Radiation-induced cationic polymerization of vinyl ethers in solution: 2. Polymerization of ethyl vinyl ether in methylene dichloride solution

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The rates and degrees of polymerization of ethyl vinyl ether (EVE) polymerized by gamma radiation in methylene chloride (CH_2Cl_2) have been studied in detail. The addition of even a small amount of CH_2Cl_2 sharply reduced the rates and degrees of polymerization. After about 0.5 ml^{-1} of CH_2Cl_2 the rates became roughly first order in monomer. It is postulated that CH_2Cl_2 strongly solvates the growing chain ends disrupting the solvation by the polymer chains themselves, leading to lower rates. The degrees of polymerization support this hypothesis. Isodielectric constant solutions of EVE in benzene–CH_2Cl_2 mixtures gave rates at the same monomer concentrations, which fitted perfectly those obtained in EVE–CH_2Cl_2 mixtures. These results indicate that the dielectric constant is not the predominating property as formerly thought but that solvation is a more important factor. The activation energies were lower in CH_2Cl_2 solution than in bulk monomer or in low dielectric constant solvents, again indicating perhaps a different state of solvation of the growing chain ends.

Keywords Polymerization; ethyl vinyl ethers; radiation; dielectric; solvation; polymer chains

INTRODUCTION

The cationic radiation-induced polymerization of EVE, studied in bulk and low dielectric constant solvents such as benzene, was described in Part I of this series[1]. It was shown that the experimental results fitted, over a large monomer concentration range, the theoretical Hayashi–Williams[2,3] kinetic equation[1]:

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

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

No significant solvation process of the propagating cations by the monomer was observed, and the very similar rate constants of polymerization determined in different low dielectric constant solvents, led to the assumption that the active cations were most probably solvated by the polymer chains.

In this paper the kinetics of the radiation-induced polymerization of EVE in methylene dichloride, are described. This is a relatively high dielectric constant solvent, which is the most commonly used polymerization medium for classical cationic chemically-induced polymerization studies.

Preliminary studies performed in these laboratories[4,5] have already shown the drastic decrease of the rate of the radiation-induced polymerization of vinyl ethers in high dielectric constant media. The extensive study of the EVE–CH_2Cl_2 system, reported here, indicates that this phenomenom is mainly due to the solvation of the radiation-generated free ions by the solvent molecules.

EXPERIMENTAL

Materials

EVE and benzene were purified as previously described[1,6]. Methylene dichloride was purified according to Sigwalt's procedure[7] and distilled from a sodium mirror immediately before use.

Polymerization

The polymerization tubes were degassed and filled as reported previously[1,6].

Irradiations were carried out in a cobalt-60 source and the polymer yield determined gravimetrically. Number average molecular weights were determined on a Hewlett-Packard vapour pressure osmometer at 37°C in toluene as the solvent.

RESULTS AND DISCUSSION

In radiation-induced ionic polymerizations the purity of the monomer and the solvent can be easily checked by the dose-rate dependence of the rate of polymerization. As shown in *Figure 1* a dependence close to the theoretical 0.5 order, expected in the absence of termination by protonic impurities, is observed for the EVE.CH_2Cl_2 system.

The influence of the monomer concentration on the rate of polymerization was examined over a monomer concentration range from 2.1 Ml^{-1} to 10.54 Ml^{-1} (bulk). The values of the polymerization rate are given in *Table 1* and the logarithmic variation of R_p with $[M]_0$ is shown in *Figure 2*. A drastic decrease in the polymerization rate is observed on adding the first small amount of methylene dichloride to the pure monomer. The variation of R_p then becomes proportional to an order close to unity with respect to the monomer.

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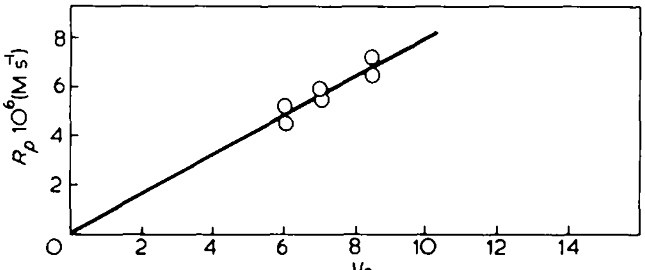

Figure 1 Dose rate dependence of the rate of polymerization of EVE in CH_2Cl_2 solution. $T = 27°C$ [M] = 5.2 Ml^{-1}

Table 1 Rates of polymerization, stationary free propagating species concentrations and rate constants of polymerization in the radiation induced polymerization of EVE in methylene dichloride, $T = 22°C$, dose-rate 71 rad. S^1

[EVE] Ml^{-1}	$R_p \times 10^{-6}$ Ml^{-1} s^{-1}	[C+] $\times 10^{10}$ Ml^{-1}	$k_p \times 10^{-3}$ Ml^{-1} s^{-1}
10.54 (bulk)	53.0	1.71	29.4
10.50	13.8	1.74	7.5
9.53	9.1	2.43	3.9
9.46	5.1	2.46	2.1
9.36	6.1	2.60	2.5
9.05	5.2	2.75	2.1
8.71	6.1	2.97	2.4
7.82	5.3	3.39	2.0
7.03	5.2	3.70	2.0
6.97	5.5	3.73	2.5
5.94	4.7	4.14	1.9
5.91	4.8	4.14	2.2
5.32	4.4	4.35	1.9
5.27	4.4	4.35	1.9
3.58	3.3	4.79	2.1
3.16	2.9	4.90	1.9
2.14	2.2	5.07	2.1

Calculations were made to take into account the variation of the concentration of the free propagating cations [C+] with the relative amounts of solvent and monomer in the mixtures.

The procedure for the calculation of [C+], based on an overall dielectric constant effect and on the contribution of the free ion yield of each component was developed in a previous paper[1]. Values of 0.14 and 0.48 were used respectively for the free ion yield of pure EVE and pure CH_2Cl_2. The solvent free ion yield value was estimated from the apparent linear dependence[9] of the free ion yields of the halogen compounds towards their dielectric constants, as shown in *Figure 3*.

As can be seen in *Table 1*, over the whole monomer concentration range examined an increase of less than a factor of three for [C+] is observed. This value must be considered as a rough estimate because the calculation does not take into account any possible preferential position of either monomer or solvent molecules around the free ions. However, as we will see later, such a process is probable. In this case, the modification of the medium around the free ions, i.e. the nature of the neighbouring molecules and the local dielectric constant, is less than the calculated value and the corresponding variation of [C+] can be considered as its maximal variation.

The logarithmic dependence of R_p/[C+] *versus* $[M]_0$ is shown in *Figure 4*. Except for monomer concentrations very close to the bulk value ($[M]_0 > 9.5$), a first order dependence with respect to the monomer is observed for the propagation reaction of EVE in this solvent. This result is in agreement with previous results reported in the literature for the chemically-induced cationic polymerization of vinyl ethers in CH_2Cl_2[10–12]. The rate constant of polymerization, given in *Table 1*, remains equal to $2.1 \pm 0.4 \times 10^3$ Ml^{-1} s^{-1} for monomer concentrations lower than 9.5 Ml^{-1}. It should be noted that this average value is about ten times lower than the reported k_p value for the chemically-induced polymerization of EVE in CH_2Cl_2[10,13,14].

Analysis of the variation of R_p with the different concentration of monomer and solvent in the mixture does not agree with a predominant effect on the rate of polymerization of the overall dielectric constant of the mixture and led us to re-examine this previous assumption.

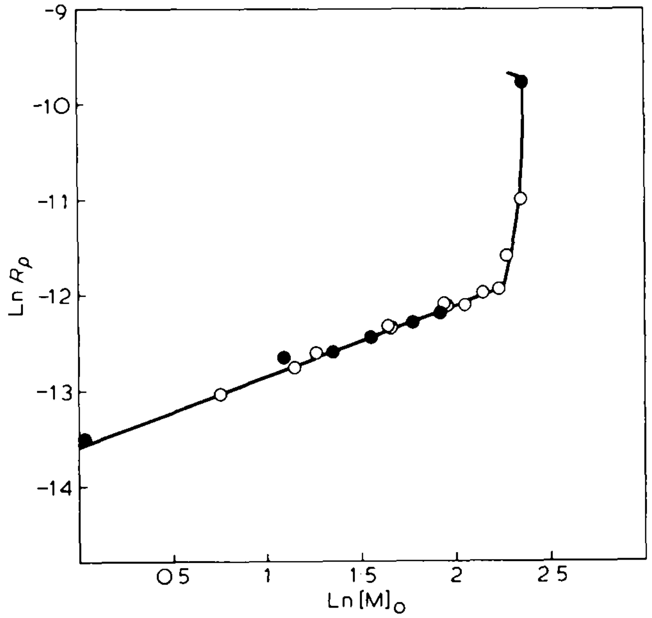

Figure 2 Dependence of rate on monomer concentration of EVE, ○ in CH_2Cl_2 solution, ○ in bulk, ● in isodielectric EVE–CH_2Cl_2–benzene mixtures. $\epsilon \approx 5.0$. $T = 22°C$. Dose rate 71 rads. per second

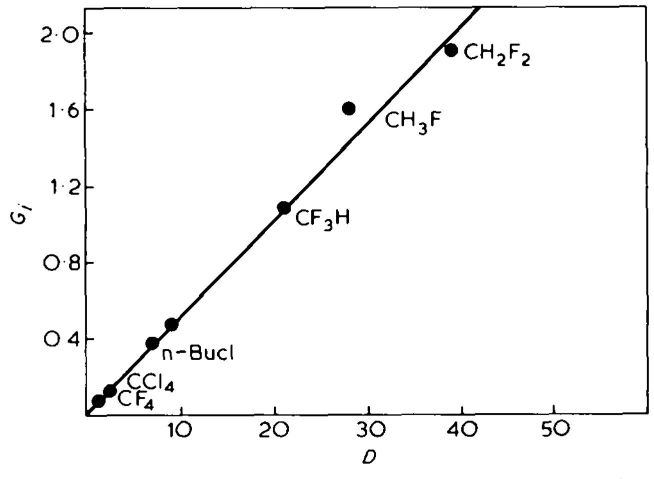

Figure 3 Determination of the free ion yield G_i of CH_2Cl_2 at 22°C from the dielectric constant, *D*. Data from Allen (ref. 8). ●, estimated CH_2Cl_2 value

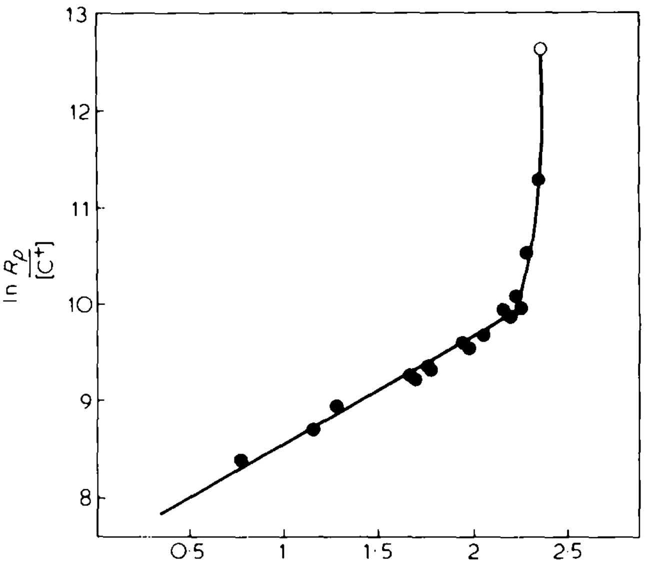

Figure 4 Dependence of $R_p/(C+)$ on the monomer concentration in CH_2Cl_2 at 22°C. ○, bulk value. Dose rate 71 rads. per second

Table 2 Rates of polymerization of EVE in isodielectric constant mixtures EVE, CH_2Cl_2, benzene T = 22°C dose rate = 71 rad. s^{-1}

[EVE] Ml^{-1}	$[C_6H_6]$ Ml^{-1}	$[CH_2Cl_2]$ Ml^{-1}	ϵ^a	$R_p \times 10^6$ $Ml^{-1}\ s^{-1}$
6.8	0	5.5	5.1	5.0
6.0	0.9	5.5	5.1	4.4
4.8	2.0	5.7	5.1	4.0
3.9	3.1	5.5	4.9	3.4
3.0	3.9	5.8	5.0	3.3
1.0	5.8	6.1	5.0	1.4

[a] Based on the molar additivity

Some experiments were performed in isodielectric mixtures EVE.CH_2Cl_2-benzene ($D = 5$) at different initial monomer concentrations ranging from 6.8 to 1 M. The results are indicated in *Table 2*. As shown in *Figure 2* the rates of polymerization determined in these experiments fit perfectly with those obtained with the EVE.CH_2Cl_2 system where the overall dielectric constant varies from 4 to 8.4.

Experiments were also performed in benzene with a same initial monomer concentration and in presence of different amount of methylene dichloride as additive. As we can see from *Table 3*, a small amount of methylene dichloride is sufficient to reduce the rate of polymerization to the value of that determined in pure CH_2Cl_2.

It is interesting to note that the identical values of R_p obtained with different ratios of methylene dichloride and benzene indicate also that the concentration of the propagating species is not appreciably affected by the composition of these mixtures.

Activation energies of the polymerization reactions were determined in pure methylene dichloride and mixtures of benzene and a small amount of CH_2Cl_2, between -5° and 43°C.

Close values of 7 ± 1 and 8 ± 1 Kcals mol^{-1} have been observed in the pure solvent and the mixture, respectively. These values are lower than those previously reported in bulk and benzene solution, probably because of the different states of solvation of the free propagating species.

An analysis of the molecular weight results is difficult. Even if for the first few percent, the molecular weights do not depend on the conversion, the chain lengths are still affected not only by kinetics parameters such as k_p, k_t, R_i and the monomer concentration, but also by accompanying, transfer reactions as well as possible irradiation grafting and degradation. However, if we assume, as a first approximation, that the two last parameters depend mainly on the total dose of irradiation some information about the transfer and the kinetic parameters can be obtained in comparing experiments performed at the same total dose of irradiation.

The molecular weights of the polymers prepared in methylene chloride with different monomer concentrations are presented in *Table 4*. As can be seen in *Figure 5*, the logarithmic dependence of $\overline{DP}$ on $[M]_0$ is very similar to that observed for R_p with $[M]_0$. After an important drop with the first small amount of CH_2Cl_2 in the medium the DP_n becomes proportional to an order of 1.25 in monomer. A similar tendency in the decrease of the rate of polymerization and of the molecular weights of polymers is observed with experiments performed in benzene, at the same initial monomer concentration and with increasing amounts of CH_2Cl_2 as can be seen in *Figure 6*.

It is interesting to note that the assumption, when adding CH_2Cl_2, of a drastic decrease of the rate of initiation would certainly lead to a decrease of R_p but at the same time to an increase in the chain length of the polymers. If we exclude any predominant role of even minute impurities in methylene dichloride, because of the half dose rate dependence observed and also because the

Table 3 Rates of polymerization of EVE and degrees of polymerization obtained in benzene in the presence of methylene chloride as additive T = 22°C dose rate = 71 rad s^{-1}

$[M]_0$ Ml^{-1}	[Benzene] Ml^{-1}	$[CH_2Cl_2]$ Ml^{-1}	$R_p \times 10^{-6}$ $Ml^{-1}\ s^{-1}$	$\overline{DP}_n{}^a$
5.4	5.5	0	8.3	85
5.4	5.4	0.25	4.9	29
5.4	4.4	1.5	4.5	26
5.3	0	7.7	4.4	21
7.2	3.6	0	20.0	
7.1	2.9	1.0	5.0	
7.0	0	5.2	5.2	

[a] Determined by vapour pressure osmometry
Total dose = 4.3 Megarads

Table 4 Number-average molecular weights and degree of polymerizations in the radiation-induced polymerizations of EVE in methylene dichloride

[EVE] Ml^{-1}	$[CH_2Cl_2]$ Ml^{-1}	$\bar{M}_n$	$\overline{DP}_n{}^a$
10.54 (bulk)	0	8600	120
10.50	0.3	4564	63
9.32	1.8	2280	32
8.71	2.7	2325	32
5.27	7.8	1370	19
3.58	10.3	670	9
3.16	10.9	620	8

[a] Determined by v.p.o.
Total dose 6 megarads

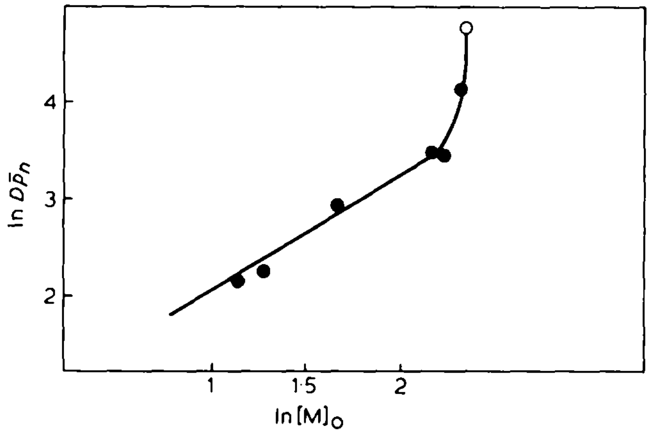

Figure 5 Dependence of $\overline{Dp}_n$ on the monomer concentration [Mo] for EVE in CH_2Cl_2. Total dose 6.0 mrads. T = 22°C. Dose rate 71 rads per second

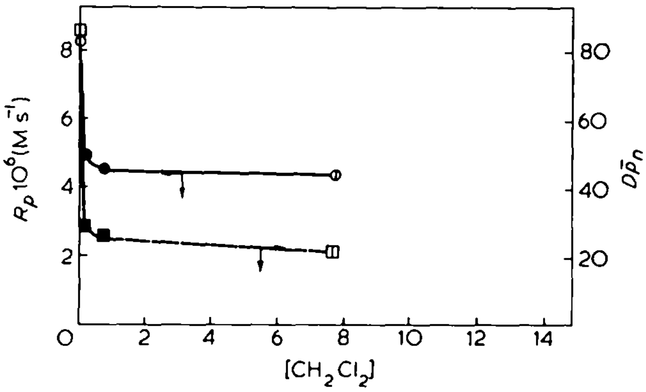

Figure 6 Variations of R_p and $\overline{DP}_n$ with the concentration of added CH_2Cl_2 in EVE-benzene solutions. (Mo) = 5.4 Ml^{-1} T = 22°C. ■, ● (CH_2Cl_2) = 0, □, ○ (Benzene) = 0. Dose rate 71 rads per second. Total dose = 4.3 mrads

effect of these impurities should be roughly proportional to the amount of methylene dichloride present in the mixture, all the reported results on the dependence of R_p, $\overline{DP}_n$ and [C+] on CH_2Cl provide considerable support to a solvation phenomenon of the free ions by the methylene dichloride molecules.

It should be noted that in the chemically-induced polymerization of cyclic ethers, Penczek's group reported an effect of the overall dielectric constant of the medium on the rate of polymerization[15-17]. They assume a predominant solvation of the propagating cations by the monomer molecules even in high polar media such as CH_2Cl_2 and CH_3NO_2. However, as pointed out by Szwarc[18] this assumption is not in agreement with the internal first order with respect to the monomer observed for the polymerization unless the solvated molecules are not incorporated in the chain, an hypothesis which seems rather improbable.

In radiation induced ionic polymerizations it is interesting to examine qualitatively the effect of solvation on the rate of polymerization. The resulting stabilization of the propagating species will reduce their reactivity resulting in a decrease in k_p. In principle the stabilization could decrease the rate of termination, k_t and possibly increse the initial yield of free ions, increasing R_i. Although these effects could, conceivably, result in an increase or decrease in the rate of polymerization it is clear that the predominant effect would be to decrease the rate. This is clearly so in the case of methylene chloride solution.

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