



Surfactant-enhanced free radical polymerization of styrene in emulsion gels

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ARTICLE INFO

Article history:

Received 12 February 2008

Received in revised form 10 May 2008

Accepted 13 May 2008

Available online 21 May 2008

Keywords:

Free radical polymerization

Emulsion gels

Polymer kinetics

ABSTRACT

The presence of a surfactant (such as hexadecyltrimethylammonium bromide, CTAB) enhanced the rate of polymerization of styrene in emulsion gels with and without silica. The emulsion gels consisted of styrene, azobisisobutyronitrile (AIBN), surfactant, water, and, in some cases, fumed silica. Polymerization of the emulsions was carried out at room temperature in one or several days depending on the composition of the emulsion. The conversion of monomer to polymer could exceed 90% in a couple of days. In contrast, very little polymerization occurred in the absence of surfactant. A simple model, incorporating a surfactant–initiator complex and standard free radical polymerization, successfully fits the experimental kinetics data. This analysis suggests that the initiator is complexed with approximately three surfactant molecules.

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1. Introduction

Emulsion polymerization is one of the most important industrial processes for the large-scale preparation of polymers. Recent developments and progress in the understanding of emulsion polymerization have been discussed in two recent reviews [1,2]. Conventional emulsion (or oil-in-water emulsion) polymerization [3] involves the polymerization of vinyl monomers at favorable rates in an aqueous medium containing a surfactant and a water-soluble initiator. The kinetic theory of emulsion polymerization developed by Smith and Ewart [4,5] has achieved good success in modeling emulsion polymerization. According to this theory, initiator radicals are generated in the aqueous phase and diffuse into soap micelles swollen with monomer. The overall polymerization rate depends on the polymerization rate within the particles, as well as on the number of particles. Another model developed by Medvedev [6] attached little importance to the number of particles, but postulated that the adsorbed surfactant layer was the principle locus of initiation. This kinetic model was applied to cases in which the initiator was water- or oil-soluble.

Concentrated emulsions have been of interest [7–14] in the past four decades because of their extraordinarily large internal phase volume (>74%), their unusual geometrical packing and their rheological properties. Because of other characteristic features, such as large dispersed phase contents, high viscosities, and translucence,

they are also referred to as emulsion gels, gel emulsions or high internal-phase emulsions (HIPE). Some concentrated emulsions have polyhedral cell structures that are separated from each other by a network of thin films formed by a continuous phase of water and surfactant [7–11]. The use of concentrated emulsions or high internal-phase emulsions as new reaction media has been probed in recent years. Ruckenstein and co-workers [15–18] have extensively investigated polymerization processes in concentrated emulsions in which organic monomers are the internal phase. Some other research groups [19–25] have explored polymerizations in the high internal-phase emulsions in which the mass ratio between the organic phase and the aqueous phase is typically 26:74.

In our lab, we became interested in an unconventional emulsion polymerization process [26,27] for the preparation of composites of silica and polymers, enzyme immobilization [28], and the room temperature decomposition [29] of AIBN in the emulsion gels. The content of organic monomer in these emulsion gels could contain more than 74% with an oil-soluble initiator. Emulsion gels can be prepared at room temperature by mixing styrene, fumed silica and initiator, such as azobisisobutyronitrile (AIBN), with an aqueous solution of surfactant, such as hexadecyltrimethylammonium bromide (CTAB). The structure of the emulsion gels has not been studied in detail and may be similar to concentrated emulsions. As a working model, we envision the surfactant to form an interface between the monomer and water, stabilizing the emulsion. Surprisingly, the emulsions described in this study can be polymerized at room temperature in 1–4 days depending on their composition, while the polymerization of styrene with AIBN alone at room

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temperature is very slow. This suggests that the free radical polymerization in this unconventional emulsion was promoted by the surfactant. The results of this study showed that the overall polymerization rate of these enhanced polymerizations depends on the concentrations of monomer, initiator and surfactant. The phenomenon of room temperature polymerization and the strong dependence of the polymerization rate on surfactant concentration indicated that the surfactant played a major role in the polymerization.

The effect of surfactant in emulsion polymerization has been investigated experimentally. A decrease in the overall activation energy [30–33] of polymerization and the increase in the polymerization rate [34], with addition of surfactant for emulsion and suspension polymerizations, have been observed. Arita et al. [34] observed that methyl methacrylate and styrene can be polymerized at 80 °C in emulsions containing sodium tetrapropylenebenzenesulfonate without initiator. Michaelis–Menten's equation for enzymatically catalyzed reactions was applied to their polymerization process [34]. They suggested that a complex of monomer and surfactant formed in emulsion, which generated free radicals. A complex was also proposed for the increased decomposition of AIBN in the presence of stannous octoate [35]. Enhanced room temperature polymerization of styrene has also been reported for other initiators in the presence of surfactant [36].

In order to understand this enhanced polymerization in our emulsion gel systems, we initially tried fitting the experimental data with the Smith–Ewart model of emulsion polymerization. The result of poor agreement between the experiment results and the Smith–Ewart model suggested that a different mechanism promoting the polymerization should be considered. In this paper, we have developed a simple kinetic model based on a surfactant–initiator complex and conventional free radical polymerization kinetics. We have recently shown that the decomposition of the initiator was enhanced in the interfacial layer of surfactant in similar systems [29]. The fit of our kinetics model to the experimental polymerization data verifies that the overall polymerization depends on the concentrations of monomer, initiator and surfactant.

2. Model development

We assume that the polymerizable emulsion consists of an aqueous phase, and a monomer (oil or bulk) phase containing the initiator, and an interfacial region (simply referred to as the interface). For the purpose of this work, the behavior of the monomer is taken to be the same as a bulk monomer phase. The interface between the water and monomer consists of a surfactant layer with the charged head groups oriented towards the water and the tails embedded in the monomer phase. We propose that the decomposition of the initiator can occur either in the monomer phase or in the interfacial region. In the interfacial region, the initiator, I_2 , is complexed by n surfactant (S) molecules to form the complex, S_nI_2 . This is schematically shown as:



where I^* , K_n (mol/l), $k_{d,b}$ and $k_{d,i}$ represent the free radical, association constant for the complex and rate constants for the decomposition of the initiator in the bulk phase (b) and at the interface (i), respectively. For simplicity, we have omitted the often used initiator efficiency, f . The total decomposition rate of the initiator, R_d , is the sum of the rates for the two pathways, or

$$R_d = R_{d,b} + R_{d,i} \quad (2)$$

where $R_{d,b}$ and $R_{d,i}$ are the decomposition rates of the initiator in the monomer phase and at the interface, respectively. We have shown [29] that the decomposition rate of the initiator at the interface is much faster than that in the bulk phase, $R_{d,i} \gg R_{d,b}$ when the surfactant is present. The surfactant and the initiator first combine to form a surfactant–initiator complex, S_nI_2 . This step is assumed to be reversible with no chemical change occurring. The surfactants and the initiator are not chemically bonded. The decomposition of the initiator occurs in a second step with the rate constant, $k_{d,i}$. The concentration of the complex may be expressed in terms of the association constant, K_n , as:

$$K_n = [S_nI_2]/([S]^n[I_2]) \quad (3)$$

where $[S]$, $[I_2]$, and $[S_nI_2]$ represent the concentrations of the free surfactant, initiator, and surfactant–initiator complex, respectively. The rate of the decomposition of the initiator and the production of the active initiator radical, I^* , from the complex is given by:

$$R_{d,i} = -d[I_2]/dt = (1/2)d[I^*]/dt = k_{d,i}[S_nI_2] \quad (4)$$

where the coefficients account for one initiator decomposing into two radicals. For simplicity, we have also omitted the efficiency factor, f , which accounts for the fraction of radicals that do not initiate polymerization [3]. To determine the rate of decomposition of the initiator in the surfactant–initiator complex, an estimation of the complex concentration is required. The total surfactant concentration, $[S]_0$, is the sum of the free surfactant and the complexed surfactant, or

$$[S] = [S]_0 - n[S_nI_2] \quad (5)$$

which yields

$$[S_nI_2] = (K_n[I_2])([S]_0 - n[S_nI_2])^n \quad (6)$$

In the limit of low concentrations of the initiator, the concentration of the surfactant–initiator complex will also be low. The expansion of the exponential term in Eq. (6) can then be truncated after the first two terms (to the first power in the complex concentration). The resulting truncated expansion yields:

$$[S_nI_2] = K_n[I_2][S]_0^n / (1 + n^2 K_n[I_2]([S]_0^{n-1})) \quad (7)$$

Substituting Eq. (7) into Eq. (4) yields:

$$R_{d,i} = (1/2)d[I^*]/dt = k_{d,i}K_n[I_2]([S]_0)^n / \{1 + n^2 K_n[I_2]([S]_0)^{n-1}\} \quad (8)$$

In order to relate Eq. (8) to the rate of free radical polymerization in the emulsion, we use the well-known mechanism of free radical polymerization in solution. The reaction is a chain reaction with three distinct steps: initiation, propagation, and termination [3]. The rate equations become solvable based on the assumption of a steady-state concentration of radicals. The total rate of the disappearance of the monomer, $[M]$, in the free radical polymerization, R_p , is the sum of the rates in the two different environments.

$$R_p = -d[M]/dt = R_{p,b} + R_{p,i} \quad (9)$$

The polymerization rate, $R_{p,b}$, in the monomer (bulk) phase can be expressed as

$$R_{p,b} = C_b[M][I_2]^{1/2} \quad (10)$$

where

$$C_b = k_{p,b}(k_{d,b}/k_{t,b})^{1/2} \quad (10a)$$

in which $k_{p,b}$, $k_{d,b}$ and $k_{t,b}$ are the rate constants for propagation, decomposition of the initiator, and termination in the monomer phase, respectively.

Similar to the development of the rate for polymerization in the bulk phase, the polymerization rate, $R_{p,i}$, for the interfacial catalyzed reaction can be written as:

$$R_{p,i} = k_{p,i}[M](R_{i,i}/2k_{t,i})^{1/2} \quad (11)$$

in which $k_{p,i}$ and $k_{t,i}$ are, respectively, the propagation rate constant and the termination rate constant for the catalyzed polymerization. The rate of initiation corresponding to the interfacially enhanced polymerization, $R_{i,i}$, is assumed to be equal to twice the rate of decomposition of the initiator, or $2R_{d,i} = R_{i,i}$. Using this and Eq. (8), we have

$$R_{p,i} = C_i[M][I_2]^{1/2}K_n([S]_0)^{n/2} / \left\{ 1 + n^2K_n[I_2]([S]_0)^{n-1} \right\}^{1/2} \quad (12)$$

where

$$C_i = k_{p,i}(k_{d,i}/k_{t,i})^{1/2} \quad (12a)$$

In this case it seems reasonable to expect that most of the addition of the monomer occurs in the monomer phase, after the initiation occurs. Combining Eqs. (9), (10) and (12) yields

$$R_p = C_b[M][I_2]^{1/2} + C_i[M][I_2]^{1/2}K_n^{1/2}([S]_0)^{n/2} / \left\{ 1 + n^2K_n[I_2]([S]_0)^{n-1} \right\}^{1/2} \quad (13)$$

where we note the dependence of $[S]_0$ to the $n/2$ power at low initiator concentrations. The constant, n , should depend on the characteristics of surfactant and initiator used. We expect that R_p should increase with an increasing concentration of the initiator. We expect standard dependence of R_p on M to the first order.

In situations where the initiator and/or surfactant concentration is small, the second term of the denominator in Eq. (13) will be negligible (*vide infra*). In that case, Eq. (13) can be simplified significantly. This also shows that C_i and $K_n^{1/2}$ enter into the equation as multiplicative constants, so that, fitting results in only their product, which we denote as C'_i .

$$R_p = C_b[M][I_2]^{1/2} + C'_i[M][I_2]^{1/2}[S]_0^{n/2} \quad (14)$$

where the new constant is defined as:

$$C'_i = k_{p,i}(k_{d,i}K_n/k_{t,i})^{1/2} \quad (15)$$

In any case, a comparison of C_b and C'_i provide a useful comparison of the polymerizations in either environment. We also note that in this formulation, C'_i has units that are dependent on the exponent n .

3. Experimental section

Styrene (Aldrich, Milwaukee, WI) was purified by distillation under reduced pressure. Azobisisobutyronitrile (AIBN, Eastman Kodak Co. Rochester, NY) was purified by recrystallization from methanol. Hexadecyltrimethylammonium bromide (Eastman Kodak Co. Rochester, NY) was used without further purification. Fumed silica (Cab–O–Sil, grade M5 from Cabot Corp. Tuscola, IL) was used as-received. This is a high surface area material ($200 \text{ m}^2/\text{g}$). The water was double distilled. HPLC grade toluene (Aldrich, Milwaukee, WI) was used as-received.

Styrene containing AIBN was introduced in a test tube containing silica. The mixture formed a gel after shaking for 1 min with a Vortex Genie Mixer. An aqueous solution of the surfactant (hexadecyltrimethylammonium bromide, CTAB) was then introduced

into the mixture. The emulsion formed after shaking the final mixture for about 1 min using the mixer.

Polymerizations were conducted in stoppered test tubes at room temperature. Conversion of styrene in the emulsions was determined as follows: basically, at different times, polymerized samples were taken out and massed. After the samples were dried at ambient conditions for 24 h and then under vacuum for 24 h, the solid containing polystyrene, fumed silica and surfactant was weighed again. The conversion of styrene into polystyrene (PS) was calculated by subtracting the mass of fumed silica and surfactant.

The samples of PS for gel permeation chromatography (GPC) measurements were prepared as follows: the solid containing PS, silica and surfactant was dissolved in toluene, and then the supernatant solution of polystyrene and toluene was taken out and dried under ambient conditions. PS does not adhere particularly strongly to Cab–O–Sil silica [37]. The resulting PS was redried under vacuum for 24 h. Molecular masses were measured using an IBM (IBM Instruments Inc. Danbury, CT) refractive index detector, a SP 8700 pump (Spectra-Physics, San Jose, CA), and a $300 \times 7.8 \text{ mm}$ column with Phenomenex phenogel of $5 \mu\text{m}$ particle size (Phenomenex, Torrance, CA). GPC measurements were performed at room temperature using tetrahydrofuran (THF, Fisher Co. Pittsburgh, PA) as solvent with a flow rate of $1.0 \text{ mL}/\text{min}$. The molecular mass calibration curve was obtained using polystyrene standards (Pressure Chemical Co., Pittsburgh, PA) of molecular masses ranging from 800 to 1,800,000 Da.

4. Results and discussion

The dependence of the formation of a kinetically stable emulsion gel on the concentration of silica and the amount of aqueous surfactant solution is shown in Fig. 1. The emulsion consisted of styrene, AIBN, and fumed silica, and an aqueous solution of surfactant. The kinetically stable emulsions, which are stable from several hours to several days without macroscopic phase separation of water, were found to be located in the region denoted I. The emulsion has a high viscosity and white appearance. It is believed that the fumed silica enhances the stability of the emulsions. The emulsions appeared to remain stable during polymerization at room temperature and macroscopic phase separation of water from the emulsion was not observed during and after polymerization. The emulsions were transformed into white powdery solids during the polymerization.

The conversions of styrene in different systems plotted against polymerization time are shown in Fig. 2. It should be noted that

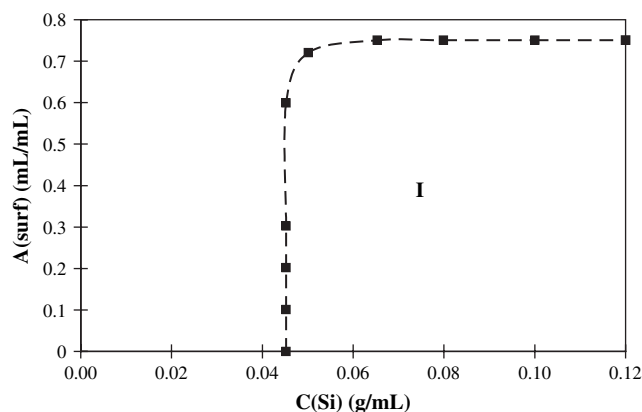


Fig. 1. Region of kinetically stable emulsion gel formation (I) for the systems of styrene, fumed silica and aqueous surfactant solution of CTAB. $C(\text{Si})$ (g/mL) is the concentration of fumed silica in entire emulsion and $A(\text{surf})$ is the volume ratio of aqueous solution of CTAB to styrene.

polymerization of styrene with AIBN at room temperature was very slow, but it still occurred in the absence of surfactant. The presence of silica did not affect the polymerization unless surfactant was present. Polymer did not form without any initiator, AIBN, in the emulsions. Enhanced polymerization (that well above that for the bulk solutions) was only observed in the emulsions containing surfactant. The effect of the surfactant on the polymerizations became more pronounced when the surfactant concentration was high. The rate of polymerization, R_p , was calculated from the initial slopes of the conversion curves.

Perhaps the most striking dependence of the rate of polymerization was on the surfactant (CTAB) concentration which is shown in Fig. 3. For these polymerizations, the concentrations of $[M] = 6.982 \text{ mol/l}$, and $[I_2] = 0.097 \text{ mol/l}$ were kept constant while $[S]_0$ was varied. At low surfactant concentrations, the polymerization rate was roughly independent of CTAB concentration and likely dominated by the polymerization in the bulk phase. At higher concentrations, the surfactant effect increased the rate of polymerization dramatically.

The model fits to the experimental data in Fig. 3 are shown as the solid curve based on Eq. (14). The fits to the data are good. The fitted parameters were: $C_b = 0.0084 (\pm 0.004) (\text{l/mol})^{1/2}/\text{h}$; $C_i' = 7.2(\pm 2) (\text{l/mol})^{n/2+1/2}/\text{h}$; and $n = 3.27 (\pm 0.25)$. The values of the fitted parameters were determined from all of the polymerization data together (Figs. 3–5) with variations of $[S]_0$, $[I_2]$, and $[M]$. The parameters were varied to minimize the squares of the normalized residuals (differences between the model and data divided by their measured values) using Mathematica [38]. The uncertainties are estimated from the best-fit parameters by varying the value in question enough to double the standard deviation of the normalized residuals, thus, corresponding to ± 1 S.D. The dependence on surfactant concentration implies that just over three surfactant molecules are, on average, involved in the surfactant-initiator complex. A similar conclusion can be reached if one considers the dependence of the $\log(R_p - R_b)$ vs $\log[S]_0$. The subtraction of the bulk polymerization rate should, in principle, negate the contribution from bulk polymerization. The resulting plot (not shown) yields a slope of 1.64 ($=n/2$) at high concentrations of surfactant. Both methods of analysis are quite consistent with each other.

The fits of the data were also performed in other ways. In essence, the best fits of the data were independent of whether Eq. (13) or Eq. (14) was used. Over the range of experiments reported, the value of the second term in the denominator was such that it made less than 0.01% difference to the model-based rate prediction.

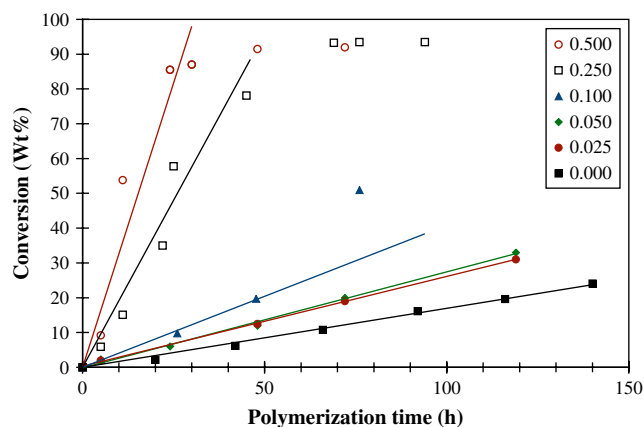


Fig. 2. Conversion of styrene to polystyrene at room temperature. The base composition of the monomer solution is 2 mL of styrene and 0.04 g of AIBN. The remainder of the samples had 0.105 g of fumed silica plus 0.5 mL of aqueous solution of CTAB of concentrations 0.0, 0.025, 0.05, 0.10, 0.25 and 0.50 M (■, ●, ◆, ▲, □, ○), respectively.

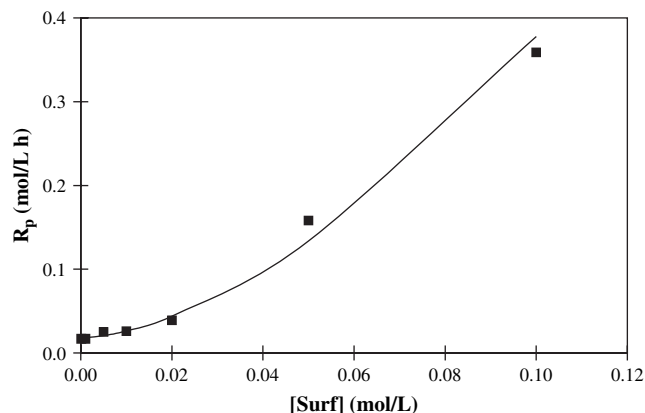


Fig. 3. Dependence of room temperature polymerization rate, R_p , of emulsions on the surfactant concentration. Compositions of emulsions: 2 mL of styrene, 0.04 g of AIBN, 0.105 g of fumed silica, 0.5 mL of aqueous solution of CTAB (varies). The best fit to Eq. (14) is shown.

Therefore, that term could be safely ignored in our analysis. This minimal dependence of the second denominator also made a determination of K_n from Eq. (13) highly uncertain, nevertheless, the determination of its product with C_i ($= C_i'$) was determined with accuracy. It is this compound constant that can be compared to the C_b with certainty. We also believe that fitting all of the data to the equation in one set is preferable to the traditional way of fitting each dependence independently. As a check, we compare, and report, each dependence in the traditional manner.

The dependence of polymerization rate on the initiator concentration, [AIBN], is shown in Fig. 4 for polymerizations made at constant concentrations of surfactant and monomer of $[M] = 6.982 \text{ mol/l}$, and $[S]_0 = 0.050 \text{ mol/l}$. The value of $[S]_0$ chosen ensured that there was a significant contribution to the surfactant assisted polymerization. The solid curve in the figure represents the fit to the data from the minimization process. The fit to the data is generally good, though not perfect. A $\log R_p$ vs $\log[I_2]$ plot (not shown) yields a line with a slope of about 0.58. This slope is a little higher than value of the 0.5 incorporated into the model. The reason for the discrepancy is not known at the present time. There are a variety of complications that have not been taken into account in our analysis, including the autoinitiation polymerization of styrene, and chain transfer to the initiator, although the latter, for AIBN to styrene, seems to be small [39].

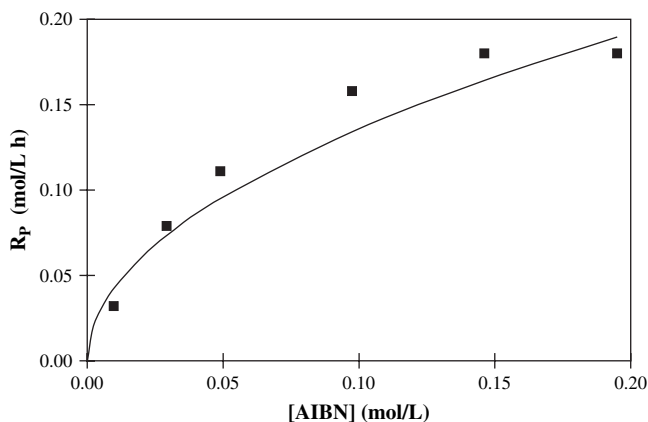


Fig. 4. Dependence of room temperature polymerization rate, R_p , of emulsions on the initiator concentration, [AIBN]. Composition of emulsions: 2 mL of styrene, AIBN (varies), 0.105 g of fumed silica, 0.5 mL of aqueous solution of CTAB (0.25 M). The best fit to Eq. (14) is shown.

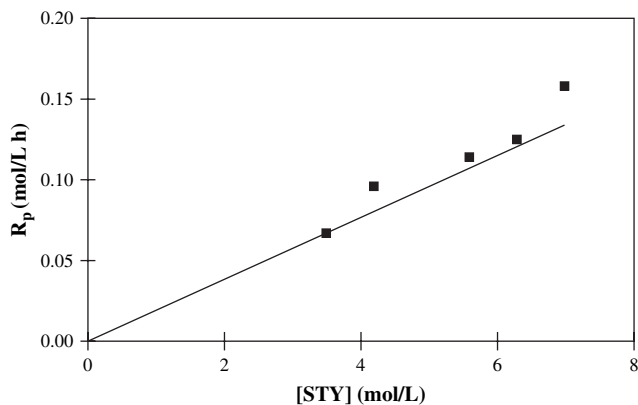


Fig. 5. Dependence of polymerization rate, R_p , of emulsions on the monomer concentration. Compositions of emulsions: 0.04 g of AIBN, 0.105 g of fumed silica, and 0.5 mL of aqueous solution of CTAB (0.25 M). Styrene was diluted with toluene to keep the organic fraction constant. The best fit to Eq. (14) is shown.

The dependence of R_p on monomer concentration is shown in Fig. 5. R_p increases linearly as expected with $[M]$ at constant concentrations of the initiator and surfactant. In these studies, the styrene was diluted with toluene to keep the fraction of organic soluble material constant. The solid line was also drawn from Eq. (14) using the previously mentioned parameters, plus known values of $[I_2] = 0.097$ mol/l, and $[S]_0 = 0.050$ mol/l. Within experimental error, the data agree with a first order dependence on the monomer concentration.

These results clearly show that the surfactant played a crucial role in the polymerization process. At high concentrations of surfactant, the rate of polymerization was enhanced by the interfacial surfactant layer by about 20 times (greater than that of the bulk polymerization of styrene). The amount of enhancement in the different samples varies with the different sample compositions. So it is difficult to make broad numerical comparisons. For the polymerizations shown in Fig. 5, for example, over 85% of the polymerizations can be attributed to the surfactant enhancement.

In our previous paper [29], we have determined that the decomposition rate constants for AIBN were $3.7 \times 10^{-8} \text{ s}^{-1}$ ($\pm 0.6 \times 10^{-8} \text{ s}^{-1}$) for the emulsion gels and $10.2 \times 10^{-8} \text{ s}^{-1}$ ($\pm 1.3 \times 10^{-8} \text{ s}^{-1}$) for the silica-containing emulsion gels. The rate constants for the decomposition of AIBN in the emulsion gels were significantly larger than those in toluene solution, which were below our measurement threshold and taken as effectively 0. Based on UV spectroscopy study, we showed that the surfactant, SDS and CTAB, strongly enhanced the decomposition of AIBN in the emulsion gels and silica-containing emulsion gels. These results agreed with the kinetic model in this paper that the enhanced decomposition of AIBN by surfactant resulted in room temperature polymerization of styrene in the emulsion gels with and without silica. Unfortunately, the numerical relationship between the dissociation of the initiator and the constant, C_i' is convoluted with the other constants whose values are unknown at this point. Nevertheless, the enhanced polymerization rates are clearly due to enhanced initiator decomposition.

The dependence of molecular mass of polystyrene on the CTAB concentration is shown in Fig. 6. The molecular mass was found to increase linearly for lower CTAB concentrations. Deviations from linear behavior begin at higher CTAB concentrations. It is our speculation that the increase of the molecular mass with CTAB concentration may be due to an interfacial effect of surfactant, which enhanced the activity of both the initiator and the monomer and reduced chain transfer rate of free radicals. The high viscosity of the emulsion gels might also make some contributions in reducing the termination rate, which may increase the molecular mass.

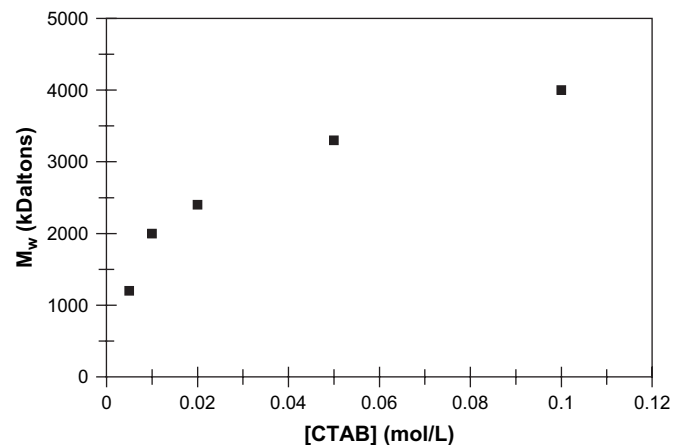


Fig. 6. Dependence of molecular weight of polystyrene on surfactant concentration at room temperature. Compositions: 2 mL of styrene, 0.04 g of AIBN, 0.105 g of fumed silica, 0.50 mL of aqueous solution of CTAB.

5. Conclusions

We have observed the enhanced polymerization due to the presence of a surfactant (CTAB) in the free radical polymerization of styrene in an emulsion gel. The major effect is the enhancement of initiator decomposition due to complexation with surfactant. Completion of polymerization of styrene in these emulsions can be achieved at room temperature in one or several days depending on their composition. It was found that the polymerization rate depends on the concentrations of surfactant, monomer, and initiator. A simple theoretical kinetic model was developed based on a surfactant–initiator complex and conventional free radical polymerization kinetics. The experimental data for polymerization of the emulsion gels are in good agreement with the model predictions. This model can be used to achieve good fits to variations in rate data from changes in monomer, initiator and surfactant concentrations. From the results of this study, it is suggested that surfactant participated in the initiation processes of polymerization. Furthermore, the model is consistent with 3.26 surfactant molecules complexing the initiator species.

Acknowledgments

We acknowledge the financial support of the National Science Foundation under grant DMR-0706197. We also thank R. O'Connor for assistance with the data fitting.

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