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Induced decomposition of persulfate by vinyl acetate

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Abstract

A study of the aqueous-phase free-radical chemistry is carried out to elucidate the reactions occurring between vinyl acetate and persulfate in the water phase; an understanding of this process is important for emulsion polymerizations involving vinyl acetate. Oligomeric species are identified using electrospray mass spectrometry. Reactions were performed between water-saturated solutions of vinyl acetate and persulfate at various concentrations, such that extensive oligomer formation occurred. These data, combined with simulations based on established models for the aqueous-phase events leading to radical entry into particles in emulsion polymerizations, suggest that the induced decomposition of persulfate seen at high initiator concentrations arises from transfer to initiator. Negligible induced decomposition of persulfate occurs at concentrations typically employed in emulsion polymerization (1–10 mM). © 2001 Published by Elsevier Science Ltd.

Keywords: Induced decomposition; Persulfate; Vinyl acetate

1. Introduction

Induced decomposition of persulfate has been observed in the presence of many monomers in emulsion polymerization. The existence and magnitude of such an effect has significant implications for the control of the rate, molecular weight distributions and mechanistic understanding of these systems. Morris and Parts [1] deduced pseudo-first-order rate coefficients for the induced decomposition of persulfate at 50°C by 0.05 mol dm^{-3} monomer in aqueous solution, for acrylonitrile, methyl acrylate and vinyl acetate (VAc) as 6.8×10^{-6}, 7.8×10^{-6} and 7.0×10^{-5} s^{-1}, respectively. This compares to 1.4×10^{-6} s^{-1} for persulfate in pure water at that temperature [2], an induced-decomposition increase by a factor of ~50 in the case of VAc. They offered no suggestions as to the mechanism of the induced decomposition or analysis of the products formed. However, they did observe for VAc that, although all the monomer was consumed, no insoluble poly(vinyl acetate) (pVAc) was formed. This suggests the possibility that the mechanism involves solubilized oligomers.

Two mechanisms have been proposed to account for the observed decomposition rates [3]. The first is the cage-complex mechanism involving cage-complex initiation, propagation and termination. The essence of the 'cage-complex mechanism' (reactions (1)–(5)) is that a polar scavenger such as VAc monomer may form a cage around a charged species such as the persulfate anion. It has been argued [3] that the high local concentration of scavenger due to a cage complex may result in the scavenging of tetraoxidosulfate (·1−) radicals ('sulfate' radicals, $SO_4^{-\cdot}$) that would otherwise have undergone geminate recombination.

$$S_2O_8^{2-} + M_{cage} \rightarrow {}^{-}SO_4M^{\cdot} + SO_4^{-\cdot} \quad (1)$$

$$SO_4^{-\cdot} + M_{(cage)} \xrightarrow{k_{p,I}} {}^{-}SO_4M^{\cdot} \quad (2)$$

$k_{p,I} \approx 10^9$ dm^3 mol^{-1} s^{-1} [4] at 50°C.

$$ {}^{-}SO_4M^{\cdot} + M \xrightarrow{k_p^1} {}^{-}SO_4M_2^{\cdot} \quad (3)$$

$k_p^1 \approx 10^4$ dm^3 mol^{-1} s^{-1} at 50°C.

$$ {}^{-}SO_4M_i^{\cdot} + M \xrightarrow{k_p^i} {}^{-}SO_4M_{i+1}^{\cdot} \quad (4)$$

$k_p^i \approx 6.7 \times 10^3$ dm^3 mol^{-1} s^{-1} at 50°C [5].

$$SO_4M_m^{\cdot} + {}^{-}SO_4M_n^{\cdot} \rightarrow {}^{-}SO_4M_{m+n}SO_4^{-} \quad (5)$$

In this scheme, the value of k_p^1 is estimated from the long chain k_p and arguments based on transition state quantum calculations [6] which suggest that k_p^1 is expected to be several times the long-chain k_p. There is also indirect evidence from model compounds [7] and empirical fits to experimental data (initiator efficiency in the persulfate/styrene system [8] and

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molecular weight distributions in PLP experiments [9,10]) that support this view.

The second proposed mechanism is reduction by aqueous-phase oligomeric radicals, in effect transfer to initiator (reaction (6)) to which we will return later.

The aim of the present paper is to characterize the oligomers formed under the conditions of the experiment of Morris and Parts (polymerization of a saturated solution of monomer in water with a high concentration of persulfate initiator) using characterization techniques (particularly, electrospray mass spectrometry) and mechanistic knowledge that were not available when this early work was performed. Electrospray mass spectroscopy (EMS) is a mild ionization technique whereby a dilute, somewhat volatile solution is discharged as a fine spray from a charged (~5 kV) capillary. In this process, the droplets acquire a net charge and, as the solvent evaporates, the charge concentrates, charged molecules are ejected and the mass spectra acquired. The decomposition rate data of Morris and Parts are then fitted to a model to yield an estimate of the rate coefficient for transfer to initiator ($k_{\mathrm{tr,I}}$). Using this value for $k_{\mathrm{tr,I}}$, the model then predicts a molecular weight distribution for the oligomers so formed which is compared to that measured with EMS.

2. Inapplicability of the cage-complex mechanism

The cage-complex mechanism proposed by Sarkar [3] produces two 'extra' radicals (over and above those produced by thermolysis of persulfate) for each induced decomposition. However, several observations argue against this mechanism.

1. *Polymerization rate independent of aqueous-phase monomer concentration*: Sarkar [3] argued that a cage complex should give a radical production rate proportional to $[\mathrm{M_{aq}}]^{1.5}[\mathrm{S_2O_8^{2-}}]^{0.5}$, where $[\mathrm{M_{aq}}]$ is the aqueous-phase concentration of monomer. If this were the case, then one would expect the polymerization rate, R_p, to decrease with decreasing $[\mathrm{M_{aq}}]$ during Interval III (that period in an emulsion polymerization where there is no separate monomer phase). However, as has often been noted in the literature, the emulsion polymerization of VAc is remarkable in that R_p is very nearly constant throughout most of Interval III [11,12].
2. *No 'extra radicals'*: Insight into the possibility of extra radical production implied by the cage-complex mechanism can be obtained from the polymerization rate in a vinyl acetate emulsion polymerization for a range of initiator types and radical concentrations. For this purpose, a series of ab initio (unseeded) emulsion polymerizations of vinyl acetate at 50°C were performed with a range of concentrations of persulfate initiator, and also with gamma-radiolysis initiation with a range of radiation fluxes. Rates were monitored using automated dilatometry; after the cessation of the induction period and particle formation, there is an extensive period of constant rate in both Intervals II and III (presence and absence of monomer droplets).

   (a) Consider first this rate in the persulfate-initiated system. The 'Maxwell–Morrison' mechanism for the entry of radicals into latex particles [13], applicable to such a system, is that the rate-determining steps for entry are aqueous-phase propagation and termination until a surface-active oligomeric radical of degree of polymerization z is formed, whereupon entry always occurs; there is extensive experimental evidence for this mechanism in anionically stabilized systems with persulfate initiator [11]. This mechanism implies that it is likely that vinyl acetate has a very high entry efficiency (>99%) in persulfate-initiated polymerization (i.e. insignificant termination of aqueous-phase oligomeric radicals under normal emulsion polymerization conditions); this is because the propagation rate coefficient of vinyl acetate [14] is high, and hence a z-mer is formed so quickly that aqueous-phase termination of smaller degrees of polymerization is kinetically insignificant (this is in contrast to the low efficiency of persulfate in styrene, for reasons that are well understood [13]).

   (b) In gamma-initiated systems, the initiating species are $\mathrm{H^{\cdot}}$, $\mathrm{OH^{\cdot}}$ and an aquated electron [15], and the lower solubility of the aqueous-phase oligomeric radicals thus formed (compared to those initiated by persulfate) suggests an even higher entry efficiency for gamma-initiated VAc oligomers.

Methods for calculating primary-radical production rates for a given concentration of persulfate and of gamma dose are well established [13,15]. With all else being equal (particle number, temperature, monomer concentration, etc.), equal radical production rates would be expected to result in equal R_ps. Fig. 1 shows observed steady-state rates as a function of radical production rate for persulfate and for gamma-radiolysis initiation. These data suggest that indeed the same radical production rate gives the same polymerization rate, independent of the initiator type. Consequently, there does not appear to be a significant contribution to radical production from induced decomposition of persulfate.

Thus, it seems that the cage-complex mechanism can be discounted, at least in the case of VAc-accelerated decomposition of persulfate, and the remainder of this paper will focus on the reductive transfer mechanism.

Reductive transfer probably occurs via a mechanism equivalent to that reported for the acrylonitrile-radical

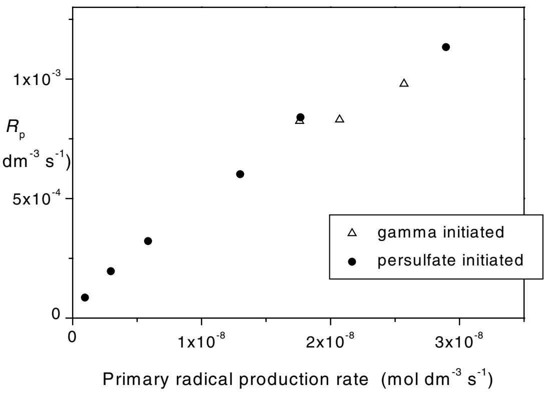

Fig. 1. Observed R_p (rate of monomer loss per liter of continuous phase), initiated by γ and persulfate at 50°C for vinyl acetate ab initio emulsion polymerization, as a function of primary radical production rate. Primary radical production rate calculated for γ initiation as described by O'Donnell and Sangster [15] and for persulfate as $2k_d[\mathrm{I}]$, using $k_d = 1.4 \times 10^6$ s^{-1} (with the initiating species being $SO_4^{-\bullet}$).

induced decomposition of persulfate [16]:

$$\begin{aligned} {}^{-}SO_4M_n\bullet + S_2O_8^{2-} &\xrightarrow{k_{tr,I}} {}^{-}SO_4M_nSO_4^{-} + SO_4^{\bullet-} \\ &\qquad\qquad M_{aq} \downarrow k_{p,I} \\ &\qquad {}^{-}SO_4M\bullet \xrightarrow{M_{aq}} \xrightarrow{M_{aq}} \xrightarrow{M_{aq}} {}^{-}SO_4M_i\bullet \end{aligned} \tag{6}$$

As can be seen in reaction (6), the reductive transfer mechanism consumes persulfate but generates no 'extra' radicals (consistent with the constant R_p observed in Interval III). Rather, it produces aqueous-phase oligomers. As is shown below, electrospray mass spectra obtained on the oligomers so formed (Fig. 2, Table 1) are consistent with this mechanism and the model developed to simulate the system.

3. Materials and methods

VAc was obtained from Aldrich inhibited with 35 ppm hydroquinone. The inhibitor was removed on a column of basic alumina. The monomer was distilled under argon at 25°C and 60 mmHg with the first and last 20% being discarded. The monomer was either used immediately or stored overnight at 4°C.

3.1. Solution polymerization of VAc in water

In this series of experiments, a solution polymerization of VAc in water is carried out, and the products analyzed by electrospray mass spectrometry.

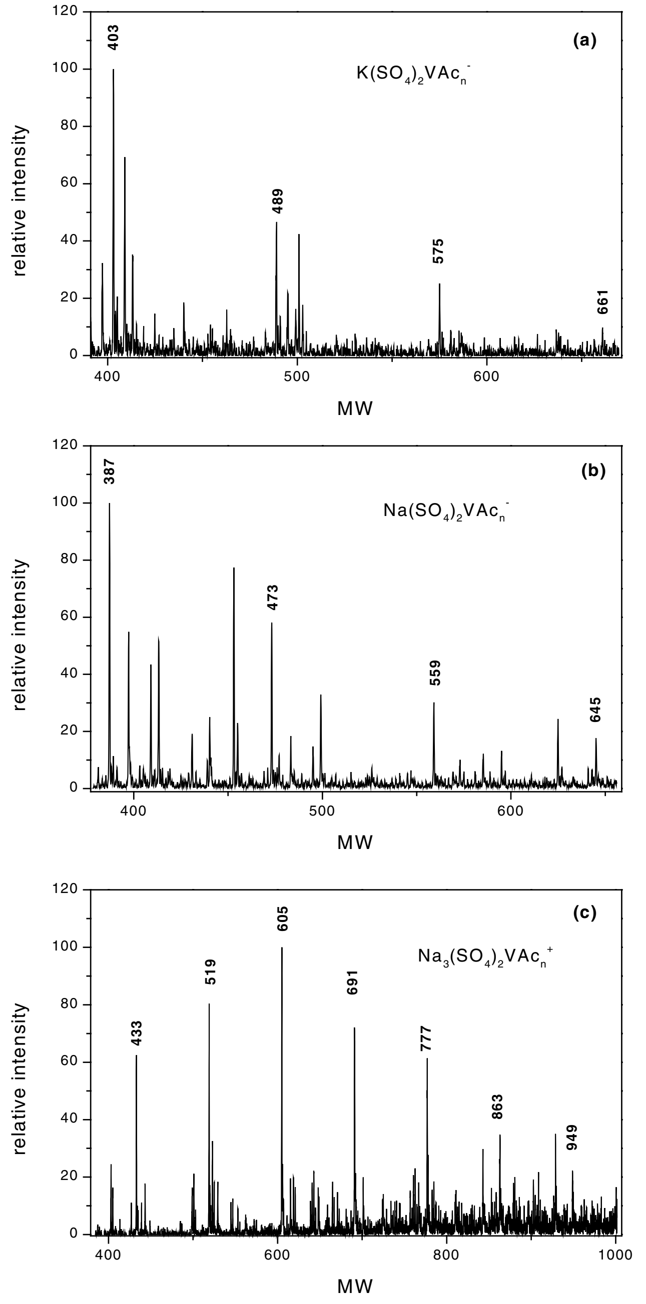

Fig. 2. (a) Electrospray mass spectrum of oligomers produced in experiment 1, (b) effect of changing counterion and (c) effect of doubling monomer concentration.

(a) Potassium persulfate obtained from Aldrich (AR grade) and recrystallized from water/ethanol was dissolved in Milli-Q water (18.2 MΩ cm^{-1}) at 50°C. To a solution (7.68 g in 250 ml water to give $[S_2O_8^{2-}] = 0.10$ mol dm^{-3}) was added potassium dihydrogenphospate (4.26 g) and potassium hydroxide (1.31 g) used as obtained from Aldrich (AR grade) to buffer the solution to pH 7.00. The water had been previously de-oxygenated by bubbling high-purity argon through for 2 h. VAc was added (1.2 g) and the solution held at 50°C under argon with stirring for 90 min. After this time, a persistent froth formed on shaking (suggesting the presence of surface-active species) and there was no smell of residual monomer. The crude oligomer solution was characterized by EMS (Fig. 2a).

Table 1
Calculated series of peaks in electrospray spectra. Numbers in italics correspond to peaks identified in spectra

	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
$K(SO_4)_2VAc_n^-$	317	*403*	*489*	*575*	*661*	747	833	919
$K_3(SO_4)_4VAc_n^+$	395	*481*	*567*	*653*	*739*	*825*	*911*	*997*
$Na(SO_4)_2VAc_n^-$	301	*387*	*473*	*559*	*645*	731	817	903
$Na_3(SO_4)_4VAc_n^+$	347	*433*	*519*	*605*	*691*	*777*	*863*	*949*

For EMS, samples of the oligomer solutions were dissolved in 50:50 methanol/H_2O and fed into the electrospray ionization unit at 0.2 ml min^{-1}. The spectra were obtained on a Finnigan Mat LCQ MS Detector with Finnigan LCQ Data Processing and Instrument Control Software; the ESI spray voltage was 5 kV, the sheathing gas was nitrogen at 60 psi and the heated capillary temperature was 200°C.

(b) In a second experiment, experiment (a) was repeated, except that sodium salts were used instead of potassium salts in order to determine the nature and number of cations attached to the oligomers detected in the electrospray/MS. The negative ion spectrum was found to be shifted downwards by 16 daltons corresponding to the substitution of one potassium by one sodium atom (Fig. 2b). Similarly, the positive ion spectrum was shifted downwards by 48 daltons corresponding to the substitution of three potassium atoms by three sodium atoms (Table 1).

(c) This was the same as experiment (a) except that less potassium persulfate was used, to give $[I] = 0.022$ mol dm^{-3}. In this experiment, a latex formed (also seen by Dunn [17]), presumably stabilized by the large number of surface-active oligomers formed under these conditions, consistent with the predictions using the simulation described below.

(d) This is the same as experiment (a) except that the monomer concentration was doubled (Fig. 2c). This had the predicted effect of approximately doubling the degree of polymerization of the aqueous-phase oligomers.

(e) This is the same as experiment (a) except that the monomer concentration was increased to 0.3 mol dm^{-3}. As in experiment (c), a latex formed, as predicted by the simulation described below.

4. Results and discussion

The kinetics of this system were modeled assuming the reductive transfer mechanism for induced decomposition. The simulation was then fitted to Morris and Parts' data in order to estimate a value for the rate coefficient for the induced decomposition of persulfate.

4.1. Simulation of oligomer distributions

The general approach used here is the model developed by Maxwell et al. [13] for entry of radicals into particles in emulsion polymerization. This comprises the following processes:

$$I - I \xrightarrow{k_d} 2I^{\bullet} \tag{7}$$

$$I^{\bullet} + M \xrightarrow{k_{p,I}} IM^{\bullet} \tag{8}$$

$$IM_i^{\bullet} + M \xrightarrow{k_{p,aq}^{i}} IM_{i+1}^{\bullet} \tag{9}$$

$$IM_i^{\bullet} + T^{\bullet} \xrightarrow{k_{t,aq}} \text{insert products}, \qquad i < z \tag{10}$$

$$IM_z^{\bullet} + \text{latex particle} \xrightarrow{\rho} \text{entry} \tag{11}$$

In this model, I is the initiator fragment (in this case $SO_4^{-\bullet}$) and z the degree of polymerization at which aqueous-phase oligomeric radicals are assumed to attain sufficient surface activity such that they irreversibly enter a particle and so are lost from the aqueous phase. However, at high initiator concentrations, such as the conditions of Morris and Parts' experiment, there may be no particle formation and aqueous-phase oligomeric radicals are lost via bimolecular termination (reaction (10)) and via transfer to initiator (reaction (6)). Hence, for the purpose of the following discussion, the definition of z will be broadened slightly to the degree of polymerization above which a negligible proportion of aqueous-phase oligomeric radicals grows, either because the radicals terminate in the aqueous phase or enter a particle.

The simulation was based on reactions (6)–(11) giving the following set of differential equations:

$$\frac{d[M_1^{\bullet}]}{dt} = 2k_d[S_2O_8^{2-}] + k_{tr,I}\sum_{i=2}^{z-1}[M_i^{\bullet}][S_2O_8^{2-}] - k_p^1[M_{aq}][M_1^{\bullet}] - k_{t,aq}[M_1^{\bullet}][T^{\bullet}] \tag{12}$$

where k_p^1 is the propagation rate coefficient for monomeric radicals with the formula $^{\bullet}MSO_4^-$, $k_{tr,I}$ the rate coefficient for transfer to initiator, $[M_1^{\bullet}]$ the concentration of aqueous-phase oligomeric radicals with degree of polymerization of one, $[M_i^{\bullet}]$ the concentration of aqueous-phase oligomeric radicals with degree of polymerization i and $[T^{\bullet}]$ the total aqueous-phase radical concentration.

There is no term in Eq. (12) for radical loss resulting from induced decomposition by $^{\bullet}MSO_4^-$. Those radicals lost in step one of reaction (6) (with $n = 1$) are immediately replaced in step two, as $k_{p,I} \approx 10^9$ dm^3 mol^{-1} s^{-1} is very high [4], and $[M_{aq}]$ is typically greater than, say, 0.05 mol dm^{-3} for VAc. Further propagation is expressed as

$$\frac{d[M_i^\cdot]}{dt} = k_p[M_{aq}][M_{i-1}^\cdot] - k_p[M_{aq}][M_i^\cdot] - k_{t,aq}[M_i^\cdot][T^\cdot] - k_{tr,I}[M_i^\cdot][S_2O_8^{2-}], \qquad i = 2,\dots,z-1 \tag{13}$$

No allowance was made in the simulation for solvent effects on k_p or chain length dependence of k_p, as these variables have not been quantified and, though they may have a significant effect on the average degree of polymerization of the oligomers, they have a negligible effect on the rate of induced decomposition. Applying the steady-state assumption yields the following:

$$[M_1^\cdot] = \left(2k_d[S_2O_8^{2-}] + k_{tr,I}\sum_{i=2}^{z-1}[M_i^\cdot][S_2O_8^{2-}]\right)\Big/\left(k_p[M_{aq}] + k_{t,aq}[T^\cdot]\right) \tag{14}$$

$$[M_i^\cdot] = k_p[M_{aq}][M_{i-1}^\cdot]/(k_p[M_{aq}] + k_{t,aq}[T^\cdot] + k_{tr,I}[S_2O_8^{2-}]), \qquad i = 2,\dots,z-1 \tag{15}$$

Eqs. (14) and (15) were solved numerically (by iteration from an initial guess) for the conditions of experiment (a). Considering that aqueous-phase termination in this system is between small species, an average value of $k_{t,aq} = 5 \times 10^8$ dm^3 mol^{-1} s^{-1} was deemed reasonable. Adjusting $k_{tr,I}$ to give accord with the induced decomposition rate determined by Morris and Parts gives a value of 3×10^3 dm^3 mol^{-1} s^{-1} for $k_{tr,I}$ which is comparable to the value of 5×10^3 dm^3 mol^{-1} s^{-1} reported for the acrylonitrile/persulfate system [16].

The probability of an *i*-meric aqueous-phase radical terminating is given by

$$P_{term}^i = \frac{k_{t,aq}[M_i^\cdot][T^\cdot] + k_{tr,I}[M_i^\cdot][S_2O_8^{2-}]}{k_{t,aq}[M_i^\cdot][T^\cdot] + k_{tr,I}[M_i^\cdot][S_2O_8^{2-}] + k_{p,aq}^i[M_i^\cdot][M_{aq}]} \tag{16}$$

where $k_{p,aq}^i$ is the propagation rate coefficient for an aqueous-phase *i*-mer. From the simulation, $[T^\cdot] < 2 \times 10^{-8}$ mol dm^{-3} and so, for any reasonable value of $k_{t,aq}$ one has

$$k_{tr,I}[M_i^\cdot][S_2O_8^{2-}] \gg k_{t,aq}[M_i^\cdot][T^\cdot] \tag{17}$$

Hence, Eq. (16) simplifies to

$$P_{term}^i \cong \frac{k_{tr,I}[S_2O_8^{2-}]}{k_{tr,I}[S_2O_8^{2-}] + k_{p,aq}^i[M_{aq}]} \tag{18}$$

Eq. (18) presents a more comprehensible physical picture of the important events that determine whether aqueous-phase oligomeric radicals will grow to a length that will confer sufficient surface activity to induce particle formation. Clearly, decreasing initiator concentration and/or increasing monomer concentration would be expected to increase the average degree of polymerization of the aqueous-phase oligomers.

4.2. Electrospray mass spectroscopy

The expectation of a high incidence of termination of relatively small oligomers from the foregoing theoretical discussion is supported by the lack of polymer formed in experiments (a) and (b). Fig. 2 is of typical electrospray spectra obtained on crude oligomer solutions. The results of electrospray mass spectrometry are presented in Table 1.

In electrospray/MS, the abscissa is *M*/*Z* (where *M* is the molecular weight and *Z* the charge on the species hitting the detector). Hence the ^{13}C isotope peak increment is 1/*Z*; as this is 1 dalton for this system, the charge on the ionic species being detected is unity and the oligomers appear in the spectrum at their actual molecular weight. Electrospray negative and positive ion mass spectra peaks were assigned to $K(SO_4)_2(VAc)_n^-$, $Na(SO_4)_2(VAc)_n^-$, $K_3(SO_4)_4(VAc)_n^+$ and $Na_3(SO_4)_4(VAc)_n^+$, as detailed in Table 1.

The average degree of polymerization of the oligomers produced under the conditions of Morris and Parts, as determined by EMS, is about 3. This is higher than the average degree of polymerization predicted by the simulation: given the assumed value of $k_{t,aq} = 5 \times 10^8$ dm^3 mol^{-1}s^{-1}, the simulation predicts an average degree of polymerization of 2 (Fig. 3).

This relatively minor discrepancy might partly be due to the simulation not taking into account the higher values of k_p^i for small *i* (especially for $i = 1$). The absence of 1-mers in the spectra may well be attributed to k_p^1 being significantly larger than k_p, an interesting observation in its own right. The effect of a large k_p^1 would be to increase the overall

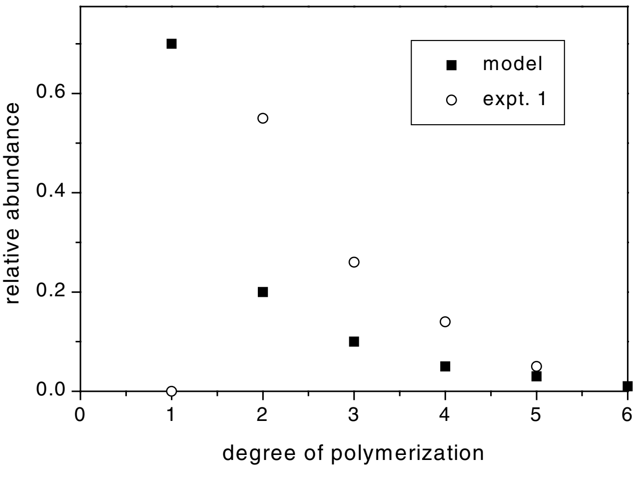

Fig. 3. Distribution of observed and calculated degree of polymerization of oligomers produced under the same conditions as those of Morris and Parts [1], $[S_2O_8^{2-}] = 0.1$ mol dm^{-3}, 50°C, $[M_{aq}] = 0.05$ mol dm^{-3}, experiment 1.

degrees of polymerization predicted by the simulation by unity — resulting in an extremely good fit to the data. Also, the decrease in [I] during the experiment and bimolecular termination by combination will tend to increase the degree of polymerization.

The Maxwell–Morrison model [13] includes an approximate relation for the critical degree of polymerization for entry:

$$z = 1 + \frac{-23\ \text{kJ mol}^{-1}}{RT\ \ln[\text{M}_{\text{aq}}^{\text{sat}}]} \tag{19}$$

where $[\text{M}_{\text{aq}}^{\text{sat}}]$ is the (saturation) solubility of monomer in the aqueous phase. If it is assumed that sufficient surface activity to guarantee entry of a singly anionically charged oligomeric radical is only attained with a degree of polymerization greater than about 8, as predicted by Eq. (19) for VAc, where $[\text{M}_{\text{aq}}^{\text{sat}}] = 0.3\ \text{mol dm}^{-3}$, then it seems reasonable to suggest that the aqueous-phase oligomers terminated by transfer to initiator will remain soluble with degrees of polymerization up to about 16, as they will include two anionic sulfate groups. Such doubly charged oligomers with degrees of polymerization less than about 16 would not be expected to support micellar nucleation. Furthermore, as can be seen in the electrospray spectra (Fig. 2), no oligomers approaching the size of a j_{crit}-mer are formed: the same reasoning, leads to Eq. (19), suggests that the critical degree of polymerization where precipitation of an oligomer occurs is given by [13]

$$j_{\text{crit}} = 1 - \frac{55\ \text{kJ mol}^{-1}}{RT\ \ln[\text{M}_{\text{aq}}^{\text{sat}}]} \tag{20}$$

for which VAc gives $j_{\text{crit}} \sim 18$. Hence, no droplet, micellar or homogeneous nucleation is possible and this explains why no latex formed under Morris and Parts' conditions.

Fig. 4 shows the dependence of the predicted distribution of oligomers as a function of initiator concentration. Clearly, at initiator concentrations less than about $0.04\ \text{mol dm}^{-3}$ (depending on the actual degree of polymerization at which surface activity is attained) a significant number of surface-active aqueous-phase oligomers and j_{crit}-mers can be expected. This is consistent with the formation of latexes (either by micellar and/or homogeneous nucleation) observed in experiments (c) and (e).

While these data are in semi-quantitative agreement with the predictions of Eqs. (19) and (20), they are certainly not definitive. It is noted that other types of experiments designed to gather such evidence, based on spin traps [18–20], have also supported the approximate validity of these semi-empirical expressions.

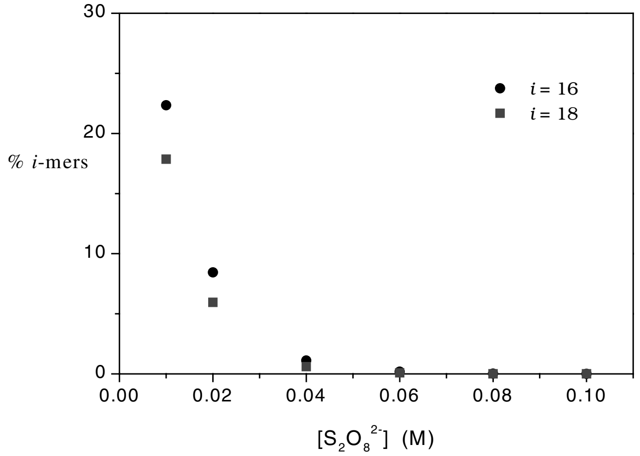

Fig. 4. Calculated proportion of aqueous-phase oligomers that grow to *i*-mers, or greater, as a function of initiator concentration and *i*, the degree of polymerization. Simulation based on Eqs. (14), (15) and (18) using $k_{\text{tr,I}} = 3 \times 10^3\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, 50°C, $[\text{M}_{\text{aq}}] = 0.05\ \text{mol dm}^{-3}$.

5. Conclusions

Experiments designed to elucidate the reason for the accelerated decomposition of persulfate by vinyl acetate monomer were based on noting that comparisons of R_{p} for chemical and radiation-induced emulsion polymerizations suggest that induced decomposition of persulfate by VAc produces no more radicals than that calculated for the thermal decomposition of persulfate. Therefore, it seems likely that the mechanism for induced decomposition is simply transfer to initiator.

Modeling of the system based on this premise, and using rate parameters fitted to the data of Morris and Parts, semi-quantitatively predicts (a) the formation of surfactant-free latexes from aqueous solutions of VAc at persulfate concentrations below about $0.02\ \text{mol dm}^{-3}$ and also (b) the absence of polymer at higher persulfate concentrations. Electrospray mass spectrometric analysis of the aqueous-phase species formed in these systems supports this supposition, and also is in semi-quantitative accord with semi-empirical expressions for the critical degrees of polymerization for entry and for homogeneous nucleation [13]. The rate coefficient for the induced decomposition of persulfate by VAc aqueous-phase oligomeric radicals, $k_{\text{tr,I}}$, was calculated from an empirical fit to the data of Morris and Parts [1] as $3 \times 10^3\ \text{dm}^3\ \text{mol}^{-1}\text{s}^{-1}$. This value of $k_{\text{tr,I}}$ suggests that negligible induced decomposition of persulfate occurs at concentrations typically employed in emulsion polymerization (1–10 mM).

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