Effect of Impurities on Emulsion Polymerization: Case II Kinetics

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Synopsis

The effects of water-soluble and monomer-soluble impurities on the kinetics of emulsion polymerization of monomers following Case II kinetics (e.g., styrene) are investigated. Experimental studies reveal that impurities can have an appreciable effect on both polymer particle nucleation and growth. These effects are shown to be well predicted by a mathematical model.

INTRODUCTION

Most studies on emulsion polymerization kinetics carried out in university and industrial research laboratories are done under extremely clean conditions. The initiators and emulsifiers are of a high purity grade, and the monomers are purified by distillation, etc. to remove the inhibitors used during storage as well as other reactive organic impurities which may act as radical scavengers or chain transfer agents. On the other hand, in industrial processes it is usually impractical to purify the monomers, etc., or at least to do so to the extent done in laboratory studies. Furthermore, in many processes where the polymerization is carried to less than complete conversion, such as in the manufacture of styrene–butadiene rubber by continuous emulsion polymerization, the unreacted monomer is recovered by steam stripping of the latex or by some other means, and then recycled to the reaction train. These recycle streams usually contain a much higher level of reactive impurities than the original feed streams due to the formation of reactive byproducts in the reactors and recovery units.

Without a good understanding of the effect of impurities on the emulsion polymerization process, it is very difficult to relate the results of laboratory kinetic studies to observations in the plant. Furthermore, one of the major reasons for batch to batch variability in latex quality and for drifting conversion and latex properties in continuous industrial reactors is the unknown variations that occur in impurity levels in the feeds. In order to better control this variability, it is necessary to have a basic understanding of how these impurities affect the kinetics of an emulsion system.

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The emulsion polymerization literature is very sparse in its coverage of impurity effects. A review of the literature reveals that there exists a general recognition that oxygen acts as a radical scavenger and inhibitor causing an induction period without having a critical impact on the subsequent course of the polymerization.[1-4] However, with the exception of Hoffman,[5] who modeled monomer- and water-soluble reactive impurity effects in Case II systems (styrene-butadiene), there appears to be little else in the published literature.

In this and a companion paper[6] we report on experimental studies and develop models to test the effect of impurities on the kinetics of emulsion polymerization. No attempt is made to investigate specific chemical impurities. Rather the objective is to investigate the general nature of the effect of water-soluble impurities and of monomer-soluble impurities on the rates of polymerization, on the particle generation kinetics, and on the molecular weights of the polymers. The study is broken into two parts: the first on emulsion polymerizations exhibiting Case II kinetics, and the second on those exhibiting Case I kinetics. Case I and Case II systems are distinguished primarily on the magnitude of radical desorption rates from the particles. Case I emulsion systems typified by vinyl chloride and vinyl acetate are characterized by monomers which have a moderate solubility in water, and by a relatively high rate of radical chain transfer to monomer during polymerization. As a result, there is a very high rate of desorption of monomeric and oligomeric radicals from the particles and the average number of radicals per particle ($\bar{n}$) is therefore much less than half. Case II emulsion systems typified by styrene, styrene/butadiene, and most acrylates are characterized by monomers having low solubility in water and low rates of radical transfer to monomer. As a result, there is a very low rate of radical desorption from the particles and, at least early in the polymerization, the average number of radicals per particle is approximately one-half.

In this paper we treat Case II systems, and follow with a treatment of Case I systems in a companion paper.[6] The reason for this division is that there is a major difference for the effect of impurities on Case I and II systems. Although we have classified the systems as following Case I or II kinetics, it should be noted that most of them eventually exhibit Case III kinetics later in the reaction when the particles become larger and $\bar{n}$ becomes considerably greater than one-half. This is especially true of acrylate systems. However, the dominant effect of impurities will be shown to be in the early stages of particle nucleation and growth.

WATER-SOLUBLE IMPURITIES

The major water-soluble impurity is usually dissolved oxygen. Oxygen acts mainly by consuming reactive free radicals in the water phase. Although the rate at which this reaction occurs is not well known, experimental evidence points to the fact that it is quite high. This high rate of radical reaction with oxygen in the water phase will lower the concentration of reactive radicals in the water phase to essentially zero until all of the oxygen is consumed. Oxygen partitions into both water and organic phases. However, as it is consumed in the water phase via reaction with initiator radicals, oxygen diffuses into the water phase until all of the oxygen is consumed. This gives rise to the
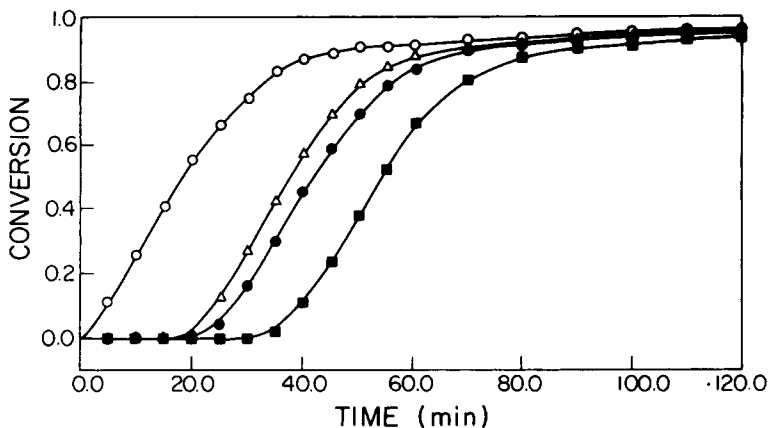
Fig. 1. Effect of water-soluble impurities (HDQ) on conversion: Emulsion polymerization of styrene. (○) 0 ppm; (△) 20 ppm; (●) 50 ppm; (■) 100 ppm.

commonly observed induction period for emulsion polymerization. Other water-soluble impurities may consume reactive radicals more slowly, and thereby allow a low level of particle nucleation by either homogeneous or micellar mechanisms.

Experimental Results

Figure 1 shows conversion time histories as determined by gravimetry for the batch emulsion polymerization of styrene. The monomer was washed with caustic solution and then distilled before the experiments. A known amount of hydroquinone (HDQ), which should act as an impurity in the water phase, was then added to the recipe, which consisted of 2000.0 g of water, 1053.0 g of styrene, 3.263 g of potassium persulfate, 63.18 g of sodium lauryl sulfate, and 2.527 g of NaHCO$_3$ at 60°C. Four runs with the identical recipe but with different levels of hydroquinone in the water were carried out. The four runs exhibit different induction times, but, once the induction time is over, the subsequent conversion histories are identical to within experimental error.

In Table I the effect of the hydroquinone level on the rate of the reaction is illustrated by taking slopes of the conversion time curves in different conversion regions. With the possible exception of the rate in the low conversion region for the highest HDQ level there appears to be no significant difference in rates. The final particle concentrations, average particle diameters, molecu-

TABLE I
Effect of HDQ on Rate of Polymerization

HDQ (ppm)	Polymerization rate for the conversion range	
	0.1 to 0.25	0.25 to ~ 0.50
0	0.028	0.032
20	0.029	0.031
50	0.028	0.031
100	0.025	0.029

TABLE II
Effect of Water-Soluble Impurities (HDQ) on the Properties of the Final Product

HDQ (ppm)	Diameter (Å)	N_p (#/mL) ($\times 10^{-15}$)	$\bar{M}_n$ ($\times 10^{-6}$)	$\bar{M}_w$ ($\times 10^{-6}$)	$\bar{M}_w/\bar{M}_n$	Viscosity (cp)
0	800	1.79	1.39	2.59	1.86	18
20	750	2.15	1.49	2.61	1.75	20
50	757	2.09	1.41	2.45	1.74	19
100	753	2.10	1.59	2.61	1.64	18

lar weights, and latex viscosities shown in Table II are identical to within experimental error for all four runs. This suggests that particle nucleation does not begin until all of the HDQ has reacted with initiator radicals in the water phase.

Hence we conclude from these results that the presence of highly reactive impurities in the water phase will have little effect on Case II emulsion polymerization beyond producing an induction period. However, with water-soluble impurities much less reactive than oxygen or hydroquinone, a significant level of radical concentration in the water phase could be established, leading to some nucleation of particles having a slow rate of growth due to a low average number of radicals per particle.

MONOMER-SOLUBLE IMPURITIES

Reactive monomer-soluble impurities may arise from a number of sources: residual inhibitors added to stabilize the monomers during storage; byproducts formed during the production of the monomers; reaction products formed in the reactors and recovery system. We are concerned here only with the impurities which will react fairly rapidly with oligomeric radicals in the polymer particles.

It is widely appreciated that these reactive monomer-soluble impurities, by reacting with radicals in the particles, will reduce the average number of radicals per particle and thereby tend to reduce the overall reaction rate. However, other more subtle effects of these impurities on the particle generation rate are much less widely appreciated. Before discussing these effects in more detail consider the following experimental results.

Conversion-time histories are shown in Figure 2 for the batch emulsion polymerization of styrene.[7] Curve A is that obtained for the emulsion polymerization of styrene that had been purified by caustic washing and subsequent distillation. Curve B was obtained using the identical procedures and the identical recipe used in obtaining curve A, except that the monomer [containing approximately 15 ppm of 4-*tert*-butyl catechol (TBC)] was not purified (see Table III for the recipe used). The most interesting aspect of these results is that in spite of a substantial initial retardation of the overall polymerization rate for the impure monomer case, the impure monomer run actually finished before the run using the purified monomer. The explanation for this is revealed in Figure 3 where the average particle diameters obtained by hydrodynamic chromatography (HDC) are plotted for these two runs. Note that for the case of the impure monomer (B), the average particle sizes
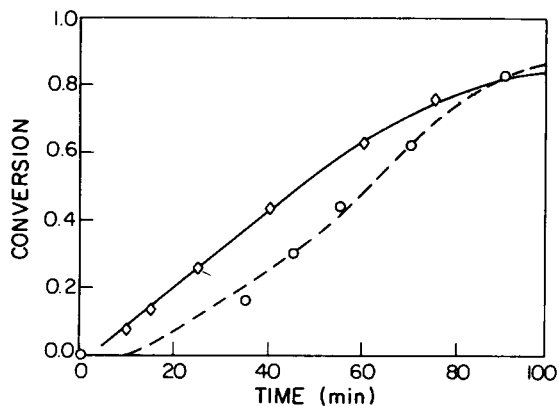
Fig. 2. Batch emulsion polymerization of styrene:[7] ($\Diamond$) purified (A) versus ($\bigcirc$) unpurified (B) case, conversion results.
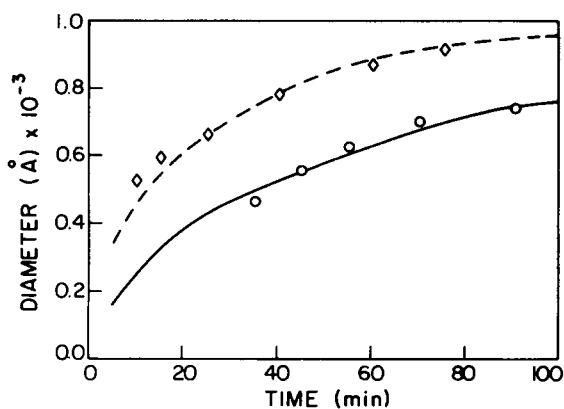

Fig. 3. Batch emulsion polymerization of styrene:[7] ($\Diamond$) purified (A) versus ($\bigcirc$) unpurified (B) case, average diameter results.

are substantially smaller than those obtained for the purified monomer. This implies that a larger number of particles have been generated by using impure monomer, and that this increased number of particles has been more than sufficient to overcome the reduced polymerization rate per particle due to the reduction of $\bar{n}$ by the reaction with impurities. Obviously, the presence of reactive monomer-soluble impurities in Case II emulsion polymerization has

TABLE III

Recipe for the Emulsion Polymerization of Styrene Shown in Figures 2 and 3

Temperature	55°C
Styrene	100 (phm)
Water	190 (phm)
Potassium persulfate	0.31 (phm)
Sodium lauryl sulfate	6 (phm)
NaHCO$_3$	0.24 (phm)

two competing effects: one on the rate and duration of particle generation, and one on the rate of polymerization per particle.

In the next section we explain these two effects by way of a mathematical model for Case II emulsion polymerizations in the presence of impurities. The solid curves in Figures 2 and 3 are the predictions of this model for these runs.

Modeling the Effect of Impurities

Following an approach used by Hoffman,[5] the monomer-soluble impurities diffuse with monomer preferentially into polymer particles and react with radicals as:

$$Im + R^0 \rightarrow P + Im^0 \tag{1}$$

where Im = impurity molecule,

R^0 = a growing polymeric radical,

P = a dead polymer chain, and

Im^0 = a stable reaction product.

The rate of consumption of impurities is given by:

$$\frac{dN_{IM}}{dt} = -k_{IM}[Im]_p N_p \bar{n}/N_A \tag{2}$$

where $[Im]_p$ = impurity concentration in the particle phase,

N_p = number of particles in the reactor,

$\bar{n}$ = average number of radicals per particle,

N_A = Avogadro's number,

N_{IM} = moles of impurity,

and k_{IM} = rate constant (L/gmol-s)

The equations of Smith and Ewart[8] can be rederived to account for reactions with impurities. First, making the stationary state hypothesis, a radical balance in the water phase gives:

$$R_I + k_{de}N_p\bar{n}/N_A = k_a C_w + k_{tw}C_w^2 + k_{wIM}C_w[Im]_w \tag{3}$$

where the left-hand side represents the rate of appearance of radicals in the water phase by initiation (R_I) and desorption from particles ($k_{de}N_p\bar{n}/N_A$), and the right-hand side gives the rate of consumption of radicals by absorption into particles ($k_a C_w$), termination in the water phase ($k_{tw}C_w^2$) and reaction with water-soluble impurities ($k_{wIM}C_w[Im]_w$). C_w is the concentration of radicals in the water phase. This can be rewritten in the standard

dimensionless form as:

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2 - W\alpha \tag{4}$$

where $\alpha = k_a C_w v / N_p k_{tp}$, $\alpha' = R_I v / N_p k_{tp}$, $m = k_{de} v / k_{tp} N_A$, $Y = N_p k_{tp} k_{tw} / k_a^2 v$, $W = k_{wIM}[Im]_w / k_a v$, and

v = volume of a polymer particle,

k_{tp} = radical termination rate constant in the particle phase.

The water phase termination term (Y) and the reaction with water-soluble impurities term (W) can usually be assumed to be negligible after the induction period.

Then, performing a balance on the number of particles containing n radicals and making a steady-state hypothesis we can write:

$$N_{n-1}\left(k_a C_w / N_p\right) + N_{n+1}(n+1)\left(k_{de} + k_{IM}[Im]_p\right)$$

$$+ \frac{N_{n+2}(n+1)(n+2)k_{tp}}{v}$$

$$= N_n\left[k_a C_w / N_p + n\left(k_{de} + k_{IM}[Im]_p\right) + (n+1)n k_{tp}/v\right] \tag{5}$$

The left-hand side gives the rate of appearance of particles containing n radicals by absorption of a radical by a particle already containing $(n-1)$ radicals, by desorption of a radical or reaction with an impurity in a particle containing $(n+1)$ radicals, and by termination of two radicals in a particle containing $(n+2)$ radicals. The right-hand side accounts for the rate of disappearance of particles containing n radicals by the same mechanisms.

Multiplying Eq. (5) through by v/k_{tp} results in the recursive equation:

$$N_{n-1}\alpha + N_{n+1}(n+1)p + N_{n+2}(n+1)(n+2) = N_n[\alpha + np + (n-1)n] \tag{6}$$

where the parameter p is given by:

$$p = \frac{k_{de}v + k_{IM}[Im]_p v}{k_{tp} N_A} \tag{7}$$

The general solution to this equation for the average number of radicals per particle was first derived by O'Toole[9] as:

$$\bar{n} = \frac{a}{4} \frac{I_p(a)}{I_{p-1}(a)} \tag{8}$$

where $I_p(a)$ and $I_{p-1}(a)$ are the modified Bessel functions of the second kind with parameter $a = (8\alpha)^{1/2}$. An approximate solution to this Eq. (6) first

developed by Ugelstad et al.[10] is given in its modified form for the present case by the expanded fraction expression:

$$\bar{n} = \cfrac{a}{p + \cfrac{2\alpha}{p + 1 + \cfrac{2\alpha}{p + 2 + \cfrac{2\alpha}{p + 3 + \cdots}}}} \tag{9}$$

The radical entry parameter α is normally unknown, but can be calculated from the water phase radical balance Eq. (4). When the desorption rate constant k_{de} is significantly greater than zero, parameter α will also depend upon $\bar{n}$ through Eq. (4). In that case, the two Eqs. (4) and (9) must be solved simultaneously for α and $\bar{n}$.

Note that these equations are identical to the usual Smith-Ewart equations except that the term p replaces the more usual m in Eqs. (8) and (9). This important parameter p defined in Eq. (7) is proportional to the ratio of the rate of disappearance of radicals from particles by desorption and by reaction with impurities to that of disappearance by mutual termination in the particles. For Case II systems the desorption term is zero.

Simulation Studies

In this section the effect of impurities on the emulsion polymerization of styrene is investigated by incorporating the impurity and radical balances of the previous section into the model presented by Broadhead et al.[11] The impurity was assumed to partition between the monomer droplet and particle phases in the same way as the monomer. Taking the recipe to be the same as that in Table III the simulation results of Figures 4, 5, and 6 were obtained using different values for the initial amount of monomer-soluble impurity in the batch. For a small amount of impurity (10 ppm) the results are very similar to the experimental results shown previously in Figure 2. The impurity reduces the average number of radicals per particle early in the reaction to a value much less than 0.5 (Fig. 6), thereby retarding the early polymerization
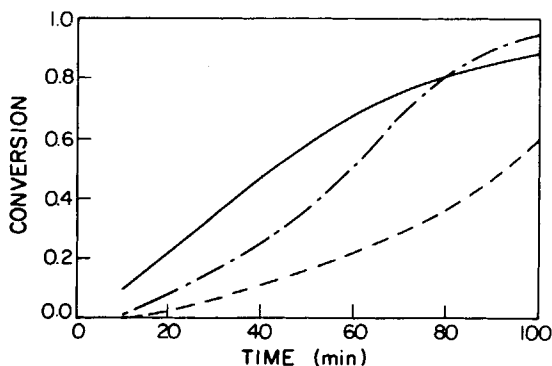

Fig. 4. Effect of monomer-soluble impurity on conversion for different initial impurity amounts: Simulation results.[7] $[Im]_0$: (—) 0 ppm; (-·-) 10 ppm; (--) 20 ppm.
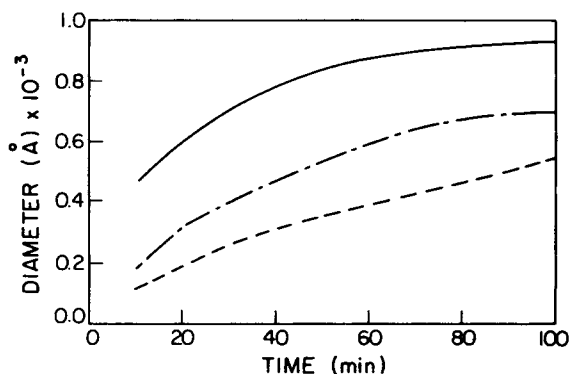
Fig. 5.   Effect of different initial impurity amounts on particle diameter: Simulation results.[7] $[Im]_0$: (—) 0 ppm; (-··-) 10 ppm; (--) 20 ppm.

rate per particle. Therefore, once new particles are generated they grow slowly, thereby creating new particle surface area at a much slower rate compared to the impurity-free case. Because of this the free emulsifier in the system that is available to form micelles and stabilize new particles is depleted at a correspondingly much slower rate than in the case with pure monomer. This results in a much longer period of particle nucleation and a correspondingly much larger number of particles being generated. This is evident in Figure 5 where the particle diameters are much smaller in the cases with impurities.

However, once the impurities have been depleted in the polymer particles, the average number of radicals rises back to the expected value of one-half a radical per particle (Fig. 6). The overall rate of polymerization then increases to a much higher value than that achieved at any time during the impurity-free run (Fig. 4) because of the larger number of particles and eventually, even though the early polymerization rate was severely retarded by the impurities, the batch with the 10 ppm impurities is completed first.

When the amount of impurity is increased to 20 ppm the effects are similar, except that since the impurity takes much longer to react and hence to be
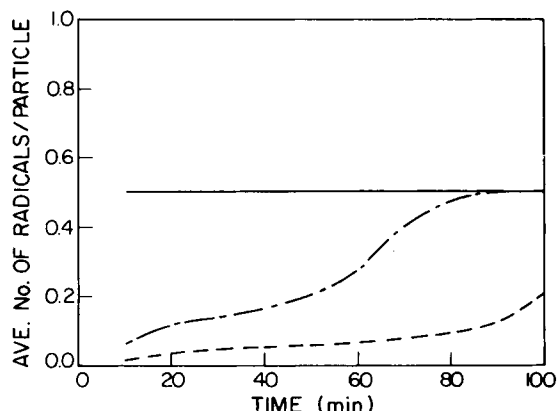

Fig. 6.   Effect of different initial amounts of monomer-soluble impurity on the average number of radicals per particle: Simulation results.[7] $[Im]_0$: (—) 0 ppm; (-··-) 10 ppm; (--) 20 ppm.
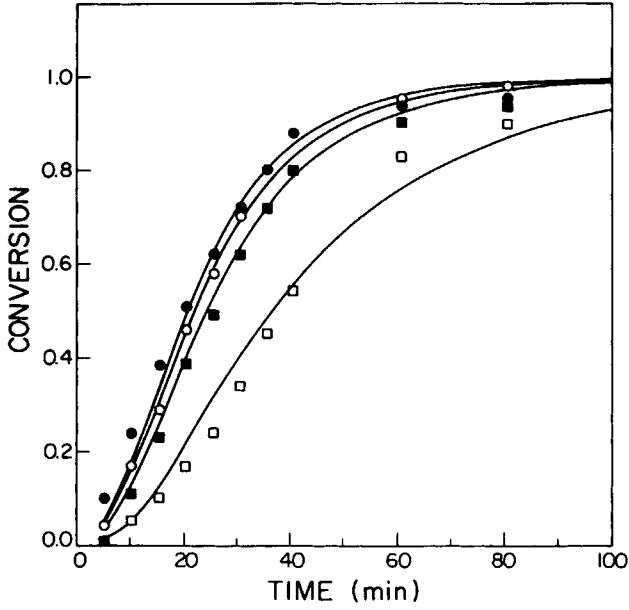
Fig. 7.   Effect of TBC levels on conversion: Emulsion polymerization of styrene. (—) Model; (●) 0 ppm; (○) 20 ppm; (■) 50 ppm; (□) 200 ppm.
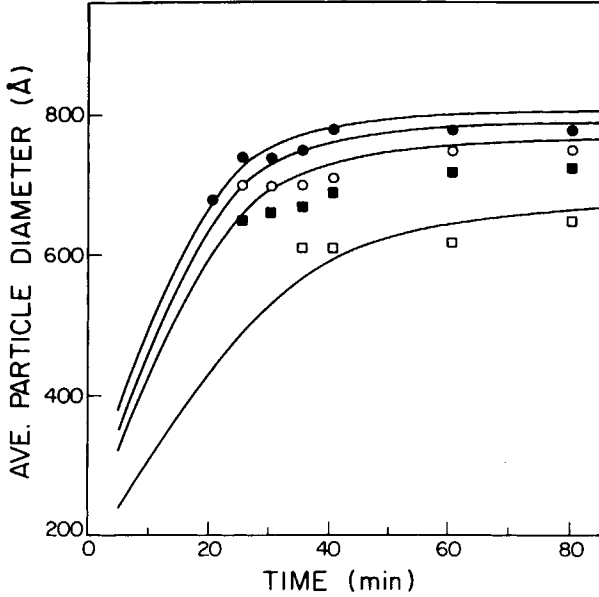

Fig. 8.   Effect of different TBC levels on average polymer particle diameter: Emulsion polymerization of styrene. (—) Model; (●) 0 ppm; (○) 20 ppm; (■) 50 ppm; (□) 200 ppm.
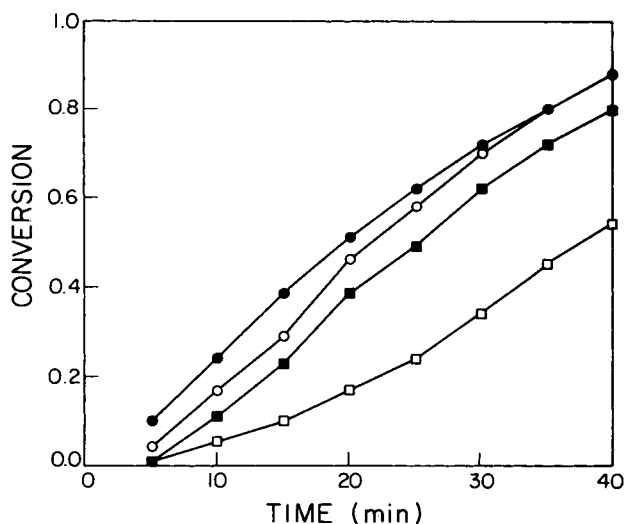
Fig. 9. Plot of the early stages of the polymerization reactions corresponding to Fig. 7. (●) 0 ppm; (○) 20 ppm; (■) 50 ppm; (□) 200 ppm.

depleted, the early retardation lasts much longer, and the batch never catches up to that of the impurity-free case. Even after 100 minutes the average number of radicals per particle is still very low.

Experimental Results

Further experimental results for the emulsion polymerization of styrene are shown in Figures 7, 8, and 9 for levels of monomer-soluble impurity (TBC) ranging from 0 to 200 ppm. The conversion data in Figure 7 were obtained by gravimetry and the particle size data in Figure 8 were obtained by hydrodynamic chromatography (HDC). The results are similar to those already discussed. To better see the effect of impurity levels on the rate of the reaction, the early part of the conversion-time histories are replotted in Figure 9 using an expanded scale and the slopes of the conversion-time curves in different conversion ranges are given in Table IV. The retardation of all the initial rates with increasing impurity levels is evident, as is the increased rate of polymerization at intermediate conversions for the smaller impurity level (20–50 ppm) runs. At very high impurity levels (200 ppm), the impurity is never fully depleted before the run is completed, and so in spite of the much

TABLE IV
Effect of TBC on Rate of Polymerization

TBC (ppm)	Polymerization rate for the conversion range	
	0.1 to 0.25	0.25 to ~ 0.50
0	0.027	0.029
20	0.024	0.034
50	0.023	0.031
100	0.021	0.030
200	0.013	0.021

TABLE V
Effect of Monomer-Soluble Impurities (TBC) on the Properties of the Final Product

TBC (ppm)	Diameter (Å)	N_p (#/mL) ($\times 10^{-15}$)	$\overline{M}_n$ ($\times 10^{-6}$)	$\overline{M}_w$ ($\times 10^{-6}$)	$\overline{M}_w/\overline{M}_n$	Viscosity (cp)
0	780	2.00	1.61	2.42	1.50	41
20	745	2.30	1.18	2.20	1.86	—
50	725	2.43	1.08	2.09	1.93	75
100	705	2.64	1.05	2.16	2.05	91
200	649	3.30	0.98	1.98	2.01	110

larger number of particles generated the overall rate of reaction never exceeds that for the purified monomer. The particle sizes shown in Figure 8 confirm that the final particle diameters are always reduced by increased impurity levels. This is a direct consequence of the increased particle nucleation period.

Other properties of the final converted latex are given in Table V for different TBC levels. The latex viscosity increase with impurity level is a direct consequence of the decrease in particle diameter. The molecular weights obtained by gel permeation chromatography (GPC) show an interesting trend. With no impurity the polydispersity is 1.50, which is the same as obtained in solution polymerization when termination by combination controls the molecular weight development. However, with increasing amounts of TBC the molecular weights fall and the polydispersity rises to 2.0, indicating that the dead polymer is dominantly formed by the reaction with the impurity (TBC). In effect, the impurity acts as a chain transfer agent (CTA) as well as a retarder.

CONCLUDING REMARKS

The general nature of the effects of reactive water-soluble and monomer-soluble impurities on Case II emulsion polymerization kinetics has been studied. Water-soluble impurities have been shown to produce an induction period proportional to the amount of impurities present, but to have little effect on the subsequent polymerization. This confirms the results reported by many authors. The effect of monomer-soluble impurities is more complex. These impurities affect the polymerization rate in two ways. First, they retard the rate of polymerization per particle by reacting with the radicals in the particles, thereby reducing the average number of radicals per particle. However, by doing this they also cause the period of particle nucleation to be extended, thereby causing the nucleation of more particles. The higher the level of impurities, the larger the number of particles produced, and the smaller the final particle diameters. These results were well predicted by the modification of an existing model for Case II emulsion polymerizations to incorporate the effect of impurities.

The consequences of these effects for industrial emulsion polymerizations can be quite serious. Inadequate control over the level of monomer-soluble impurities can lead to varying batch times, and more importantly, to highly variable particle concentrations and sizes. Also of some consequence may be the fact that the larger number of particles generated at a higher impurity

level may lead to inadequate stabilization of the particles and subsequent coagulation, or to inconsistent behavior of the latex when used in subsequent formulations (e.g., when using associative rheological modifiers). Another consequence during production may be higher rates of polymerization due to higher particle concentrations and thus heat-generation rates which cannot be removed through the cooling surfaces, thereby resulting in undesirable temperature excursions and potential runaway polymerizations.

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