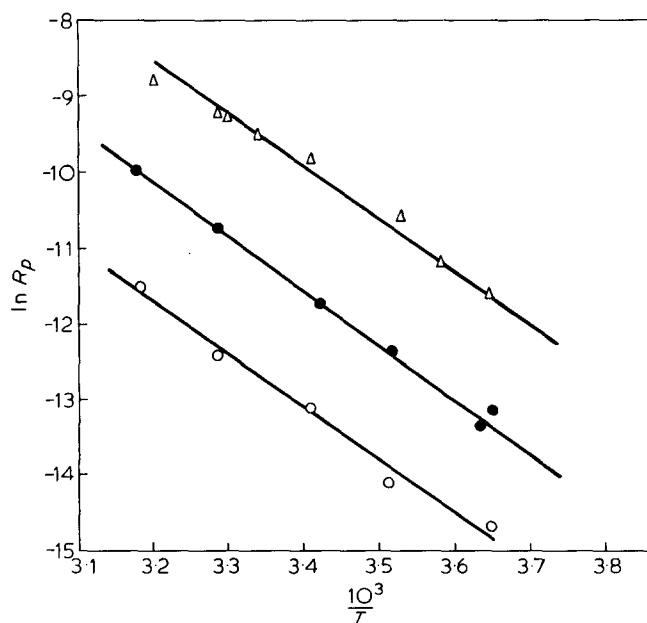

Figure 6 Arrhenius plots for EVE. △, In bulk; ●, 5.4 molar in benzene; ○, 2.1 molar in benzene. Dose rate, 71 rad s^{-1}

Table 4 Rate of polymerization, estimated free ion yields and rate constants of polymerization in the radiation induced polymerization of EVE in low dielectric constant solvents. $T = 30°C$; dose rate 71 rad s^{-1}

| Solvent	ϵ	$[M]_0 M I^{-1}$	$R_p \times 10^5$ $M I^{-1} s^{-1}$	$G_{im} \left(\dfrac{\text{free ions}}{100 \text{ eV}} \right)^a$	$k_p{}^c \times 10^4$ $I M^{-1} s^{-1}$
Neo-pentane	2.39	5.2	3.6	0.20 (0.50)[b]	6.0 (2.4)[b]
n-Pentane	2.42	5.2	2.5	0.14	3.8
Benzene	2.64	5.3	2.2	0.09	4.4
EVE (bulk)	~3	10.5	9.5	0.14	6.0
Di-isopropyl ether	3.7	5.2	3.2	0.21	3.1
Diethyl ether	3.9	5.2	2.9	0.23	2.6

[a] Calculated by Allen method. The other method gives very similar values, except for neo-pentane
[b] Value determined by the simple additivity method
[c] Determined from equation (1) assuming an order close to one in monomer for the reaction. This was checked for benzene and diethyl ether

Table 5 Rates of polymerization in the radiation-induced polymerization of EVE in bulk and benzene solution in the presence of methylene chloride or glyme as additives. $T = 20°C$; dose-rate 71 rad s^{-1}

Solvent	$[M]_0$ (M)	Additive (A)	$[A]$ $M I^{-1}$	$R_p \times 10^5$ $M I^{-1} s^{-1}$
Bulk	10.54	None	—	5.27
''	10.16	CH_2Cl_2	0.6	0.56
''	9.52	Glyme[a]	0.5	7.50
Benzene	5.4	None	—	0.83
''	5.4	CH_2Cl_2	0.25	0.49
''	5.2	Glyme[a]	0.21	3.9

[a] Bis-2 methoxy ethyl ether

effect. Such a solvation can be written as follows:
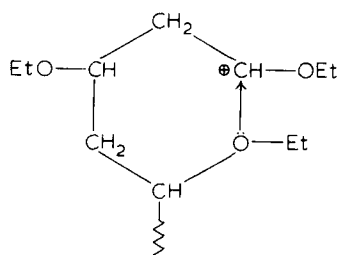
Changes in the solvation of the ionic species by the polymer chain probably occur with the dilution decreasing the intermolecular solvation on the one hand, while the intramolecular solvation is left unchanged on the other. This could provide an explanation for the relatively fast decrease of the polymerization rates at high monomer concentrations.

The similar values for the estimated k_p values shown in *Table 4* for a number of different solvents including both hydrocarbons and ethers also support solvation by the polymer chain assuming no unusual effects of the solvent molecules[15,16].

Introduction of polar or highly solvating molecules as additives, such as methylene chloride or diglyme, however, can act to destroy the assumed solvation by the polymer. As shown in *Table 5*, this creates drastic changes in the rates of polymerization, tending to confirm the important role of the polyether chain in the polymerization process of EVE in low solvating power media.

This work represents the first detailed study of a solution radiation-induced ionic polymerization. We

have shown that the experimental results are in good agreement with the Hayashi–Williams expression, and that this equation can be applied to solution systems. The calculated values of k_{tm} and R_{im}, which must be considered as a rough estimate of their magnitude, show that the variation of these parameters is relatively small and that the variation of R_p represents mainly the variation of the propagation factors.

Kinetic results in bulk, in benzene, and in other low dielectric constant solvents can be explained by a solvation of the propagating species by the polymer chain. These results appear to indicate that there is little or no solvation by the monomer. Experiments on radiation-induced polymerization in other solvents are in progress to improve our knowledge of this kind of polymerization.

ACKNOWLEDGEMENT

REFERENCES

1 Williams, F., Hayashi, Ka., Ueno, K., Hayashi, K. and Okamura, S. *Trans. Faraday Soc.* 1967, **63**, 1501
2 Williams, F. (Fundamental Processes in Radiation Chemistry' (Ed. P. Ausloos), Interscience, New York (1968)
3 Kubota, H., Kabanov, V. Ya, Squire, D. R. and Stannett, V. J. *Macromol. Sci. (A)* 1978, **12**, 1299
4 Stannett, V., Kubota, H., Hsieh, W. C. and Squire, D. R., 'Proceedings of the Sixth International Congress on Radiation Research', Tokyo, May 1979, pp. 365–373
5 Hsieh, W. C., Kubota, H., Squire, D. R. and Stannett, V. *J. Polym. Sci. Polym. Chem. Edn.* 1980, **18**, 2773
6 Hayashi, Ka, Hayashi, K. and Okamura, S. *J. Polym. Sci. (A-1)* 1971, **9**, 2305
7 Schmidt, W. F. and Allen, A. O. *J. Phys. Chem.* 1968, **72**, 11, 3730
8 Schmidt, W. F. and Allen, A. O. *J. Chem. Phys.* 1970, **52**, 2345
9 Goineau, A. M., Kohler, J. and Stannett, V. *J. Macromol. Sci. (A)* 1977, **11**, 99
10 Suzuki, Y., Chudgar, A., Rooney, J. M. and Stannett, V. *J. Macromol. Sci. (A)* 1977, **11**, 115
11 Matyjaszewski, K., Kubisa, P. and Penczek, S. *J. Polym. Sci. Polym. Chem. Edn.* 1979, **17**, 69
12 Matyjaszewski, K., Slomkowski, S. and Penczek, S. *J. Polym. Sci. Polym. Chem. Edn.* 1979, **17**, 69
13 Matyjaszewski, K., Slomkowski, S. and Penczek, S. *J. Polym. Sci. Polym. Chem. Edn.* 1979, **17**, 2413
14 Szwarc, M. *Macromolecules* 1978, **11**, 1053
15 Kazanskii, K. S., Solovyanov, A. A. and Tarasov, A. N. *Int. Symp. Macromol. Helsinki* 1972, **2**, 535
16 Ugelstad, J., Mork, P. C. and Jensen, B. *Acta Chem. Scand.* 1963, **17**, 1455