

Kinetics of the emulsion copolymerization of styrene and butyl acrylate

Lourdes López de Arbina, María J. Barandiaran, Luis M. Gugliotta* and José M. Asua[†]

Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco/Euskal Herriko Unibertsitatea, Apdo. 1072, 20080 San Sebastián, Spain

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The kinetics of the chemically initiated seeded emulsion copolymerization of styrene and butyl acrylate was investigated in experiments in which the diameter of the seed, the number of seed particles, and the concentration of initiator were widely varied. The experimental data were fitted with a model in which the rate coefficients for radical entry and exit were the adjustable parameters. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Because of its practical significance, emulsion copolymerization has been extensively investigated. However, only a limited effort has been devoted to discriminate the mechanisms involved in this process by estimating the corresponding parameters^{1–3}. This might be due to the difficulties associated with the experimental procedure. Data of the time evolution of both the overall conversion and copolymer composition during the approach to the steady state of the average number of radicals per particle, \bar{n} , in seeded emulsion copolymerizations are particularly useful for the kinetic investigation of this process. To determine these properties, sampling is required, the overall conversion is measured by gravimetry and the copolymer composition by either gas chromatography (g.c.), or n.m.r. Only a limited number of samples can be withdrawn from the reactor and there is a serious risk of introducing oxygen, that affects the kinetics of the process, into the reactor. In addition, the steady state value of \bar{n} is reached at low monomer conversion, and the calculation of the composition of the copolymer formed from g.c. measurements of the unreacted monomer might involve important relative errors. On the other hand, the presence of the seed, makes difficult the determination of the composition of the newly formed copolymer by n.m.r.

Reaction calorimetry offers the possibility of continuous and accurate monitoring of polymerization processes. Although, only information related to the overall conversion is directly available from the heat of polymerization, Urretabizkaia *et al.*⁴ developed an approach to estimate the evolution of the copolymer

composition in batch emulsion copolymerization systems using calorimetric data. This method requires knowledge of the reactivity ratios and the monomer partitioning between the different phases. Recently, Barandiaran *et al.*⁵ demonstrated by simulation the feasibility of estimating the kinetic parameters of emulsion copolymerization systems using only calorimetric measurements. It has to be pointed out that the approaches developed by Urretabizkaia *et al.*⁴ and Barandiaran *et al.*⁵ can be applied to any kind of frequent monitoring of the overall conversion such as dilatometric and densitometric measurements.

In the present paper, the kinetics of the chemically initiated seeded emulsion copolymerization of styrene and butyl acrylate carried out in a calorimeter reactor under a wide range of experimental conditions was investigated. Styrene–butyl acrylate latexes are extensively used for paints and adhesives. The dependence of the estimated absorption and desorption rate coefficients on the polymer particle diameter was used to speculate about the mechanisms involved in this process. A better knowledge of these mechanisms will allow us to develop mathematical models with improved predictive capabilities.

EXPERIMENTAL

Butyl acrylate (BuA), was washed several times first with a 10 wt% solution of NaOH and afterwards with deionized water until the wash water was neutral. Then it was dried over CaCl₂ and distilled under reduced pressure. Styrene (St) was purified by distillation under reduced pressure. The purified monomers were stored at –18°C until use. K₂S₂O₈ (Merck, Germany), Na₂S₂O₈ (Merck), NaH₂PO₄ (Merck) and sodium lauryl sulfate (SLS, Henkel, Germany) were used as received. Deionized water was used throughout the work.

*On leave from INTEC (Consejo Nacional de Investigaciones Científicas y Técnicas and Universidad Nacional del Litoral, Santa Fe, República Argentina)

[†] To whom the correspondence should be addressed

Two seeds of St/BuA = 60/40 weight composition and different sizes were prepared. The smaller one, S1, was prepared in two stages. The first was carried out at 70°C in a batch reactor using the recipe given in Table 1. The resulting latex was used as a seed for the second stage that was carried out at 75°C under starved conditions in a semicontinuous reactor using the recipe given in Table 1. The second seed, S2, was prepared by swelling seed S1 with a monomer mixture and polymerizing it in batch at 60°C afterwards. The recipe for this polymerization is also included in Table 1. The seeds were kept at 80°C for 48 h to decompose the initiator completely. The diameters of these seeds were: S1 = 64 nm and S2 = 100 nm. Kinetic runs were conducted at 60°C under Interval II conditions in a calorimeter reactor (Mettler RC1). Table 2 presents a summary of the polymerizations carried out in which both the number of polymer particles and the concentration of initiator were varied for each seed. Prior to the polymerization, the seed and all of the components of the recipe with the exception of the initiator and 6 cm³ of water, were mixed in a 2.5 l bottle and kept under agitation for at least 15 h at room temperature. During this time, which was enough to reach the equilibrium swelling, the bottle was purged with nitrogen (purity:

99.995%; flow rate: 4.4 l h⁻¹). The reactor was purged with nitrogen before introducing the reaction mixture from the swelling bottle. The reactor was calibrated and stabilized and a sample was withdrawn from the reactor to check for thermal polymerization. No thermal polymerization was observed in any run. The polymerization was started by injecting the initiator dissolved in 6 cm³ of water. The polymerizations were carried out under a nitrogen blanket (flow rate: 6.3 l h⁻¹). At the end of the process, a sample was withdrawn from the reactor to determine the overall gravimetric conversion and the copolymer composition (by g.c.). The final latexes were examined by TEM. No secondary nucleation was observed.

MATHEMATICAL MODEL

Assuming that the extent of the aqueous phase polymerization is negligible, the material balances for the monomers are:

$$\frac{dX_i}{dt} = (k_{pA} P_A^p + k_{pB} P_B^p) [i]_p \frac{\bar{n} N_T}{M_{i0} N_A} \quad i = A, B \quad (1)$$

where X_i is the molar conversion of monomer i , $k_{p_{ij}}$ the

Table 1 Recipes used to prepare the styrene/butyl acrylate seeds (all in grams)

Seed S1								Feeding time (h)
	St	BuA	SLS	H ₂ O	NaH ₂ PO ₄	K ₂ S ₂ O ₈	T (°C)	
First stage	256.8	171.4	37.8	1427	4.1	3.9	70	–
Second stage	447.8	298.4	–	2600	–	5	75	9
Seed S2								T (°C)
	St	BuA	SLS	H ₂ O	Seed S1	Na ₂ S ₂ O ₈		
	55.6	37.1	1.1	829.9	31.1	0.4		60

Table 2 Summary of the kinetic runs

Seed	N_T (particles cm ⁻³ of water)	[Na ₂ S ₂ O ₈] (mol cm ⁻³ of water)	\bar{n}
S1	2.6×10^{14}	5.1×10^{-7}	0.18
		10.1×10^{-7}	0.21
		20.1×10^{-7}	0.26
		39.5×10^{-7}	0.31
		78.1×10^{-7}	0.37
	5.2×10^{14}	159.4×10^{-7}	0.41
		5.0×10^{-7}	0.15
		10.1×10^{-7}	0.19
		19.9×10^{-7}	0.22
		40.4×10^{-7}	0.27
S2	1.0×10^{14}	10.1×10^{-7}	0.32
		20.1×10^{-7}	0.36
		40.1×10^{-7}	0.40
	2.0×10^{14}	10.2×10^{-7}	0.27
		41.0×10^{-7}	0.36

propagation rate constants, $[i]_p$ the concentration of monomer i in the polymer particles, \bar{n} the average number of radicals per particle, N_T the number of polymer particles per cm^3 of water, M_{i0} the number of moles of monomer i per cm^3 of water initially charged into the reactor, N_A the Avogadro's number, and P_i^p the time averaged probability of finding a free radical with ultimate unit of type i in the polymer particles. These probabilities are obtained from the pseudo-steady state approximation for the growing radicals

$$P_A^p = \frac{k_{pBA}[A]_p}{k_{pBA}[A]_p + k_{pAB}[B]_p} \quad (2)$$

$$P_B^p = 1 - P_A^p \quad (3)$$

The concentration of the monomers in the polymer particle was calculated using the equilibrium equations and the overall material balances by means of an iterative algorithm inspired by the method proposed by Omi *et al.*⁶ and successfully applied by Urretabizkaia and Asua⁷. The partition coefficients used in this calculation are given in Table 3.

Under the conditions used in this work, \bar{n} in all of the polymerizations was below 0.5. \bar{n} was calculated from the steady-state part of the time evolution of the overall calorimetric conversion, X_{TC} , from

$$\frac{dX_{TC}}{dt} = \frac{\sum_{i=A,B} (k_{pAi}P_A^p + k_{pBi}P_B^p)[i]_p(-\Delta H_i)}{M_{A0}(-\Delta H_A) + M_{B0}(-\Delta H_B)} \left(\frac{\bar{n}N_T}{N_A} \right) \quad (4)$$

where $(-\Delta H_i)$ is the heat of homopolymerization of monomer i . The values of \bar{n} calculated using equation (4) are given in Table 2. Since \bar{n} is always less than 0.5, namely the 'zero-one' assumption holds and $\bar{n} \times N_T$ equals N_1 . The form of the population balance for polymer particles containing one radical depends on the level of description of the free radicals in the aqueous phase. López de Arbina *et al.*⁸ used models of different complexity to fit the evolution of the conversion in the chemically initiated seeded emulsion polymerization of styrene carried out under a wide range of experimental conditions. The simplest model made no distinction between radicals in the aqueous phase, whereas the other models distinguished between initiator-derived radicals and transfer-derived radicals in the aqueous phase. López de Arbina *et al.*⁸ reported that all models fitted in a similar way the experimental data, i.e. that no advantage was observed by increasing the complexity of

the mathematical model by including the distinction between initiator-derived radicals and transfer-derived radicals in the aqueous phase. Therefore, a mathematical model in which no distinction between radicals in the aqueous phase is made was used in the present work. The population balance for particles containing one radical is given by

$$\frac{dN_1}{dt} = k_a[R]_w(N_T - 2N_1) - \bar{k}_d N_1 \quad (5)$$

where k_a is the radical entry rate coefficient, \bar{k}_d the overall rate coefficient for radical desorption, and $[R]_w$ the concentration of free radicals in the aqueous phase, which can be calculated through the material balance for free radicals in the aqueous phase

$$\frac{d[R]_w}{dt} = 2fk_1[I_2] + \frac{\bar{k}_d N_1}{N_A} - \frac{k_a[R]_w N_T}{N_A} - 2\bar{k}_{tw}[R]_w^2 = 0 \quad (6)$$

where f and k_1 are the efficiency factor and the rate coefficient, respectively, for initiator decomposition, $[I_2]$ the number of moles of initiator per cm^3 of water, and \bar{k}_{tw} the average termination rate coefficient in the aqueous phase. It has been demonstrated that the pseudo-steady state approximation for the free radical concentration in the aqueous phase can be safely used⁹, and hence equation (6) equals zero. The average termination rate coefficient in the aqueous phase is given by

$$\bar{k}_{tw} = k_{twAA}(P_A^w)^2 + 2k_{twAB}P_A^wP_B^w + k_{twBB}(P_B^w)^2 \quad (7)$$

where k_{twij} is the rate constant for termination of radicals of types i and j in the aqueous phase and P_i^w the time averaged probability of finding a radical with ultimate unit of type i in the aqueous phase. P_i^w is defined as P_i^p [equations (2) and (3)] but using the concentrations of the monomers in the aqueous phase. In reaction calorimetry, X_A and X_B are not directly measured but the overall calorimetric conversion, X_{TC} , can be considered the observable variable. Assuming that the cross-propagation heat $(-\Delta H_{ij})$ is equal to the heat homopolymerization $(-\Delta H_j)$, the relationship between X_{TC} and X_i is⁴

$$X_{TC} = \frac{M_{A0}X_A(-\Delta H_A) + M_{B0}X_B(-\Delta H_B)}{M_{A0}(-\Delta H_A) + M_{B0}(-\Delta H_B)} \quad (8)$$

The calorimetric conversion was calculated from the measured polymerization heat flow as

$$X_{TC}(t) = \frac{\int_0^t Q_r(t) dt}{\sum_{i=A,B} X_{if} M_{i0}(-\Delta H_i)} X_{TCif} \quad (9)$$

where X_{if} is the molar conversion of monomer i at the end of the process determined by gravimetry and g.c., and X_{TCif} the calorimetric conversion calculated from X_{if} by means of equation (8).

PARAMETER ESTIMATION

Equations (1), (5) and (6) are a system of initial value stiff differential equations containing several parameters that, in principle, can be estimated by means of the approach detailed in ref. 9. However, de la Cal *et al.*² found that the

Table 3 Parameter values taken from literature

$k_{pAA}^{22}, k_{pBB}^{19}$ ($\times 10^{-5}$) ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	3.76	1.27
r_A^{20}, r_B^{20}	0.75	0.20
$k_{twAA}^{23}, k_{twBB}^{19}$ ($\times 10^{-10}$) ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	7	0.00018
$k_t(s^{-1})^{21}, f^{21}$	5.78×10^{-6}	0.6
$(-\Delta H_A)^{24}, (-\Delta H_B)^4$ (kJ mol^{-1})	74	78
m_{dAw}, m_{pAw}^{11}	2714	1629
m_{dBw}, m_{pBw}^{11}	724	471

A = Styrene
B = Butyl acrylate

cross-propagation rate constants cannot be estimated accurately even when both X_A and X_B are directly measured and they advised the use of the approach proposed by de la Cal *et al.*¹⁰ for estimation of the reactivity ratios from data obtained in emulsion polymerization to calculate $k_{p_{ij}}$. On the other hand, Asua *et al.*⁹ demonstrated that k_a and $\bar{k}_{d,w}$ are correlated and they cannot be unambiguously determined unless some independent measurement of the concentration of radicals in the aqueous phase is available. Therefore, in the present work only k_a and \bar{k}_d were estimated by fitting the experimental data taking the values for the other parameters from literature (Table 3). The objective function minimized to estimate k_a and \bar{k}_d was

$$S = \sum_{j=1}^M \frac{1}{G_j} \sum_{i=1}^{G_j} (X_{TC_e} - X_{TC_c})_{i,j}^2 \quad (10)$$

where M is the number of experiments, G_j the number of experimental points in experiment j , X_{TC_e} the measured calorimetric conversion, and X_{TC_c} the calorimetric conversion predicted by the model.

Different mechanisms have been proposed for the radical entry process. Gardon¹¹ treated the entry as a collisional process predicting that k_a is proportional to the square of the particle diameter. Ugelstad and Hansen¹² proposed that the rate-determining step for entry is the diffusion of soluble oligomeric species from the aqueous phase into the polymer particle. In this model, a linear dependence of the entry rate coefficient on the particle diameter (d_p) is predicted. Penboss *et al.*¹³ proposed the colloidal model, where k_a is proportional to d_p . Maxwell *et al.*¹⁴ have proposed the so-called propagational model but its use in the frame of the mathematical model used in the present work may be inconsistent⁸. Therefore, in order to take into account the effect of the particle diameter on k_a , the entry rate coefficient was written as

$$k_a = k_a^* d_p^{\alpha_1} \quad (11)$$

where α_1 can vary between 1 and 2.

The overall exit rate coefficient depends on the individual exit rate coefficients¹⁵

$$\bar{k}_d = k_{d_A} + k_{d_B} \quad (12)$$

This means that \bar{k}_d depends on the monomer molar ratio in the system. In this paper, the same initial monomer molar ratio was used in all of the polymerizations and as the final overall conversion was relatively low ($\approx 20\%$), only a limited composition drift is expected to occur during the polymerization. Therefore, the effect of the composition of the monomer mixture on \bar{k}_d was not taken into consideration. On the other hand, Asua *et al.*¹⁶ developed a general equation for k_d that unless very small particles are involved reduces to

$$k_d = (k_{fm_A} P_A^P + k_{fm_B} P_B^P) [i]_p \frac{K_{0i}}{\beta_i K_{0i} + k_{p_{iA}} [A]_p + k_{p_{iB}} [B]_p} \quad (13)$$

For sparingly water-soluble monomers $\beta_i \rightarrow 0$, whereas for highly water-soluble monomers $\beta_i \rightarrow 1$. In addition, if the exit occurs by diffusion with no additional resistance in the interface, $K_{0i} \propto (1/d_p^2)$ ¹⁷.

Therefore

$$k_d \propto (1/d_p^2) \quad \text{if} \quad k_{p_{iA}} [A]_p + k_{p_{iB}} [B]_p \gg \beta_i K_{0i} \quad (14)$$

$$k_d \neq f(d_p) \quad \text{if} \quad k_{p_{iA}} [A]_p + k_{p_{iB}} [B]_p \ll \beta_i K_{0i} \quad (15)$$

Both monomers used in this work, styrene and butyl acrylate, are sparingly soluble in water. Therefore, the dependence of \bar{k}_d on d_p is expected to be close to the limit given by equation (14), and \bar{k}_d was expressed as

$$\bar{k}_d = k_d^* d_p^{-\alpha_2} \quad (16)$$

where α_2 can vary between 0 and 2.

k_a^* and k_d^* were estimated using the approach proposed by Asua *et al.*⁹ and different values of α_1 and α_2 . The results are presented in Table 4 where it can be seen that the best fitting was obtained for values of α_2 lower than 1, whereas similar fitting was obtained with both $\alpha_1 = 1$ and $\alpha_1 = 2$. The confidence intervals of k_a^* and k_d^* for the values of α_1 and α_2 that provided the best fitting are also included in Table 4. Figures 1 and 2 present the comparison between experimental results and model predictions for $\alpha_1 = 1$ and $\alpha_2 = 0.5$. Although these results are only approximate because α_1 and α_2 were not estimated but discrete values were used, they show that the information contained in the data was not enough to discriminate between the diffusional¹², colloidal¹³ and collisional¹¹ mechanisms for radical entry. This uncertainty may be due to the fact that the seeds were not monodisperse but narrowly distributed. On the other hand, the dependence of \bar{k}_d on d_p was substantially lower than what was expected for sparingly water soluble monomers like styrene and butyl acrylate [equation (14)]. This result is qualitatively in agreement, although with lower values of α_2 , with that found by the present authors for the seeded emulsion polymerization of styrene⁸. This dependence may be explained taking into consideration the profile of radical concentration in the polymer particles due to the anchoring of the entering radicals onto the surface of the polymer particle. Through Monte Carlo simulations, de la Cal *et al.*¹⁸ showed that the more pronounced the radical concentration profile the higher the rate for radical desorption. Larger particles have more pronounced radical concentration profiles, and hence comparatively faster radical desorptions that can counteract the effect of d_p on \bar{k}_d predicted by equation (14) leading to a lower value of α_2 . The lower value of α_2 as compared with that found for the seeded polymerization of styrene⁸ might be due to the fact that the water solubility of butyl acrylate is higher than that of styrene.

CONCLUSIONS

The kinetics of the chemically initiated seeded emulsion copolymerization of styrene and butyl acrylate was investigated. Diameter of the seed, number of seed particles and concentration of initiator were varied in these experiments and the process monitored by reaction calorimetry. The experimental data were fitted with a mathematical model in which the rate coefficients for free radical entry and exit were the adjustable parameters. The dependence of the entry rate coefficient on d_p could not be determined because similar fitting was obtained with both $k_a \propto d_p$ and $k_a \propto d_p^2$. On the other hand, the dependence of k_d on d_p was substantially lower than

Table 4 Values of the entry and exit rate coefficients assuming different size dependences

α_1	α_2	k_a^*	k_a ($d_p = 150$ nm)	k_d^*	k_d ($d_p = 150$ nm)	S
1	0	1.80×10^{14}	2.70×10^9	0.52×10^{-1}	5.24×10^{-2}	1.18×10^{-3}
1	0.5	1.48×10^{14}	2.22×10^9	0.15×10^{-3}	3.80×10^{-2}	7.66×10^{-4}
1	1	1.49×10^{14}	2.23×10^9	0.46×10^{-6}	3.07×10^{-2}	9.43×10^{-4}
1	1.5	1.87×10^{14}	2.81×10^9	1.67×10^{-9}	2.87×10^{-2}	1.66×10^{-3}
1	2	2.49×10^{14}	3.73×10^9	0.61×10^{-11}	2.72×10^{-2}	2.80×10^{-3}
2	0	1.58×10^{19}	3.57×10^9	0.47×10^{-1}	4.70×10^{-2}	6.59×10^{-4}
2	0.5	2.30×10^{19}	5.17×10^9	0.19×10^{-3}	4.85×10^{-2}	8.82×10^{-4}
2	1	3.33×10^{19}	7.50×10^9	0.71×10^{-6}	4.71×10^{-2}	1.43×10^{-3}
2	1.5	4.87×10^{19}	10.96×10^9	2.51×10^{-9}	4.33×10^{-2}	2.24×10^{-3}
2	2	7.27×10^{19}	16.36×10^9	0.86×10^{-11}	3.81×10^{-2}	3.28×10^{-3}

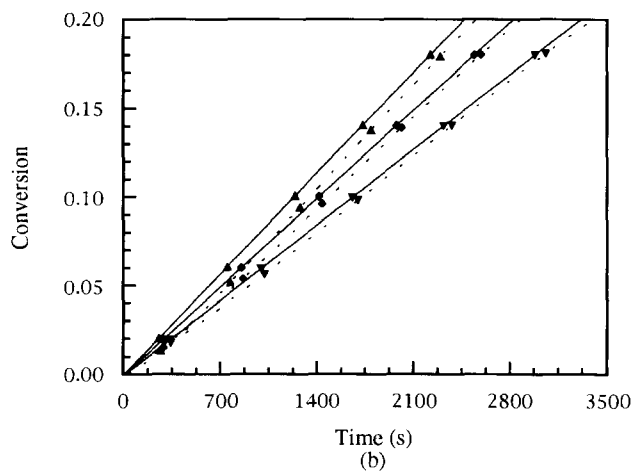
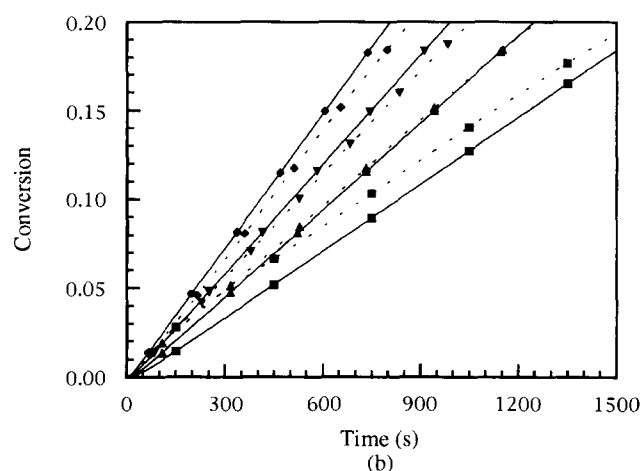
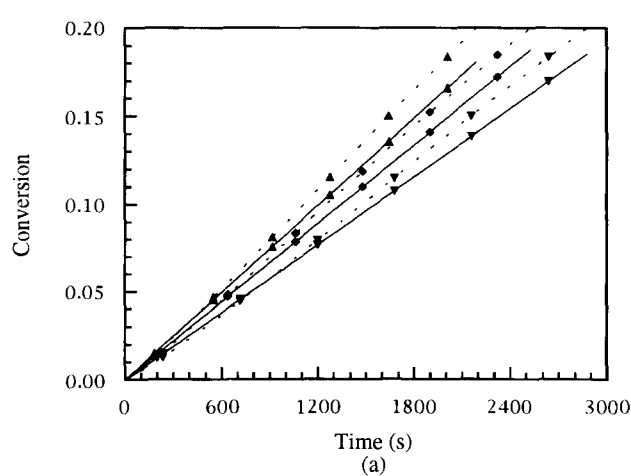
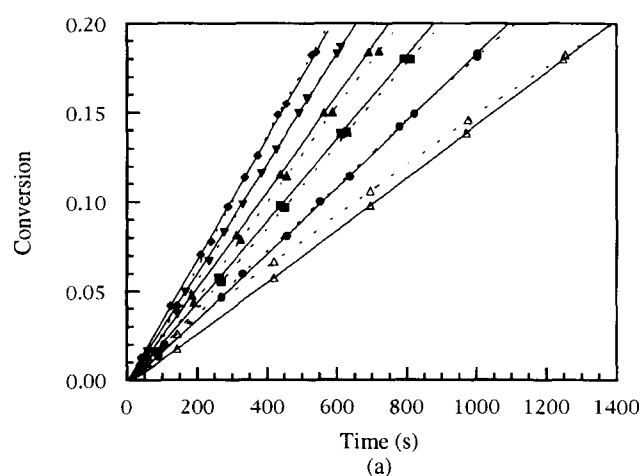


Figure 1 Comparison between experimental results (---) and model predictions (solid lines) for $\alpha_1 = 1$ and $\alpha_2 = 0.5$. (a) Seed: S1, $N_T = 2.6 \times 10^{14}$ particles cm^{-3} of water, $[I_2] \times 10^7$ mol cm^{-3} of water: (Δ) 5.1, (\bullet) 10.1, (\blacksquare) 20.1, (\blacktriangle) 39.5, (\blacktriangledown) 78.1, (\blacklozenge) 159.4. (b) Seed: S1, $N_T = 5.2 \times 10^{14}$ particles cm^{-3} of water, $[I_2] \times 10^7$ mol cm^{-3} of water: (\blacksquare) 5.0, (\blacktriangle) 10.1, (\blacktriangledown) 19.9, (\blacklozenge) 40.4

Figure 2 Comparison between experimental results (---) and model predictions (solid lines) for $\alpha_1 = 1$ and $\alpha_2 = 0.5$. (a) Seed: S2, $N_T = 1.0 \times 10^{14}$ particles cm^{-3} of water, $[I_2] \times 10^7$ mol cm^{-3} of water: (\blacktriangledown) 10.1, (\blacklozenge) 20.1, (\blacktriangle) 40.1. (b) Seed: S2, $N_T = 2.0 \times 10^{14}$ particles cm^{-3} of water, $[I_2] \times 10^7$ mol cm^{-3} of water: (\blacktriangledown) 10.2, (\blacklozenge) 20.1, (\blacktriangle) 41.0

what was expected for sparingly water soluble monomers. This suggests that the anchoring of the initiator radicals on the surface of the polymer particle might have a significant role in the desorption mechanism.

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APPENDIX

$[A]_j, [B]_j$	Concentration of monomers A and B, respectively, in the phase j (mol cm^{-3})
d_p	Diameter of the monomer swollen polymer particle (cm)
f	Efficiency factor for initiator decomposition.
G_j	Number of experimental points in experiment j
$[I_2]$	Concentration of initiator (mol cm^{-3})

k_a	Entry rate coefficient ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)
k_a^*	Parameter defined by equation (11)
k_d	Overall desorption rate coefficient (s^{-1})
k_d^*	Parameter defined by equation (16)
$k_{d,i}$	Desorption rate coefficient for radicals of the type i (s^{-1})
$k_{tm,i}$	Monomer chain transfer constant ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)
k_I	Rate coefficient for initiator decomposition (s^{-1})
$K_{0,i}$	Rate of exit of a monomeric radical of the type i from a polymer particle (s^{-1})
$k_{p,j}$	Propagation rate constant ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)
$k_{p,i,j}$	Propagation rate constant of a monomeric radical ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)
$k_{tw,i,j}$	Termination rate constant in the aqueous phase ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)
\bar{k}_{tw}	Average termination rate constant in the aqueous phase ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)
m_{diw}	Partition coefficient of monomer i between monomer droplets and aqueous phase
m_{piw}	Partition coefficient of monomer i between polymer particles and aqueous phase
M	Number of experiments
M_{i0}	Amount of monomer i initially charged into the reactor (mol cm^{-3})
\bar{n}	Average number of radicals per particle
N_A	Avogadro's number
N_1	Number of polymer particles containing one radical, per cm^3 of water
N_T	Total number of polymer particles, per cm^3 of water
P_i^j	Time averaged probability of finding a radical with ultimate unit of type i in the phase j
Q_r	Overall heat of reaction (kJ)
$[R]_w$	Concentration of radicals in the aqueous phase (mol cm^{-3})
r_A, r_B	Reactivity ratios
S	Residual sum of squares
t	Reaction time (s)
X_j	Conversion of monomer i
X_{TC}	Overall calorimetric conversion
X_{TC_c}	Measured overall calorimetric conversion
X_{TC_p}	Overall calorimetric conversion predicted by the model

Greek symbols

α_1, α_2	Parameters defined by equations (11) and (16)
β_i	Probability that a monomeric radical of type i reacts in the aqueous phase by either propagation or termination
$(-\Delta H_i)$	Heat of homopolymerization of monomer i (kJ mol^{-1})

Subscript

tf	Final reaction time (s)
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