Efficiency of initiation by azodiisobutyronitrile in the emulsion polymerization of styrene*

W. A. -G. Al-Shahib† and A. S. Dunn
Chemistry Department, University of Manchester Institute of Science and Technology, P. O. Box 88,
Manchester M60 1QD, UK

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Oil-soluble initiators can produce rates of emulsion polymerization similar to those obtained with the water-soluble initiators which are normally used. Although radicals are generated in pairs in the oil phase, escape of a radical to the aqueous phase leaves an isolated radical in the oil phase: this is the essential condition for an emulsion polymerization. A concentration of azodiisobutyronitrile was found which produced the same number of latex particles in the emulsion polymerization of styrene as was obtained with a typical concentration of potassium peroxydisulphate. The rate of nucleation of latex particles can then be equated to that obtained with the known rate of decomposition of peroxydisulphate. Comparison with the rate of decomposition of azodiisobutyronitrile shows its efficiency to be only 4% in emulsion polymerization in contrast with the efficiency of ~50% obtained in bulk or solution polymerization.

INTRODUCTION

Emulsion polymerization is characterized by high rates of polymerization occurring simultaneously with the production of high molecular weight polymer. Haward[1] pointed out that this is a consequence of the isolation of single radicals polymerizing in loci of small dimensions so that the normal mutual termination step between polymer radicals is excluded from the polymerization mechanism in favour of termination by primary radicals derived from the initiator. Normally water-soluble initiators such as potassium persulphate or redox systems based on hydrogen peroxide are preferred for emulsion polymerizations but, provided a surfactant is used to stabilize the latex particles formed, similar rates of polymerization can be obtained using oil-soluble initiators such as benzoyl peroxide[2,3] and azodiisobutyronitrile[4,5]. Interfacial initiation using an oil-soluble hydroperoxide and a water-soluble reducing agent provides another possible variation[6,7]. Oil-soluble initiators produce free radicals in pairs so that the isolation of a polymer radical in a latex particle is dependent on the probability of one radical escaping into the aqueous phase by partition or by transfer to an emulsifier molecule[8]. Theories of emulsion polymerization have generally been restricted to the case of decomposition of the initiator in the aqueous phase[9,10] and although Medvedev[11] considered both aqueous-phase and oil-phase initiation, the experimental observations which led him to reject Harkins's theory[12] have subsequently been found to be unsound[5,13].

It has not yet been possible to calculate the rate of escape of radicals from micelles or latex particles by diffusion of primary radicals into the water phase, or by transfer to an adsorbed emulsifier molecule with subsequent exchange of the emulsifier radical with an emulsifier molecule dissolved in the aqueous phase. But according to the Smith–Ewart–Gardon theory[9,10] the number of latex particles, N, generated in the initial stage (Interval I) of a batch emulsion polymerization depends on the 2/5th power of the rate of initiation, R_i (equation 1). If, therefore, conditions can be found in which the number of latex particles formed using an oil-phase initiator is the same as that produced by a known concentration of a water-soluble initiator for which the rate of initiation is known, it can be inferred that this is also the rate of initiation in emulsion polymerization by the oil-soluble initiator. Because of the cage effect[14] the rate of initiation in bulk polymerization by such initiators as azodiisobutyronitrile is only about half their rate of decomposition. Since, in emulsion polymerization, the initiator radicals must not only escape from the cage of monomer molecules in which they are dissolved but also one of them must escape entirely from the micelle or latex particle in which it was produced, an even lower efficiency of initiation may be expected. The subsequent rate of polymerization, $-\mathrm{d}(M)/\mathrm{d}t$, during Interval II (equation 2) might also be expected to be the same as that observed with the water-soluble initiator at the same rate of initiation because this depends directly on the number of latex particles per unit volume, N, which has been produced during Interval I provided the rate of initiation is sufficient to maintain the average number of radicals per latex particle, $\bar{n} = \frac{1}{2}$. k_p is the propagation rate constant of the monomer, (M) the monomer concentration in the latex particles, (S) the emulsifier concentration in the aqueous phase, and L the Avogadro Number.

$$N = (\mathrm{Constant})R_i^{2/5}(S)^{3/5} \quad (1)$$

$$-\mathrm{d}(M)/\mathrm{d}t = (\bar{n}Nk_p(M))/L \quad (2)$$

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† Present address: Department of Chemistry, College of Education, University of Baghdad, Wazzeria, Baghdad, Iraq

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Table 1 Efficiency of azodiisobutyronitrile in nucleating latex particles 60°C. Emulsifier: sodium octadecyl sulphate 0.060 mol dm^{-3} on the water phase

10^5 (Oil-phase conc.) AIBN/mol cm^{-3}	$10^3 R_p$ mol dm^{-3} s^{-1}	$\bar{r}_T$/nm^{-1}	$\bar{r}_{LS}/\bar{r}_T$	10^{-15} N/cm^{-3} water	10^6 x Equivalent persulphate conc/mol cm^{-3}	Efficiency relative to persulphate (%)
0.96	1.51	40.0	1.15	1.6	(0.18)	3.1
4.84	2.52	29.9	1.31	3.6	(1.51)	5.1
30.5	3.51	24.6	1.39	6.6	(7.40)	4.0
–	5.73	24.2	1.15	6.9	7.40	–

Table 2 Effect of sodium alkyl sulphates on the emulsion polymerization of styrene using azodiisobutyronitrile. Total concentration of emulsifier 6.0 x 10^{-2} mol dm^{-3} on water phase. Azodiisobutyronitrile 4.86 x 10^{-3} mol dm^{-3} in oil phase. 60°C

Alkyl chain length	10^3 (C.M.C.) mol dm^{-3}	10^2 $(S - S_m)$ mol dm^{-3}	$\bar{r}$/nm	$\bar{r}_{LS}/\bar{r}_T$	10^{-15} N/cm^3 water	10^3 Rp mol dm^{-3} s^{-1}
C 10	34.0	2.6	46.5	1.08	1.0	0.91
C 12	9.0	5.1	40.2	1.07	1.6	1.51
C 14	2.4	5.8	32.7	1.23	2.9	2.09
C 16	0.62	5.9	32.7	1.21	2.9	2.21
			33.3	1.16	2.8	2.24
C 18	0.16	6.0	29.9	1.33	3.6	2.52

EXPERIMENTAL

Rates of polymerization were determined gravimetrically: the precise technique has been described previously[15]. Styrene (BDH) was redistilled twice under vacuum. The monomer and the water were deoxygenated by passing oxygen-free' nitrogen for 30 min: passage through alkaline pyrogallol solution was used to remove residual oxygen from the nitrogen stream. Azodiisobutyronitrile (BDH) was recrystallized twice from ethanol. Sodium alkyl sulphate emulsifiers were prepared and purified by the method described previously[15]. The amounts of the emulsifiers used were those required to give a 0.060 mol dm^{-3} solution in 212 cm^3 water which was 0.10 mol dm^{-3} in sodium hydroxide. The volume of styrene used was 80 cm^3. Polymerizations were conducted in a three-necked flask immersed in a thermostat at 60°C. Conversions exceeded 60% within the first hour in most experiments. Samples for particle size measurement were left in the thermostat overnight to complete the polymerization and were measured within 24 h. Particle numbers were calculated from the turbidity-average diameter:

$$\bar{d}_T = \left(\frac{\Sigma n_i d_i^6}{\Sigma n_i d_i^3}\right)^{1/3}$$

determined by a light-scattering method[16]. This method also yields an even higher average diameter:

$$\bar{d}_{LS} = \left(\frac{\Sigma n_i d_i^8}{\Sigma n_i d_i^6}\right)^{1/2}$$

The difference between the radii $\bar{r}_T$ and $\bar{r}_{LS}$ (*Tables 1* and *2*) shows that the particle-size distribution are not monodisperse. Since the turbidity-average diameter is significantly larger in a polydisperse distribution than the root–mean-cube average diameter:

$$\bar{d}_{rmc} = \left(\frac{\Sigma n_i d_i^3}{\Sigma n_i}\right)^{1/3}$$

which should be used[10] in particle number calculations, a systematic error is introduced into the calculated particle numbers which were estimated to be ~25% low on the basis of one sample which was examined by electron microscopy[16]. However since the principal conclusions of the present work depend on the identification of samples which have equal values of $\bar{d}_T$, this error is irrelevant provided the samples have similar particle-size distributions.

RESULTS

Variation of the initiator concentration

The number of latex particles formed (*Table 1*) varies approximately with the 2/5th power of the initiator concentration, but the dependence of the rate of polymerization during Interval II on the initiator concentration is lower than this, indicating that the Interval II rate is less than directly proportional to the number of latex particles present as required by equation (2). This is similar to that found in the emulsion polymerizations of vinyl acetate and vinyl chloride, following the Smith–Ewart Case I kinetics, in which the transfer of radicals from the particles to the aqueous phase is not negligible and in which the average number of radicals per particle $\bar{n} \ll ½$. This might be expected since the possibility of using an oil-soluble initiator for emulsion polymerization depends on the transfer of radicals to the aqueous phase. *Table 1* shows that the size (and, assuming similar particle-size distribution, the number) of latex particles formed, using a concentration of azodiisobutyronitrile in styrene of 3.07 x 10^{-4} mol cm^{-3}, was the same as that obtained using a much lower concentration (7.40 x 10^{-6} mol cm^{-3}) of potassium persulphate in water. It is believed that all radicals formed from potassium persulphate nucleate latex particles in the initial stages of an emulsion polymerization. Therefore the rate of formation of isolated radicals which nucleate latex particles from azodiisobutyronitrile may be equated to twice the known rate of decomposition of persulphate in alkaline aqueous solution. If the rate constant for this decomposition is taken[17] as $k_d = 5.0 \times 10^{-6}$ s^{-1} at 60°C, the rate of initiation at this initiator concentration is $R_i = 7.40 \times 10^{-11}$ mol cm^{-3} s^{-1}. Multiplication by the Avogadro constant gives Gardon's[10] R, the number of radicals generated per cm^3 of the water phase per second as 4.46×10^{13} cm^3 s^{-1}. This must also be the value for the concentration of azodiisobutyronitrile used because the same number of latex particles are formed. Taking the rate constant[18] for the decomposition of azodiisobutyronitrile at 60°C to be 1.6×10^{-5} s^{-1}, and the percentage of isobutyronitrile radicals which avoid mutual reaction and escape from the solvent cage (being available for the initiation of polymerization) to be 50%[19], the rate of radical production in the oil-phase is calculated as $R_r = 2k_df(\mathrm{I}) = 4.92 \times 10^{-9}$ mol cm^{-3} s^{-1}. Since the ratio of the volumes of the oil phase and the water phase is 80:212 or 1:2.65, this would be equivalent to a rate of radical generation in the water phase of 1.85×10^{-9} mol cm^{-3} s^{-1} if all these radicals escaped into the water phase. The fraction which do nucleate latex particles is $7.40 \times 10^{-11}/1.85 \times 10^{-9} = 0.040$. That is only 4% of the radicals available for the initiation of polymerization in the oil-phase nucleate latex particles: presumably the remainder do initiate polymerization in the oil phase. However, because of the small volume of latex particles, the radical concentration must be very high when two radicals are present so that mutual termination is rapid, and only a small amount of low molecular weight oligomer, which is likely to remain in solution when the polymer is isolated by precipitation, is produced. For persulphate initiation $N \propto R_i^{2/5}$ hence the persulphate concentrations, needed to nucleate the same number of particles as the lower concentrations of azodiisobutyronitrile, can be calculated and the corresponding efficiencies of azodiisobutyronitrile in particle nucleation can be evaluated. The results are given in *Table 1*.

Variation of alkyl chain length

A series of experiments was carried out in which the chain length of the alkyl sulphate emulsifier was varied between 10 and 18 carbon atoms, keeping the total concentration constant at 0.060 mol dm^{-3} on the aqueous phase and using a constant concentration of azodiisobutyronitrile (4.86×10^{-3} mol dm^{-3}) in the oil phase. The results (*Table 2*) were similar to previous experiments in which a water-soluble initiator was used[15]. The area, a_S, occupied by an emulsifier molecule in a saturated monolayer at the polymer/water interface is constant at 0.52 nm^2 for this series of emulsifiers. According to the Smith–Ewart theory[10] $N \propto (a_S[S])^{3/5}$, and it would be expected that the same number of latex particles would be formed if this was determined by the total emulsifier concentration. *Table 2* shows that this is not the case. The lower members of the series have relatively high critical micelle concentrations (S_m). Proportionality of N to $(S - S_m)^{3/5}$, (i.e. to the 3/5th power of the concentration of micellar emulsifier) is sufficient to account for the change in the number of particles formed between the C10 and C12 emulsifiers, but is inadequate to account for the differences between the higher members of the series for which the difference between (S) and ($S - S_m$) is comparatively small. Perhaps the probability of transfer to the emulsifier increases with the length of the alkyl chain, increasing the probability of radicals escaping into the aqueous phase. The increase in number of latex particles formed between C12 and C18 is double that observed in experiments[15] using potassium persulphate as initiator at the same emulsifier concentration.

DISCUSSION

Provided that the rate of initiation is sufficient to maintain the average number of radicals per latex particle $\bar{n} = 0.5$, the Interval II rate of polymerization should be the same for lattices with the same number of latex particles N, according to equation (2) if Smith–Ewart[10] Case II kinetics (neglecting escape of radicals from the latex particles) can be applied. Radical escape is essential to the present case and it has been argued above that Case I kinetics should be applied. Nevertheless the rates observed at the two lower azodiisobutyronitrile concentrations do correspond to those expected for the persulphate concentrations which would nucleate equal numbers of particles. Therefore it appears that $\bar{n} = 0.5$ can be maintained during Interval II at these particle concentrations. At the highest azodiisobutyronitrile concentration (*Table 1*) the rate of polymerization is lower than would be expected with the persulphate concentration which nucleates an equal number of particles, and corresponds to $\bar{n} = 0.3$. Berezhnoi, Khomichovskii, and Medvedev[18] find that the rate of polymerization of styrene using an alkyl sulphonate emulsifier, becomes independent of azodiisobutyronitrile concentration at high concentrations (similar to the highest concentration in *Table 1*), and that the rate (in this range of initiator concentration) is directly proportional to the emulsifier concentration. The authors' original interpretation of these results was a polymerization occurring within the adsorbed emulsifier layer. Reinterpretation shows a transition from Case II kinetics, at low initiator concentrations, to Case I kinetics at the highest initiator concentrations.

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