

Non-classical free-radical polymerization: Degradative addition to monomer in the polymerization of 1-vinylimidazole

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A study of the free-radical polymerization of 1-vinylimidazole at 70°C is described; most attention has been devoted to the (homogeneous) reaction in ethanol, but polymerizations in *N,N*-dimethylformamide (DMF), water and bulk monomer are also considered. The polymerization in ethanol is unusual in that the rate becomes effectively zero-order in monomer *M* at moderately high [*M*]. Kinetic results indicate the occurrence of a degradative reaction between propagating radicals and monomer (see below); the available molecular weight data suggest that bimolecular termination takes place by radical combination. Polymerization in DMF is generally similar although the kinetic treatment is rather less satisfactory. At high [*M*] there are indications of occlusion phenomena in DMF and these latter are marked in the (heterogeneous) bulk polymerization. In water, significant interactions between solvent and monomer, evidenced by viscosity-composition behaviour, affect the kinetics of polymerization, which, however, resemble those with the other solvents. Of considerable interest is the influence of pH on rates and degrees of polymerization, which change in the same sense and to nearly the same extent. We believe these findings imply suppression of the degradative reaction by protonation of the monomer. The degradative reaction between propagating chains and monomer is thought to be formation of a relatively unreactive radical by addition to position 2 of the monomer, rather than by chain transfer. Evidence for this is adduced from molecular weight data, which are not consistent with transfer, the existence of occlusion phenomena and the observations on the pH dependence in aqueous solution. Molecular weight distributions expected in polymerizations of this type are calculated in the Appendix. Reinitiation by the adduct radical, which probably occurs only to a limited extent under non-occlusion conditions, becomes important when occlusion is significant. A kinetic treatment of these phenomena is presented.

INTRODUCTION

The interest shown in imidazole-containing polymers in recent years stems from a number of causes. Many proteins contain imidazole rings in the form of L-histidine, and these groups are thought to be responsible for most of the buffering capacity of proteins in the physiological pH range¹ and also appear to be the principal sites for metal binding². The fact that the imidazole ring in histidine occurs in the active sites of several hydrolytic enzymes has stimulated study of the catalytic properties of poly[4(5)-vinylimidazole] and its copolymers in activated ester hydrolysis³. Several features of enzyme-catalysed processes were observed with the synthetic polymers, including high rates arising from cooperative effects, selectivity, saturation kinetics and competitive inhibition.

Further, the ability of imidazoles to complex with metals and bind dyes, the hydrophilicity of the monomers and polymers, and the latter's polyelectrolyte behaviour have stimulated interest in imidazole-containing polymers for potential industrial uses.

Although 1-vinylimidazole (1-VIM) has been known

for some time, relatively little has been published on its homopolymerization. Skushnikova *et al.*⁴ and Konsulov⁵ reported that in methanol the reaction orders with respect to monomer and initiator are 1.6 and 0.7 respectively. The high order in monomer was thought to involve hydrogen-bond formation between 1-VIM and methanol and the high initiator exponent was attributed to active centre deactivation by chain transfer to solvent.

In this paper we describe a detailed study of the homopolymerization of 1-VIM in ethanol, together with ancillary observations on the polymerization in *N,N*-dimethylformamide (DMF), water and bulk.

EXPERIMENTAL

Techniques

Polymerizations in solution were followed dilatometrically and the bulk polymerization was followed gravimetrically at $(70 \pm 0.01)^\circ\text{C}$. The contraction factor, $(\rho_p - \rho_m)/\rho_p$ (ρ = density), for the homopolymerization of 1-VIM was found to be 0.207; this was confirmed by dilatometric and gravimetric determinations of rates of polymerization. The corresponding value for 2-methyl-1-vinylimidazole (MVIM) was found to be 0.157.

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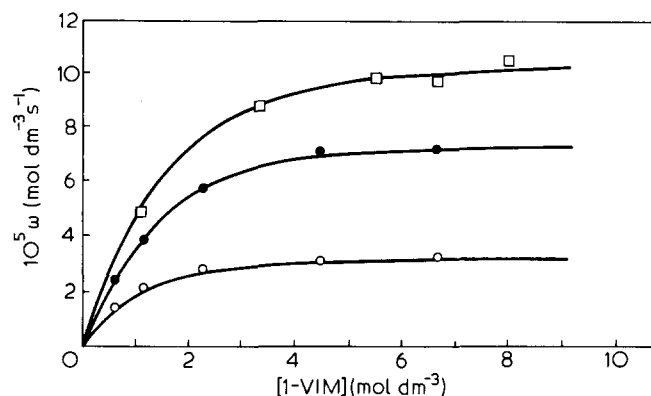


Figure 1 Polymerization of 1-VIM in ethanol at 70°C. Dependence of rate of polymerization ω on [1-VIM]. 10^3 [azobis(isobutyronitrile)]/mol dm⁻³: □, 9.88; ●, 6.53; ○, 2.60. Experimental points and curves calculated from equation (12)

Reaction mixtures were degassed under high vacuum by the conventional freeze-thaw technique. Five cycles were usually sufficient to attain a residual gas pressure $<10^{-5}$ torr.

For polymerizations of 1-VIM in water azobis(4-cyanovaleric acid) was used as initiator. At low pH and room temperatures this is only sparingly soluble, but it dissolves readily at 70°C. Polymerization at low pH could not be followed for more than about 20 min since the column of liquid in the dilatometer capillary tended to break on account of gas evolution. The rate of decomposition of the initiator was shown spectrophotometrically to vary somewhat with pH, but the variation ($<20\%$) could make only minor contributions to observed changes in ω (Figure 5).

Molecular weights were determined viscometrically with 5M aqueous sodium chloride as solvent.

Materials

1-VIM (ex. BASF) was dried over molecular sieves, purified by successive fractional distillations (b.p. 80°C/7 torr) to give a purity of $>99.9\%$ as estimated by g.l.c. The monomer was partially prepolymerized in the presence of a trace amount of azobis(isobutyronitrile) and redistilled before use.

MVIM (ex. BASF) purified similarly to 1-VIM had b.p. 71°C/5 torr.

2,2'-Azobis(isobutyronitrile) (ex. BDH) was recrystallized from methanol (once) and chloroform (twice) before use.

Ethanol A.R. (ex. James Burrough) was refluxed for 2 h in the presence of sodium and diethyl phthalate, fractionally distilled and stored under argon.

N,N-Dimethylformamide was dried over molecular sieves and fractionally distilled immediately before use.

Water was triply distilled.

RESULTS AND DISCUSSION

All rates of polymerization were measured at low conversion ($<5\%$) and all conversion *versus* time curves for polymerization of 1-VIM in ethanol, DMF or water were linear, except at high monomer concentrations (>8.5 mol dm⁻³ approximately), when some polymerizations became increasingly heterogeneous. All our results in so-

lution pertain to $[1\text{-VIM}] < 8.5$ mol dm⁻³, in which case the polymerizations were homogeneous.

The dependence of rate of polymerization ω of 1-VIM in ethanol as a function of monomer concentration $[M]$ is shown in Figure 1 for three initiator concentrations $[I]$. The rate increases with increasing monomer concentration at low $[M]$ but eventually reaches a plateau value, above which it is effectively zero-order in $[M]$. It will be noticed from Figure 1 that the monomer concentration at which the plateau is effectively attained is higher for higher $[I]$. All the data in Figure 1 refer to homogeneous polymerizations.

Since the curves in Figure 1 consist of two well-defined portions, viz. the initial and plateau regions, we have studied the dependence of ω on $[I]$ at values of $[M]$ corresponding to these two regions. The dependence of ω on $[I]$, demonstrated by Figures 2 and 3 is summarized by equations (1):

$$\begin{aligned} \text{at low } [M], \quad \omega &\propto [M][I]^{0.5} \\ \text{at high } [M], \quad \omega &\propto [M]^0[I]^{1.0} \end{aligned} \quad (1)$$

Kinetics

The classical relation for free radical vinyl polymerization is given by equation (2), where k_p and k_t are the propagation and termination rate coefficients

$$\omega \equiv -\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}} [M] \mathcal{J}^{1/2} \quad (2)$$

respectively, and \mathcal{J} is the rate of initiation. Equation (2)

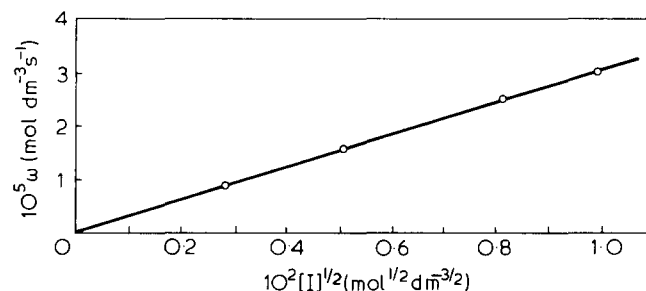


Figure 2 Polymerization of 1-VIM in ethanol at 70°C. Dependence of rate of polymerization ω on [azobis(isobutyronitrile)]^{1/2}, [1-VIM] = 0.55 mol dm⁻³

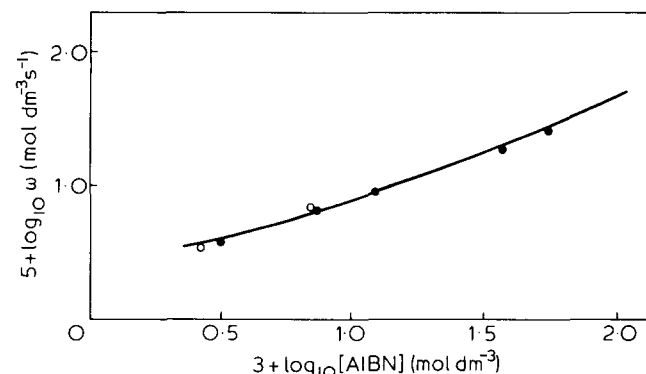


Figure 3 Polymerization of 1-VIM in ethanol at 70°C. Plot of $\log \omega$ versus $\log [\text{azobis(isobutyronitrile)}]$ for $[1\text{-VIM}] = 4.4$ mol dm⁻³

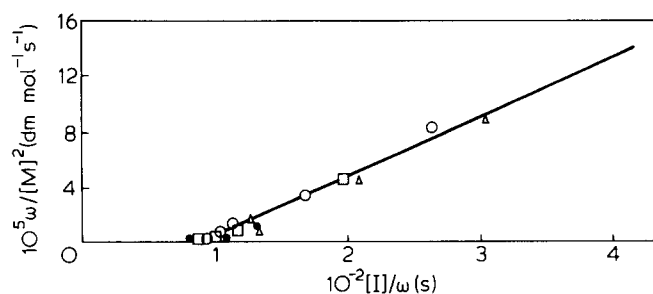
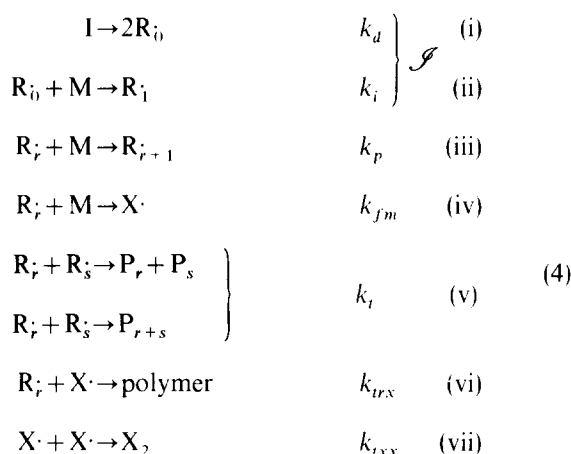


Figure 4 Polymerization of 1-VIM in ethanol at 70°C. Plot of $\omega/[M]^2$ versus $[I]/\omega$ (see equation (7))

indicates that ω is linearly dependent on $[M]$ and $[I]^{0.5}$, since \mathcal{J} can be expressed by

$$\mathcal{J} = 2fk_d[I] \quad (3)$$

where f is the efficiency of initiation and k_d is the initiator decomposition rate coefficient. Many monomers obey equations (2) and (3) over a wide range of conditions, but clearly these relations have limited application in the polymerization of 1-VIM in ethanol [equation (1)]. At low $[M]$, the system behaves classically, but at high $[M]$ there appears to be retardation by monomer (Figure 1). We propose that this arises from degradative chain transfer to monomer. The latter would also account for the observed changes in the initiator concentration exponent. A simple kinetic scheme (4), incorporating this behaviour is written below.



Degradative chain transfer to monomer is represented by equation (4 iv). There are two possibilities: abstraction of a hydrogen atom from the monomer by the growing radical R_r ; or addition of R_r to the monomer (in a manner other than that in the propagation step) to give the unreactive radical $X\cdot$. Arguments are presented later which indicate that the latter is more probable, but for the present kinetic treatment distinction is unnecessary. No reinitiation step is included. $X\cdot$ can be removed by reaction with R_r (equation 4 vi) or by dimerization (equation 4 vii); however, the very low reactivity of $X\cdot$ suggests that (equation 4 vii) can be effectively ignored⁶.

Under steady-state conditions,

$$\frac{d[R\cdot]}{dt} = \mathcal{J} - k_i[R\cdot]^2 - k_{rx}[R\cdot][X\cdot] - k_{fm}[R\cdot][M] = 0 \quad (5a)$$

$$\frac{d[X\cdot]}{dt} = k_{fm}[R\cdot][M] - k_{rx}[R\cdot][X\cdot] = 0 \quad (5b)$$

where $[R\cdot]$ and $[X\cdot]$ represent the total concentrations of the two radical species, regardless of size. From these equations together with equation (6), which is valid for a large mean chain length,

$$\omega = k_p[R\cdot][M] \quad (6)$$

we obtain the relation (7)

$$\frac{k_i}{k_p^2} \cdot \frac{\omega^2}{[M]^2} + \frac{2k_{fm}}{k_p} \cdot \omega - \mathcal{J} = 0 \quad (7)$$

which on solution yields

$$\omega = \frac{k_{fm}k_p}{k_i}[M]^2 \left\{ \left(1 + \frac{k_i}{k_{fm}^2}[M]^2 \right)^{1/2} - 1 \right\} \quad (8)$$

We see from equation (8) that at low and high $[M]$, the limiting expressions for ω are given by equations (9) and (10), respectively.

$$\omega = \frac{k_p}{k_i^{1/2}} [M] \mathcal{J}^{1/2} \quad (9)$$

$$\omega = \frac{k_p \mathcal{J}}{2k_{fm}} \quad (10)$$

These relations are clearly consistent with the experimental observations summarized by equation (1).

According to equation (7), a plot of $\omega/[M]^2$ versus \mathcal{J}/ω should be linear, with slope (k_p^2/k_i) and intercept on the \mathcal{J}/ω axis $2k_{fm}/k_p$. In agreement with this a plot of $\omega/[M]^2$ versus $[I]/\omega$ is satisfactorily linear as shown in Figure 4, which contains the data in Figures 1, 2 and 3. Rates of initiation may be estimated from equation (3) if k_d and f are known. We assume the conventional value⁷ $k_d = 3.4 \times 10^{-5} \text{ s}^{-1}$, which we have confirmed by spectrophotometric determinations in ethanol, and we take $f = 0.54$, a value in the normal range⁸ chosen for reasons mentioned later.

From Figure 4 we thus obtain

$$\begin{aligned} \frac{k_i}{k_p^2} &= 91.8 \text{ mol dm}^{-3} \text{ s} \\ \frac{k_{fm}}{k_p} &= 1.65 \times 10^{-3} \end{aligned} \quad (11)$$

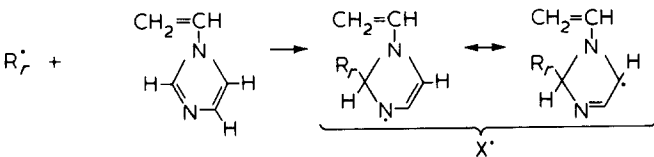
Substitution of these values into equation (7) gives:

$$91.8 \frac{\omega^2}{[M]^2} + 3.3 \times 10^{-3} \omega - \mathcal{J} = 0 \quad (12)$$

which is the general equation for the homopolymerization of 1-VIM in ethanol. For given values of \mathcal{J} , equation (12) can be used to generate theoretical ω versus $[M]$ curves and this has been done for the initiator concentrations corresponding to Figure 1. The solid lines in Figure 1 are the theoretical curves and it will be appreciated that there is an excellent correlation between theoretical and observed data.

Chemical nature of degradative reaction

As previously mentioned, degradative chain transfer to monomer may involve either hydrogen atom abstraction or radical addition to a monomer molecule. It is not obvious that a stabilized radical can be obtained from 1-VIM by hydrogen abstraction, but such a species can be formulated if the growing polymer radical adds to 1-VIM in the 2-position to give a resonance-stabilized radical on the 3-nitrogen. We therefore propose that X[•] has this structure.



If this hypothesis is correct, then blocking position 2 with a sufficiently bulky group, e.g. methyl, should hinder attack by the growing polymer radicals and thus dramatically reduce degradative chain transfer. In such a case a linear ω versus $[M]$ curve in accordance with equation (2) would be anticipated. We have found that such a relationship holds for the polymerization of 2-methyl-1-vinylimidazole in ethanol (Figure 5). It is interesting that rates of polymerization are significantly higher with MVIM, especially at high $[MVIM]$, consistent with the absence of retardation.

It seems to us that 'degradative chain-transfer' is a misnomer when applied to an addition reaction between radical and monomer (or other unsaturated species) such as that discussed above, since no chain-transfer occurs. We suggest calling this type of process 'degradative addition'.

In some respects degradative addition leads to fewer kinetic complications than degradative transfer; for exa-

mple, in the absence of chain transfer, degradative addition does not affect the simple relations existing between degree of polymerization and rates of initiation and polymerization. This matter will be referred to later.

Molecular weights

Scheme (4) includes two termination reactions (v), (vi) occurring between the two species of polymer radical R_p[•] and X[•]; which, in principle, may occur either by disproportionation or combination. The number- and weight-average degrees of polymerization deduced from scheme (4) for the two cases are given in equation (13), in which the nature of the termination is denoted by the suffix *d* or *c* following \bar{P}_n or \bar{P}_w .

1 / P_{n,d} = (2k_{fm}/k_p) + (k_t/k_p²) * (ω/[M])² (13a)

1 / P_{w,d} = 1 / P_{n,c} = (k_{fm}/k_p) + (k_t/2k_p²) * (ω/[M])² (13b)

1 / P_{w,c} = (k_{fm}/1.5k_p) + (k_t/3k_p²) * (ω/[M])² (13c)

Expressions for the molecular weight distributions, used in deducing weight-averages in equation (13), are presented in the Appendix.

Polymer molecular weights have been determined viscometrically on samples prepared at low monomer conversion with the aid of Mark-Houwink *K* and α values derived for fractions by Tan and Sochor⁹. For our polymers, if we assume the distribution given by equation (A15) (Appendix), *K* must be increased¹⁰ by a factor $\Gamma(3 + \alpha)/2^{1+\alpha} = 1.195$, so that the appropriate relations are

[η] = 9.83 × 10⁻⁴ M_{n,c}^{0.54} ; [η] = 7.90 × 10⁻⁴ M_{w,c}^{0.54} (14)

(see (A18), Appendix). Results calculated from equation (14) are presented in Table 1.

According to equation (13), 1/ \bar{P}_n and 1/ \bar{P}_w should be linear in ω/M^2 ; Figure 6 presents such plots derived from equation (13) with the parameters in equation (11), together with the experimental data (Table 1). There is reasonable agreement between the 'combination' lines and experiment. As will be apparent, the parameters in equation (11) depend on the efficiency of initiation and the value $f=0.54$ was chosen to secure the best fit with the molecular weight data. The 'disporportionation' lines in Figure 6 could be made compatible with experiment by

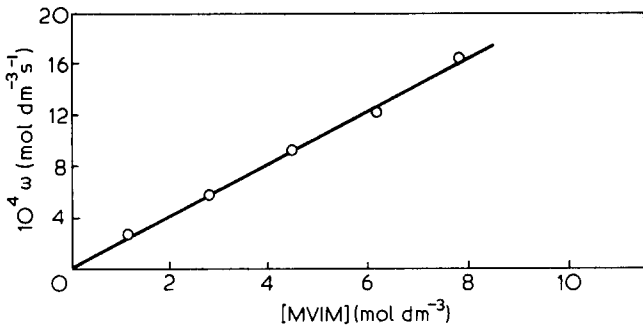


Figure 5 Polymerization of MVIM in ethanol at 70°C. Dependence of ω on $[MVIM]$. $[Azobis(isobutyronitrile)] = 2.59 \times 10^{-3} \text{ mol dm}^{-3}$

Table 1 Molecular weights of polymers prepared at 70°C in ethanol under various conditions

$[M]$ (mol dm ⁻³)	10 ³ $[I]$ (mol dm ⁻³)	10 ⁵ ω (mol dm ⁻³ s ⁻¹)	10 ⁶ $\frac{\omega}{[M]^2}$ (mol ⁻¹ dm ³ s ⁻¹)	$\bar{P}_{n,c}^*$	$\bar{P}_{w,c}^*$
2.2	10.16	7.75	16.0	381	572
5.5	2.64	2.84	0.94	567	850
5.5	2.67	2.87	0.95	623	934
5.5	6.79	7.03	2.32	585	878
5.5	9.87	9.98	3.30	564	846
5.5	9.98	10.06	3.33	637	955

* Calculated from equation (14)

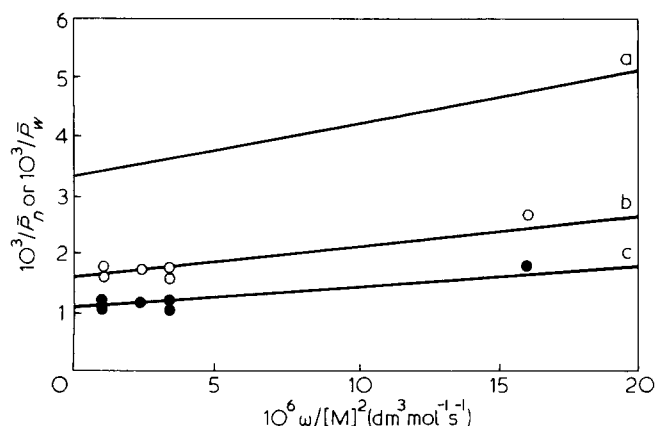


Figure 6 Polymerization of 1-VIM in ethanol at 70°C. Plot of reciprocal degrees of polymerization *versus* $\omega/[M]^2$ (a) $10^3/\bar{P}_{n,d}$; (b), $10^3/\bar{P}_{n,c}$ or $10^3/\bar{P}_{w,d}$; (c), $10^3/\bar{P}_{w,c}$. Lines calculated using parameters in equation (11). Experimental points from viscometric measurements and equation (14) \circ , $\bar{P}_{n,c}$; \bullet , $\bar{P}_{w,c}$. Polymers prepared as in Table 1

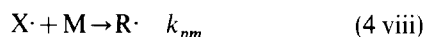
assuming $f=0.33$. This seems unreasonably low and in our view termination by combination is much more likely, although the present results do not establish this conclusively. This conclusion, if correct, clearly confirms the degradative reaction with monomer as an addition process.

Radical occlusion and re-initiation

Poly(1-vinylimidazole) is insoluble in the monomer and precipitates when the latter is polymerized at 70°C in bulk. Under these conditions the rate of polymerization increases with increasing conversion, as shown in Figure 7. The conversion *versus* time curve is similar to those obtained in the polymerization of other monomers under precipitation conditions (e.g. acrylonitrile in bulk¹¹) and the steadily increasing rate may be explained in terms of progressive radical occlusion by precipitated polymer. Related phenomena are observed in solution in *N,N*-dimethylformamide at high monomer concentrations. For $[M]>8.5 \text{ mol dm}^{-3}$, approximately, the solution becomes turbid during polymerization and the ω *versus* $[M]$ curve, virtually horizontal for lower $[M]$, begins to bend upwards.

According to the hypothesis we have proposed, chains are terminated at high $[M]$ almost exclusively by degradative interaction with monomer so that it would appear at first sight that there should be no significant occlusion phenomena. However, if, as we believe, the degradative reaction is an addition process forming a polymer radical $X\cdot$, reaction (4 vi) could be diffusion-controlled and influenced by occlusion. Although occlusion would result in an increase in $[X\cdot]$, this would not bring about an increase in reaction rate at high $[M]$ in the absence of reinitiation by $X\cdot$. So far, we have considered this process to be insignificant under non-occlusion conditions; we now investigate how far this view is compatible with the occlusion phenomena observed.

The reinitiation reaction is represented by (4 viii)



and its inclusion leads to relation (15) between ω , $[M]$ and \mathcal{J} .

$$\frac{k_t k_{trx}}{k_p^3 k_{pm}} \frac{\omega^3}{[M]^4} + \left\{ 1 + \frac{2k_{trx} k_{fm}}{k_{pm} k_t} \right\} \frac{k_t}{k_p^2} \frac{\omega^2}{[M]^2} - \frac{k_{trx}}{k_p k_{pm}} \frac{\mathcal{J} \omega}{[M]^2} - \mathcal{J} = 0 \quad (15)$$

Equation (15) is closely related to an expression derived for polymerizations with degradative transfer to solvent which was applied to the polymerization of vinyl chloride⁶. No information is available about the rate coefficients k_t, k_{trx} of the two termination processes (4 v), (4 vi), respectively; the reactions are probably both diffusion-controlled and for present purposes we shall assume that $k_t = k_{trx} = \lambda$. With this simplification, which is unlikely to affect the general character of the results, equation (15) may be written in the following form:

$$a^3 b \frac{\omega^3}{[M]^4} + \left\{ 1 + \frac{2bc}{a} \right\} a^2 \frac{\omega^2}{[M]^2} - \mathcal{J}_{ab} \frac{\omega}{[M]^2} - \mathcal{J} = 0 \quad (16)$$

in which

$$\frac{k_t}{k_p^2} = \frac{\lambda}{k_p^2} = a^2; \quad \frac{k_t}{k_{pm}^2} = \frac{\lambda}{k_{pm}^2} = b^2; \quad \frac{k_{fm}}{k_p} = c;$$

so that $k_{pm} = \frac{a}{b} k_p$ and $\frac{k_{fm}}{k_{pm}} = \frac{bc}{a}$ (17)

Experimental values of a^2 and c are given in equation (11) and we shall take $\mathcal{J} = 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$, a value close to that holding for the experiments depicted in the lowest curve in Figure 1. ω *versus* $[M]$ curves have been calculated from equation (16) with the aid of these parameters for a series of values of b , i.e. for a range of values of k_{pm}/k_p . Results are presented in Figure 8. Curves a–e correspond to decreasing b (increasing k_{pm}); for $b = \infty$ ($k_{pm} = 0$, curve a) equation (16) reduces to equation (7) so that curve (a) is essentially the same as the lowest curve in Figure 1, while $b = 0$ (curve e) equation (16) reduces to the classical relation (1). For $b = 10^7 \text{ mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{1/2}$ ($k_{pm} = 9.58 \times 10^{-7} k_p$) (curve b) the calculated rates differ insignificantly from those obtained experimentally; deviations occur to an increasing extent with decreasing b (increasing k_{pm}).

The effect of occlusion is to reduce λ ; for purposes of

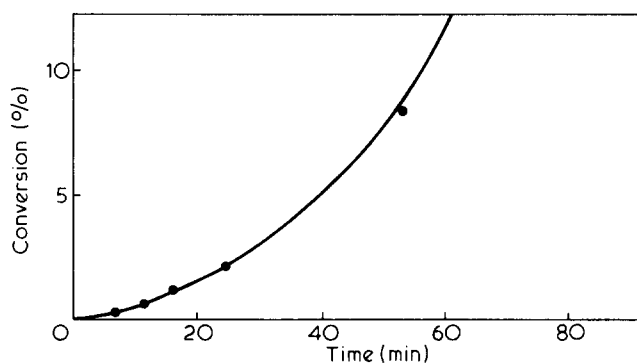


Figure 7 Typical conversion *versus* time curve for bulk polymerization of 1-VIM at 70°C. [Azobis(isobutyronitrile)] = $1.02 \times 10^{-2} \text{ mol dm}^{-3}$

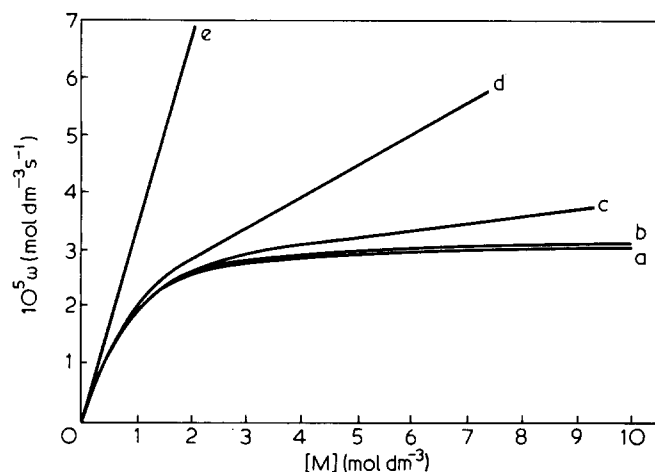


Figure 8 Influence of reinitiation; dependence of ω on $[M]$ calculated from equation (16) for various values of b , with $a^2 = 91.8 \text{ mol dm}^{-3} \text{ s}$, $c = 1.65 \times 10^{-3}$, $J = 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$. Values of b ($\text{mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{1/2}$) (see equation (17)): (a), ∞ ; (b), 10^7 ; (c), 10^6 ; (d), 10^5 ; (e), 0

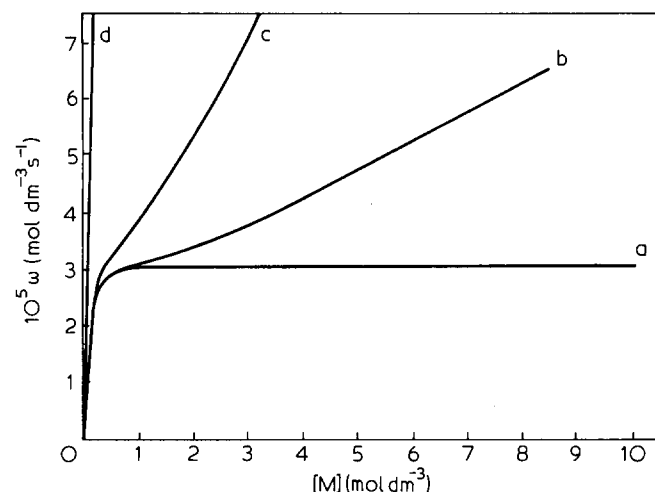


Figure 9 Influence of reinitiation under occlusion conditions; dependence of ω on $[M]$ calculated from equation (16) for various values of b , with $a^2 = 0.918 \text{ mol dm}^{-3} \text{ s}$, $c = 1.65 \times 10^{-3}$, $J = 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$. Values of b ($\text{mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{1/2}$) (see equation (17)): (a), ∞ ; (b), 10^6 ; (c), 10^5 ; (d), 0

illustration we have supposed λ to be reduced by a factor 100. In these circumstances $a^2 = 0.918 \text{ mol dm}^{-3}$ while c remains unaffected, since neither degradative addition nor propagation would be influenced by a relative mild degree of occlusion. Calculated ω versus $[M]$ curves are presented in Figure 9. Comparison with Figure 8 shows that for $b = \infty$ ($k_{pm} = 0$, curve a) the plateau of ω is not changed by occlusion while at low $[M]$, when bimolecular terminations are important, ω is increased strongly, as anticipated. For $b = 10^6 \text{ mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{1/2}$ ($k_{pm} = 9.58 k_p$) the calculated curve (Figure 9, curve b) shows ω increasing markedly with increasing $[M]$ over the whole range examined, without attaining a plateau value. More pronounced changes of the same kind appear with $k_{pm} = 9.58 \times 10^{-6} k_p$ (curve c). We may therefore conclude that a small degree of reinitiation, corresponding to $k_{pm} \sim 10^{-6} k_p$, is without significant influence on the rate of polymerization under non-occlusion conditions, but becomes important and leads to marked kinetic changes when radical occlusion prevails.

It is of interest to estimate the fraction of $X\cdot$ radicals formed which reinitiate under various conditions. This is given by

$$F = \frac{k_{pm}[X\cdot][M]}{k_{fm}[R\cdot][M]} \quad (18)$$

$[X\cdot]$ may be obtained in terms of $[R\cdot]$ by writing the stationary-state equation for reactions (4 iv, vi, viii) then expressing $[R\cdot]$ in terms of ω according to equation (6). The result is

$$F = \frac{1}{1 + k_{trx}\omega/(k_{pm}k_p[M]^2)} = \frac{1}{1 + \omega(ab/[M]^2)} \quad (19)$$

(assuming as hitherto that $k_{trx} = k_t = \lambda$).

F is shown in Figure 10 as a function of $[M]$ for $k_{pm}/k_p = 9.58 \times 10^{-6}$ and 9.58×10^{-7} , for non-occlusion and occlusion conditions ($a^2 = 91.8$ and $0.918 \text{ mol dm}^{-3} \text{ s}$, respectively). In conformity with our previous discussion, the figure indicates that at the lower value of k_{pm} only a minute fraction of the $X\cdot$ formed reinitiates in the absence of occlusion, but the fraction becomes very significant at high $[M]$ when occlusion is present.

Other solvents

Polymerization of 1-vinylimidazole in *N,N*-dimethylformamide solution yields ω versus $[M]$ curves which are rather similar to those obtained in ethanol, although, for given initiator concentration, the rates in DMF are higher. Individual curves may be fitted approximately to an expression of the type (7), but the agreement for a series of different initiator concentrations is unsatisfactory. We have already mentioned that at high monomer concentrations the solution becomes turbid on polymerization; the poor solvent power of DMF for the polymer may well influence the termination reactions and enhance the extent of reinitiation. Qualitatively, however, the approach to a plateau in ω is consistent with the occurrence of degradative chain addition to monomer.

Two features of the polymerization in water solution are of particular interest. First, the ω versus $[M]$ curve, obtained with use of the soluble initiator 4,4'-azobis(4-cyanovaleric acid), has the unusual shape shown in Figure 11, exhibiting a maximum near $[M] = 8.5 \text{ mol dm}^{-3}$. At

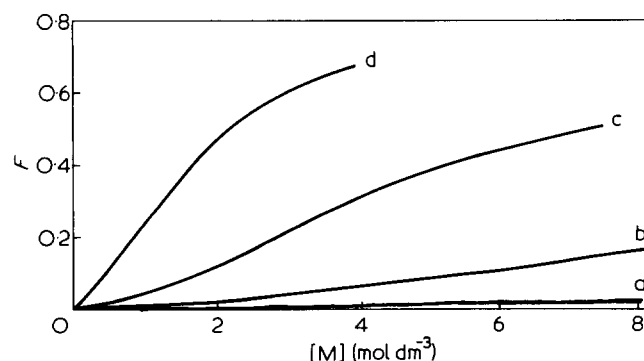


Figure 10 Fraction of $X\cdot$ radicals which reinitiate, calculated from equation (19). Non-occlusion: $a^2 = 91.8 \text{ mol dm}^{-3} \text{ s}$: curve (a), $k_{pm}/k_p = 9.58 \times 10^{-7}$; curve (b), $k_{pm}/k_p = 9.58 \times 10^{-6}$. Occlusion: $a^2 = 0.918 \text{ mol dm}^{-3} \text{ s}$: curve (c), $k_{pm}/k_p = 9.58 \times 10^{-7}$; curve (d), $k_{pm}/k_p = 9.58 \times 10^{-6}$

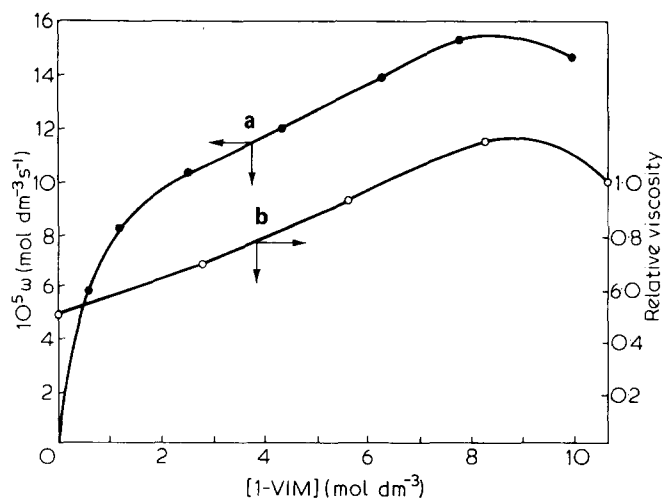


Figure 11 The 1-VIM-water system. (a), Polymerization at 70°C: dependence of ω on [1-VIM]. 10^3 [azobis(4-cyanovaleric acid)] = 7.69×10^{-3} mol dm $^{-3}$. (b), Relative viscosities of 1-VIM-water mixtures

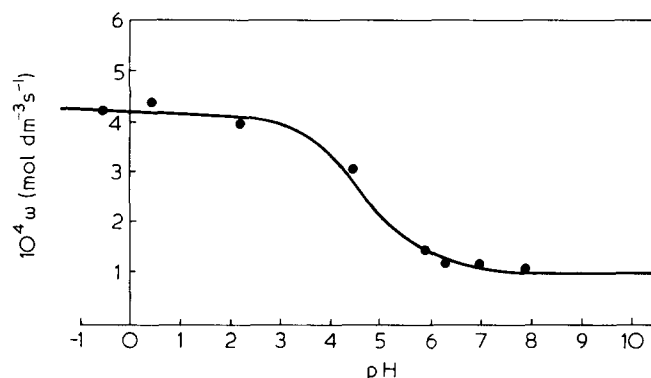


Figure 12 Polymerization of 1-VIM in water at 70°C. Dependence of ω on pH. 10^3 [azobis(4-cyanovaleric acid)] = 7.95×10^{-3} mol dm $^{-3}$; [1-VIM] = 2.2 mol dm $^{-3}$

this point water and monomer are present in approximately equal concentrations. The complex form of the curve may arise in part from the influence of strong monomer-water interactions superimposed on degradative chain addition, the situation resembling that encountered in the polymerization of *N*-vinylpyrrolidone in water reported by Senogles¹². In the present system the reality of such interactions is illustrated by the appearance of a maximum in the viscosity of 1-vinylimidazole-water mixtures at $[M] = 8.5$ mol dm $^{-3}$ (Figure 11). This would influence the termination reactions directly, and would contribute to the maximum in ω ; propagation may also be affected by reactivity changes brought about by complexation of monomer with water. No comparable effects were found with DMF or ethanol as solvent, viscosity changes in these systems being relatively small.

In our view, some of the phenomena noted by Senogles point to the occurrence of degradative chain transfer or addition in his systems.

Secondly, the rate of polymerization in water depends markedly on pH, as shown in Figure 12; the rate assumes constant values at low and high pHs, being higher at the lower pHs, with a transition region extending over pH 3.5–6, approximately. Degrees of polymerization are similarly influenced by pH, as illustrated in Table 2; note

Table 2 Polymerization of 1-VIM in water at 70°C $[M] = 2.2$ mol dm $^{-3}$, [azobis(cyanovaleric acid)] = 7.95×10^{-3} mol dm $^{-3}$. Dependence of $\bar{P}_{n,c}$ (determined viscometrically) on pH

pH	$\bar{P}_{n,c}$
0.8	2518
4.5	1888
7.8	591

that the ratio of the degrees of polymerization at the extremes of pH examined is close to that of the corresponding rates (approximately 4). Since 1-vinylimidazole is protonated at pHs below 4.5 it is most likely that the effects described arise from protonation of the monomer and radicals.

We have already referred to some simplifying consequences of degradative addition. These may be expressed quantitatively by the relations (20), which are classical in form and hold in the absence of transfer.

$$\bar{P}_{n,d} = \omega / \mathcal{J} \quad ; \quad \bar{P}_{n,c} = 2\omega / \mathcal{J} \quad (20)$$

While intuitively obvious, they follow from equations (7) and (13 a, b). Thus for given \mathcal{J} , $\bar{P}_{n,d}$ and $\bar{P}_{n,c}$ are proportional to ω ; as shown in the Appendix the proportionality extends to $\bar{P}_{w,d}$ and $\bar{P}_{w,c}$. These conclusions are clearly consistent with the experimental findings presented in Figure 12 and Table 2. Equation (20) should be valid regardless of the precise origin of the changes in rates and degrees of polymerization. In the present system all the rate coefficients may be affected by protonation, but we consider that the predominant effect is a large decrease in k_{fm} . Protonation at position 3 gives rise to a system strongly stabilized by resonance involving both nitrogen atoms; since the resonance energy would be lost on addition of a radical at position 2 the latter process is strongly suppressed by protonation of the monomer.

In summary, we believe that the experimental data on the polymerization of 1-VIM in aqueous solution are all consistent with degradative addition to monomer.

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APPENDIX

Molecular weight distributions

From scheme (4) we obtain equations (A1)–(A3) for the case in which there is no significant occlusion, i.e. reinitiation is negligible, and concentrations of all reactants are effectively constant. Square brackets, representing concentrations, have been omitted for clarity.

$$\frac{dR_r}{dt} =$$

$$k_p R_{r-1} M - k_p R_r M - k_{fm} R_r M - k_t R_r R \cdot - k_{trx} R_r X \cdot = 0, \quad r > 1. \quad (A1)$$

$$\frac{dR_1}{dt} = \mathcal{J} - k_p R_1 M - k_{fm} R_1 M - k_t R_1 R \cdot - k_{trx} R_1 X \cdot = 0 \quad (A2)$$

$$\frac{dX_r}{dt} = k_{fm} R_{r-1} M - k_{trx} R \cdot X_r = 0, \quad r > 1 \quad (A3)$$

In these equations, as before,

$$R \cdot = \sum_1^{\infty} R_r \cdot, \quad X \cdot = \sum_2^{\infty} X_r \cdot \quad (A4)$$

Note that X_2 is the smallest $X \cdot$ possible, since the $X \cdot$ species are formed by addition of $R_r \cdot$ to M .

From equations (5a, b) we obtain

$$\mathcal{J} - 2k_{fm} R \cdot M - k_t R^2 = 0 \quad \text{and} \quad (A5a)$$

$$X \cdot = \frac{k_{fm} M}{k_{trx}} \quad (A5b)$$

Equations (A1, A2, A3, A5b) yield the relations shown in (A6)

$$\frac{R_r}{R_{r-1}} = \frac{k_p M}{k_p M + 2k_{fm} M + k_t R \cdot} \equiv \frac{k_p M}{\Delta} \quad (A6a)$$

$$R_1 = \frac{\mathcal{J}}{k_p M + 2k_{fm} M + k_t R \cdot} \equiv \frac{\mathcal{J}}{\Delta} \quad (A6b)$$

from which it follows that

$$R_r = \frac{\mathcal{J}}{\Delta} \alpha^{r-1}, \quad (A7)$$

$$X_r = \frac{\mathcal{J} k_{fm} M}{\Delta k_{trx} R \cdot} \alpha^{r-2}, \quad r > 2$$

$$\text{where} \quad \alpha = \frac{k_p M}{k_p M + 2k_{fm} M + k_t R \cdot} \quad (A8)$$

If the termination reactions (4v, vi) both occur by disproportionation, the rate of formation of polymer molecules containing r units is given by equation (A9)

$$\frac{dP_r}{dt} = k_t R_r R \cdot + k_{trx} R_r X \cdot + k_{trx} X_r R \cdot, \quad r > 1 \quad (A9)$$

which, with the aid of equations (A5b, A6a, A7) leads to

$$\frac{dP_r}{dt} = \mathcal{J} (1 - \alpha) \left(1 + \frac{k_{fm}}{k_p} \right) \alpha^{r-1}, \quad r > 1 \quad (A10)$$

Similarly,

$$\begin{aligned} \frac{dP_1}{dt} &= k_t R_1 R \cdot + k_{trx} R_1 X \cdot \\ &= \mathcal{J} \left(1 - \alpha - \frac{k_{fm}}{k_p} \alpha \right) \end{aligned} \quad (A11)$$

Equations (A10), (A11) give the form of the molecular weight distribution. By conventional methods we may derive the following relations for the zeroth, first and second moments.

$$\begin{aligned} \frac{d}{dt} \sum_1^{\infty} P_r &= \mathcal{J} \\ \frac{d}{dt} \sum_1^{\infty} r P_r &= \frac{\mathcal{J}}{1 - \alpha} \left(1 + \frac{k_{fm}}{k_p} \alpha \right) \end{aligned} \quad (A12)$$

$$\frac{d}{dt} \sum_1^{\infty} r^2 P_r = \frac{\mathcal{J}}{(1 - \alpha)^2} \left\{ 1 + \alpha + \frac{k_{fm}}{k_p} \alpha (1 - \alpha) \right\}$$

The number- and weight-average degrees of polymerization deduced from equation (A12) are shown in equations (A13).

$$\bar{P}_{n,d} = \frac{1}{1 - \alpha} \left(1 + \frac{k_{fm}}{k_p} \alpha \right) \quad (A13)$$

$$\bar{P}_{w,d} = \frac{1}{1 - \alpha} \left\{ 1 + \alpha + \frac{k_{fm}}{k_p} \alpha (3 - \alpha) \right\}$$

The corresponding results for the case in which both terminations (4v, vi) are combination processes may be deduced in a similar manner from equations (A5–A8) and are summarized below. For this case

$$\frac{dP_r}{dt} = \frac{1}{2} k_t \sum_{s=1}^{r-1} R_s R_{r-s} + k_{trx} \sum_{s=1}^{r-2} R_s X_{r-s} \quad (A14)$$

Note that for the first and second terms on the right of equation (A14), $r > 1$ and $r > 2$, respectively. Using equation (A7), we deduce from equation (A14), the required distribution (A15).

$$\frac{dP_r}{dt} = \left(\frac{\mathcal{J}}{\Delta} \right)^2 \left\{ \frac{1}{2} k_t (r-1) \alpha^{r-2} + k_{fm} \frac{M}{R \cdot} (r-2) \alpha^{r-3} \right\}, \quad (A15)$$

$r \geq 2$

Relations for the first three moments are presented in equation (A16), and the number- and weight-average degrees of polymerization in equation (A17).

$$\frac{d}{dt} \sum_2^r P_r = \frac{1}{2} \mathcal{J}$$

$$\frac{d}{dt} \sum_2^r r P_r = \frac{\mathcal{J}}{1-\alpha} \left(1 + \frac{k_{fm}}{k_p} \alpha \right) \quad (A16)$$

$$\frac{d}{dt} \sum_2^r r^2 P_r = \frac{\mathcal{J}}{(1-\alpha)^2} \left(2 + \alpha + \frac{k_{fm} M (5-\alpha)}{\Delta} \right)$$

$$\bar{P}_{n,c} = \frac{2}{1-\alpha} \left(1 + \frac{k_{fm}}{k_p} \alpha \right) \quad (A17)$$

$$\bar{P}_{w,c} = \frac{2 + \alpha + k_{fm} M (5-\alpha) / \Delta}{(1-\alpha) \left(1 + \frac{k_{fm}}{k_p} \alpha \right)}$$

When $k_{fm}=0$, equations (A10–13) and equations (A15–17) reduce to their conventional forms. For long chains ($\alpha \rightarrow 1$, $\Delta \rightarrow k_p M$) we see from equations (A13) and (A17) that

$$2\bar{P}_{n,d} = \bar{P}_{n,c} = \bar{P}_{w,d} = \frac{1}{1.5} \bar{P}_{w,c} \quad (A18)$$

These distribution relations were used in developing equations (13) and (14) and in constructing *Figure 6*.

The two cases in which the termination reactions (4v) and (4vi) are different in nature have not been investigated; the appropriate distribution formulae may be derived by methods similar to those presented above, starting from equations (A5–A8).