# Ultrasonically Initiated Free Radical-Catalyzed Emulsion Polymerization of Methyl Methacrylate (II): Radical Generation Process Studies and Kinetic Data Interpretation

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ABSTRACT: In the previous work, we have studied the effects of acoustic intensity, argon gas flow rate, surfactant concentration, and initial monomer concentration on polymerization rate, polymer particle number, and polymer molecular weight in the ultrasonically initiated emulsion polymerization of methyl methacrylate. In this study, radical trapping experiments were used to investigate the effect of acoustic intensity, argon gas flow rate, and sodium lauryl sulfate concentration on the extent of free radical generation in aqueous sodium dodecyl sulfate solutions. In these radical trapping experiments, aqueous solutions of sodium lauryl sulfate were ultrasonically irradiated in the presence of a radical scavenger. The sodium lauryl sulfate molecule degraded under ultrasound to form free radicals in the water. It was found that the extent of free radical generation increased as: (1) the 0.60 power of the acoustic intensity, (2) the 0.44 power of the argon gas flow rate, (3a) the 0.35 power of the surfactant concentration within the 0.035M-0.139M surfactant concentration range, and (3b) the 1.09 power of the surfactant concentration within the 0.139M - 0.243Msurfactant concentration range. The generated free radical concentration, the number of polymer particles produced, and the polymerization rate exhibit an increasing trend with an increasing (1) acoustic intensity, (2) argon gas flow rate, and (3) surfactant concentration. Increases in surfactant concentration correspond to: (1) an increase in generated free radical concentration and (2) a decrease in polymer molecular weight. These relationships confirm the previous assumptions that (1) the polymerization rate increases with increasing acoustic intensity and argon gas flow rate due to an increase in the radical generation rate and the reaction temperature; (2) the polymerization rate increases with increasing surfactant concentration due to an increase in the radical generation rate, the micellar, homogeneous nucleation, and the reaction temperature; and (3) the polymer molecular weight decreases with increasing surfactant concentration due to an increase in the radical generation rate. These results are helpful in understanding the kinetics of the ultrasonically initiated emulsion polymerization of methyl methacrylate. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 827-834, 1999

Key words: ultrasound; radical traps; radical scavenger; GC/MS

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## INTRODUCTION

In the previous paper,<sup>1</sup> we have reported the ultrasonically initiated emulsion polymerization of methyl methacrylate (MMA) at ambient temper-

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ature using sodium lauryl sulfate as the surfactant in the absence of a conventional initiator. We have also reported the preliminary radical generation process study<sup>2</sup> and a specially designed gas chromatography/mass spectroscopy (GC/MS) analytical method to identify the source of free radicals that served as initiators<sup>3</sup> in this ultrasonically initiated emulsion polymerization of MMA.

Ultrasound was shown to be a useful tool for initiating the radical emulsion polymerization of MMA at low temperatures. The initiation of the polymerization was postulated to result from the ultrasonically induced degradation of surfactant molecules (sodium lauryl sulfate), presumably in the aqueous phase, to give alkyl radicals and a sulfate radical. The polymerization rate, the polymer particle number, and the polymer molecular weight were found to increase with increasing acoustic intensity to a point, and then decrease. The polymerization rate, the polymer particle number, and the polymer molecular weight were found to increase with increasing argon gas flow rate. The polymerization rate and the polymer particle number were found to increase with increasing surfactant concentration, and the polymer molecular weight was found to decrease with increasing surfactant concentration within the 0.035*M*-0.243*M* surfactant concentration range.

To have a better understanding of the kinetics of the ultrasonically initiated emulsion polymerization of MMA, radical trapping experiments were performed in this study by ultrasonically irradiating aqueous sodium lauryl sulfate solutions in the presence of a radical scavenger (bromoform) to investigate the effects of the different reaction parameters on the quantity of radicals generated at constant sonication time. The concentration of the primary free radical generated from the sodium lauryl sulfate molecule in aqueous solution was found to depend on three parameters: (1) acoustic intensity, (2) argon gas flow rate, and (3) sodium lauryl sulfate concentration. A qualitative correlation was found between the effect of the above three parameters on the generated free radical concentration, and the effect of the above three parameters on both the polymerization rate, polymer particle number, and the polymer molecular weight. This qualitative correlation is helpful in understanding the kinetics of the ultrasonically initiated emulsion polymerization of MMA.

## **EXPERIMENTAL**

#### Apparatus

The apparatus used was described in the previous paper.  $^{1\!-\!3}$ 

#### Materials and Reagents

Sodium lauryl sulfate [assayed as sodium dodecyl sulfate (SDS), 70% dodecyl sulfate, 25% tetradecyl sulfate, and 5% hexadecyl sulfate sodium salt] and bromoform (99%) were obtained from Aldrich Chemical Company (Milwaukee, WI) and used as received. *n*-Propanol, suitable for the use in liquid and gas chromatography, was obtained from Omnisolv Chemical Company (Jackson, MS) and used as received.

#### **Radical Trapping Experiments**

Different solutions containing water, sodium lauryl sulfate, and bromoform were ultrasonically irradiated under various (1) acoustic intensities, (2) argon gas flow rates, and (3) surfactant concentrations to study the effect of these three parameters on the amount of the free radicals generated. The solution was prepared by adding surfactant, and then bromoform to water, with constant stirring at room temperature for 15 min. This solution was then introduced to the reactor. a 17 cm high  $\times$  6 cm diameter flat-bottomed pyrex glass tube. It was deoxygenated with argon gas for 3 min and then subjected to ultrasonic irradiation. The horn was always placed 3 cm from the bottom of the reaction vessel. The glass tube was surrounded by an ethylene glycol and water mixture cooling bath maintained at  $-10^{\circ}$ C. During ultrasonic irradiation, dry argon was bubbled continuously through the solution to promote cavitation by providing nuclei for the formation of the bubbles. The reactor was ultrasonically irradiated for 30 min and then immediately removed from the cooling bath. Then, 100 mL of *n*-propanol was added to each sample to completely dissolve the precipitated materials in the solution. The sample was then subjected to GC/MS analysis.

#### **GC/MS** Analysis

GC/MS analysis was performed on a Hewlett-Packard Model 5970 mass selective detector interfaced to a Hewlett-Packard Model 5890 gas chromatograph as described in the previous paper.<sup>3</sup> In the quantitative analysis procedure, the

No.	Acoustic Intensity $(W \text{ cm}^{-2})$	$\begin{array}{c} C_a{}^{\rm b} \\ ({\rm mg\ mL^{-1}}) \end{array}$	$\begin{array}{c} {C_b}^{\rm c} \\ ({\rm mg}~{\rm mL}^{-1}) \end{array}$	${R_p}^{ m d} imes 10^4 \  m (mol~L\text{-s}^{-1})$	${M_w}^{ m e}  imes 10^{-6} \ ({ m g \ mol}^{-1})$
1	6.8	0.63	0.44	3.49	3.04
2	7.6	0.69	0.48	3.58	3.08
3	9.2	0.76	0.52	4.34	3.24
4	11.0	0.84	0.58	5.25	3.37
5	13.0	0.96	0.66	5.90	3.47
6	14.4	0.86	0.59	4.57	3.29

 Table I
 Effect of Acoustic Intensity on Radical Concentration, Polymerization Rate, and Polymer

 Molecular Weight for the Ultrasonically Initiated Emulsion Polymerization of MMA<sup>a</sup>

<sup>a</sup> Sample solution used for radical concentration studies was prepared with 100 mL of water, 4.2 mL of bromoform, and 1 g of SDS. Argon gas flow rate used was 0.74 mL s<sup>-1</sup>, sonication time was 30 min, and cooling bath temperature was  $-10^{\circ}$ C.

 ${}^{\rm b}C_a$  is total concentration in mg per mL of water of 1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane detected from SDS aqueous solution.

 $^{c}C_{b}$  is total alkane free radical concentration calculated from  $C_{a}$ .

 ${}^{d}R_{p}^{o}$  is polymerization rate cited from ref. 1.

 ${}^{e}M_{w}$  is the weight average molecular weight cited from ref. 1.

characteristic ions of the long-chain alkylbromides with m/z 135, 137, 149, and 151 were chosen to build the total ion chromatogram.

Sodium lauryl sulfate and bromoform degrade in the presence of ultrasonic irradiation to produce free radicals that combine to give stable compounds. Compounds detected included 1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane in the same ratio as the respective compound distribution in the original SDS. The free radical concentrations generated from different sample solutions with ultrasound at different reaction conditions can be determined by detecting the total amount of the alkylbromides found in the GC/MS analysis. The library search of mass spectra of 1-bromododecane, 1-bromohexadecane, and 1-bromotetradecane was conducted and used for qualitative analysis. The mass spectrum of 1-bromododecane was also obtained from a standard sample to confirm the result.

A 100-mL portion of *n*-propanol was added to each of the ultrasonically irradiated sample solutions to obtain better distribution of the alkylbromide compounds in the solutions to perform a quantitative analysis. For quantitative analysis, the selective ion monitoring data acquisition model was chosen to reduce the analytical time. Each value on the calibration curve was taken from the average of five data points, and each measured radical concentration was obtained from the average of five data points, both with relative experimental errors of less than  $\pm 5.0\%$ . The standard samples used for quantitative analysis were prepared by adding 1-bromododecane, 1-bromotetradecane, or 1-bromohexadecane in a stock solution containing 1.0 g of SDS, 100 mL of water, and 100 mL of *n*-propanol.

#### **RESULTS AND DISCUSSION**

## Effect of Acoustic Intensity on Free Radical Concentration, Polymerization Rate, Polymer Particle Number, and Polymer Molecular Weight

The effect of acoustic intensity on free radical concentration generated by ultrasound was studied by ultrasonically irradiating a SDS aqueous solution containing 0.035 mol of SDS (1% based on the aqueous phase) and 0.48 mol of bromoform/L of water at different acoustic intensities under an argon gas flow rate of 0.74 mL s<sup>-1</sup> in a  $-10^{\circ}$ C cooling bath. The examples of mass spectra obtained from a sample solution, which was ultrasonically irradiated at an acoustic intensity of 13.0 W cm<sup>-2</sup> under a 0.74 mL s<sup>-1</sup> argon flow rate were shown in Figure 2 in the previous paper.<sup>1</sup> The results of the effect of acoustic intensity on polymerization rate and polymer molecular weight at constant argon gas flow rate, surfactant concentration, and initial monomer concentration were obtained from the previous work<sup>1</sup> and are summarized in Table I.

The total concentration of alkylbromide  $(C_a)$ and alkane free radical concentration  $(C_b)$  was reported in units of milligrams per milliliter of water. The log-log plots of acoustic intensity versus polymerization rate, acoustic intensity versus polymer particle number and acoustic intensity versus polymer weight average molecular weight



**Figure 1** Effect of acoustic intensity on radical concentration in SDS aqueous solution. (Water = 100 mL, bromoform = 4.2 mL, SDS = 1 g, argon gas flow rate = 0.74 mL s<sup>-1</sup>, sonication time = 30 min, cooling bath temperature =  $-10^{\circ}$ C.)

were shown in Figures 4, 5, and 7 in the previous paper.<sup>1</sup> The result of the effect of acoustic intensity on free radical concentration generated in SDS solution and the corresponding log–log plot of acoustic intensity *versus* free radical concentration are shown in Table I and Figure 1.

The mass spectra shown in the previous papers<sup>1,3</sup> gave the examples of the identification of 1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane detected by GC/MS analysis from the ultrasonically irradiated sample solutions. The total amount of these three alkylbromide compounds detected were used to calculate the free radical concentration generated from ultrasonically irradiated sample solutions. The detailed work dealing with the GC/MS analysis was described in the previous paper.<sup>3</sup>

In the previous paper,<sup>1</sup> the polymerization rate, polymer particle number, and the polymer molecular weight were shown to increase as the 0.98, 1.23, and the 0.21 power of the acoustic intensity, respectively, as the acoustic intensity increased from 6.8 to 13.0 W cm<sup>-2</sup>. These values then decreased at an acoustic intensity of 14.4 W cm<sup>-2</sup>. The increase in polymerization rate with increasing acoustic intensity was attributed to an increase in total polymer particles generated, assumed to result from an increase in radical generation rate. It was also attributed to a reaction rate constant increase as reaction temperature increases with acoustic intensity. The increase in polymer molecular weight with increasing acoustic intensity was attributed to gel effect.<sup>1</sup>

From the data given in Table I and Figure 1, it appears that the free radical concentration generated in the SDS aqueous solution increased as the 0.60 power of the acoustic intensity, with acoustic intensity increasing from 6.8 to 13.0 W  $cm^{-2}$ . This increase in the extent of radical generation is attributed to an increase in the number of cavitation bubbles when the acoustic intensity used in the ultrasonically initiated emulsion polymerization system is increased. The free radical concentration then decreased at an acoustic intensity of 14.4 W cm<sup>-2</sup>. This decrease in the extent of radical generation is attributed to a decrease in the number of cavitation bubbles after a maximum intensity peak.<sup>1</sup> The free radical concentration, the polymer particle number, and polymerization rate all exhibit an increasing trend with increasing acoustic intensity. This similar increasing trend confirms the previous assumption<sup>1</sup> that an increase in the acoustic intensity, resulting in increasing radical generation, thus produces more polymer particles and enhances polymerization rate.

The rate of emulsion polymerization per liter of water and number of average degree polymerization can be expressed as follows<sup>4-6</sup>:

$$R_p = \bar{n}NK_p[M]_p \tag{1}$$

$$X_n = R_p / R_i = n N K_p [M]_p / R_i$$
(2)

where *n* is the average number of radicals per particle,  $[M]_p$  is the monomer concentration in a polymer particle in mol/L,  $K_p$  is the propagation constant in L/mol s<sup>-1</sup>, *N* is the number of polymer particles per liter of water, and  $R_i$  is initiation rate in mol/L s<sup>-1</sup>.

Because the argon gas flow rate and emulsion recipes were held constant in this part of the study, increasing the acoustic intensity in this ultrasonically initiated emulsion polymerization system resulted in three phenomena: (1) an increase in the total number of polymer particles Ndue to the increase of radical generation rate resulting from an increase in the number of cavitation bubbles; (2) an increase in the propagation rate constant due to the increase in reaction temperature resulting from an increase of the number of cavitation bubbles, an increase of the heat generated from horn vibration and the polymerization; and (3) gel effect. As a result, the poly-





Figure 2 Summaries of the relationship between acoustic intensity, extent of radical generation, polymerization rate, and polymer molecular weight.

merization rate will increase with increasing acoustic intensity due to the increase of the radical generation rate and reaction temperature and gel effect. These relationships are shown in Figure 2.

Normally, in an emulsion polymerization system, the polymer molecular weight decreases with increasing initiation rate. The fact that polymer molecular weight increases with acoustic intensity implies that gel effect contributes to the increase of molecular weight at higher acoustic intensities. Without the gel effect, increasing the acoustic intensity will increase the initiation rate and lower molecular weight. This gel effect phenomenon was observed at higher acoustic intensity based on the molecular weight development curve shown in the previous paper.<sup>1</sup>

### Effect of Argon Gas Flow Rate on Free Radical **Concentration, Polymerization Rate, Polymer** Particle Number, and Polymer Molecular Weight

The effect of argon gas flow rate on free radical concentration generated by ultrasound was studied by ultrasonically irradiating a SDS aqueous solution containing 0.035 mol of SDS (1% based on the aqueous phase) and 0.48 mol of bromoform/L of water at an acoustic intensity of 9.2 W  $\mathrm{cm}^{-2}$  under different argon gas flow rates in a  $-10^{\circ}$ C cooling bath. The results of the effect of the argon gas flow rate on polymerization rate and polymer molecular weight at constant acoustic intensity, surfactant concentration, and initial monomer concentration were obtained from the previous work<sup>1</sup> and are summarized in Table II. The log-log plots of argon gas flow rate versus polymerization rate, argon gas flow rate versus polymer particles number, and argon gas flow rate versus polymer weight average molecular weight were shown in Figures 9, 10, and 12 in the previous paper.<sup>1</sup> The result of the effect of argon gas flow rate on free radical concentration generated in SDS aqueous solution and the corresponding log-log plot of argon gas flow rate *versus* free radical concentration are shown in Table II and Figure 3.

In the previous paper,<sup>1</sup> the polymerization rate, polymer particle number, and the polymer molecular weight were shown to increase as the 0.086, 0.16, and the 0.02 power of the argon gas flow rate, respectively. This increase in polymerization rate with increasing argon gas flow rate was attributed<sup>1</sup> to an increase in total polymer particles generated, assumed to result from an increase in radical generation rate. It was also attributed to a slight reaction rate constant increase as reaction temperature increased with argon gas flow rate. The increase in polymer molecular weight with increasing argon gas flow rate was attributed to gel effect.<sup>1</sup>

No.	Argon Flow Rate $(mL s^{-1})$	$C_a{}^{ m b}$ (mg mL <sup>-1</sup> )	$\frac{C_b{}^{\mathbf{c}}}{(\mathrm{mg}\;\mathrm{mL}^{-1})}$	${R_p}^{ m d} imes 10^4 \  m (mol~L{\cdot}s^{-1})$	${M_w}^{ m e}  imes 10^{-6} \ ({ m g \ mol}^{-1})$
1	0.25	0.61	0.42	3.83	3.02
2	0.32	0.76	0.52	4.22	3.22
3	0.42	0.84	0.58	4.30	3.23
4	0.54	0.94	0.65	4.42	3.25
5	0.67	1.04	0.72	4.48	3.27

Table II Effect of Argon Gas Flow Rate on Radical Concentration, Polymerization Rate, and Polymer Molecular Weight for the Ultrasonically Initiated Emulsion Polymerization of MMA<sup>a</sup>

<sup>a</sup> Sample solution used for radical concentration studies was prepared by 100 mL of water, 4.2 mL of bromoform, and 1 g of SDS. Acoustic intensity used was 9.2 W cm<sup>-2</sup>, sonication time was 30 min, and cooling bath temperature was  $-10^{\circ}$ C.

<sup>b</sup> C<sub>a</sub> is total concentration in mg per mL in water of 1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane detected from SDS aqueous solution.

 $^{c}C_{b}$  is total alkane free radical concentration calculated from  $C_{a}$ .

 ${}^{c}{}^{b}{}^{b}{}^{b}$  is polymerization rate cited from ref. 1.  ${}^{e}{}^{M}{}^{w}{}^{w}$  is the weight average molecular weight cited from ref. 1.



**Figure 3** Effect of argon gas flow rate on radical concentration in SDS aqueous solution. (Water = 100 mL, SDS = 1 g, bromoform = 4.2 mL, acoustic intensity = 9.2 W cm<sup>-2</sup>, sonication time = 30 min, cooling bath temperature =  $-10^{\circ}$ C.)

From the data given in Table II and Figure 3, it seems that the free radical concentration generated in the SDS aqueous solution increased as the 0.44 power of the argon gas flow rate due to an increase in the number of cavitation bubbles. The increasing trend of free radical concentration with increasing argon gas flow rate is similar to the increase of polymer particle number generated and polymerization rate with increasing argon gas flow rate. This similar increasing trend confirms the previous assumption<sup>1</sup> that increasing argon gas flow rate resulted in increasing radical generation, thus producing more polymer particles and an enhanced polymerization rate.

Because the acoustic intensity and emulsion recipes were held constant in this part of the study, increasing the argon gas flow rate in this ultrasonically initiated emulsion polymerization system resulted in three phenomena: (1) an increase in the total number of polymer particles Ndue to the increase in radical generation rate resulting from an increase in the number of cavitation bubbles, (2) a slight increase in the propagation rate constant due to the slight increase in reaction temperature resulting from an increase in the number of cavitation bubbles and an increase in the heat generated from the polymerization, and (3) gel effect. As a result, the polymerization rate will increase with increasing argon gas flow rate due to the increase in radical generation rate, reaction temperature, and gel effect. These relationships are shown in Figure 4.

The fact that polymer molecular weight increases slightly with increasing argon gas flow rate again indicates that the gel effect contributes to the molecular weight increase at higher argon gas flow rate. Without the gel effect, increasing argon gas flow rate will increase the initiation rate and lower the molecular weight.

### Effect of Surfactant Concentration on Free Radical Concentration, Polymerization Rate, Polymer Particle Number, and Polymer Molecular Weight

The effect of surfactant concentration on free radical concentration generated by ultrasound was studied by ultrasonically irradiating SDS aqueous solutions containing a different amount of surfactant and 0.48 mol of bromoform/L of water at an acoustic intensity of  $9.2 \text{ W cm}^{-2}$  under an argon gas flow rate of 0.32 mL s<sup>-1</sup> in a  $-10^{\circ}$ C cooling bath. The results of the effect of surfactant concentration on polymerization rate and polymer molecular weight at constant acoustic intensity, argon gas flow rate, and initial monomer concentration were obtained from the previous work<sup>1</sup> and are summarized in Table III. The loglog plots of surfactant concentration versus polymerization rate, surfactant concentration versus polymer particle number, and surfactant concentration versus polymer weight average molecular weight were shown in Figures 15, 16, and 18 in the previous paper.<sup>1</sup> The result of the effect of surfactant concentration on free radical concentration generated in SDS solution and the corresponding log-log plot of surfactant concentration versus free radical concentration are shown in Table III and Figure 5.

From the previous paper,<sup>1</sup> the polymerization rate and polymer particle number were shown to



**Figure 4** Summaries of the relationship between argon gas flow rate, extent of radical generation, polymerization rate, and polymer molecular weight.

No.	$[\text{SDS}] \\ (\text{mol } L^{-1})$	$\begin{array}{c} C_a{}^{\rm b} \\ ({\rm mg~mL^{-1}}) \end{array}$	$\begin{array}{c} {C_b}^{\rm c} \\ ({\rm mg} \ {\rm mL}^{-1}) \end{array}$	${R_p}^{ m d} imes 10^4 \  m (mol~L\text{-s}^{-1})$	${M_w}^{ m e}  imes 10^{-6} \ ({ m g mol}^{-1})$
1	0.04	0.71	0.49	4.22	3.22
2	0.07	0.86	0.59	4.45	3.07
3	0.10	0.98	0.68	4.61	2.88
4	0.14	1.10	0.76	4.71	2.71
5	0.17	1.39	0.96	5.30	2.55
6	0.21	1.73	1.20	5.84	2.38
7	0.24	1.98	1.37	6.54	2.14
2 3 4 5 6 7	$\begin{array}{c} 0.07 \\ 0.10 \\ 0.14 \\ 0.17 \\ 0.21 \\ 0.24 \end{array}$	$0.86 \\ 0.98 \\ 1.10 \\ 1.39 \\ 1.73 \\ 1.98$	0.59 0.68 0.76 0.96 1.20 1.37	$\begin{array}{c} 4.45 \\ 4.61 \\ 4.71 \\ 5.30 \\ 5.84 \\ 6.54 \end{array}$	3.07 2.88 2.71 2.55 2.38 2.14

 Table III
 Effect of Surfactant Concentration on Radical Concentration, Polymerization Rate, and

 Polymer Molecular Weight for the Ultrasonically

<sup>a</sup> Sample solution used for radical concentration studies was prepared by 100 mL of water, 4.2 mL of bromoform, and various amount of SDS. Acoustic intensity was 9.2 W cm<sup>-2</sup>, argon gas flow rate was  $0.32 \text{ mL s}^{-1}$ , sonication time was 30 min, and cooling bath temperature was  $-10^{\circ}$ C.

 $^{\rm b}C_a$  is total concentration in mg per mL of water of 1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane detected from SDS aqueous solution.

 $^{c}C_{b}$  is total alkane free radical concentration calculated from  $C_{a}$ .

 ${}^{d}R_{p}$  is polymerization rate cited from ref. 1.

 ${}^{e}M_{w}$  is the weight average molecular weight cited from ref. 1.

increase as the 0.08 and 0.3 power of the surfactant concentration, respectively, when the surfactant concentration increased from 0.035M– 0.139M. The polymerization rate and polymer particle number then increased as the 0.58 and 1.87 power of the surfactant concentration, respectively, when the surfactant concentration increased from 0.139M to 0.243M. This increase in polymerization rate with increasing surfactant



Log Surfactant Concnetration

**Figure 5** Effect of surfactant concentration on radical concentration in SDS aqueous solution. (Water = 100 mL, bromoform = 4.2 mL, acoustic intensity = 9.2 W cm<sup>-2</sup>, argon gas flow rate = 0.32 mL s<sup>-1</sup>, sonication time = 30 min, cooling bath temperature =  $-10^{\circ}$ C.)

concentration was assumed<sup>1</sup> to be due to the increase in radical generation rate, micellar nucleation, homogeneous nucleation, and reaction temperature. The polymer weight average molecular weight was shown to decrease as the 0.12 power of the surfactant concentration when the surfactant concentration increased from 0.035M to 0.139M. The polymer weight average molecular weight then decreased as the 0.34 power of the surfactant concentration when the surfactant concentration increased from 0.139M to 0.243M. This decrease in polymer molecular weight with increasing surfactant concentration was assumed<sup>1</sup> to be due to an increase in radical generation rate resulting from an increase in the number of surfactant molecules that serve as initiators.

From the data given in Table III and Figure 5, it seems that the free radical concentration generated in the SDS aqueous solution increased as the 0.35 power of the surfactant concentration when the surfactant concentration increased from 0.035M to 0.139M. The free radical concentration generated then increased as the 1.09 power of the surfactant concentration when the surfactant concentration increased from 0.139M to 0.243M. The increase in free radical concentration with increasing surfactant concentration is similar to the increase in polymer particles generated and polymerization rate with increasing surfactant concentration. This similarity in the increasing trend confirms the assumption<sup>1</sup> that increasing surfactant concentration resulted in an increased



**Figure 6** Summaries of the relationship between surfactant concentration, extent of radical generation, polymerization rate, and polymer molecular weight.

radical generation, thus producing more polymer particles and enhancing polymerization rate.

Because the acoustic intensity and argon gas flow rate were held constant in this part of the study, increasing surfactant concentration in this ultrasonically initiated emulsion polymerization system resulted in three phenomena: (1) an increase in the total number of polymer particles Ndue to the increase in radical generation rate resulting from an increase in the number of surfactant molecules that serve as initiators; (2) an increase in the propagation rate constant due to the increase in reaction temperature resulting from an increase in the heat generated from the polymerization; and (3) an increase in micellar nucleation and homogeneous nucleation. As a result, the polymerization rate will increase with increasing surfactant concentration due to the increases in radical generation rate, micellar nucleation, homogeneous nucleation, and reaction temperature. Figure 6 summarizes these relationships.

The fact that polymer molecular weight decreases with increasing surfactant concentration suggests that the effect of increasing  $R_i$  (initiation rate), which leads to lower molecular weight, is larger than the effect of increasing  $N \times K_p$ , which leads to higher molecular weight. This explains our assumption<sup>1</sup> that the decrease in polymer molecular weight with increasing surfactant concentration is due to an increased radical generation rate resulting from an increase in the number of surfactant molecules that serve as initiator.

#### **CONCLUSIONS**

1. The radical generation rate, the polymer particles number generated, and the poly-

merization rate all increase with increasing acoustic intensity from 6.8 to 13.0 W  $\rm cm^{-2}$ . The increase in polymerization rate with increasing acoustic intensity is attributed to an increase in radical generation rate, reaction temperature, and gel effect.

- 2. The radical generation rate, the polymer particles number generated, and polymerization rate all increase with increasing argon gas flow rate from 0.25 to 0.67 mL s<sup>-1</sup>. The increase in polymerization rate with increasing argon gas flow rate is attributed to an increase in radical generation rate, reaction temperature, and gel effect.
- 3. The radical generation rate, the polymer particles number generated, and the polymerization rate increase with increasing surfactant concentration from 0.035M to 0.243M. The increase in polymerization rate with increasing surfactant concentration is attributed to an increase in the radical generation rate, micellar nucleation, homogeneous nucleation, and reaction temperature. Polymer molecular weight decreases with increasing surfactant concentration from 0.035M to 0.243M. The decrease in polymer molecular weight with increasing surfactant concentration is attributed to an increase in radical generation rate resulting from an increase in the number of surfactant molecules that serve as initiator.

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