New Views on Cationic Polymerizations Induced by Ionizing Radiations

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Phil. Trans. R. Soc. Lond. A 1993 **342**, 469-504
doi: 10.1098/rsta.1993.0029

New views on cationic polymerizations induced by ionizing radiations

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Contents

This paper is about a reinterpretation of the cationic polymerizations of hydrocarbons (HC) and of alkyl vinyl ethers (VE) by ionizing radiations in bulk and in solution. It is shown first that for both classes of monomer, M, in bulk ($[\mathrm{M}] = m_{\mathrm{B}}$) the propagation is unimolecular and not bimolecular as was believed previously. This view is in accord with the fact that for many systems the conversion, Y, depends rectilinearly on the reaction time up to high Y. The growth reaction is an isomerization of a π-complex, $\mathrm{P}_n^+\mathrm{M}$, between the growing cation P_n^+ and the double bond of M. Therefore the polymerizations are of zero order with respect to m, with first-order rate constant k_{p1}^+. The previously reported second-order rate constants k_{p}^+ are related to these by the equation

$$k_{\mathrm{p1}}^+ = k_{\mathrm{p}}^+ m_{\mathrm{B}}.$$

If the monomer contains a group, other than the double bond, that can complex with the carbenium ion, such as an aromatic ring or a heteroatom, the resulting complexes, $\mathrm{P}_n^+\mathrm{G}$, are not propagators; in such systems the concentration of the propagators, $[\mathrm{P}_n^+\mathrm{M}]$, is less than the total concentration, c, of cations. This newly recognized effect makes the k_{p1}^+ of most monomers calculated from c too small; it may be at least partly responsible for the rate of polymerization of styrene being

Phil. Trans. R. Soc. Lond. A (1993) **342**, 469–504

Printed in Great Britain

significantly less than that of isobutene, and for the rate of polymerization of the VE being much less than that of the HC.

The behaviour patterns ensuing when bulk monomers are diluted by solvents are very varied. The most detailed information concerns the VE. My re-examination of the results shows that, contrary to current belief, no one kinetic scheme will fit all the systems over the whole range of m. My interpretations were facilitated considerably by the availability of the dependence of c on m, which for most systems can be expressed by a linear equation of the form $c = Am+B$, where in some systems A is positive, in others negative. By making this substitution in the kinetic equations it becomes obvious why for most systems the external kinetic order with respect to m is greater than unity, an effect noted, but hitherto not explained convincingly.

Both for ethyl vinyl ether (EVE) and isopropyl vinyl ether (IPVE) in benzene the unimolecular character of the propagation persists down to $m \approx 7$ mol dm^{-3}. Below that, a bimolecular propagation becomes dominant, of first order in m. The behaviour of EVE in Et_2O and in diglyme [bis(2-ethoxyethyl)ether] is apparently similar, but detailed examination shows marked differences. In Et_2O the propagation is of second order over most of the range of m. The rate of polymerization in diglyme goes through a sharp maximum near $m = 8.5$ mol dm^{-3}, which requires a more complicated explanation.

For EVE and 4-methoxystyrene in CH_2Cl_2 the addition of the solvent produces a dramatic fall in rate. This is explained by a change from unimolecular to bimolecular propagation at high m, near m_B. The rate of polymerization of styrene in toluene and in CH_2Cl_2 from $m \approx 2$ mol dm^{-3} up to $m = m_B$ shows a marked discontinuity, and the rate for isobutene in four very different solvents goes through a maximum near $m = 5$ mol dm^{-3}.

Many of these phenomena point to the solvent affecting the rate of the unimolecular propagation at high m, which seems paradoxical. The following new theory of what is essentially a new type of unimolecular reaction accounts for the phenomena. My new idea is this: The k^+_{p1}, through its free energy of activation, depends upon the strength of the π-bond between the carbenium ion and the double-bond of the monomer. But this depends on the 'electrostatic environment' of the complex, which in the present context means primarily the strength of the dipole at the 'back-side' of the near-planar carbenium ion. The stronger that dipole is, the weaker is the π-bond, and consequently the greater is the k^+_{p1}.

The dependence of the degree of polymerization (DP) on m is available only for EVE and isobutene in CH_2Cl_2 and for styrene in toluene. For all three systems, the discontinuities in the dependence of the DP on m betray changes in reaction mechanism corresponding to the indications from the kinetics. The dependences can be interpreted by the conventional Mayo equation for the low-m region where bimolecular propagation prevails, and by the corresponding, new, equation for unimolecular propagation at high m.

The new rate-constants resulting from my analysis are listed. The lessons from these theoretical investigations will also be useful in the context of chemically initiated cationic polymerizations, especially for those in which propagation by unpaired ions is dominant.

1. Preamble

In the present context the term 'cationic polymerization' refers to reactions in which compounds with C═C bonds are added to carbenium ions, $R'R''R'''C^+$, with the re-formation of the carbenium ion after each addition, and the eventual formation of polymers in this way. The polymerizations via oxonium ions are excluded, as are pseudo-cationic polymerizations (Plesch 1988).

In the course of reviewing the propagation rate-constants of cationic polymerizations in general (Plesch 1993), I came to suspect certain inconsistencies in the interpretations of the rates of the cationic polymerizations initiated by ionizing radiations. I found that there was no general theory covering the polymerizations in bulk and in various solvents. Therefore I examined in detail the primary data and scrutinized the existing theories, and this paper is the result of what turned out to be a very lengthy enquiry. I would not have attempted to develop a comprehensive theory, if the experimental work had not been of such very high quality and recorded in such an accessible manner. Because the theory presented here is mainly concerned with accounting for the changes in the rate of polymerization brought about by some change in the chemical circumstances, it is useful to clarify just what is involved.

Generally, the rate of a polymerization depends on several factors, which include the nature of the monomer, the presence and nature of any solvent, the nature and number of the propagating species, and the concentration of each of these, which together is called the population of propagators. If there is but one species, the system is monoeidic, if there is more than one, it is enieidic (these terms were introduced by Biddulph *et al.* (1965) and Plesch (1973)). The system as a whole is characterized by the reactivity of each species, measured by its rate constant for attack on the monomer. This is determined by the chemical nature of the propagator and of the monomer, the solvent, the temperature, pressure and the population of other compounds in solution. Rate constants can be of two kinds: simple, e.g. the second-order rate constant of a bimolecular reaction, or composite, containing several simple rate constants and one or more equilibrium constants and/or concentrations. In all polymerizing systems the rate depends on the concentration of one or more reagents which may, but need not, include the monomer.

The purpose of this Preamble is to remind the reader that when we attempt to explain a change of rate brought about, for example, by dilution with a solvent that may be more or less polar than the monomer, we are attempting to visualize and rationalize the resulting changes in the physico-chemical circumstances and the consequent changes in the population of the propagators, and in the equilibrium constants and rate constants involved. That is what this paper is about. (In this work the term 'population' is shorthand for 'nature and concentration'.)

2. Introduction

Ever since 1962, when Williams, Okamura, and their associates started to publish propagation rate-constants k_p^+ for the cationic bulk polymerization of cyclopentadiene, isobutene, styrene, α-methylstyrene and isopropylvinyl ether by ionizing radiations, these constants have been accepted as the best, most likely, values for the k_p^+ of unpaired cations in a medium of low-polarity, and those obtained subsequently by Stannett and his collaborators, using similar methods, enjoyed the same status. (The *loci classici* are Bates *et al.* (1962), Bonin *et al.* (1964), Taylor & Williams (1969)

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and the three papers by Ueno *et al.* (1967), Hayashi *et al.* (1967) and Williams *et al.* (1967).)

The fundamental chemistry of the events leading to polymerizations initiated by ionizing radiations are largely agreed to be as follows. The reactive species formed in hydrocarbons by the ionizing radiation, which survive the very fast geminate recombinations in what might be called a 'Coulombic cage', are organic cations and anions. The cations are those normally generated by the removal of an electron, i.e. radical cations and, in unsaturated hydrocarbons, conventional carbenium ions are formed in times that are short on the timescale of the subsequent reactions caused by these carbenium ions, in particular, cationic polymerizations (Williams 1968, 1972). For isobutene (IB) the initiation is represented as (Aquilanti 1967; Hayashi 1969):

$$\left.\begin{aligned}&\mathrm{CH_2{=}CMe_2 + e^- \longrightarrow {}^{\bullet}CH_2{-}C^{+}Me_2 + 2e^-},\\&\mathrm{{}^{\bullet}CH_2{-}C^{+}Me_2 + CH_2{=}CMe_2 \longrightarrow Me_3C^{+} + CH_2{=}C(Me)CH_2{}^{\bullet}}\end{aligned}\right\} \tag{2.I}$$

According to the traditional view, the $\mathrm{Me_3C^+}$ adds to the monomer in a bimolecular reaction of second order, generating a new carbenium ion, and repetitions of this process produce the growing polymer of chain length n, P_n^+; we shall show below that this simple view needs to be refined.

The anions originate from the attachment of an electron to whatever electron acceptors are available in the system; in bulk hydrocarbon monomer this results in the formation of radical anions. Because the electron affinities of alkenes are much lower than the ionization potentials of hydrocarbon radicals, the neutralization reaction between the cations and the anions, one possible version of which,

$$\mathrm{R{-}CH_2{-}CMe_2^{+} + CH_2{=}CMe_2^{-} \longrightarrow R{-}CH_2{-}CMe_2{}^{\bullet} + CH_2{=}CMe_2}, \tag{2.II}$$

is highly exo-energetic. However, not all hydrocarbons are the same in this respect, and for α-methylstyrene, which forms a more stable cation and radical anion than isobutene, the rate constant, k_t, of reaction (2.II) is smaller than for isobutene (Taylor & Williams 1969).

The rate, R_t, of the termination reaction is therefore

$$R_\mathrm{t} = k_\mathrm{t} c^2, \tag{2.1}$$

where c is the total concentration of either species of ion, and k_t can be calculated by the simple diffusion equation (see below). Equation (2.1) implies that k_t is the same, whatever the nature of the anion, and that it is also independent of the state of the cation, i.e. whether, and if so by what, it is complexed or solvated. In view of the fact that such neutralizations involve large, negative ΔH and a positive ΔS because of the release of the ion-solvating molecules, this is probably a sound approximation.

The theory of polymerizations by ionizing radiations gives the rate of initiation R_i(ions cm^{-3} s^{-1}) as

$$R_\mathrm{i} = IG_\mathrm{i}/100, \tag{2.2}$$

where I(eV cm^{-3} s^{-1}) is the dose-rate and G_i(ions (100 eV)$^{-1}$) is the yield of free ions. In the steady state

$$R_\mathrm{i} = R_\mathrm{t} \tag{2.3}$$

and therefore

$$c = (10^{-2} G_\mathrm{i} I/k_\mathrm{t})^{\frac{1}{2}}. \tag{2.4}$$

The traditional equation for the rate of polymerization is given in our symbols as

$$R = k_\mathrm{p}^{+}[\mathrm{P}_n^{+}\mathrm{Sv}]\, m, \tag{2.5}$$

where Sv is a molecule of solvent. In bulk monomer, where $m = m_B$, M replaces Sv.

If, according to the traditional view,

$$c = [\mathrm{P}_n^+\mathrm{Sv}], \tag{2.6}$$

it follows from (2.4) and (2.5) that

$$R = k_p^+(10^{-2}\,G_i\,I)^{\frac{1}{2}}\,m/k_t^{\frac{1}{2}}. \tag{2.7}$$

The dependence of R on $I^{\frac{1}{2}}$ became a corner-stone of the theory of the polymerizations by ionising radiations. If an experiment gave an exponent of I greater than 0.5, it was concluded that chain-breakers other than the anions, e.g. impurities such as water, were intervening. It was common practice to continue purification of apparatus, monomer and solvent until the exponent approached 0.5. Conversely, it was concluded that if the exponent was 0.5, then the propagation must be by unpaired ions; but the question whether other types of termination might give the same dependence of R on $I^{\frac{1}{2}}$ has not been examined explicitly, probably because there was no obvious need. However, since the time when this theoretical framework was established by Williams and his collaborators our understanding of the mechanisms of ionic reactions in organic media has developed, especially with regard to the kinetic importance of ion pairs. It is therefore useful to examine briefly the hypothetical termination reactions (2.III) and (2.IV) with rate R_t in which ion pairs react with free ions or with their own kind to give a non-ionic product Nt:

$$\mathrm{Q^+R^-} + \mathrm{Q^+} \longrightarrow \mathrm{Nt} + \mathrm{Q^+}, \tag{2.IIIa}$$

$$\mathrm{Q^+R^-} + \mathrm{R^-} \longrightarrow \mathrm{Nt} + \mathrm{R^-}, \tag{2.IIIb}$$

$$2\mathrm{Q^+R^-} \longrightarrow 2\mathrm{Nt}. \tag{2.IV}$$

If, as before, we designate the total concentration of either positive or negative ions by c, we find that reactions (2.IIIa) and (2.IIIb) give $R_t = f(c^{\frac{3}{2}}, c^{\frac{1}{2}})$ and reaction (2.IV) gives $R_t = f(c^2, c^{\frac{3}{2}}, c^{\frac{1}{2}})$.

Only the reaction

$$\mathrm{Q^+} + \mathrm{R^-} \longrightarrow \mathrm{Nt} \tag{2.V}$$

gives $R_t = f(c^2)$ and hence $R_p = f(I^{\frac{1}{2}})$. Departures from the latter behaviour have traditionally been attributed to termination by impurities or solvent, or by the products formed by electron capture fragmentation of monomer, polymer, or solvent. To this list must now be added the possible intervention of ion pairs. However, this brief analysis has established that only if the half-power dependence of R on the dose-rate prevails, the only propagating species that needs to be considered is the unpaired cation.

In polymerizations by ionizing radiations in the presence of strong electron acceptors which reduce the reactivity of the electrons, the termination reaction is inhibited, the concentration of ions grows and under these conditions the participation of paired cations becomes relevant (Hayashi *et al.* 1977; Yamamoto *et al.* 1977).

The propagation rate-constants mentioned in the first paragraph of this section were calculated by Williams and his successors in the following manner on the assumption that there is only one kind of cation, and that this is the propagator. The G_i in (2.7) for different compounds is known from independent experiments. The k_t can be obtained by two independent methods.

(*a*) The Einstein–Smoluchowski equation for the rate of encounter of two ions gives

$$k_{\mathrm{t}} = 4\pi e^2 D/\epsilon \bar{k} T, \tag{2.8}$$

where e is the electronic charge, D is the average diffusion coefficient of the two ions, ϵ is the dielectric constant of the medium, and $\bar{k}$ is Boltzmann's constant. Substitution of (2.8) into (2.7) gives

$$R = k_{\mathrm{p}}^{+}\, m (G_{\mathrm{i}} I \epsilon T/D)^{\frac{1}{2}} (\bar{k}/\pi)^{\frac{1}{2}}/20\, e. \tag{2.9}$$

The greatest sources of uncertainties are G_{i}, what value should be given to ϵ, and the size of the ions, which is implicit in D.

(*b*) The second method involves measuring the electrical conductivity, κ, of the polymerizing system, and using Langevin's equation (2.10) to obtain k_{t} in terms of κ:

$$k_{\mathrm{t}} = 4\pi e \Lambda/\epsilon, \tag{2.10}$$

where Λ is the ionic conductivity which can be calculated from Stokes' equation. Since

$$\Lambda = \kappa/ec, \tag{2.11}$$

$$k_{\mathrm{t}} = 4\pi\kappa/\epsilon c, \tag{2.12}$$

we substitute for c from (2.4) and obtain

$$k_{\mathrm{t}}^{\frac{1}{2}} = 4\pi\kappa/\epsilon(10^{-2} G_{\mathrm{i}} I)^{\frac{1}{2}}. \tag{2.13}$$

Substitution of this into (2.7) gives

$$R = k_{\mathrm{p}}^{+}\, m G_{\mathrm{i}} I \epsilon/400\pi\kappa. \tag{2.14}$$

To summarize: m, I and ϵ are given by the materials and the experimental conditions; R and κ are the measured variables, but G_{i} is assumed by analogy with similar systems; the weakness of this procedure is acknowledged. The two methods have generally given reasonably concordant results (see, for example, Deffieux *et al.* 1981).

We shall see that there are good reasons for supposing that not all cations are propagators, and that there may be more than one kind of non-propagating cation and more than one kind of propagator. If the propagators are designated as before by P_n^+ and the non-propagators by R_n^+

$$c = \Sigma\,[\mathrm{P}_n^+] + \Sigma\,[\mathrm{R}_n^+]. \tag{2.15}$$

These ideas are new, since traditionally non-propagating cations have not been considered; and the polymerizations by ionizing radiations have been thought of as monoeidic, the sole propagator being the cation P_n^+, solvated of course, but otherwise unencumbered.

To clarify what is implied, it must be understood that the propagators considered below include cations complexed by the solvent (solvated) $\mathrm{P}_n^+\mathrm{Sv}$, and cations complexed by the monomer through its double bond, $\mathrm{P}_n^+\mathrm{M}$; and that the principal non-propagators are cations complexed by an aromatic ring or a heteroatom in the monomer, $\mathrm{P}_n^+\mathrm{G}$.

It is possible that polar or polarizable side-groups of polymers, e.g. RO from VE, can complex with the growing cations, but for the reasons explained (Plesch 1993) this effect will not be considered in detail (see also §3*a*).

The theory developed for the hydrocarbons was transferred virtually without change to the polymerization of alkyl vinyl ethers (Ueno *et al.* 1967), and it was not realized that these monomers might behave rather differently, for several reasons.

1. The ionization of the alkyl vinyl ethers generates radical cations which break up into radicals and cations. The question how an alkyl vinyl ether would split into a cation and an anion was considered by Hamann *et al.* (1949), and following their arguments it seems likely that the split would produce an alkyl cation R^+ and a vinyloxy radical, $ViO^{\bullet}$, thus:

$$\text{R–O–Vi} \xrightarrow{e^-} R^+ + \text{Vi–O}^{\bullet} + 2e^- \xrightarrow{\text{R–O–Vi}} RCH_2C^+HOR. \qquad (2.VI)$$

The difference from the hydrocarbons is that the oxocarbenium ion resulting from the addition of R^+ to the monomer becomes solvated by the strong dipoles of the monomer (for EVE $\mu = 1.14$ Debye (Taskinen *et al.* 1978)).

2. The irradiation of alkyl vinyl ethers leads to dissociative electron capture. Yoshida *et al.* (1972) showed that dimethyl ether decomposes according to

$$Me_2O + e^- \longrightarrow Me^{\bullet} + MeO^-. \qquad (2.VII)$$

The calculations of Hamann *et al.* quoted above indicate that an alkyl vinyl ether would fragment according to

$$ROCH{=}CH_2 + e^- \longrightarrow R^{\bullet} + CH_2{=}CHO^-. \qquad (2.VIII)$$

The vinyloxy anion formed in this way is much less reactive than hydrocarbon anions and it might be expected that therefore the termination reaction with the propagating cation would be slower.

3. The vinyl ethers, being polar, are much better solvating agents than alkenes, so that both cations and anions have a stabilizing solvation shell. (Hayashi *et al.* 1971).

4. The dielectric constants, ϵ, of the vinyl ethers are around 3.5, whereas for alkenes it is *ca.* 2, for styrene 2.4 and for α-methylstyrene 2.6.

It seems that these essential differences between alkenes and vinyl ethers were ignored when the kinetic interpretation of the polymerizations of alkenes by ionizing radiations were extended to the vinyl ethers, but any or all of them may help us to understand the behavioural differences between hydrocarbons and heteroatomic monomers (see §4*c*).

3. The kinetics of bulk polymerization

(*a*) *Theory*

Fontana *et al.* (1948, 1952) showed that the kinetics of the cationic polymerization of C_3H_6 by $AlBr_3$ and HBr in a hydrocarbon solvent can be explained on the assumption that the alkene forms complexes with the growing cations, which might be unpaired or paired:

$$P_n^+ + M \rightleftharpoons P_nM^+, \quad \text{equilibrium constant } K_M^+, \qquad (3.I)$$

$$A^-P_n^+ + M \rightleftharpoons A^-P_n^+M, \quad \text{equilibrium constant } K_M^{\pm}, \qquad (3.II)$$

and this idea has been used since then by so many authors that it has become part of the general theory of cationic polymerizations, and it is hardly possible to give adequate references. These complexes are not *ad hoc* inventions, but are closely related to those formed by alkenes with Ag^+ (Dewar 1951; Salomon 1953) and other cations. If the monomers are hydrocarbons, these complexes are π-complexes; but for aryl alkenes (styrene, etc.) both the aromatic ring and the double bond can be coordinated to the carbenium ion, and only the latter type of complex can rearrange to the lengthened chain; in other words, the former complex is not a propagator. Other monomers that can form two types of complexes with the carbenium ion are those containing heteroatoms, such as 4-methoxystyrene and the alkyl vinyl ethers. The two kinds of complex are the π-complex with the double-bond and the n-complex involving the heteroatom. (The interaction of both the double bond and the O-atom with the carbenium ion seems to have been suggested first by Higashimura *et al.* (1969).) These features have been discussed in some detail (Plesch 1989, 1990). The complexing with the heteroatom of the monomer to give a non-propagating complex, P_n^+G, will be considered further in a later section. Evidently, any polymers containing heteroatoms can also complex through these with the cations, but I shall show that this is probably relatively unimportant, except possibly at high conversions. However, Stannett and his co-workers, the most prolific workers with alkyl vinyl ethers, accorded great importance to the complexing of the growing carbenium ion with the polymer, but disregarded its complexing with the monomer, and they stated explicitly at the end of the first paper on solvent effects (Deffieux *et al.* 1981): ‘These results appear to indicate that there is little or no solvation by the monomer’. In the light of other evidence, their arguments seem rather less convincing.

We now consider the polymerizations in bulk, i.e. without a solvent, of hydrocarbon monomers by ionizing radiations in the light of the monomer complexing of cations which has been noted for polymerizations in solution. If in a solvent of low polarity this complexing is kinetically important, then it follows *a fortiori* that in bulk monomer it is likely to be dominant. In the absence of a solvent, and especially at low conversion, the solvation shell consists entirely of monomer molecules, one of which is in the special position of being the electron donor to the carbenium ion. A mono-alkene can form such a complex only through its double bond, giving P_n^+M, but an aryl alkene can form this or it can complex through its aromatic ring, giving one form of P_n^+G; and a vinyl ether can form the π-complex through the double bond and an n-complex through the O-atom, which is another variety of the non-propagating P_n^+G. The first part of the following discussion concentrates on monomers which can only form the π-complex with their double bond.

According to Fontana's theory, the rate-determining step in a polymerization involving a monomer-complexed cation is a unimolecular isomerization of the complex, which is kinetically of first order:

$$R = k_{p1}^+[P_n^+M]. \tag{3.1}$$

This means that the rate constants derived from ionizing radiation experiments with bulk monomers are not the second-order k_p^+ given by (2.5), but first-order rate constants, k_{p1}^+, given by (3.1). A comparison of these equations shows that the putative k_p^+ reported in the literature are related to the k_{p1}^+ by (3.2),

$$k_{p1}^+ = k_p^+ m_B, \tag{3.2}$$

where m_B is the concentration of bulk monomer. Because for all the usual monomers the m_B lie in the range of 9 ± 2 mol dm^{-3}, the k_{p1}^+ are numerically about one order of

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Table 1. *Examples of systems in which Y increases rectilinearly with dose or with time*

	monomer	T/°C	dose-rate, I/(rad s^{-1}) (*a*)	Y^*(%) (*b*)	figure number in reference	references
1	isobutene	−78	5.6	22	1	Stannett *et al.* (1964)
2	cyclopentadiene	−78	7.2 to 75	2	1	Bonin *et al.* (1965)
3	β-pinene	25	66	60	1	Bates *et al.* (1962)
4	α-methylstyrene	30	67	(*c*)	2–4	Best *et al.* (1962)
5	α-methylstyrene	30	96	30	1, 2	Hubman *et al.* (1966)
6	EVE	0	9.1	16	4	Suzuki *et al.* (1977)
7	EVE	30	70.6	60	1	Hsie *et al.* (1980)
8	IPVE	26	71	27	1	Deffieux *et al.* (1983)
9	IPVE	30	70.6	28	3	Ma *et al.* (1979)
10	IBVE	0, 30 and 60	various	60	tables I and II	Bonin *et al.* (1964)

(*a*) Converted from the original authors' units at the rate of 1 rad = 6.242×10^{13} eV g^{-1}.
(*b*) Y^* is the yield (% conversion) up to which the rate of polymerization is constant.
(*c*) Some of the curves show slight acceleration.

magnitude greater than the ‘k_p^+’, which henceforth shall be put between inverted commas. Since the k_{p1}^+ have the dimension of a first-order rate constant (time^{-1}), they cannot be compared with any second-order k_p^+. Because of this misidentification, the numerous attempts at comparing the putative second-order rate constants ‘k_p^+’ with the genuine second-order k_p^+ obtained in dilute solutions by chemical initiation, have been futile.

This is not the first time that the kinetics of bulk polymerizations has been analysed critically. Szwarc (1978) has made the same objection to the identification of the rate constant for the chemically initiated bulk polymerization of tetrahydrofuran as a second-order rate constant, $k_p^{\pm}$, and he related the correct, unimolecular, rate constant to the reported $k_p^{\pm}$ by an equation identical to (3.2). Strangely, this fundamental revaluation of kinetic data was dismissed in three lines in a major review (Penczek *et al.* 1980). Evidently, it is likely to be relevant to all rate constants for cationic bulk polymerizations, e.g. those of trioxan, lactams, epoxides, etc. Because of its general importance I will refer to this insight as ‘Szwarc's correction’ and to (3.2) as ‘Szwarc's equation’.

It is necessary now to find out whether my theoretical conclusion is supported by experimental evidence; in fact, there are many results for bulk polymerizations that indicate a first-order growth reaction. The experimental support that I seek would be found in the shape of the curves relating the conversion, Y, to the total received dose of radiation or to the time at a constant dose-rate. If the polymerizations are of zero order with respect to m, the conversion curves will be rectilinear instead of concave to the dose (or time) axis. Rectilinear conversion curves are actually much more common than ‘first-order type’ curves, and some instances of this behaviour are listed in table 1. In example 8 of table 1 the experimental points are actually on a straight line, but a curve has been drawn past them.

The plots in the figures quoted in table 1 all show such a small scatter from a straight line up to conversions of 20% or more, that they are incompatible with a first-order curve. (For a first-order reaction, the rate R at $Y = 20\%$ is 20% less than the initial rate R_0, and therefore also 20% less than the rate which the reaction would have at that stage if it were of zero order. Such a deviation would be easily detectable, as it is well outside the scatter of the experimental points.) I therefore conclude that the experimental evidence supports amply the theoretical conclusion, and can but wonder why this was ignored by so many workers.

Can my new view explain why alkenes, e.g. isobutene, polymerize so much more rapidly than aryl alkenes, e.g. styrene? (See table 2.) I think that since the activation enthalpies for both types of monomer are very small, and the activation entropies are probably very similar, the effect arises from the difference in the concentrations of the propagating π-complexes. As mentioned above, the simple alkenes can interact with the carbenium ion only through their double bond, whereas the aryl alkenes can also be held by their aromatic ring, and for the fraction thus held a considerable rearrangement would be required before the new bond can be formed. This means that there are actually two types of complexed cations, those π-bonded to the double bond, P_n^+M, which can propagate, and those π-bonded to the aromatic ring, P_n^+G, which cannot. The same considerations can be applied to a comparison of the vinyl ethers (VE) with the hydrocarbon monomers, thus: the VE form complexes with the carbenium ions mainly through the O-atom; this view leads to the same conclusion as in the comparison of alkenes with arylalkenes, namely that this is the principal reason why the VE polymerize more slowly than the alkenes. It can be put differently. The VE polymerize more slowly than the alkenes mainly because the concentration of propagators, $[P_n^+M]$, is smaller, even when the total concentration of cations, $[P_n^+M]+[P_n^+G]$, is the same. The fact that IPVE polymerizes more rapidly than EVE is likely to be at least partly due to the fact that for stereochemical and polarity reasons $[P_n^+M]/[P_n^+G]$ is greater for the IPVE. These matters will be discussed further in the section on the alkyl vinyl ethers.

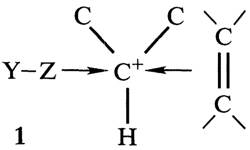
Stannett and his co-workers suggested that the differences between the hydrocarbons and the vinyl ethers and between the various vinyl ethers are due to the following effect. One of the O-atoms in the polymer chain, probably from the penultimate unit, was believed by them to be complexed with the carbenium ion, so that in comparison to the hydrocarbon monomers the access of monomer to the reaction site is impeded; and with increasing bulk of the alkyl group this obstruction by the polymer diminishes, so that the rate constant increases. It seems unlikely to me that the complexing of polymer can play an important part in the bulk polymerization of the vinyl ethers, for the following reason. Let the cation complexed by a heteroatom of its own or of some other polymer chain be represented by P_n^+P. The reaction pattern then depends on the ratio $[P_n^+P]/[P_n^+M]$. The only way in which a cation complexed by a hetero-atom pendent from a chain, or indeed by any species other than the monomer, can propagate is bimolecularly. Therefore if this ratio is large, i.e. if $[P_n^+P]$ is dominant, we must have a second-order polymerization, the rate of which is given by

$$R = k_p^+[P_n^+P]\,m, \tag{3.4}$$

a conclusion which is in conflict with the observations.

However, in solution the participation of the species P_n^+P is probable, especially with polar monomers in non-polar solvents, but because of the difficulty of diagnosing when this occurs, I will ignore it during most of the subsequent discussions.

It is useful to anticipate here that my analysis of the kinetics of the polymerizations in solution indicates the prevalence of unimolecular propagation in some systems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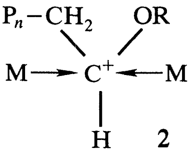
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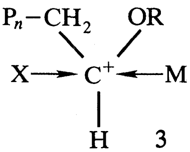
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down to quite low m. Moreover, we will see that the corresponding first-order rate constant is influenced by the nature of the diluent. Such an effect seems paradoxical, and as it appears to be a newly recognized phenomenon, I will present here my explanation of it which is as follows.

The k^+_{p1} characterizes a unimolecular transformation of the π-complex between the cation and the double-bond of the monomer, to the newly formed cation, which now has the previously complexed monomer molecule added to the chain. The rate of this process, or rather the activation energy, is determined by the strength of the π-bond, and this must depend to some extent on the electrical environment of the complex. What I have in mind is this: If there is a dipole Y–Z at the side of the near-planar trigonal carbenium ion opposite to where the complexed monomer is held, the π-bond will be weakened and the reaction accelerated. This idea is represented schematically by **1**. This model will help us to account for the apparently paradoxical fact that the rate of the unimolecular growth reaction is evidently influenced by the polarity of the solvent. If we pursue the idea that R depends on what is attached to the 'backside' of the carbenium ion, it follows that if there is present a compound other than the monomer, e.g. a solvent, the rate R is composite, consisting of at least two components, one representing the more reactive species having the stronger dipole at the backside, and one having the weaker; and one of these usually is the monomer, so that we have species **2** and **3** propagating with rate constants $k^{+\mathrm{M}}_{\mathrm{p1}}$ and $k^{+\mathrm{X}}_{\mathrm{p1}}$. It follows that (3.1) should be written as

$$R = k^{+\mathrm{M}}_{\mathrm{p1}}[\mathrm{MP}^+_n\mathrm{M}] + k^{+\mathrm{X}}_{\mathrm{p1}}[\mathrm{XP}^+_n\mathrm{M}]. \tag{3.5}$$

The relative magnitude of the two concentrations evidently depends on the magnitude of the equilibrium constants and of the concentrations of M and X. Two further points need to be made. (i) It is likely that the formation of **3** from **2** will be favoured, i.e. the equilibrium constant will be enhanced, by a statistical factor akin to an entropy of mixing. (ii) For the species **2** there is no 'front' and 'back', the $\mathrm{MP}^+_n\mathrm{M}$ is symmetrical, and therefore the probability of the propagation, i.e. the k^+_{p1}, is twice as great as it would be for $\mathrm{XP}^+_n\mathrm{M}$, even if the free energy of complexing is the same for X and M.

I have refrained from introducing these refinements explicitly into the algebra, but the ideas will explain at least qualitatively some otherwise puzzling and hitherto unexplained phenomena to be discussed in §4.

My idea that in bulk monomer and in some solutions the propagation is a unimolecular reaction is supported strongly by the way in which the DP depends on the monomer concentration. At low m, $1/DP$ increases rectilinearly with $1/m$, as demanded by the conventional Mayo equation for bimolecular propagation; but at high m, $1/DP$ increases rectilinearly with m, as is required for unimolecular propagation (see §5).

Table 2. *Alleged rate constants k_p^+ for bulk polymerizations and first order k_{p1}^{+B} calculated from them*

result number	$T/°C$	$m_B/(\text{mol dm}^{-3})$	$k_p^+/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$ (*a*)	$k_{p1}^{+B}/\text{s}^{-1}$ (*b*)	references
cyclopentadiene					
1	−78	13.6	$5.8\times10^{8\pm1}$	7.9×10^9	Bonin *et al.* (1965)
isobutene					
2	0	11.0	1.5×10^8	1.6×10^9	Taylor and Williams (1969)
3	−78	12.6	1.5×10^8	1.9×10^9	
styrene					
4	15	8.75	$(2\pm0.5)\times10^6$	1.8×10^7	Williams *et al.* (1967)
5	40	8.54	$(2.9\pm1)\times10^6$	2.5×10^7	Hayashi *et al.* (1973)
6	25	8.66	$(2.4\pm0.9)\times10^6$	2.1×10^7	
α-methylstyrene					
7	0	7.75	4.4×10^6	3.4×10^7	Williams *et al.* (1967)
8	35	7.58	6.5×10^5	3.0×10^6	Chawla & Huang (1975)
9	20	7.71	9.9×10^5	7.6×10^6	
10	0	7.75	1.30×10^6	1.0×10^7	
11	−20	8.05	1.18×10^6	9.5×10^6	
4-methoxystyrene					
12	20	7.45	3×10^6	2.2×10^7	Deffieux *et al.* (1980)
ethyl vinyl ether					
13	30	10.3	9.4×10^4	9.7×10^5	Hsieh *et al.* (1980)
14	23	10.5	3.5×10^4	3.7×10^5	
15	20	10.54	2.9×10^4	3.1×10^5	Deffieux *et al.* (1981)
16	0	10.8	7.2×10^3	7.8×10^4	Goineau *et al.* (1977)
17	0	10.8	8.3×10^3	9.0×10^4	Suzuki *et al.* (1977)
isopropyl vinyl ether					
18	30	8.65	1.3×10^6	1.1×10^7	Hsieh *et al.* (1980)
19	26	8.72	1.2×10^6	1.0×10^7	Deffieux *et al.* (1983)
20	0	9.0	9.0×10^5	8.1×10^6	Goineau *et al.* (1977)
21	0	9.0	9.2×10^5	8.3×10^6	Hsieh *et al.* (1980)
isobutyl vinyl ether					
22	50	7.3	6×10^5	4.4×10^6	Hayashi *et al.* (1971)
23	42.5	7.4	1.1×10^6	8.1×10^6	Ueno *et al.* (1971)
24	30	7.6	3.4×10^5	2.6×10^6	Williams *et al.* (1971)
25	25	7.6	1.2×10^5	6.2×10^5	Hayashi *et al.* (1971)
26	0	7.9	3.8×10^4	3.0×10^5	
27	0	7.9	3.8×10^4	3.0×10^5	Goineau *et al.* (1971)
tertbutyl vinyl ether					
28	0	*ca.* 8.0	5×10^4	4×10^4	Goineau *et al.* (1977)

(*a*) The k_p are the constants calculated by the original authors.

(*b*) The k_{p1}^{+B} are the unimolecular rate-constants calculated by (3.2). As explained in the text, they are probably minimum values for all systems except 1, 2, and 3.

(*b*) *New rate-constants for bulk polymerizations*

In table 2 we present the new unimolecular propagation rate-constants k_{p1}^{+B} for bulk polymerizations, calculated from the published bimolecular 'k_p^+' by Szwarc's equation (3.2). The bulk concentrations m_B of the monomers are from standard sources. These rate-constants fall into three groups.

1. Cyclo-pentadiene and isobutene, for which the k_{p1}^{+B} are of the order of $10^9\ \text{s}^{-1}$. These monomers have but one 'attachment point' to the carbenium ion, but there

is no means of ascertaining what fraction of these is complexed; it is likely to be high. The 'k_p^+' were originally calculated on the assumption that the concentration of propagators, which is $[\mathrm{P}_n^+]$ on the traditional view, equals c, and by implication therefore also our $[\mathrm{P}_n^+\mathrm{M}] = c$. This means that if indeed $[\mathrm{P}_n^+\mathrm{M}] = c$, my $k_{\mathrm{p1}}^{+\mathrm{B}}$ for these monomers are the true values, but if that equality does not hold, then they are 'apparent' and minimum values. Over the whole range of conditions for which the conversion curves are rectilinear any bimolecular propagation by whatever species of propagator must be kinetically unimportant. This means that whenever the polymerizations are of zero order with respect to m, our assumption that effectively only one reaction, namely complexing, results directly from the encounter of the P_n^+ with M, is vindicated.

2. The results for styrene and its two derivatives are all of the order of $10^7\ \mathrm{s}^{-1}$. Because for these monomers the c comprises not only $[\mathrm{P}_n^+\mathrm{M}]$, but also $[\mathrm{P}_n^+\mathrm{G}]$, so that $[\mathrm{P}_n^+\mathrm{M}]$ is a fraction of c, these apparent $k_{\mathrm{p1}}^{+\mathrm{B}}$ are necessarily minimum values. The same holds for the VE, and it is easy to show from our equations that if $R = k_{\mathrm{p1}}^{+\mathrm{B}}[\mathrm{P}_n^+\mathrm{M}]$ and the minimum value $(k_{\mathrm{p1}}^{+\mathrm{B}})$ is calculated from $R = (k_{\mathrm{p1}}^{+\mathrm{B}})c$, the true $k_{\mathrm{p1}}^{+\mathrm{B}}$ is given by

$$k_{\mathrm{p1}}^{+\mathrm{B}} = (k_{\mathrm{p1}}^{+\mathrm{B}})(K_{\mathrm{G}}+K_{\mathrm{M}})/K_{\mathrm{M}}, \tag{3.6}$$

where K_{M} and K_{G} are defined by (4.2) and (4.3) below.

Therefore further progress in this area depends on the measurement of equilibrium constants. At this stage I simply cannot say how much of the difference of two powers of 10 between the $k_{\mathrm{p1}}^{+\mathrm{B}}$ of the alkenes and the styrenes is to be attributed to an intrinsic difference in reactivity and how much to the existence of the $\mathrm{P}_n^+\mathrm{G}$ complexes. The negative temperature coefficient of the rate constant for α-methyl styrene found by Chawla & Huang (1975) is a strong indication in favour of my view that the propagation is not a simple bimolecular reaction.

3. The $k_{\mathrm{p1}}^{+\mathrm{B}}$ of the VE cover the range from 10^4 to $10^7\ \mathrm{s}^{-1}$ and it is not obvious what determines the differences between them, and in particular why IPVE appears to be so outstandingly reactive. Evidently, for these monomers too, the $k_{\mathrm{p1}}^{+\mathrm{B}}$ are minimum values, but it is not obvious which are the main factors depressing these 'apparent' $k_{\mathrm{p1}}^{+\mathrm{B}}$ below the true value given by $R/[\mathrm{P}_n^+\mathrm{M}]$; in particular, what is the origin of the great differences between the $k_{\mathrm{p1}}^{+\mathrm{B}}$ of the various VE; this problem will be encountered again in the context of the k_{p1}^{+} for the polymerizations in solution. In seeking a solution it must be remembered that the VE differ not only in terms of their stereochemistry and polarity, factors which affect their complexing with the carbenium ion and the rate of the subsequent isomerization, but they also differ with respect to the dissociative electron capture of both the monomers and their polymers and the production of inhibiting species (Suzuki *et al.* 1977). It is because of such effects that MeVE does not polymerize cationically under ionizing radiations, although it does so with typical cationic initiators (Desai *et al.* 1977).

4. The kinetics of polymerizations in solution

(*a*) *Development of the general kinetic equations*

When considering the polymerizations by ionizing radiations in solution, I adopt a point of view opposite to that customary in conventional reaction kinetics. In these it is normal practice to progress from dilute to more concentrated solutions, usually up to no more than *ca.* 2 mol dm^{-3}. In the present context, the actual experimental practice determines that we think in terms of a gradual dilution of the bulk monomer; this also happens to be heuristically fruitful.

To develop the required kinetic equations, we start from the proposition that it is unlikely that the same species, namely the monomer-complexed cation, P_n^+M, can propagate both unimolecularly and bimolecularly. However, unimolecular and bimolecular propagation by different species can be going on simultaneously. This is my interpretation of the fact that all the R against m plots (except possibly that for 4-MeO-styrene) and the DP against m plots have a more or less prominent inflection. This is the region of dieidic propagation in which P_n^+M and P_n^+Sv coexist in kinetically significant concentrations. The m at which the R against m plot from $m = 0$ begins to curve upwards we denote by m_C, the critical m at which the previously monoeidic second-order propagation begins to be dieidic. The rate R of such a dieidic polymerization, consisting of a bimolecular component R_2 and a unimolecular component R_1 is given by

$$R = R_2 + R_1 = k_p^+[P_n^+Sv]\, m + k_{p1}^+[P_n^+M], \tag{4.1}$$

on the assumption that the concentration of the bare cation, $[P_n^+]$ is kinetically insignificant. This means that all the P_n^+-species are involved in competitive equilibria. The complexing of the monomer with P_n^+ through its double bond is therefore represented as

$$P_n^+Sv + M \rightleftharpoons P_n^+M + Sv, \tag{4.I}$$

which gives the equilibrium equation

$$K_M^+ = [P_n^+M]\,[Sv]/[P_n^+Sv]\, m. \tag{4.2}$$

The non-propagating species P_n^+G, in which the monomer is complexed with P_n^+ through a heteroatom or a phenyl ring is involved in the equilibrium

$$P_n^+Sv + M \rightleftharpoons P_n^+G + Sv, \tag{4.II}$$

described by

$$K_G^+ = [P_n^+G]\,[Sv]/[P_n^+Sv]\, m. \tag{4.3}$$

As before, we define c as the total concentration of positively charged species, which is the same as what Stannett's group designate as $[C^+]$, the total concentration of cations which have escaped geminate recombination, so that

$$c = [C^+], \tag{4.4}$$

and therefore

$$c = [P_n^+M] + [P_n^+G] + [P_n^+Sv]. \tag{4.5}$$

From (4.2), (4.3) and (4.5) we obtain

$$[P_n^+M] = K_M^+\, mc/(m[K_M^+ + K_G^+] + [Sv]), \tag{4.6}$$

and

$$[P_n^+Sv] = c[Sv]/(m[K_M^+ + K_G^+] + [Sv]), \tag{4.7}$$

and by means of the simplification

$$K_{GM}^+ = K_G^+ + K_M^+ \tag{4.8}$$

and (4.1) we arrive at the general rate-equation which has two useful forms:

$$R = mc(k_{p1}^+ K_M^+ + k_p^+[Sv])/(K_{GM}^+\, m + [Sv]) \tag{4.9a}$$

and

$$R = k_{p1}^+ K_M^+\, c/(K_{GM}^+ + [Sv]/m) + k_p^+\, cm/(1 + K_{GM}^+\, m/[Sv]). \tag{4.9b}$$

The [Sv] can be expressed as a function of m in terms of the molar volumes of monomer, v_{M}, and solvent, v_{S}, by

$$[\mathrm{Sv}] = (1-mv_{\mathrm{m}})/v_{\mathrm{S}}. \tag{4.10}$$

If (4.10) is introduced into (4.9) we obtain

$$R = [k_{\mathrm{p}}^{+}\,mc(v_{\mathrm{s}}^{-1}-mv_{\mathrm{m}}\,v_{\mathrm{s}}^{-1})+k_{\mathrm{p1}}^{+}\,K_{\mathrm{M}}^{+}\,mc]/[m(K_{\mathrm{GM}}^{+}-v_{\mathrm{m}}\,v_{\mathrm{s}}^{-1})+v_{\mathrm{s}}^{-1}]. \tag{4.11}$$

The somewhat clumsy (4.11) is a necessary stage in the development of the complete rate-equation with m as the single independent variable. The c can be eliminated by taking advantage of the fact that the comprehensive results from Stannett's group enable us to express c as a function of m for their systems. I introduce this innovation because of the self-consistency of the c values and their trends, and despite the warning of the original authors, that they are afflicted with some uncertainties. For most of the systems these variables are related over a considerable range of concentrations by an equation of the form

$$c = Am+B, \tag{4.12}$$

where A can be positive or negative. The fact that c is itself a function of m is sufficient to account for the fact, repeatedly noted by Stannett's group, that the external order of the polymerizations with respect to monomer is consistently greater than unity. The introduction of (4.12) into (4.11) gives the general rate-equation (4.13), whereby we obtain R as the ratio of two polynominals in m:

$$\begin{aligned}&[m(v_{\mathrm{m}}\,v_{\mathrm{s}}^{-1}-K_{\mathrm{GM}}^{+})-v_{\mathrm{s}}^{-1}]R\\ &\quad = m^{3}Ak_{\mathrm{p}}^{+}\,v_{\mathrm{m}}\,v_{\mathrm{s}}^{-1}-m^{2}(Ak_{\mathrm{p1}}^{+}\,K_{\mathrm{M}}^{+}+Ak_{\mathrm{p}}^{+}\,v_{\mathrm{s}}^{-1}-Bk_{\mathrm{p}}^{+}\,v_{\mathrm{m}}\,v_{\mathrm{s}}^{-1})-mB(k_{\mathrm{p1}}^{+}\,K_{\mathrm{M}}^{+}+k_{\mathrm{p}}^{+}\,v_{\mathrm{s}}^{-1}).\end{aligned} \tag{4.13}$$

The form of (4.13) offers a ready explanation for the fact that the formal order of the polymerizations, $\mathrm{d}(\ln R)/\mathrm{d}(\ln m)$, as shown by the bilogarithmic plots of Stannett *et al.*, varies with m. Equation (4.13) is such that both the first derivative $\mathrm{d}R/\mathrm{d}m$ and the second derivative $\mathrm{d}^2R/\mathrm{d}m^2$ can be zero; the former applies to the polymerization of isobutene for which the R against m curves have a maximum (figures 9 and 10), the latter to the VE and styrene, the R against m curves for which all show inflections. The pursuit of this line of enquiry, though possibly rewarding, would take us too far from the main theme of this paper.

The development of the equations for analysing the kinetic results now proceeds as follows. Note that to make an analysis of the data feasible, it is essential to assume that the equilibrium constants do not vary with m, i.e. with the changing polarity of the medium. Since none of the equilibria involve a change of charge, this is reasonable. The same is not true of both the rate constants k_{p}^{+} and k_{p1}^{+}. The variation of the second-order rate constant k_{p}^{+} with the polarity of the medium, usually expressed in terms of its dielectric constant, is well known and needs no comment at this stage. As noted in §3, the k_{p1}^{+} does depend on the solvent, but the effect is different in kind from that on k_{p}^{+}. The reason is that for the unimolecular propagation there are at most three species to be considered: $\mathrm{MP}_n^{+}\mathrm{M}$, $\mathrm{SvP}_n^{+}\mathrm{M}$, and $\mathrm{PP}_n^{+}\mathrm{M}$, the relative concentrations of which change throughout the reaction, but the k_{p1}^{+} of each of these species is probably not influenced strongly by the composition of the solvation shell, in contrast to k_{p}^{+}. However, having made this warning signal, I will not attempt to include solvent effects formally in my considerations.

Table 3. *Particulars of the systems, the results for which are plotted in figures 1–15*

figure	M	T/°C	m_B/(mol dm^{-3})	diluent	I/(rad s^{-1})	reference
1	EVE	20	10.54	C_6H_6	71	Deffieux *et al.* (1981)
2	IPVE	26	8.72	C_6H_6	71	Deffieux *et al.* (1983)
3	EVE	23	10.54	Et_2O	71	Hsieh *et al.* (1982)
4	EVE	23	10.54	$Me(OC_2H_4)_2OMe$	71	
5, 12	EVE	22	10.54	CH_2Cl_2	71	Deffieux *et al.* (1982)
6, 13	styrene	10	8.5	toluene	9.7	Ueno *et al.* (1966*c*)
7, 14	styrene	23	8.5	toluene	53	
8	styrene	10	8.5	CH_2Cl_2	9.7	
9	isobutene	−78	12.6	CS_2, $CHCl_3$	7.5	Ueno *et al.* (1966*b*)
10, 15	isobutene	−78	12.6	CH_2Cl_2, C_6H_{14}	7.5	
11	4-MeO-styrene	0	7.4	CH_2Cl_2	70.5	Deffieux *et al.* (1980)

So far I have conducted my kinetic analysis on the basis of a 'worst case scenario' applicable over the whole range of m, and the resultant (4.13) is not suitable for the calculation of the rate constants and equilibrium constants.

Therefore, since c and therefore A and B, are given at least for the systems studied by Stannett's group, we go back to (9*b*), and we will use the first term to analyse the region of high m, near m_B, where [Sv]/m is small, so that

$$R_1 = k^+_{p1}\,\mathrm{K}^+_M\,c/K^+_{GM} = k^+_{p1}\,W(Am+B), \tag{4.14}$$

where $W = K^+_M/K^+_{GM}$. From appropriate plots we can determine $k^+_{p1}\,W$. However, for most systems the $k^+_{p1}\,W$ increases strongly with m, so that the $k^{+B}_{p1}\,W$ cannot be used to calculate W.

At low m, we use the approximation

$$R_2 = k^+_p\,cm, \tag{4.15}$$

since m/[Sv] is small. The calculation of k^+_p from (4.15) is the method used by the original authors, so that we obtain essentially similar results for low m. These, however, differ from those that they calculated by the best line for the whole bilogarithmic plots and which therefore generally differ from my values.

A guide to the behaviour of all the systems is the shape of the R against m plots, and the DP against m plots, shown in figures 1–15. The detailed information for all the figures in this paper is compiled in table 3.

(*b*) *The alkyl vinyl ethers*

The VE are discussed first because very detailed information is available for them from Stannett's group. Then we will investigate whether the ideas evolved concerning the VE are useful for interpreting the rather scantier results for other monomers. During these studies it became clear that if the original authors had plotted simply R against m for all their systems instead of making bi-logarithmic plots, the very different shapes of the various curves and their inflections might have caused them some misgivings about applying to all systems the simple second-order kinetics according to (2.5) and (4.15), in their symbols

$$R_p = k_p[C^+]\,[M] \tag{4.16}$$

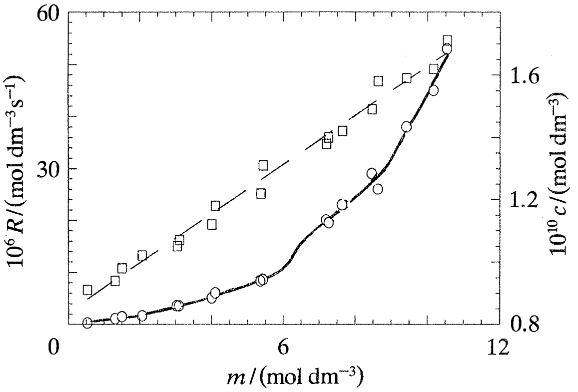

Figure 1. The dependence of R (○) and of c (□) on m for EVE in C_6H_6.

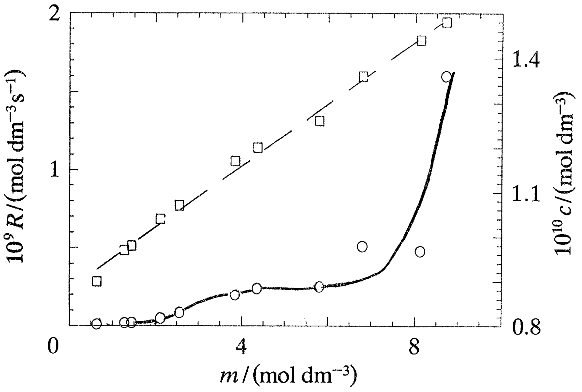

Figure 2. The dependence of R (○) and of c (□) on m for IPVE in C_6H_6.

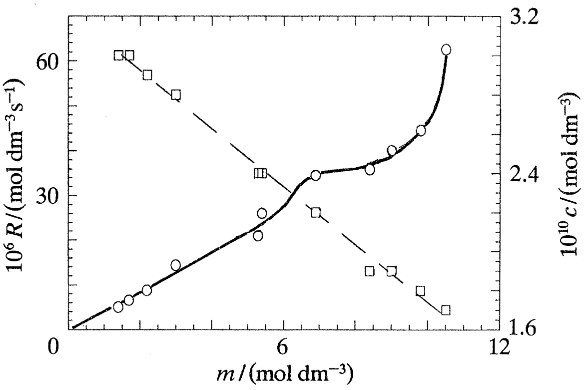

Figure 3. The dependence of R (○) and of c (□) on m for EVE in Et_2O.

A synoptic view of the rate-curves shown in figures 1–5 shows that they all consist of several regions. Figures 1–3 and 5 show a sharp drop in R from $m = m_B$ to the first dilution point; figure 4 shows R rising to a maximum. All five figures show an inflection near the middle of the concentration range. If an inflection had occurred only once and if it had been feeble, as that in figure 1, I might have ignored it, but I prefer to draw curves *through* the experimental points, especially when they are as

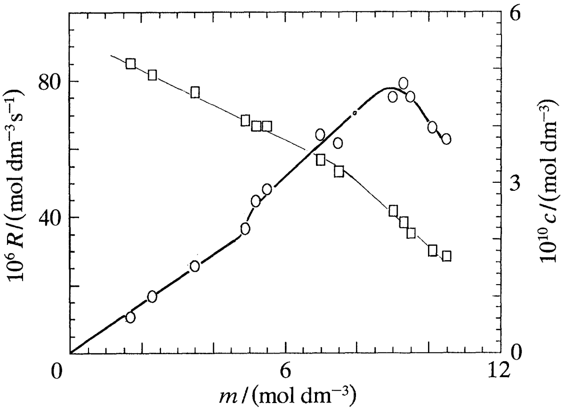

Figure 4. The dependence of R (○) and of c (□) on m for EVE in diglyme.

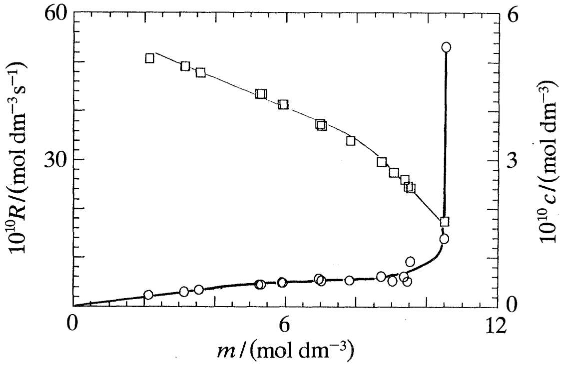

Figure 5. The dependence of R (○) and of c (□) on m for EVE in CH_2Cl_2.

well documented by duplication as in figure 1, rather than to draw a curve born of prejudice *past* the experimental points. Finally, at lowest m all the plots are rectilinear. These different regions are the symptoms of different kinetic régimes, i.e. ranges of m over which the different propagating species dominate the kinetics. My interpretations are not complete; in particular, I have not attempted to introduce into my picture the species P_n^+P, which is very likely to play a part and which may eventually help in a more detailed comprehension of the facts. What does seem clear and common to all these systems is (*a*) that the statistical factor explained at the end of §3*a* must produce a reduction in R at or near to the first dilution step, and (*b*) that in the low m region the principal propagating species is P_n^+Sv with an indeterminable contribution from P_n^+P, which will be larger or smaller, according to the outcome of the competition between Sv and the pendent OR groups.

For the following detailed analysis I now divide the systems into three groups.

1. Solutions in benzene, for which at higher monomer concentrations the complexing of P_n^+ by the solvent is assumed to be negligible compared to its complexing by the much more polar monomer, and therefore R_2 of (4.1) is assumed to be negligible over that part of the concentration range.

2. Solutions in diethyl ether and diglyme, whose behaviour, despite their chemical similarity, is different and rather more difficult to understand.

3. Solutions in CH_2Cl_2, for which the complexing by the solvent is so strong, that

the monomer is effectively excluded from the solvation shell of the cation, and therefore the propagation becomes predominantly a bimolecular reaction, i.e. the R_1 of (4.1) is negligible after a very small degree of dilution.

(i) *EVE and IPVE in benzene*

The R against m plots together with the c against m plots are shown in figures 1 and 2, and it is clear that the kinetic patterns are not simple. Both systems show a drop in rate upon the first dilution which is much greater for IPVE, and at the $m = 0$ end a threshold value of $m = m_{\mathrm{i}} \approx 0.5\ \mathrm{mol\ dm^{-3}}$, below which the rate is negligibly small. I will not attempt to account for the apparent thresholds, as it is probable that they arise from impurity effects that are always more important at low concentrations of the reagents. For the kinetic analysis of the reactions at high m we use (4.14). From this point it is more useful to discuss the two systems separately.

EVE in benzene. From figure 1 we find that the slope S_1 of the line from the first dilution point below m_{B} down to *ca.* 8.5 mol dm^{-3} is

$$S_1 = (45.2-27.6)\times 10^{-6}/(10.17-8.55) = 9.17\times 10^{-6}\ \mathrm{dm^6\ mol^{-2}\ s^{-1}}.$$

Because $A = (1.65-0.84)\times 10^{-10}/10 = 8.1\times 10^{-12}$, $k^+_{\mathrm{p1}} W = S_1/A = 1.1\times 10^6\ \mathrm{s^{-1}}$. Because by definition $K^+_{\mathrm{GM}} > K^+_{\mathrm{M}}$, this gives a maximum value of k^+_{p1}. A second value of $k^+_{\mathrm{p1}} W$ can be obtained thus. When $m = 10.17\ \mathrm{mol\ dm^{-3}}$, $R = 4.52\times 10^{-5}\ \mathrm{mol\ dm^{-3}\ s^{-1}}$, therefore $k^+_{\mathrm{p1}} W = 4.52\times 10^{-5}/(10.17A+B)$, and since $B = 8.6\times 10^{-11}$, $k^+_{\mathrm{p1}} W = (4.52/16.84)\times 10^6 = 2.7\times 10^5\ \mathrm{s^{-1}}$, which gives another, rather lower, maximum value for k^+_{p1}. In view of the considerable uncertainties, especially in the A and B values, the disagreement in the $k^+_{\mathrm{p1}} W$ values by a factor of *ca.* 4 is not astonishing; the mean value of $k^+_{\mathrm{p1}} W = 7\times 10^5\ \mathrm{s^{-1}}$. As we do not know the magnitude of K^+_{M} and K^+_{GM}, there is no means of estimating k^+_{p1} at present. Figure 1 shows that the slope R/m increases strongly as $m \rightarrow m_{\mathrm{B}}$. This means that $k^+_{\mathrm{p1}} W$ increases and since, as discussed above, the equilibrium constants, and *a fortiori* their ratio, are likely to be insensitive to the concurrent change of medium, we attribute this mainly to the change in the k^+_{p1} which is caused by the change in the population of propagators, the $[\mathrm{MP}^+_n\mathrm{M}]$ increasing at the expense of the $[\mathrm{SvP}^+_n\mathrm{M}]$ as $m \rightarrow m_{\mathrm{B}}$ (see (3.5) in which the X is Sv in the present application). It is because of this increase of k^+_{p1} with m that we cannot use the value of $k^{+\mathrm{B}}_{\mathrm{p1}}$ to calculate W for this and similar systems.

At $m \lesssim 7\ \mathrm{mol\ dm^{-3}}$ a different polymerization mechanism appears to gain prominence, so that we then have a dieidic reaction, which is followed by a monoeidic regime below $m \approx 3\ \mathrm{mol\ dm^{-3}}$. For this region we calculate k^+_{p}, as the original authors did, from (4.15). If the result at the lowest m is neglected, their 'k_{p}' values give for $m = 1.32$ to $3.10\ \mathrm{mol\ dm^{-3}}$ a $k^+_{\mathrm{p}} = (9.9\pm 1.8)\times 10^3\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$.

IPVE in benzene. Figure 2 shows that the dependence of R on m near m_{B} is too ill-defined to make a calculation of $k^+_{\mathrm{p1}} W$ possible. However, a simple comparison of the rates R_{B} at $m = m_{\mathrm{B}}$ gives $R_{\mathrm{B}}(\mathrm{IPVE})/R_{\mathrm{B}}(\mathrm{EVE}) = 1600/55 \approx 30$.

Because of the very low rates at $m < 3\ \mathrm{mol\ dm^{-3}}$ a plausible value of k^+_{p} cannot be calculated reliably by the method used in the previous section, despite the apparent similarity of the plots. Estimates by means of various lines through the experimental points give values of k^+_{p} of $(10\pm 5)\times 10^5\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$.

I do not propose any explanation for the great differences in $k^+_{\mathrm{p1}} W$, and therefore probably in the k^+_{p1}, for the two VE, but the fact that both rate constants (k^+_{p} and k^+_{p1}) are so different indicates some profound difference in the kinetic properties of these two monomers. The exceptional kinetic position of secondary alkyl ethers is not news, since Eley & Saunders (1954) found cyclohexyl VE to be eight times more reactive than EVE in polymerizations initiated by iodine. The dramatic drop in rate at the first dilution step for IPVE is different in magnitude and shape from what was seen with EVE, and the ideas used in the following sections to explain apparently similar phenomena with other monomers and solvents do not seem to be applicable here; it remains a mystery.

(ii) *EVE in* Et_2O *and diglyme*

The R against m plots for these two solvents (figures 3 and 4) show that they behave differently. In view of the fact that the di(2-methoxyethyl) ether (diglyme) molecule is much larger than Et_2O and contains three O-atoms, this is not too strange, and therefore I shall treat the systems separately.

Et_2O *solvent*. Figure 3 shows that R increases with m by a factor of *ca*. 40, whereas c decreases by a factor of *ca*. 1.8. The original authors concluded from their usual bilogarithmic plot that there is a normal bimolecular propagation over the whole concentration range, according to (4.15). However, my interpretation of the points in figure 3 shows several régimes.

In the region of high m there are insufficient results to define the curve adequately for an interpretation like that given for EVE in benzene. At the other end one can use (4.15) and thus I found that as m goes from 1.4 to 3 mol dm^{-3}, the k_p^+ goes from 1.1×10^4 to 1.5×10^4 $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, which is the same as found by the original authors, and k_p^+ continues to increase with growing m. For this change, at any rate throughout the region of bimolecular propagation, I suggest the following, fairly obvious, qualitative explanation. Since the dielectric constant (DC) of Et_2O at the relevant temperature is *ca*. 5 and that of EVE is lower by about one unit, one may be seeing here the normal acceleration of an (ion + molecule) reaction as the DC of the medium decreases with increasing m. The sharp fall in rate as m goes from m_B (10.5 mol dm^{-3}) to 10 mol dm^{-3} can be explained in terms of my theory, as follows. Because both the monomer and the solvent have the same dipole moment of 1.14 Debye (Taskinen *et al*. 1978) it cannot be due to a polarity effect and I conclude therefore that one has here the case discussed at the end of §3*a*, namely that this deceleration is a manifestation of the statistical factor.

Diglyme solvent. The kinetic plot for this system (figure 4) differs from those of all the other VE systems in several respects, and it shows clearly that the behaviour pattern consists of several parts. As the bulk monomer is diluted with diglyme, there is a marked rise in the polymerization rate, in contrast to the deceleration seen in all other VE systems, accompanied by a fairly steep rise in c down to $m \approx 8.5$ mol dm^{-3}. After a sharp maximum, the rate falls continuously but with an inflection towards $m = 5.5$ mol dm^{-3}, and c rises less steeply and near-rectilinearly, as for the Et_2O system. The interpretation of the behaviour from about 2 to 9 mol dm^{-3} might be by the same model as used by the original authors and by us for Et_2O solvent, were it not for the inflection and that R/m *increases* by *ca*. 40% with increasing m, whereas the coefficient of k_p^+ in (4.15), $Am+B = c$, *decreases* from around 5×10^{-10} to 2.5×10^{-10} mol dm^{-3}. It follows that k_p^+ must be increasing too. This, however, is contrary to the prediction of simple transition state theory, since for diglyme $\epsilon = 7.3$ (Hsieh *et al*. 1982), so that as m increases, ϵ falls. Probably one is seeing here an effect characterizing large solvents comprising several (in this case three) linked dipoles (CH_2OCH_2 groups), and which definitely fall outside the scope of the simple

Table 4

$m/(\mathrm{mol\ dm^{-3}})$	2–4.5	4.5–10	$m_{\mathrm{B}} = 10.5$
propagators	$\{\mathrm{SvP}_n^+\mathrm{Sv}$	$\mathrm{SvP}_n^+\mathrm{M}$ $\mathrm{SvP}_n^+\mathrm{Sv}$	$\mathrm{MP}_n^+\mathrm{M}$
eidetity	monoeidic	dieidic	monoeidic
molecularity	bimolecular	unimolecular + bimolecular	unimolecular

transition state theory. The k_{p}^+ calculated by the original authors, ranging from 1.2×10^4 to $2.7 \times 10^4\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ as m goes from 1.2 to 7 mol dm^{-3} appear to us to be valid.

However, the behaviour near $m = m_{\mathrm{B}}$ needs some other explanation. My proposal involves the specific solvation of the 'backside' of the carbenium ion by the strong dipole of the solvent; this displaces the monomer molecule which is located there in the absence of the solvent, so that the π-bond to the monomer at the 'front' is weakened and the unimolecular isomerization–propagation becomes accelerated, despite the statistical factor which, alone, would produce a deceleration, as explained at the end of §3*a*. As the dilution proceeds from $m = m_{\mathrm{B}}$ downwards, the polymerization goes through a dieidic phase, in which the unimolecular propagation by the species $\mathrm{SvP}_n^+\mathrm{M}$, which are 'backside solvated' by diglyme, coexists with bimolecular propagation by the species $\mathrm{SvP}_n^+\mathrm{Sv}$, in which the P_n^+ is completely solvated by diglyme. As m decreases, the polymerization becomes monoeidic, i.e. purely bimolecular, as discussed in the previous paragraph. The whole sequence of changes is illustrated in table 4.

(iii) *EVE in* $\mathrm{CH_2Cl_2}$

The R against m plot for this system (figure 5) resembles at first sight that for IPVE in benzene, and indicates a change of mechanism at very small dilution, i.e. very near $m = m_{\mathrm{B}}$. It is an obvious step to seek the explanation in terms of a preferential solvation of the propagating cation by the added solvent which has a dipole moment of 1.6 Debye, whereas that of EVE is 1.14 Debye. A similar view was expressed by the original authors (Deffieux *et al.* 1982). I am aware of $\mathrm{CH_2Cl_2}$ being a much weaker donor than any ether (Gutmann 1978) and of the fact that near m_{B} the ether monomer has the mass-action advantage. None the less, my view offers the following self-consistent picture. As $\mathrm{CH_2Cl_2}$ is added progressively to the monomer, the ratio $[\mathrm{P}_n^+\mathrm{Sv}]/[\mathrm{P}_n^+\mathrm{M}]$ increases so that in the then dieidic polymerization the contribution from the fast unimolecular propagation diminishes so that the slower bimolecular propagation gradually takes over, and from $m \approx 5$ mol dm^{-3} downwards the polymerization is monoeidic and bimolecular. This means that the only type of cation needing consideration is $\mathrm{P}_n^+\mathrm{Sv}$ and therefore from (4.15) $R/mc = k_{\mathrm{p}}^+$. In other words, for the lower part of the concentration range the interpretation of the original authors is valid, their k_{p} is our k_{p}^+, and it is what they believed it to be; its slight upward drift as m increases, i.e. as the mean ϵ of the mixture decreases, is what one expects for an (ion + molecule) reaction. The fact that even a small amount of $\mathrm{CH_2Cl_2}$ admixed to another solvent reduces the rate to that prevalent in $\mathrm{CH_2Cl_2}$ only has also been found in small-molecule kinetics and fits into the picture of specific or selective solvation (Clark & Wayne 1969).

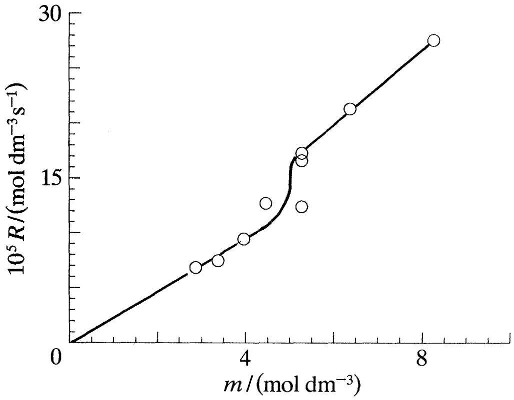

Figure 6. The dependence of R on m for styrene in toluene at $I = 9.7$ rad s^{-1}.

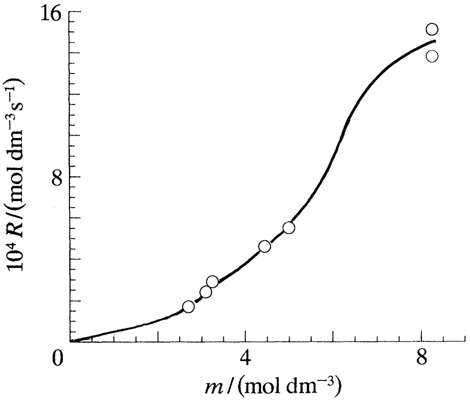

Figure 7. The dependence of R on m for styrene in toluene at $I = 53$ rad s^{-1}.

(c) *Other monomers*

The polymerizations of hydrocarbon monomers by ionizing radiations differ from those of the VE in several respects which have been set out at the end of §2. I now show that the reaction patterns of the hydrocarbons and the ways in which they differ from those of the VE can be explained adequately by my theory. Unfortunately, c is not known for any of these systems, so that no rate-constants can be calculated by the established method, but another method has been devised based on DP information.

(i) *Styrene in solution*

The only extensive set of kinetic results, including DPs, was obtained by Ueno *et al.* (1966*a*). Before these are analysed, the reader must be warned that they are presented in a dangerously misleading manner, because the rate is given in units of percent per minute as a function of mol (%) of monomer. In their figure 4 the rate is 0.2 % min^{-1} at $m = 8$ mol dm^{-3} and also at 6 mol dm^{-3}; but at $m = 8$ mol dm^{-3}, $R = 2\times10^{-3}\times8 = 1.6\times10^{-2}$ and at $m = 6$ mol dm^{-3} it is 1.2×10^{-2} mol dm^{-3} min^{-1}! Their kinetic results for styrene in toluene are shown, recalculated by us, in figures 6 and 7 as $R/(\text{mol dm}^{-3}\,\text{s}^{-1})$ against $m/(\text{mol dm}^{-3})$. At first sight the two sets of

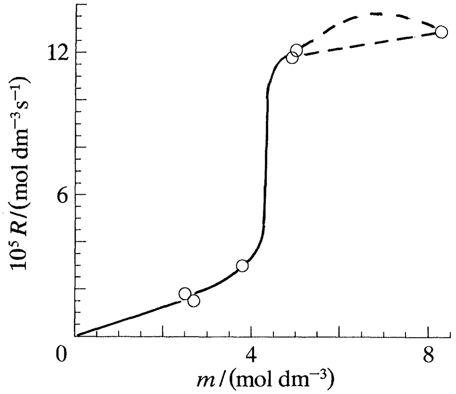

Figure 8. The dependence of R on m for styrene in CH_2Cl_2 at $I = 9.7$ rad s^{-1}.

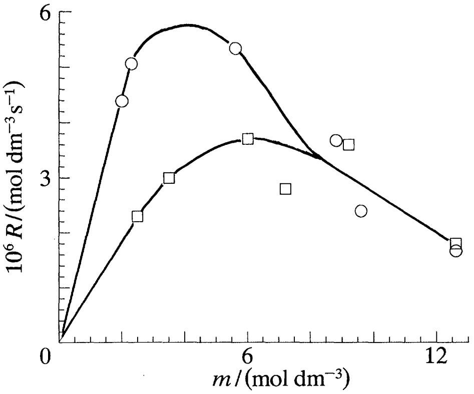

Figure 9. The dependence of R on m for isobutene in CS_2 (○) and $CHCl_3$ (□).

points seem hardly compatible, but by my interpretation they can both be considered to evince the same reaction pattern which involves a change of kinetics near $m = 5$ mol dm^{-3}. In terms of my theory we are seeing at high m a unimolecular propagation and at low m a normal bimolecular propagation, with a dieidic régime in between.

In the same paper, figure 6 purports to show that under similar polymerization conditions the dilution of styrene with CH_2Cl_2 produces a sharp *increase* in rate to a maximum R_X and then a decrease. Figure 8, in which the same results are plotted as $R/(\text{mol dm}^{-3}\ \text{s}^{-1})$ against m, shows this to be illusory, and in fact the dependence of R on m at high m is unknown. What is clear is that a drastic deceleration sets in at or above 5 mol dm^{-3}, and that below *ca.* 3 mol dm^{-3} probably normal bimolecular propagation prevails. In §5*b* (ii) I show how the DP information for this system makes it possible to calculate a k_p^+.

(ii) *Isobutene in solution*

The influence of various solvents on the rate of polymerization of isobutene at −78 °C by ionizing radiation has been described by Ueno *et al.* (1966*b*). The dilution of isobutene with *n*-hexane, chloroform, CH_2Cl_2, or carbon disulphide accelerated the polymerizations, the effect increasing in the order given, and the acceleration by CS_2 being much the greatest. The dependence of the rate on m appears to show two

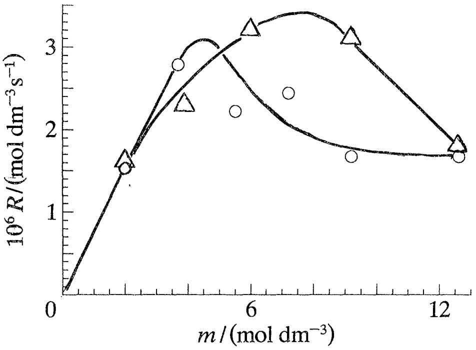

Figure 10. The dependence of R on m for isobutene in CH_2Cl_2 (○) and hexane (△).

different behaviour patterns. Their figure 4 shows that for CS_2 and CH_2Cl_2 the rate increases with dilution to a maximum, R_x, near 5 mol dm^{-3} and then declines steeply to $m = 2$ mol dm^{-3}. For CS_2 the ratio $R_X/R_B \approx 3.2$, for CH_2Cl_2 $R_X/R_B \approx 1.6$. For $CHCl_3$ and hexane, their figure 7 appears to show that over the whole range of m the rate increases as m decreases, but – in contrast to figure 4 – the rate is given in percent per hour. When it is recalculated to mol dm^{-3} s^{-1} one finds that for these solvents, too, R goes through a maximum, near m = 7 mol dm^{-3}, with $R_X/R_B \approx 2$ for both solvents; see figures 9 and 10.

For the experiments with CH_2Cl_2, $CHCl_3$ ($\epsilon = 6.8$), and CS_2 the same explanation as used for styrene will serve, although the strong acceleration by CS_2 seems odd at first sight in view of its zero dipole moment. However, because of its exceptionally high polarizability it behaves like a solvent of high ϵ, although its ϵ is only 2.6 (−78 °C). Its irregular behaviour in cationic polymerizations, as if it were a solvent of high polarity, has been known for many years (Hersberger *et al.* 1945). The similarity of the curves for the four solvents is remarkable, and the fact that the polyisobutene formed in CH_2Cl_2 is precipitated as a gel, whereas it is soluble in the other solvents, seems only to have distorted the relevant curve. However, the cause of the acceleration by the non-polar, non-polarizable hexane remains obscure.

The increase in the rate of polymerization of isobutene as it is diluted with a polar solvent had been reported earlier by Popova *et al.* (1965). These authors found that for polymerizations with $I = 70$ rad s^{-1} at −78 °C the dilution with CH_2Cl_2 gave $R_X/R_B \approx 2$ at *ca.* 50 mol (%) (*ca.* 7 mol dm^{-3}), and dilution with CF_2Cl_2 gave $R_X/R_B \approx 5$ at *ca.* 80 mol (%) isobutene. However, in one of the earliest studies of the effects of solvents on polymerizations by ionizing radiations (Stannett *et al.* 1964) it was found that the rate of polymerization of isobutene in CH_2Cl_2 at −78 °C and I = 5.6 rad s^{-1} with m = 9.5 and 11 mol dm^{-3} was only about one third of the rate for bulk monomer. In view of the earliness of this investigation its disagreement with later results may not be significant, especially in view of the well-known difficulty of purifying adequately the CH_2Cl_2 available at that time. (The changes in the nature and amounts of the impurities in commercial chemicals, particularly solvents, with time, and differences between countries, are far too little known and appreciated.)

(iii) 4-*Methoxystyrene*

The polymerization of 4-methoxystyrene (MeOSt) by ionizing radiations at 20 °C in CH_2Cl_2 is reported briefly by Deffieux *et al.* (1980). Because this monomer

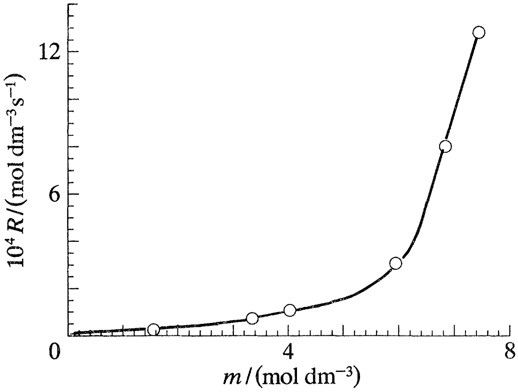

Figure 11. The dependence of R on m for 4-MeO-styrene in CH_2Cl_2.

resembles the VE in its polarity, one expects it to resemble these monomers in its polymerization behaviour. Indeed, as figure 11 shows, the drop in rate, $R_B/R_{0.8B}$, between $m = m_B$ and the arbitrarily chosen $m = 0.8m_B$ is 4.3, and for EVE it is 2.5. There is no obvious inflection signalling the change of mechanism as there is for EVE, but the scanty points are certainly compatible with one. The behaviour is markedly different from that of styrene.

(*d*) *The rate constants in solution*

(i) *The unimolecular rate constants*

The experiments show that the dilution of all the monomers leads to a change of rate, and I contend that at the earliest stage of dilution the polymerizations are still mainly unimolecular and I offer an explanation for the effects of solvents on the rate of the unimolecular reactions. Since the rate constants, k^+_{p1}, are defined by (4.1) and (4.14) they can only be calculated if $[P^+_nM]$ is known. As explained in §3*b*, there are reasons for believing that for cyclopentadiene and for isobutene $[P^+_nM] = c$, but for the former there are no results for solutions, and for the latter no c values are available, so that for these monomers k^+_{p1} could only be calculated for the bulk polymerizations.

(ii) *The bimolecular rate constants*

According to my view, the polymerizations by ionizing radiations at the lowest m are bimolecular reactions, propagated by the species P^+_nSv. For these reactions there are no ambiguities, and $[P^+_nSv] = c$, so that k^+_p is defined by (4.1) and (4.15). The available values, including those calculated in this section and in §5, are collected in table 5.

The new features of this table are: (i) the values calculated by me (1, 2 and 3); (ii) the recognition that the values quoted apply only over a range of m which depends on the nature of the solvent; (iii) the k^+_p for styrene and EVE in solvents of low polarity are very similar. In my view none of these values and others in the literature are sufficiently reliable for any activation energies calculated from them to afford useful information. I have refrained from attempting a correlation of the rate constants with the dielectric constant of the diluent because in my view even the same cation in each different solvent is a different species, so that the fundamental hypothesis of theories of the Laidler type is not valid.

Table 5. *Values of* k_p^+

result	T/°C	diluent	$k_p^+/(\mathrm{dm^3\ mol^{-1}\ s^{-1}})$ this work (*a*)	$k_p^+/(\mathrm{dm^3\ mol^{-1}\ s^{-1}})$ original authors	references
			isobutene		
1	−78	CH_2Cl_2	10^4	—	Ueno *et al.* (1966*b*)
			styrene		
2	10	toluene	2.0×10^4 (*b*)	—	Ueno *et al.* (1966*c*)
3	23	toluene	3.2×10^4 (*c*)	—	
			ethyl vinyl ether		
4	20	benzene	$(1.5\pm0.8)\times10^4$	0.7×10^4	Deffieux *et al.* (1981)
5	23	Et_2O	$(2.4\pm1.5)\times10^4$	$(1.2\text{–}2.6)\times10^4$	Hsieh *et al.* (1982)
6	23	diglyme	$(1.3\pm0.3)\times10^4$	$(1.2\text{–}2.7)\times10^4$	
7	22	CH_2Cl_2	$(2\pm0.2)\times10^3$	*ca.* 2×10^3	Deffieux *et al.* (1982)
			isopropyl vinyl ether		
8	26	benzene	$(10\pm5)\times10^5$	$(1.4\text{–}3)\times10^5$	Deffieux *et al.* (1983)

(*a*) Calculated for $m < m_C$.
(*b*) $I = 9.7$ rad s^{-1}.
(*c*) $I = 53$ rad s^{-1}.

5. The degree of polymerization

(*a*) *General treatment*

The DP of polymers formed by ionizing radiations is more difficult to interpret than that of polymers formed by chemical initiation, because after quite a low degree of conversion the degradation of the polymers by the radiation may become significant (Stannett *et al.* 1964; Deffieux *et al.* 1982). It is not known to what extent this fragmentation and to what extent various transfer and termination processes are responsible for the well-documented fact that the observed DP is generally smaller, in some systems very much smaller, than the ideal DP given by the ratio $G(-m)/G_i$, where $G(-m)$ is the amount of monomer consumed and G_i is the yield of propagating ions per 100 eV (see (2.2)). In all the pioneering papers dealing with the bulk polymerizations, the lowness of the DP was attributed to the proton transfer to monomer that was well documented in the chemically initiated polymerizations, and was treated in terms of a bimolecular process. Therefore, those discussions, referring to bulk conditions and ignoring fragmentation, are of no relevance here. What we have to decide is whether all the DP information is to be ignored because of our ignorance of the extent of fragmentation in the different systems, or whether we attempt a partial understanding by ignoring the possibility of fragmentation. Actually, the scant information available appears to be reasonably consistent, it can be interpreted by our theories, and some quantitative results can be extracted from it, so that it may be that the importance of the fragmentation has been exaggerated. To utilize the DP of the unimolecular reactions, the conventional theory, expressed essentially by the Mayo equation, had to be generalized to include the DP of polymers formed by a propagation of zero order with respect to monomer. This was done first in the context of a more general discussion (Plesch 1968), and the present treatment follows from it.

This analysis starts conventionally. The DP is given by R_p/R_b, where R_p is the rate of propagation and R_b is the sum of the rates of all chain-breaking processes. In the systems considered here, $R_p = R$ and is given by (4.1). As before, it is more useful to treat the two ends of the monomer concentration range separately. For the region $m < m_C$ where second-order propagation by P_n^+Sv predominates, the corresponding rate R_2 is given by (4.15). At high m the species that $[P_n^+Sv]$ is kinetically insignificant, so that $c = [P_n^+M] + [P_n^+G]$ and correspondingly R_1 is given by (4.14) in the form

$$R_1 = k_{p1}^+ cW. \tag{4.14a}$$

Hence

$$R = k_{p1}^+ cW + k_p^+[P_n^+Sv]\, m. \tag{5.1}$$

With regard to chain-breaking, note that in the systems under consideration here the dependence of the polymerization rate on $I^{\frac{1}{2}}$ indicates that there are no terminating impurities, and that the principal termination is the neutralization of the cations by electrons.

According to my view, and in contrast to the treatments by earlier authors, there are three such reactions, represented below:

$$P_n^+M + e^- \longrightarrow P_n^{\cdot} + M, \tag{5.Ia}$$

$$P_n^+G + e^- \longrightarrow P_n^{\cdot} + M \tag{5.Ib}$$

and

$$P_n^+Sv + e^- \longrightarrow P_n^{\cdot} + Sv. \tag{5.II}$$

The fate of the radicals $P_n^{\cdot}$ (see (2.II)) does not concern us here.

I know of no reason why the rate constants of these three diffusion-controlled reactions should be markedly different, and so they are given the same symbol, k_t. If no cations other than P_n^+M, P_n^+G and P_n^+Sv are present, the concentration $[A^-]$ of terminating electrons attached to an acceptor A, is c, the total concentration of ions of either charge, and therefore

$$R_t = k_t c^2. \tag{5.2}$$

It will be convenient to replace only one of the c in (5.2) by means of (4.5) so that the rate of termination is then

$$R_t = k_t([P_n^+Sv] + [P_n^+M] + [P_n^+G])\, c. \tag{5.3}$$

The total rate of chain breaking is the sum of the rate of termination and the rates of all other chain-breaking processes, R_r:

$$R_b = R_t + R_r. \tag{5.4}$$

The most important of these in chemically initiated polymerizations are the transfer reactions with solvent, rate R_s and rate-constant k_s, and with monomer, rate R_m and rate-constant k_m. Solvent transfer was shown to be important by Ueno *et al.* (1966*c*) for the polymerization of styrene in toluene, and it will be discussed below. The chemistry of the transfer with an aromatic compound ArH, discovered by Plesch *et al.* (Plesch 1953; Brackman & Plesch 1958; Penfold & Plesch 1961), can be represented as

$$P_n^+X + ArH \longrightarrow P_nArH^+X, \tag{5.III}$$

$$P_nArH^+X + M \longrightarrow P_nAr + HM^+X, \tag{5.IV}$$

where the reaction (5.III) is rate-determining. Therefore

$$R_s = k_s[P_n^+X]\,[Sv], \tag{5.5}$$

where $[P_n^+X]$ is any or all of the propagating cations. The chain transfer by non-aromatic solvents is of course chemically different, but the formalism is similar. The question to be decided now is which of the propagating species can take part in this type of transfer. Because in chemically initiated polymerizations k_s is usually much smaller than k_p^+ and $k_p^+ m_B < k_{p1}^+$, we propose to neglect the solvent transfer at high m, i.e. when [Sv] is small; thus (5.5) becomes

$$R_s = k_s[P_n^+Sv][Sv]. \tag{5.6}$$

Monomer transfer is a more difficult phenomenon to analyse, because in principle both P_n^+M and P_n^+G can react unimolecularly and bimolecularly thus:

$$P_n^+M \quad \text{or} \quad P_n^+G \longrightarrow P_n + HM^+, \tag{5.V}$$

and

$$P_n^+M \quad \text{or} \quad P_n^+G + M \longrightarrow P_n + HM^+. \tag{5.VI}$$

In view of the fact that proton transfer to monomer is the most general and effective alternative to propagation in chemically initiated bimolecular polymerizations, it seems sensible to include here the reactions (5.V). For $m < m_C$ we need to include the normal bimolecular process,

$$P_n^+Sv + M \longrightarrow P_n + HM^+ \tag{5.VII}$$

especially since monomer transfer was recognized as an important feature in the polymerization of IBVE in CH_2Cl_2 by Du Plessis *et al.* (1974).

The bimolecular processes (5.VI) is neglected for the same reason that bimolecular propagation by P_n^+M and P_n^+G was discarded.

It follows that the rate of chain breaking by monomer is given by

$$R_m = k_m[P_n^+Sv]\,m + k_{mM}[P_n^+M] + k_{mG}[P_n^+G]. \tag{5.7}$$

By means of (5.3), (5.6) and (5.7) we obtain from (5.4) the general chain-breaking equation

$$R_b = k_t([P_n^+Sv]+[P_n^+M]+[P_n^+G])\,c + k_s[P_n^+Sv][Sv] + k_m[P_n^+Sv]\,m + k_{mM}[P_n^+M] + k_{mG}[P_n^+G]. \tag{5.8}$$

The general DP equation, derived from R_p/R_b by means of (5.1) and (5.8), is evidently cumbersome and not really useful because of the variation of all the rate-constants with m, especially when the polarities of M and Sv are very different. Recognizing this limitation, we shall once again consider separately the two ends of the range of m.

(i) *Bimolecular propagation*

For $m < m_C$, where the only kinetically significant propagator is P_n^+Sv, the DP is given by the second term of (5.1) divided by the appropriate modification of (5.8) in which $[P_n^+M] = [P_n^+G] = 0$, so that

$$DP = k_p^+ m/(k_t c + k_s[Sv] + k_m m). \tag{5.9}$$

The inversion of (5.9) yields (5.10), which resembles the conventional Mayo equation, except that it contains the c:

$$1/DP = k_m/k_p^+ + (k_s[Sv] + k_t c)/k_p^+ m. \tag{5.10}$$

To visualize the dependence of the DP on m we need to substitute for c in terms of (4.12) and we thus obtain

$$1/DP = (k_t A + k_m)/k_p^+ + (k_t B + k_s[Sv])/k_p^+ m, \tag{5.11}$$

which has the same form (5.12) as the conventional Mayo equation:

$$1/DP = \alpha'' + \beta''/m \tag{5.12}$$

with α'' and β'' constant for high [Sv]; in contrast to the Mayo equation for chemically initiated polymerizations, α'' may be negative, because we have seen that for some solvents A is negative. For $m > m_C$ one can generalize (5.10) and (5.11) further by substituting for [Sv] in terms of (4.10). This procedure gives

$$1/DP = (k_m - k_s v_m/v_s)/k_p^+ + (k_s/v_s + k_t c)/k_p^+ m \tag{5.13a}$$

and

$$1/DP = (k_t A + k_m - k_s v_m v_s^{-1})/k_p^+ + (k_t B + k_s v_s^{-1})/k_p^+ m. \tag{5.13b}$$

These equations give the same dependence of the DP on m as (5.12), but one can only expect them to be valid over a range of m for which the DC of the reaction mixture remains sufficiently constant for the rate constants to be unaffected. Equation (5.13*a*) is used for the system styrene in toluene where this condition is fulfilled.

(ii) *Unimolecular propagation*

For the region of high m the rate of chain-breaking is given by

$$R_{b1} = k_t([P_n^+M] + [P_n^+G])\,c + k_{mM}[P_n^+M] + k_{mG}[P_n^+G]. \tag{5.14}$$

Since there seems little prospect at present of being able to determine k_{mM} and k_{mG} separately, we will combine the second and third terms as $k_{m1}([P_n^+M] + [P_n^+G])$, and since by hypothesis the two types of complexed cations are the only cations, (5.14) takes the simple form

$$R_{b1} = (k_t c + k_{m1})\,c. \tag{5.15}$$

Therefore, from (4.14*a*) (given at the beginning of this section) we obtain

$$DP = k_{p1}^+ W/(k_t c + k_{m1}) \tag{5.16}$$

and

$$1/DP = k_t c/k_{p1}^+ W + k_{m1}/k_{p1}^+ W. \tag{5.17}$$

To find the dependence of the DP on m, we substitute for c from (4.12) and obtain thus

$$1/DP = (k_t B + k_{m1})/k_{p1}^+ W + k_t A m/k_{p1}^+ W, \tag{5.18}$$

which is of the form

$$1/DP = \alpha' + \beta' m. \tag{5.19}$$

The corresponding equation for chemically initiated unimolecular polymerizations is of the same form (Plesch 1968), and it was pointed out on that occasion that in favourable cases one can discriminate between polymerizations of first and zero order with respect to m from the way the DP depends on m.

(*b*) *Applications of the* DP *equations*

(i) *EVE in* CH_2Cl_2

The results of Deffieux *et al.* (1982, table 2) for EVE in CH_2Cl_2 are plotted according to (5.12) and (5.19) in figure 12*a*, *b*. It is fortunate that the apparently off-the-line point near $m = 5\ \text{mol dm}^{-3}$ is reinforced by two further determinations (Deffieux *et al.* 1982, table 3; Hsieh *et al.* 1982, table 5), so that the general shape of the curve is fairly closely defined, except near m_B. The original authors made no attempt at a detailed interpretation and presented the results once again as a log–log plot, thus obscuring their most interesting features. We know from the kinetic

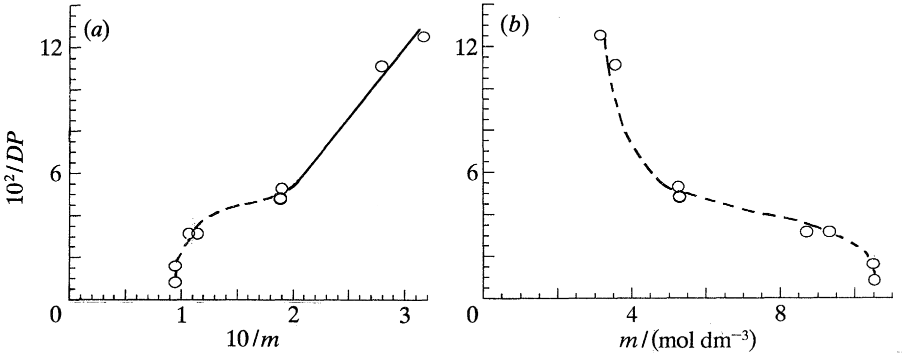

Figure 12. Plot (*a*), $10^2/DP$ against $10/m$ and plot (*b*), $10^2/DP$ against m for EVE in CH_2Cl_2. Two additional points near $m = 5$ mol l^{-1} from Deffieux *et al.* (1982), Table 3 and Hsieh *et al.* (1982), Table 5.

analysis that for $m \lesssim 6$ mol dm^{-3} the polymerization is bimolecular, so that (5.11) applies, and we are concerned with the right-hand side of figure 12. There is no means of knowing whether this is rectilinear, but if we assume it to be as shown, with minimum slope and minimum intercept, and make some simplifying assumptions, we can obtain an order-of-magnitude for k_t. We assume that $k_m = k_s = 0$ and thus obtain

$$1/DP = k_t A/k_p^+ + k_t B/k_p^+ m. \tag{5.20}$$

Because for this system A is negative, the figure 12*a* gives us the intercept

$$I_{20} = k_t A/k_p^+ = -6.8 \times 10^{-2}$$

and with $A = -2.65 \times 10^{-11}$ we obtain $k_t/k_p^+ = 2.6 \times 10^9$. From the slope

$$S_{20} = k_t B/k_p^+ = 7 \times 10^{-1}$$

and with $B = 6.7 \times 10^{-10}$ we obtain $k_t/k_p^+ = 1.0 \times 10^9$ and an average $k_t/k_p^+ = 1.8 \times 10^9$. The value of k_p^+ from the kinetic data is 2.2×10^3 dm^3 mol^{-1} s^{-1} so that the average $k_t = 4 \times 10^{12}$ dm^3 mol^{-1} s^{-1}. It is encouraging that our two values of k_t/k_p^+ agree within a factor of 2. One cannot use (5.10) in this instance to determine k_m by assuming c is constant, as I_{20} is negative. Deffieux *et al.* (1981) calculated k_t from (2.8) as $k_t \approx 4 \times 10^{11}$ dm^3 mol^{-1} s^{-1}. In view of the assumptions involved in both calculations, the discrepancy is probably not significant.

Next, we examine the dependence of the DP on m in the region near m_B, where (5.18) is applicable. Both the kinetic plot and figure 12 show that the consequences of introducing even a very small quantity of CH_2Cl_2 into the EVE are so dramatic that an attempt to account for them by an equation is unpromising (consider, that one would need to know the d/dm for each of the rate constants and equilibrium constants). I conclude from this analysis that my theory, based on a change of propagation mechanism with decreasing m, can account adequately for the observations.

(ii) *Styrene in toluene*

The dependence of the DP of polystyrenes formed by ionizing radiations in toluene has been reported by Ueno *et al.* (1966*c*) in the form of plots of molecular weight against mole fraction of monomer for two values of I and slightly different T. These results, converted to DP dependence on m, are shown in figures 13*a*, *b* and 14*a*, *b*. The

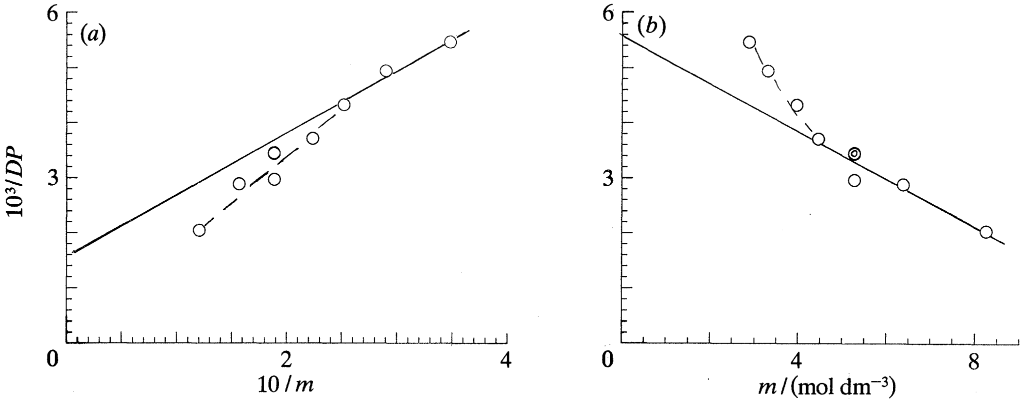

Figure 13. Plot (*a*), $10^3/DP$ against $10/m$ and plot (*b*), $10^3/DP$ against m for styrene in toluene.

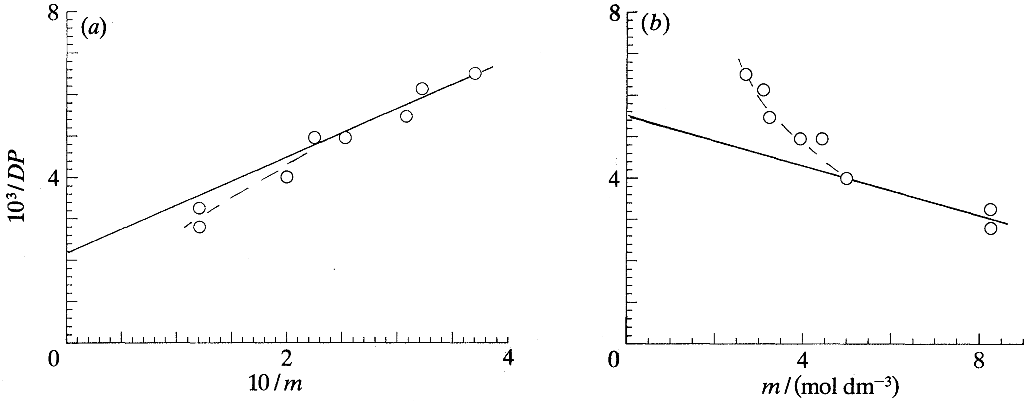

Figure 14. Plot (*a*), $10^3/DP$ against $10/m$ and plot (*b*), $10^3/DP$ against m for styrene in toluene.

rate curves discussed in §4*b*(i) indicate a marked change of régime near $m = 5\ \text{mol dm}^{-3}$, which I attributed to bimolecular propagation being prevalent below that, and unimolecular propagation being dominant at high m, and the DP plots can be interpreted in the same way. However, in contrast to the VE system discussed in the previous section, we have no information on c for this system, but since the yield of ions from a given dose-rate depends mainly on the dielectric constant, it can be assumed that in the mixtures of aromatic hydrocarbons with which we are dealing here, the c and the rate constants are independent of m, so that we can use (5.10) and (5.14), treating c as constant.

However, (5.14) does not help to provide new information, because even if we assume $k^+_{\mathrm{p}1} = k^{+\mathrm{B}}_{\mathrm{p}1}$ and calculate k_{t} from the diffusion equation, we still have the two unknowns W and c.

At low m, equations (5.13*a*, *b*) are relevant, and since A and B are unknown for this system, we shall use (5.13*a*). The intercepts for both systems (figures 13*a* and 14*a*) are effectively the same, so that

$$I_{13} = (k_{\mathrm{m}} - k_{\mathrm{s}} v_{\mathrm{m}}/v_{\mathrm{s}})/k^+_{\mathrm{p}} = (2 \pm 0.5) \times 10^{-3}.$$

Since $v_{\mathrm{m}} \approx v_{\mathrm{s}}$, the fact that I_{13} is positive shows that $k_{\mathrm{m}} > k_{\mathrm{s}}$, which is in agreement with the results obtained by the original authors by a slightly different method (Ueno *et al.* 1966).

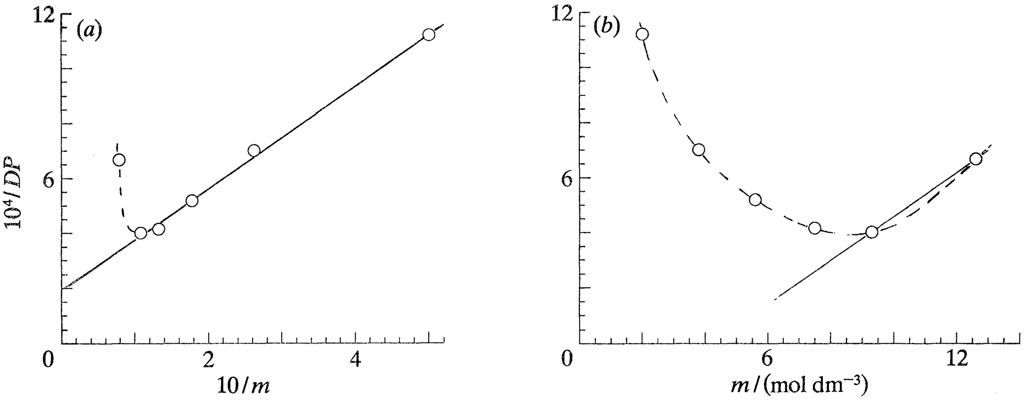

Figure 15. Plot (*a*), $10^4/DP$ against $10/m$ and plot (*b*), $10^4/DP$ against m for isobutene in CH_2Cl_2.

Table 6. *Values of* k_p^+

figure number	$10^2 S_{13}$	$(10^5 R/m)/s^{-1}$	$10^4 k_p^+/(\text{dm mol}^{-1}\ s^{-1})$
13	1.13	2.3	2.0×10^4
14	1.16	6	3.2×10^4

The slope is

$$S_{13} = (k_t c + k_s/v_s)/k_p^+$$

from which we can estimate k_p^+ if we assume that k_s/v_s can be neglected compared to $k_t c$; this can be justified by reference to various findings from chemically initiated polymerizations. Further, at low m equation (4.1) gives $c = R/mk_p^+$, so that the above equation for S_{13} becomes

$$k_p^+ = (k_t R/S_{13}\, m)^{\frac{1}{2}}. \tag{5.21}$$

By means of (5.21) and the data in table 6, together with the value of $k_t = 2 \times 10^{11}$ dm^3 mol^{-1} s^{-1} used previously, the two values of k_p^+ shown in table 6 have been calculated. Because both I and T are different, it is not possible to apportion the reasons for the difference in k_p^+; if indeed it is significant. However, the close agreement as to order of magnitude of the two values obtained from the two sets of experiments is reassuring. It is unfortunate that for styrene in CH_2Cl_2 the results of Ueno *et al.* (1966*b*) are too scanty and too scattered to permit similar calculations.

(iii) *Isobutene in* CH_2Cl_2

Ueno *et al.* (1966*b*) have given results for the DP of polyisobutenes formed in CH_2Cl_2 at −78°, which we show as plots of $1/DP$ against $1/m$ and $1/DP$ against m in figure 15*a*, *b*. These can be exploited, together with the rate data for the same system (figure 10), to obtain an estimate of k_p^+.

Note that the rate goes through a maximum near $m = 5$ mol dm^{-3} (figure 10) and that the DP has a maximum near 8 mol dm^{-3} (figure 15).

Equation (5.17) is more useful for this system than for most others, because for isobutene there is only one complexing site so that $W = 1$, and (5.17) takes the form

$$1/DP = k_t c/k_{p1}^+ + k_{m1}/k_{p1}^+. \tag{5.22}$$

Since $c = R_1/k^+_{\mathrm{p1}}$, (5.17) gives for $m = m_{\mathrm{B}}$,

$$k_{\mathrm{m1}} = k^{+\mathrm{B}}_{\mathrm{p1}}/DP_{\mathrm{B}} - k_{\mathrm{t}} R_1/k^{+\mathrm{B}}_{\mathrm{p1}}. \tag{5.23}$$

The original data give $DP_{\mathrm{B}} = 1.5 \times 10^3$, R_1 at $m = m_{\mathrm{B}}$ as 1.7×10^{-6} mol dm^{-3} s^{-1}, and $k^{+\mathrm{B}}_{\mathrm{p1}} = 2 \times 10^9$ s^{-1} (table 2), so that

$$k_{\mathrm{m1}} = 2 \times 10^9/1.5 \times 10^3 - 10^{12} \times 1.7 \times 10^{-6}/2 \times 10^9 \approx 10^6\ \mathrm{s}^{-1}.$$

This result means that at any rate for bulk isobutene at −78° the DP is governed by the unimolecular proton transfer to the monomer.

To estimate k^+_{p} by means of (5.13*a*) we make the approximation $k_{\mathrm{s}}/v_{\mathrm{s}} \ll k_{\mathrm{t}} c$, replace c by $R/k^+_{\mathrm{p}} m$ and thus obtain the slope S_{13} as

$$S_{13} = k_{\mathrm{t}}(R/m)/(k^+_{\mathrm{p}})^2$$

so that

$$k^+_{\mathrm{p}} = (k_{\mathrm{t}} R/S_{13} m)^{\frac{1}{2}}. \tag{5.24}$$

With $S_{13} = 1.82 \times 10^{-3}$, $R/m = 7.5 \times 10^{-7}$, and $k_{\mathrm{t}} = 2 \times 10^{11}$ dm^3 mol^{-1} s^{-1}, we thus obtain $k^+_{\mathrm{p}} = 10^4$ dm^3 mol^{-1} s^{-1}. This is of the same order of magnitude as the $k^+_{\mathrm{p}} = 1.2 \times 10^4$ dm^3 mol^{-1} s^{-1} for isobutene in MeCl at −45° (Magagnini *et al.* 1977 and preceding papers). The rate-constant determined by these authors was identified as k^+_{p} by Plesch (1993). (The k^+_{p} calculated in this section was wrongly given as 10^5–10^6 by Plesch (1993).)

6. Conclusions

In this paper many sets of results on the polymerization of various alkenic monomers by ionizing radiations from several research groups have been re-examined by means of a new theoretical model which consists of several connected parts. The first comprises the idea that for polymerizations of monomers in bulk or in solution at high concentrations, the propagation is a unimolecular isomerization of a complex consisting of a monomer molecule which is π-bonded by its double bond to the carbenium ion at the growing end of the chain. This idea, due to Fontana *et al.* (1948, 1952), has not been used previously in the context of polymerizations by ionizing radiations, nor have its implications been examined before. The kinetic evidence shows that at conversions up to *ca.* 30 % the polymerizations are of zero order with respect to monomer, which supports my theory and indicates that the earlier interpretation of the rates in terms of a second-order reaction was erroneous. The new first-order rate constants, k^+_{p1}, calculated by me from the published data, are collected in table 2.

The second part of the theory, which is a logical consequence of the first, is that monomers that have more than one basic site, e.g. an aromatic ring or an oxygen atom, can form more than one type of complex with the carbenium ion; this idea was first proposed by Plesch (1990) in the context of chemically initiated polymerizations. It helps to explain why aryl alkenes and alkyl vinyl ethers polymerize more slowly than isobutene and cyclopentadiene. The reason is that all the complexes formed by the alkyl alkenes are propagators, whereas for the aryl alkenes and vinyl ethers only a fraction of the population of complexes can propagate.

To explain the very varied behaviour patterns shown by the various monomers in various solvents, use has been made of a further, hitherto unrealized, implication of the model, namely that the rate of the isomerization–propagation must depend upon the electrochemical environment of the complex. This vague idea has been given precision by concentrating attention on the species which occupies the site at the 'back-side' of the near-planar carbenium ion, the 'front-side' of which is π-bonded to the double bond of the monomer. The idea is that the stronger the dipole at the back, the weaker is the π-bond, and the lower is the energy of the transition state, and therefore the greater is the rate.

As the dilution of the monomer progresses, the solvent takes over from the monomer as the principal solvator of the carbenium ions, and the propagation becomes of second order. The ensuing reaction pattern, i.e. the way in which the rate and the DP change with the monomer concentration, depends upon the relative polarity of the solvent and the monomer, and an understanding of these relations has made possible a self-consistent interpretation of the multifarious phenomena of these reactions. As far as possible these ideas have been expressed algebraically and rate constants have thus been extracted from the data (table 5).

The ideas propounded here about the solvation of carbenium ions in different circumstances are capable of further development. I hope that they will be tested and refined by a resumption of work in this now neglected field; in particular, it seems that recent results on copolymerizations by ionizing radiations (Wood *et al.* 1989; Wood & Stannett 1992) will need to be reassessed. The many results on polymerizations by ionizing radiations of monomers mixed with electron-acceptors should also now be re-examined in the light of the new theory. Further, it seems likely that its application to chemically initiated cationic polymerizations would be rewarding.

It is a pleasure to acknowledge that this work would not have been possible without the old-fashioned, detailed publication of primary data by Stannett and his group and by the earlier workers; the currently fashionable omission of primary data by most authors is a serious obstacle to all investigations which involve the reinterpretation of established results.

I also acknowledge with deep gratitude the generous advice and critical encouragement of many colleagues, especially (in alphabetical order) M. K. Abraham, A. Deffieux, A. Gandini, G. A. Salmon, V. T. Stannett and Ff. Williams.

This is part XI of 'Developments in the theory of cationic polymerization'. For part X see Plesch (1991) and for part IX see Plesch (1990).

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Received 18 October 1991; revised 19 February 1992; accepted 14 April 1992