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Emulsion Polymerization of Vinyl *neo*-Decanoate, a “Water-Insoluble” Monomer

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ABSTRACT: Rate and particle size data for the emulsion polymerization of vinyl *neo*-decanoate, where inhibitor/retarder effects are obviated through rigorous purification, can be quantitatively fitted by conventional mechanisms for particle formation and growth, even though the monomer has a very low water solubility. These mechanisms are (1) radical entry is by an oligomeric radical (z-mer) arising from aqueous-phase propagation at a critical degree of polymerization (z between 1 and 2 for this monomer) where the species becomes surface-active, (2) radical loss is by transfer to a species which desorbs into the aqueous phase and eventually terminates (after reentry into another particle) rather than undergoing further propagation, and (3) particle formation is by a z-mer entering a micelle. These hypotheses are consistent with γ relaxation data which give direct information on radical loss.

Introduction

While the dominant mechanisms for particle formation and growth in conventional emulsion polymerizations are moderately well understood,[1] other mechanisms may replace these events for monomers of very low water solubility, above and/or below the critical micelle concentration,[2,3] since many of the mechanistic steps in conventional systems involve aqueous-phase monomer.[4,5] For example, radical activity in particles starts with entry from the aqueous phase; one of the fundamental mechanistic tenets of conventional emulsion polymerization is that entry occurs by propagation of an initiator-derived radical in the water phase until it reaches a critical degree of polymerization z such that it irreversibly enters a particle to propagate therein.[6] The value of z is related to the solubility of monomer in water[6] (eq 3) and for example with persulfate as initiator is ∼2−3 for styrene and ∼4−5 for methyl methacrylate. If the monomer is of very low water solubility, there could well be difficulties in this mechanism being able to provide a sufficient radical flux into particles to sustain a reasonable reaction rate. On the other hand, when such oligoradicals enter particles, they will have a low probability of exiting, so termination may also be restricted. The determination of the applicability of this conventional mechanism, and of a value for z, is thus a critical facet of the mechanism of initiation and growth for such systems.

Vinyl *neo*-decanoate (VnD) is an important industrial hydrophobic monomer used in manufacturing latexes for water-borne coatings.[7] The commercial monomer is a mixture of isomers of formula $CH_2CHOCOCCH_3RR'$, where the total number of carbons in R and R′ is 7. The water solubility of the monomer has been reported[8] as ≈4×10^{-5} M at 50 °C. Data have been obtained by Balic[8] for rates and particle sizes of the ab initio (unseeded) emulsion polymerization of this low water solubility monomer, with sodium persulfate (NaPS) as initiator at 50 °C. It was found that the emulsion polymerization kinetics could be strongly influenced by inhibitor and retarder effects; however, if the monomer was rigorously purified by reaction−distillation[9] (polymerization to ∼25% conversion followed by distillation), then significant retardation effects were absent. A clear steady state in the polymerization rate was observed for ∼3×10^4 s for [NaPS] = 0.9 mM to ∼1×10^4 s for [NaPS] = 4.7 mM; the rates for the highest concentration of NaPS showed a maximum rather than a steady state, but these maximum values clearly lie on a smooth curve with the steady-state values for lower [NaPS], as shown in Figure 1.

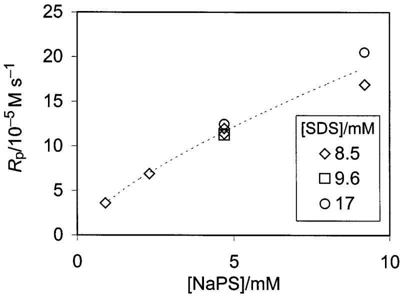

Figure 1. Points: observed dependence of steady state or maximum polymerization rate in ab initio emulsion polymerization of VnD with persulfate initiator, as a function of initiator concentration, for various concentrations of SDS, at 50 °C; data from Table 1. Line is empirical fit $R_p/10^{-5}$ M s^{-1} = 3.88×10^{-5}([NaPS]/mM)$^{0.71}$.

The observation of a steady state is consistent with either (a) a system undergoing interval II emulsion polymerization (polymerization in particles in the presence of monomer droplets, with a constant particle number) and/or a system in both intervals II and III (interval III is the absence of monomer droplets and a constant particle number) obeying limit 2b kinetics,[1] as discussed below.

It is the objective of this paper to see whether these data (Table 1) can be fitted by conventional emulsion polymerization mechanisms.

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Table 1. Observed[8] Steady-State Interval II Rates (R_p) and Particle Concentrations (N_c) for VnD Emulsion Polymerization at 50 °C, for Varying Concentrations of Initiator (Sodium Persulfate, NaPS) and Surfactant (Sodium Dodecyl Sulfate, SDS); Monomer Was Purified by Reaction–Distillation[11] [a]

run	[SDS],[b] mM	[NaPS],[b] mM	R_p [b] 10^{-5} M s^{-1}	particle diam,[b] nm	final solids,[b] g dm^{-3}	N_c,[b] 10^{-17} dm^{-3}	$\bar{n}$
1	8.5	0.9	3.6	150	231	1.9	0.010
2	8.5	2.3	6.9	155	196	1.5	0.024
3	8.5	4.7	12	125	226	3.3	0.019
4	8.5	4.7	11.4	131	236	3	0.020
5	8.5	9.2	16.9	123	233	3.7	0.024
6	9.6	4.7	11.3	95	120	3.4	0.017
7	17	4.7	12.5	96	239	7.8	0.008
8	17	9.2	20.5	102	244	6.7	0.016

[a] Note: run 6 commenced with approximately half the monomer of runs 1–5, 7, and 8. Slight variation in final solids due to variation in final conversions. [b] From ref 8.

Theory

The rate, R_p, in an emulsion polymerization is given by

$$R_p = -\frac{dn_M}{dt} = k_p[M]_p\bar{n}\frac{N_c}{N_A} \quad (1)$$

where n_M is the number of moles of monomer per unit volume of aqueous phase, k_p the propagation rate coefficient, $[M]_p$ the monomer concentration in particles, $\bar{n}$ the average number of radicals per particle, N_c the number of particles per unit volume of aqueous phase, and N_A Avogadro's constant. The particle size (as unswollen particle radius r_{us}) is trivially related to particle number by

$$N_c = \frac{m_p}{{}^4/_3\pi r_{us}{}^3 d_p} \quad (2)$$

where m_p is the initial mass of polymer (as dried weight of seed latex) per unit volume of the aqueous phase and d_p the density of polymer. It is convenient to use N_c rather than r_{us} when comparing models with experiment. (Nucleation models are set out in terms of particle number which depends only on the kinetics, while particle size has an additional trivial dependence on the amount of monomer m_p present in the system.) The rate data of Balic[8] (Table 1) can be converted to $\bar{n}$ using eq 1 and the value of $k_p = 5.3 \times 10^3$ M^{-1} s^{-1} at 50 °C as measured by pulsed-laser polymerization.[10]

The two observables in the data of Table 1 are the steady-state rate (equivalent to $\bar{n}$) and the particle number N_c. Models for these quantities will now be considered.

Average Number of Radicals per Particle. The data of Table 1 show that all $\bar{n}$ values are $\ll {}^1/_2$, which is a necessary (but by no means sufficient) condition that the system may obey "zero-one" kinetics. This is when entry of a radical into a particle already containing a growing chain results in instantaneous termination; it is noted that small values of $\bar{n}$ can be also obtained in a system following "pseudo-bulk" (rather than zero-one) kinetics, where termination is rate-determining.[1]

The "zero-oneness" issue can be theoretically resolved by calculating the probability of an entering radical terminating in the presence of a long-chain radical, following the method derived by Maeder and Gilbert.[11] This calculates the termination rate between an *i*-meric radical and a long radical using established models (based on diffusion theory) and parameter values.[12–14] Results for the cumulative probability of an entering radical not terminating, using the formulas derived in ref 11 and rate parameters given in the present paper, are shown in Figure 2. The calculation was performed for two different assumed values for k_p^1 (the propagation rate coefficient for a monomeric radical): (1) $k_p^1 = k_p$ (the long-chain value) and (2) $k_p^1 = k_p/100$; the latter small value is to mimic the behavior assumed appropriate for a monomeric radical resulting from transfer that is relatively stable to propagation. It can be seen (Figure 2) that a small value of k_p^1 implies that instantaneous termination is probable for a reentering radical in a particle that already contains another radical. The value of k_p^1 for a species such as $^{\bullet}MSO_4^-$ (a 1-mer initiated with persulfate, discussed further below) is unknown, and surface-anchoring effects (a possible effect of the SO_4^- chain end being attached to the surface) may reduce the probability that it terminates rapidly with a preexisting radical inside the particle. However, because transfer to a propagating species is a rapid event in this system (see below), then although an entering *z*-meric radical might not undergo instantaneous termination on entering a particle containing a growing chain, termination will nevertheless be extremely rapid, perhaps after several transfer events. A value of the transfer rate coefficient to monomer, k_{tr}, has been reported[8] as 4 M^{-1} s^{-1} for VnD at 50 °C using the number molecular weight distribution method,[15] with appropriate account taken of branching. The

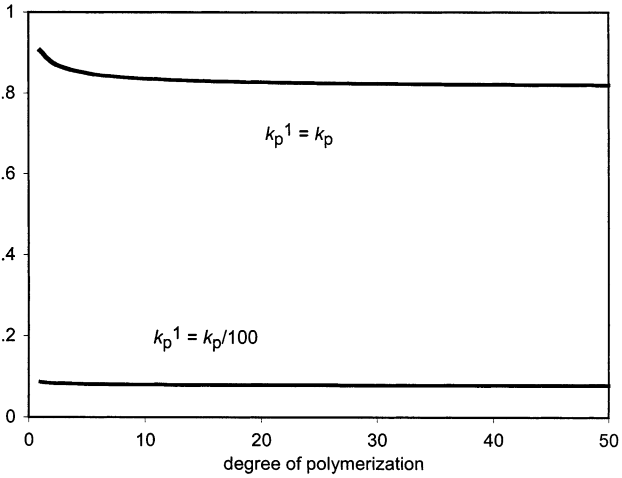

Figure 2. Calculated probability that a radical of degree of polymerization *i* will not have terminated after entering as monomeric radical into a particle containing a long growing chain. Calculations performed with two different values of k_p^1 (the rate coefficient for propagation of a monomeric radical) using parameters appropriate for the VnD examined here, with the diffusion model for the chain-length-dependent termination rate coefficient.

results of Figure 2 suggest therefore that termination is likely within about 1 s, and thus zero-one kinetics are applicable to this system.

The rate data of Table 1 show that R_p is approximately independent of particle number for a given initiator concentration, i.e., approximately independent of particle size. This is consistent with limit 2b zero-one kinetics of emulsion polymerization,[1] whereby a monomeric radical resulting from transfer to monomer goes from particle to particle by desorption and reentry until it eventually enters a particle containing a growing radical, whereupon it undergoes very rapid bimolecular termination. This supposition requires that a radical resulting from transfer is relatively stable to propagation and for simplicity can be considered to be nonpropagating. For the case of VnD there are several possible radical species that may result from transfer to monomer. If one (or more) of these is nonpropagating, then limit 2b kinetics may apply. In such a case, transfer to monomer may be characterized by two transfer coefficients: one for transfer that generates *nonpropagating* radicals and a second that includes all transfers that generate *propagating* monomeric radicals. Transfer to polymer is kinetically unimportant, and in the rest of this paper "transfer", unless otherwise specified, refers to transfer to monomer (or another small species) capable of exiting the particle.

To gain further information on radical loss events, direct measurements of this process were carried out in the present work using γ-radiolysis relaxation in a seeded system,[1,16] as detailed in a later section.

The critical degree of polymerization for entry of persulfate-derived radicals can be estimated from[6]

$$z = 1 - \frac{23\ \text{kJ mol}^{-1}}{RT\ \ln[\text{M}]_\text{w}} \qquad (3)$$

where $[\text{M}]_\text{w}$ is the monomer solubility in water in mol dm^{-3}. Using the value of $[\text{M}]_\text{w}$ given above, this yields $z = 1.8$. The assumption that entry is only through radicals of degree of polymerization z or greater as a "yes/no" condition for entry is a simplification, and in actuality[6] it is likely that the rate of irreversible entry of oligomeric species of degree of polymerization i increases with i and becomes so fast for $i \geq z$ that no other fate is likely. In the case of VnD, k_p is very large (5.3×10^3 M^{-1} s^{-1} at 50 °C[8]), and $k_p^{\text{IM}\bullet}$ (the propagation rate coefficient for a monomeric radical derived from initiator, $^\bullet\text{MSO}_4^-$) is likely to be about 10 times this value.[17−19] Assuming that the monomer concentration at the surface of the particle is about the same as in the bulk of the particle (1.8 M), the first propagation step would take only about 1×10^{-5} s. This is in the middle of the range of desorption times for surfactant molecules from SDS (sodium dodecyl sulfate) micelles (10^{-4}−10^{-6} s).[20] Consequently, it may be argued that a 1-mer ($^\bullet\text{MSO}_4^-$ where M is a VnD molecule) may be most likely to propagate and enter a particle even though it is sufficiently water-soluble to desorb quite rapidly. Even if it does not enter the first particle it encounters, it is likely to encounter many particles before propagating to a 2-mer or terminating with another aqueous phase radical. Hence, a value of $z = 1.8$ from eq 3 could be interpreted as irreversible entry being probable for $i = 1$ and absolute for $i = 2$. Since the entry model is most simply implemented for integer values of z, modeling will be performed for $z = 1$ and 2.

Limit 2b kinetics implies that first-order radical loss should have a rate coefficient given by $2k_{\text{tr,np}}[\text{M}]_\text{p}{}^1$ (measured in the γ relaxation experiment described below); that is, the average number of radicals per particle obeys

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho(1 - 2\bar{n}) - k\bar{n}, \quad k = 2k_{\text{tr,np}}[\text{M}]_\text{p} \qquad (4)$$

where $k_{\text{tr,np}}$ is the rate coefficient of transfer to form nonpropagating monomeric radicals and ρ is that for entry of radicals into particles. The accepted model for entry[6] in conventional emulsion polymerizations gives (under certain approximations)

$$\rho \approx \frac{2k_\text{d}[\text{I}]N_\text{A}}{N_\text{c}}\left\{\frac{\sqrt{2k_\text{d}[\text{I}]k_{\text{t,w}}}}{k_{\text{p,w}}[\text{M}]_\text{w}} + 1\right\}^{1-z} \qquad (5)$$

(assuming that there is no significant "spontaneous", or "thermal", component to the entry rate coefficient); here [I] is the initiator concentration, k_d is the initiator dissociation rate coefficient, $k_{\text{p,w}}$ and $k_{\text{t,w}}$ are the propagation and termination rate coefficients in the water phase, and $k_{\text{t,w}}$ is defined so that the total loss of radicals in the water phase is $\mathrm{d}[\text{T}^\bullet]/\mathrm{d}t = -2k_{\text{t,w}}[\text{T}^\bullet]^2$ (taking cognisance of the recommendation of an IUPAC Working Party to give the explicit definition of k_t in such cases where there is an ambiguous factor of 2). Calculated initiator efficiencies depend strongly on the value of z.[6] The efficiency is the ratio of the actual value of ρ to that predicted in the absence of aqueous-phase termination, i.e., $\rho\,(100\%) = 2k_\text{d}[\text{I}]N_\text{A}/N_\text{c}$. For [NaPS] ~ 1 mM at 50°C, and using established values[1] for the other rate coefficients ($k_\text{d} = 1.2 \times 10^{-6}$ s^{-1}, $k_{\text{p,w}} = k_\text{p}$, $k_{\text{t,w}}, = 1.8 \times 10^9$ M^{-1} s^{-1}), eq 5 predicts an initiator efficiency of 100% for $z = 1$ and ~5% for $z = 2$.

Particle Number. Extensive models have been given for nucleation (i.e., calculating the particle number, and hence particle size, through eq 2) in emulsion polymerization. A well-established model will be used incorporating the above mechanistic precepts. For this, we use the implementation developed by the present group,[1,21] as follows. Rate equations are written down for aqueous-phase radicals arising from initiator, together with loss by entry into micelles and into preexisting particles, the time and particle-volume dependence of concentrations of particles containing no radicals ($n_0(V,t)$), particles containing a monomeric radical formed by transfer, $n_1^\text{m}(V,t)$, which is assumed to be unable to propagate (on the time scale of interest) but able to desorb with rate coefficient $2k_{\text{tr,np}}[\text{M}]_\text{p}$ and has no other fate except to terminate radical activity by reentry into a particle which already contains a growing radical, and particles containing a growing (polymeric) radical, $n_1^\text{P}(V,t)$. Entry of an initiator-derived radical into a particle containing a growing radical results in very rapid termination. The evolution equations are, for example,

$$\frac{\partial n_1{}^\text{P}(V,t)}{\partial t} = \rho(V)(n_0 - n_1{}^\text{P}) - k_{\text{tr,np}}[\text{M}]_\text{p}n_1{}^\text{P} - \frac{\partial}{\partial V}Kn_1{}^\text{P} + \delta(V - V_0)[\text{IM}_z]k_{\text{e,micelle}}[\text{micelle}] \qquad (6)$$

where the propagational growth rate coefficient $K = k_\text{p}M_0[\text{M}]_\text{p}/N_\text{A}d_\text{p}$, the δ function is for creation of particles

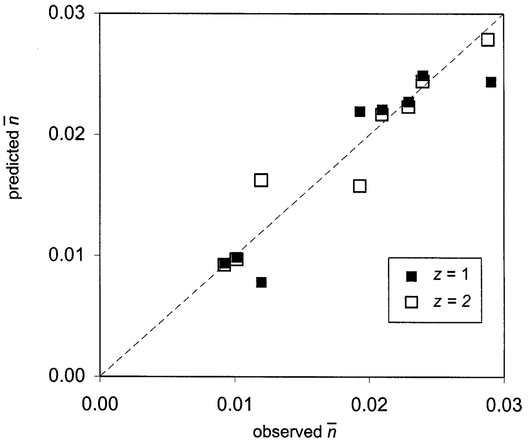

Figure 3. Observed and predicted values of $\bar{n}$ for VnD ab initio emulsion polymerization data of Table 1 (NaPS initiator, 50 °C). Predicted values from eq 4. Values of $k_{\mathrm{tr,np}}$ were obtained by fitting to the observed $\bar{n}$. The dashed line shows $\bar{n}$(observed) = $\bar{n}$(predicted).

of volume V_0 by entry of a z-meric initiator-derived radical $\mathrm{IM}_z^{\bullet}$ into a micelle with rate coefficient $k_{\mathrm{e,micelle}}$, and [micelle] is the concentration of micelles. This last is found by mass balance assuming that the particles are completely covered with surfactant. Coagulation of precursors particles is ignored. Full details of the equations have been given elsewhere,[1,21] except for minor simplifications in the evolution equations to take account of the assumption that nonpropagating transferred radicals can only terminate. Parameter values for the model (e.g., the critical micelle concentration for SDS, etc.) have also been given elsewhere,[1] except for those quantities such as $k_{\mathrm{tr,np}}$ which are particular for VnD and which are specified in the present paper. For the range of [NaPS] and [SDS] used here, the simulations are insensitive to most input parameters (e.g., to V_0, the cmc, and the aggregation number of micelles). The full time evolution of the particle size distribution equations (e.g., eq 6) is obtained by numerical integration of the corresponding finite-difference equations.

Because this treatment ignores coagulation (which occurs for small precursor particles, even above the cmc), it provides an upper estimate for N_c. More sophisticated calculations that include coagulative nucleation[22] show a significant although not large reduction in the predicted N_c.

Model and Experiment

$[\mathrm{M}]_p$ was calculated from the unswollen and swollen diameters of a VnD latex as determined by photon correlation spectroscopy (PCS). It was found to be 1.8 M at 25 °C, in good accord with the value of 2.2 M determined by Balic.[8]

Given a value of $k_{\mathrm{tr,np}}$, then from eq 4 and the established[6] model for ρ (which leads to eq 5), one may compare calculated with observed steady-state values of $\bar{n}$ given in Table 1. As it is not clear what the nonpropagating species could be (recalling that VnD is a mixture of isomers), the value of $k_{\mathrm{tr,np}}$ was treated as a parameter whose value was fitted to give accord with the observed steady-state $\bar{n}$. The calculated values for $\bar{n}$ using fitted values of $k_{\mathrm{tr,np}} = 0.24$ and 0.011 $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ for $z = 1$ and 2, respectively, are shown in Figure 3. It is seen that the predicted values of $\bar{n}$, fitting only the single parameter $k_{\mathrm{tr,np}}$, are in good accord with experiment over the whole range of initiator concentrations. This is consistent with the model assumptions.

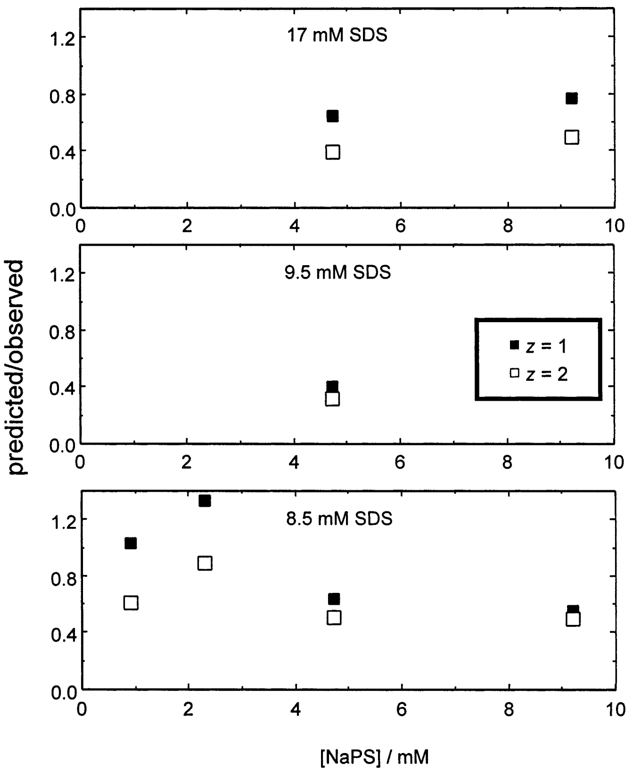

Figure 4. Ratios of predicted to observed particle numbers, for the conditions and results of Table 1, for $z = 1$ and for $z = 2$.

These fitted values of $k_{\mathrm{tr,np}}$ are both less than the value of 4 $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ reported for transfer to monomer obtained from moelcular weight distributions.[8] This implies that if $z = 1$ (i.e., the entering species are all $^{\bullet}\mathrm{MSO}_4^-$), then ~6% of chain transfer to monomer must produce nonpropagating monomeric radicals, and if $z = 2$, then this becomes 0.3%. Thus, the chain-stopping event which dominates the MWD (k_{tr}) might give a radical that does not desorb: that is, one transfer event might dominate the molecular weight distribution while another ($k_{\mathrm{tr,np}}$) dominates exit.

Figure 4 gives (as the ratio predicted/observed) the results of the simulations and experiment for particle number, for both $z = 1$ and 2 (using the corresponding values of $k_{\mathrm{tr,np}}$ in each case). For both values of z, the model predicts values that are remarkably close to experiment, although usually producing a value that is ~50% lower than that observed. The level of agreement between observed and experimental particles in this calculation, which is completely without adjustable parameters, is impressive: in the literature, agreement within a factor of as much as 5 for a totally a priori calculation is regarded as good (e.g., refs 1 and 22). It is emphasized that for this system, although the model contains many parameters, results are only sensitive to (physically reasonable) changes in k_{tr} and z, of those quantities cannot be determined independently. Note that while the simulated values vary monotonically with both [NaPS] and [SDS], the experimental values show scatter. Now, particle size used to infer the particle number was obtained by capillary hydrodynamic fractionation, which has some attendant uncertainty (perhaps ±30%) which might lead to uncertainty in particle number through eq 2 of as much as a factor of 2 in N_c.

However, the trends and scatter in Figure 4 show the inference that the calculations using these two values of z are consistent with the observed behavior is still valid even with this uncertainty.

It is emphasized that the simulations have no adjustable parameters except the value of $k_{\mathrm{tr,np}}$, which was fixed to give agreement with the observed values of $\bar{n}$. The results of Figure 4 offer little distinction between $z = 1$ or 2.

γ Relaxation. The values for k_{tr} obtained above also yield a rate for radical loss which can be compared to that observed directly from γ radiolysis and the inferences, leading to eq 4. This predicted rate is $2k_{\mathrm{tr,np}}[\mathrm{M}]_{\mathrm{p}}$, for which the calculated values (at 50 °C in interval II) are 0.8 s^{-1} for the $z = 1$ model and 0.04 s^{-1} s for the $z = 2$ model at 50 °C.

Radical loss studies employed techniques described extensively elsewhere in the literature[16,23] wherein the rate of reaction of a seeded emulsion polymerization is monitored after rapid removal from a radical source (^{60}Co), prior to which the system had been exposed to the radical flux for sufficient time to achieve a significant polymerization rate.

A VnD seed latex was prepared as follows. To 800 g of water was added 1.25 g of Dowfax 2A1 (1-dodecyl-3-(phenoxy-3-sulfonate)benzene-4-sulfonate, 47% w/w, chosen by trial and error), 0.5 g of potassium persulfate (KPS), 0.2 g of potassium hydrogen carbonate, and 0.05 g of sodium metabisulfite. The solution was heated to 85 °C for 1 h whereupon 30.4 g of VnD was added and held at 60 °C for 4 h. A further 130 g of VnD was added and held at 55 °C for 18 h, after which another 0.1 g of KPS was added. After 24 h at 55 °C another 0.1 g of KPS was added, and the solution was heated to 75 °C for 24 h. The final latex contained 7.4% w/w polymer, with particles of diameter 127 nm (measured by PCS).

The detailed technique used here was identical to that used previously for vinyl acetate (VAc).[23] 0.41 g of AMA-80 (sodium dihexyl sulfosuccinate, Cyanamid) and 0.3 g of sodium acetate (Merck) were dissolved in 21.44 g of thoroughly degassed water. (Sodium acetate was used as a buffer rather than the more common $\mathrm{NaHCO_3}$, since acetate will not liberate $\mathrm{CO_2}$ with changes in pH; $\mathrm{CO_2}$ liberation can create bubbles which would vitiate the dilatometric monitoring of rate used here.) To this was added 6.42 g of distilled VnD; the mixture was emulsified with a magnetic stirrer and added to 130 g of seed, which was allowed to swell for 7 days at room temperature. The lengthy swelling period was necessary to overcome monomer creaming. Milli-Q water, of conductivity 18.2 μS cm^{-1}, was used throughout. A portion of the swollen latex was placed in a water-jacketed thermostated 60 cm^3 dilatometer and equipped with an RTD temperature probe. The dilatometer was then placed in a γ source (^{60}Co, 0.083 Gy s^{-1}). Upon reaching a steady state, the dilatometer was removed from the γ source and the relaxation behavior monitored.

Precautions need to be taken to account for exothermicity effects, particularly in rapidly relaxing systems.[23] It was impossible to eliminate these exothermicity artifacts at the temperature of the data in Table 1, 50 °C. Furthermore, eq 4 suggests that the loss rate coefficient should show a significant activation energy (largely that of $k_{\mathrm{tr,np}}$); hence, relaxations proceed more slowly, thereby allowing for the collection of better quality data as the meniscus tracking device used in the automated dilatometer can only acquire data at intervals greater than about 3 s. It was therefore decided to perform radical loss studies at 0.5 °C because there was no measurable temperature change in the dilatometer on removal from the γ source at this temperature and also because the thermal expansion coefficient for water (which is the major component of the emulsions studied) is very small at this temperature. Consequently, the results for this rate coefficient at lower temperatures will be a lower bound for that at 50 °C.

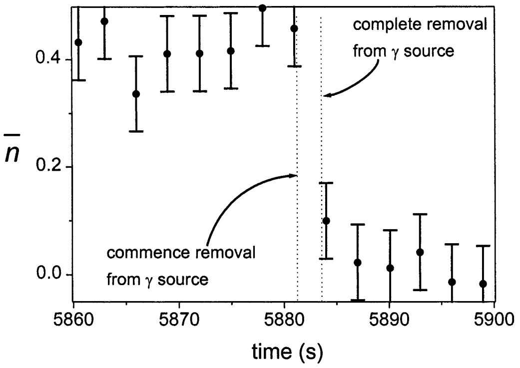

Figure 5. γ relaxation data (as time evolution of $\bar{n}$) for VnD seeded emulsion polymerization at 0.5 °C in a poly(VnD) seed.

Table 2. Observed $\bar{n}$ of Seeded Emulsion Polymerization in γ Source (0.083 Gy s^{-1}) over a Range of Temperatures

temperature (°C)	$\bar{n}$
0.5	0.52 ± 0.1
11.9	0.45 ± 0.1
21.4	0.47 ± 0.1

Data from a typical γ relaxation, converted from the experimental observable (time dependence of conversion obtained by dilatometry) to the time dependence of $\bar{n}$ using eq 1, are shown in Figure 5. Data are shown for poly(VnD) seed swollen with VnD monomer. Data obtained with multiple insertions into and removals from the radiation source in a single run show this same behavior with each removal, implying that there is no artifact arising from inhibitor or retarder (i.e., leaving the system in the radiation source for a sufficient time before the first removal successfully “burns out” all inhibitors and retarders present).

The relaxation at 0.5 °C was so fast (a few seconds or less) that it is comparable to the mechanical time taken to physically remove the dilatometer from the radiation source (~3 s). Hence, the only quantitative information that can be gained from these experiments is that there is a radical loss process that is faster than ~0.3 s^{-1} at 0.5 °C and presumably faster still at 50 °C. However, this is in fact a very useful result for mechanistic understanding. This suggests that $z = 1$ (which implies a radical loss process with rate ~0.8 s^{-1} at 50 °C) is consistent with the observed rapid relaxation (Figure 5). On the other hand, $z = 2$ implies a radical loss process rate ~0.04 s^{-1} at 50 °C. This strongly suggests that $z = 1$ is the best description for this system.

The γ studies also support the notion that the system is indeed zero-one as the observed value of $\bar{n}$ *within* the source is always close to 0.5 (within experimental error) regardless of temperature from 0.5 to 21.4 °C (Table 2). This $\bar{n}$ (which is large compared to that seen in the KPS initiated experiments of Table 1) can be understood as follows. In the γ source, the primary radical flux is very high (and independent of temperature), approximately

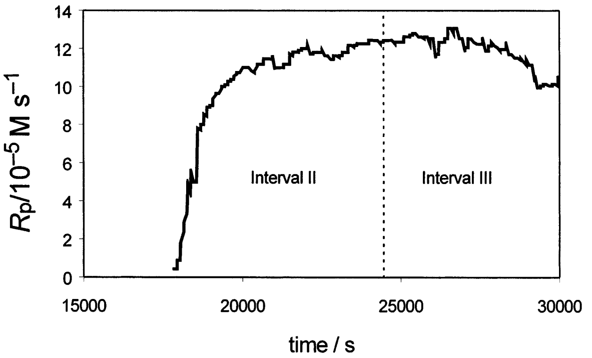

Figure 6. Rate as a function of time for run with [NaPS] = 4.7 mM from Table 1, showing the transition from interval II to interval III, and exhibiting an extensive constant R_p in interval III, consistent with limit 2b kinetics. Data reprocessed from ref 8.

equivalent to 20 mM KPS at 50 °C. In the γ experiments, the transfer rate coefficient over the range 0.5–21.4 °C must be much less that that at 50 °C (activation energies for transfer reactions involving H atoms being ~50 kJ mol^{-1}), and hence the exit rate coefficient must be much less than at 50 °C. Hence, a value of $\bar{n} = {}^1/_2$ at the lower temperatures is simply the well-known Smith–Ewart case 2 limit.

In view of the similarities between the γ relaxation results for vinyl acetate[23] and VnD (this work) and the chemical structures of the monomers, it seems likely that they share the same (or a chemically similar) relaxation mechanism. Most transfer events in the VAc system would be expected to be via abstraction of an alkyl hydrogen[24] to produce an extremely reactive radical. The vinyl acetyl radical is chemically almost identical to the (*tert*-butoxy)carbonylmethyl radical, which has been shown to react very rapidly with vinyl acetate monomer, with a propagation rate coefficient of 1.3×10^5 M^{-1} s^{-1}.[25] However, it is possible that the occasional abstraction of a vinylic hydrogen from VAc monomer produces a relatively unreactive radical[26] which may then exit and terminate via the limit 2b mechanism. In the case of VnD, the ester group is a mixture of branched C_{10} alkanes.[27] Thus, it seems likely that most transfer will also be via abstraction of an alkyl hydrogen. As with VAc, the occasional abstraction of a vinylic hydrogen might produce a relatively unreactive radical, as could abstraction from a sterically hindered tertiary carbon on the branched alkyl group.

An interesting feature of limit 2b kinetics is that it predicts that R_p should be independent of conversion (i.e., that conversion be linear in time) in interval III.[12] This is seen immediately by substituting the steady-state form of eq 4 into eq 1, whence one obtains

$$R_p = \frac{k_p}{2k_{tr,np}} \rho \frac{N_c}{N_A} \tag{7}$$

which is independent of conversion, i.e., independent of $[M]_p$. Linearity of conversion with time in interval III has been reported by many authors for vinyl acetate.[28] For VnD emulsion homopolymerization the boundary between intervals II and III is at 50–60% depending on the value of $[M]_p$ used; the limit 2b inference thus explains the observation[8] that systems which show an extensive steady state do so over most of interval III. This behavior is exemplified in Figure 6; the rate data are noisy, being the numerical derivative of conversion data from dilatometry, but these results show the existence of an approximately constant dn_M/dt in interval III. In Kitzmiller et al.'s miniemulsion experiments on the similarly highly water-insoluble vinyl 2-ethylhexanoate[29] (e.g., their Figure 2B, experiment E), there also appears to be an extensive steady state to about 80% conversion.

It may seem counterintuitive that a monomer that is as hydrophobic as VnD could ever exit. The exit rate coefficient for a monomeric radical, k_{dM}, can be found from[30]

$$k_{dM} = \frac{3D_w}{r_S^2} \frac{[M]_w}{[M]_p} \tag{8}$$

where D_w is the diffusion coefficient of the monomeric radical and r_S the swollen particle radius. Using the parameters given above, together with a typical value for $D_w = 1.5 \times 10^{-5}$ cm^2 s^{-1}, one obtains $k_{dM} \sim 10$ s^{-1}, corresponding to a desorption time of ~0.1 s. While this is slower than the corresponding time for styrene (~10^{-3} s), it is still sufficiently fast to be consistent with the inferences given above.

Conclusions

Figure 4 shows that the experimental particle number over a range of initiator and surfactant concentrations is fitted quite adequately by the alternative values ($z = 1$ or 2) of the critical degree of polymerization for entry, the only adjustable parameter being the transfer rate coefficient to a nonpropagating species which is fitted to the observed steady-state rate. Additional data using γ relaxation suggest that $z = 1$ is more applicable to this system. VnD behaves as a standard zero-one system obeying limit 2b kinetics: radical loss by transfer to a nonpropagating (or slowly propagating) species and (to a much lesser extent) by termination following entry of a z-mer into a particle which already contains a growing radical. The limit 2b assumption that the nonpropagating radical resulting from transfer always undergoes termination (by successive desorption and reentry) implies that the kinetics are independent of the water solubility of this radical: although the rate coefficient for exit of a radical depends on the solubility of this radical,[31,32] this step is not rate-determining when one assumes limit 2b kinetics. Even though the exiting radical is probably of low water solubility, the radiolysis relaxation data (Figure 5) show clearly that radical loss is very fast.

In summary, the emulsion polymerization of this highly water-insoluble monomer follows normal zero-one emulsion polymerization mechanisms for both particle formation and growth.

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