Radiation-induced cationic polymerization of vinyl ethers in solution: 3. The influence of monomer and solvent concentrations on the rate of polymerization of ethyl vinyl ether in ether solvent

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The influence of the monomer concentration on the rate of propagation of the radiation-induced polymerization of super-dry ethyl vinyl ether has been examined in detail in two ether solvents, diethyl ether and diglyme, chosen for their different dielectric constants and their different abilities to solvate ions. Estimations of the rate of initiation and of the rate of termination have made possible the evaluation of the rate constants of polymerization. Very similar values were obtained in both ethers. Experiments were also performed in benzene–diglyme and diglyme–methylene chloride mixtures. The results are in good agreement with the previous studies, made in benzene and methylene dichloride, and confirm the important role of the solvation of the free propagating species concerning the reactivities observed in the radiation-induced polymerization of EVE in solution.

Keywords Polymerization; monomer; concentration; ethyl vinyl ether; initiation; termination; propagation

INTRODUCTION

In the first two articles of this series[1,2] the radiation-induced polymerization of EVE was studied in detail in benzene and methylene dichloride solutions. Except at the highest monomer concentrations, the experimental rates of polymerization were observed to follow the theoretical Hayashi–Williams[3,4] kinetic equation, leading, for the propagation reaction, to an external order with respect to monomer close to unity. However, in benzene, and more generally in low polar solvents such as hydrocarbons, or some ethers, the results were interpreted by a predominant solvation of the free propagating cations by the polymer chain whereas in methylene dichloride solution the ionic species appeared to be solvated by the solvent molecules. In this article kinetics are described of the cationic radiation-induced polymerization of EVE in two ethers, chosen for their different dielectric constants and their different abilities to solvate ions, i.e. diethyl ether ($\varepsilon=4.2$) and diglyme ($\varepsilon=7.3^5$). Some experiments were also performed in the mixed solvents benzene–diglyme and methylene dichloride–diglyme. As in the previous studies the influence of monomer and solvent concentrations on the rates of polymerization and on the stationary concentration of propagating species have been investigated.

The results obtained with these solvents agree with the previous interpretations and confirm the important role of the solvation of the free propagating species towards the reactivity observed in the radiation-induced polymerization of EVE in solution.

EXPERIMENTAL

Materials

EVE (Aldrich Co.), benzene, and methylene dichloride were purified as described previously[1,2,6].

Diethyl ether and diglyme [(2-methoxyethyl) ether, Fisher Scientific] were stored over potassium hydroxide, and then distilled over calcium hydride. The final drying was carried out over sodium mirrors until the sodium remained unattacked and a stable blue colour was observed with the diglyme.

Polymerization

Polymerization experiments were performed as described previously[1], number average molecular weight determinations were carried out on a Hewlett–Packard vapour pressure osmometer at 37°C in toluene.

RESULTS AND DISCUSSION

As in the previous papers, the purity of the monomer and the solvents was initially checked by the dose-rate dependence of the rates of polymerization. As shown in *Figure 1*, the dependence observed was close to 0.5 in both

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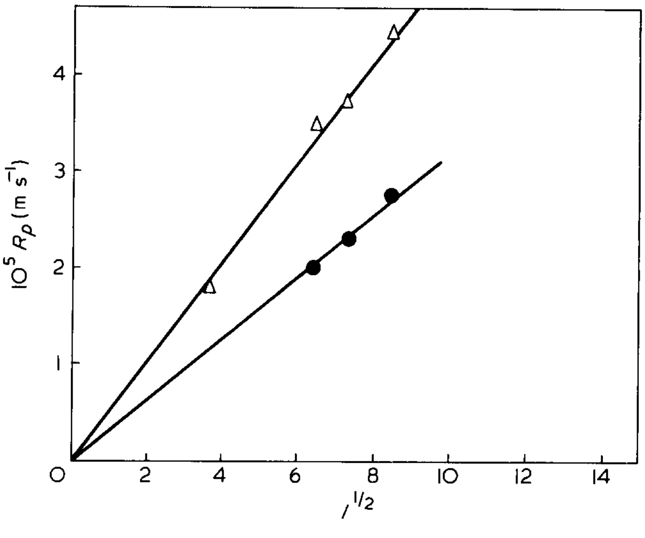

Figure 1 Dose rate dependence of the rate of polymerization of EVE. ● in diethyl ether, △ in diglyme at 23°C. $[M]_0 = 5.2$ m l^{-1}

Table 1 Rates of polymerization, estimated free cation concentrations and rate constants of polymerization in the radiation-induced polymerization of EVE in diethyl ether. ($T° = 23°$C; dose rate 71 rad s^{-1})

[EVE] (m l^{-1})	$R_p \times 10^6$ (m l^{-1} s^{-1})	[C+] 10^{10} (m l^{-1})	k_p 10^{-4} (l m^{-1} s^{-1})
10.5 (bulk)	62.5	1.7	3.5
9.8	44.5	1.8	2.6
9.0	40.0	1.9	2.4
8.4	35.8	1.9	2.2
6.9	34.5	2.2	2.3
5.4	26.0	2.4	2.0
5.3	21.0	2.4	1.7
3.0	14.4	2.8	1.7
2.2	8.7	2.9	1.3
1.7	6.5	3.0	1.3
1.4	5.0	3.0	1.2
(pure solvent)	–	3.3	–

solvents and, therefore, allowed us to neglect the influence of a termination reaction by protonic impurities.

The influence of the initial monomer concentrations on the rates of polymerization of EVE was studied in diethyl ether and diglyme solutions over a range of from 1–10.54 ml^{-1} (bulk). The values of the polymerization rates are given in *Tables 1* and *2* and the logarithms of the polymerization rates are plotted against the logarithms of the monomer concentrations, in *Figure 2*. In the main parts of the ranges examined the rates of polymerization are respectively proportional to an order of 1.1 and 1.2 with respect to monomer in diethyl ether and diglyme. Note that for the high monomer concentrations in diglyme solutions the apparent rates of polymerization increase with dilution leading to higher rates than in bulk. After reaching a maximal value for about 9 ml^{-1} the rates decrease normally according to the dilution effect.

Calculations were made to estimate the variations of the stationary-free propagating cation concentrations, with the different amounts of monomer and solvent present in the mixtures. This calculation, as described previously[1], is based on the estimation of the free ion yields of mixtures, G_{im}, by Allen's theory[7,8] and on the assumption of a global dielectric constant effect on the rate of charge neutralization k_{tm}. The local dielectric constant would certainly be more valid but is unknown. As shown by Williams and Hayashi[3,4]:

$$[\mathrm{C}+]=\left(\frac{10\,I\,G_{im}}{N\,kt_m}\right)^{1/2}$$

where I is the dose rate and N the Avogadro number. Values of 0.35 and 0.65 were used respectively for the free ion yields of diethyl ether and diglyme. The free ion yield of diglyme was estimated from the dependence of the free ion yields of ethers on their dielectric constants[10], as shown in *Figure 3*.

The values of [C+], are given in *Tables 1* and *2*. They must be considered as rough estimates. The logarithmic variations of R_p/[C+] are plotted against the logarithms of the monomer concentration in *Figure 4*. Results previously obtained in benzene[1] are also indicated on the figure. It is remarkable that in these three solvents of

Table 2 Rates of polymerization, estimated free-cation concentrations and rate constants of polymerization in the radiation-induced polymerization of EVE in diglyme. ($T° = 23°$C; dose-rate, 71 rad s^{-1})

[EVE] (m l^{-1})	$R_p \times 10^6$ (m l^{-1} s^{-1})	[C+] 10^{10} (m l^{-1})	k_p 10^{-4} (l m^{-1} s^{-1})
10.5 (bulk)	62.5	1.7	3.5
10.1	66.0	1.8	3.6
9.5	75.0	2.1	3.6
9.3	79.0	2.3	3.7
9.0	75.0	2.5	3.3
7.5	61.5	3.2	2.6
7.0	64.0	3.4	2.7
5.5	48.0	4.0	2.2
5.2	44.5	4.0	2.1
4.9	36.5	4.1	1.8
3.5	25.5	4.6	1.6
2.3	16.5	4.9	1.5
1.7	10.5	5.1	1.2
(pure solvent)	–	5.6	–

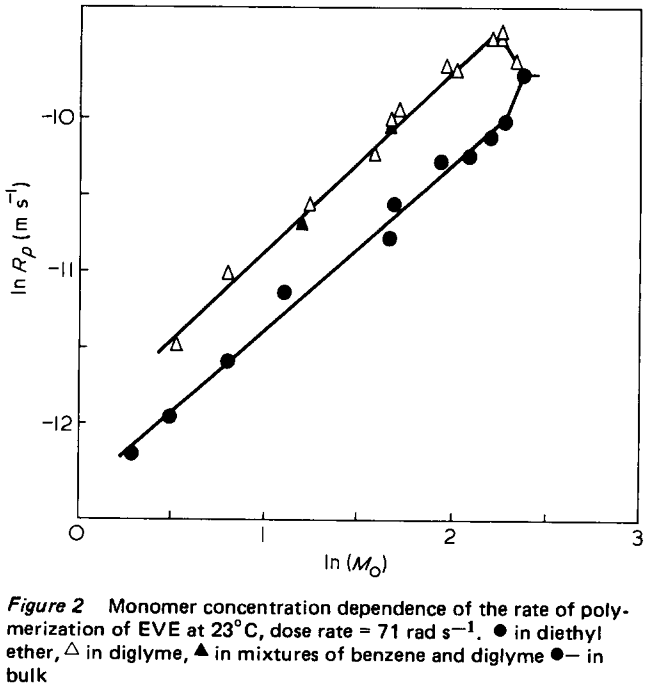

Figure 2 Monomer concentration dependence of the rate of polymerization of EVE at 23°C, dose rate = 71 rad s^{-1}. ● in diethyl ether, △ in diglyme, ▲ in mixtures of benzene and diglyme ●— in bulk

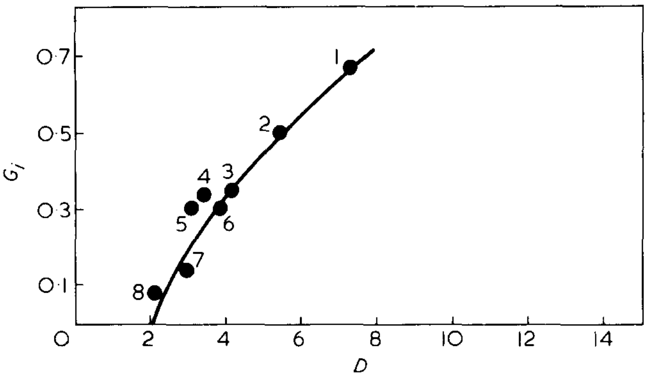

Figure 3 Free ion yields, G_i, of various ethers versus their dielectric constants, D, used to estimate the diglyme value. Data of Allen[9]. 1. Tetrahydrofuran, 2. Tetrahydropyran, 3. Diethyl ether, 4. Di-n-propyl ether, 5. Di n-butyl ether, 6. Di-isopropyl ether, 7. Ethyl vinyl ether, 8. 1,4-Dioxane

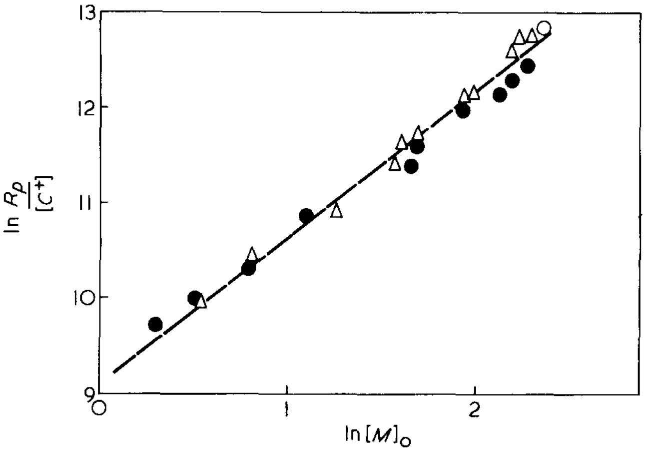

Figure 4 Variation of $\ln R_p/(C^+)$ with $\ln[M_0]$ for EVE at 23°C. ● in diethyl ether, △ in diglyme and ○ in bulk. The dashed line is for benzene solutions extrapolated from 20°C[1]

different physical properties and different solvating ability the data fit, within the experimental error on the same line, indicating that the rate constants of propagation for EVE are very close in these solvents. The variations observed lead to an order of ~1.4 with respect to monomer for the propagation reaction.

This order is slightly higher than the first order dependence expected for the propagation, according to the previous results[1,2]. This comes probably from the assumptions made in the calculations of the free propagating cation concentrations.

Values of the rate constants of polymerization, according to an order of unity in monomer are indicated in *Tables 1* and *2*. The activation energies of the polymerization reaction were measured in diethyl ether at several monomer concentrations over a temperature range of 0°–40°C. The results are given in *Table 3*. Those previously obtained in bulk benzene and methylene dichloride solutions are also included. No significant variations in the activation energies of the polymerization reaction are observed at the different monomer concentrations. Moreover the values obtained in diethyl ether are close to those determined in other low dielectric constant solvents. This confirms the hypothesis of a relatively similar state of the propagating species.

Experiments were also performed in mixed solvents, benzene–diglyme and methylene dichloride–diglyme. The results are reported in *Tables 4* and *5*.

In the first system the rates of polymerization obtained show that the influence of the diglyme, even added in small quantities, is largely predominant over the benzene. The results, plotted in *Figure 5* fit quite closely with those obtained in pure diglyme.

On the contrary in the methylene dichloride–diglyme mixtures, the chlorinated solvent is predominant over the diglyme and determines the rates of polymerization. These rates, indicated in *Table 5* appear to be independent of the relative amount of each solvent component, and correspond closely to those determined in pure methylene dichloride, see *Figure 5*. As reported in *Table 5*, the number average molecular weights of the polymers

Table 3 Activation energies in the radiation-induced polymerization of EVE in bulk and in solution

Solvent	Monomer concentration $[M]$	E_a kcal M^{-1}	Ref
Bulk	10.5	13 ± 0.5	(1)
Benzene	5.4	13.9 ± 0.5	(1)
Benzene	2.1	13.5 ± 0.5	(1)
Diethyl ether	6.9	11.6 ± 0.5	this work
Diethyl ether	5.3	11.5 ± 0.5	this work
Diethyl ether	2.9	12.3 ± 0.5	this work
Methylene dichloride	5.2	7 ± 1	(2)
Methylene dichloride + Benzene	5.2	8 ± 1	(2)

Table 4 Rate of polymerization in the radiation-induced polymerization of EVE in mixtures of diglyme and benzene ($T° = 23°C$; dose-rate = 71 rad s^{-1})

[EVE] (m l^{-1})	[Benzene] (m l^{-1})	[Diglyme (m l^{-1})	$R_p \times 10^6$ (m l^{-1} s^{-1})
5.4	6.0	0	8.3
5.2	5.6	0.2	39.0
5.3	0	3.5	44.5
3.1	8.2	0	3.6
3.3	7.2	0.4	31.5
3.4	0	4.8	36.5

Table 5 Rates of polymerization in the radiation-induced polymerization of EVE in mixtures of diglyme and CH_2Cl_2 at 23°C. (Dose rate 71 rad s^{-1})

$[EVE]_0$ (m l^{-1})	[diglyme] (m l^{-1})	$[CH_2Cl_2]$ (m l^{-1})	$R_p \times 10^6$ (m l^{-1} s^{-1})	$\bar{M}_n$†
8.6*	1.3	0	74.0	–
8.6	0.7	1.4	6.1	–
8.7	0	2.8	6.1	–
7.5	2.0	0	61.5	–
7.5	1.2	1.7	5.5	–
7.8	0	4.0	5.3	–
5.2	3.5	0	44.5	6100
5.0	3.0	1.6	4.0	2150
5.3	1.8	3.9	4.1	1400
5.1	0.9	6.1	4.2	1450
5.3	0	7.8	4.4	1500

* Extrapolated from *Figure 2*
† Total dose 4.25 Mrad

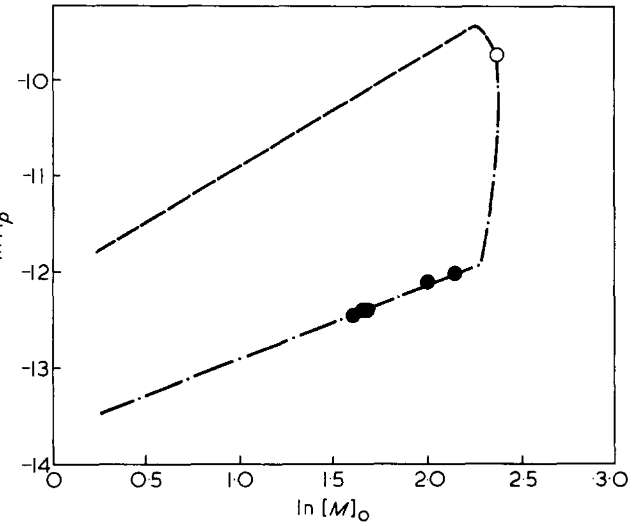

Figure 5 Rates of polymerization for EVE, ● in mixtures of diglyme and methylene chloride, ○ in bulk value — — — — in pure diglyme; —·—·—·— in pure methylene chloride; all at 23°C, dose rate 71 rads s^{-1}

prepared in pure diglyme, pure methylene dichloride and in mixtures of these solvents, confirm the tendency observed with the rates.

DISCUSSION

The rate constants of the radiation-induced polymerization of EVE have been determined in different hydrocarbon and ether solvents. In spite of relatively important changes in the dielectric constant, and in the solvating ability towards the cations of these media, the rate constants of polymerization were found to be practically identical and unaffected by the physical properties of these solvents. In a previous paper[1] this peculiar phenomenom was discussed and interpreted by the predominant solvation of the propagating species by the polyether polymer chains which, in surrounding the cations act as a shield and reduce the influence of the external medium. Such a phenomenom has been reported in other cases[11,12]. The rather surprising fact with the present results, is the predominant effect of the polymer chain over the diglyme molecules. However both compounds are polyether types, and a cooperative effect of several oxygens of the polymer chain, chelating effects, comparable to the one which occurs with the glyme molecules can probably explain this result. Moreover, a self-solvation of the propagating cations by their own chains, is a process which is entropically and sterically favoured in comparison with any inter-solvation processes which could also be postulated.

Another interesting point is the predominant effect of the methylene dichloride over the polymer chain and the diglyme. These results were checked with different sets of products to eliminate the hypothesis of any possible effect of an impurity. A long distance effect of the methylene dichloride, due to its polarity, through the solvation shell of the polymer seems rather improbable mainly because of the small concentration of methylene dichloride needed[2] and also because a comparable effect should be observed with the diglyme ($\varepsilon = 7.3$). A final comment concerns the identical values of the rates of polymerization observed in mixed solvents benzene CH_2Cl_2[2], diglyme–CH_2Cl_2 and pure methylene dichloride on the one hand, and benzene–diglyme and pure diglyme on the other. These results firstly imply the same rate constants of propagation, but also the same concentrations of propagating species in the media. In the mixed solvents examined, the concentrations $[C+]$ appear to be independent of the ratio of the components and only dependent on the nature of the more polar or more solvating component present in the medium, which seems able to govern the escaping and recombination process of the ions. These observations show the limits of our estimation of $[C+]$ with the composition of the mixtures, mainly when one of the components is a polar or solvating molecule. However, even in this case the limit of variations of $[C+]$ remains between the values of $[C+]$ of the pure components, which are relatively close, and do not greatly affect the order of magnitude of the concentrations but only their law of variations with the composition of the medium.

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