Ultrasonically Initiated Free Radical-Catalyzed Emulsion Polymerization of Methyl Methacrylate (I)

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SYNOPSIS: The emulsion polymerization of methyl methacrylate initiated by ultrasound has been studied at ambient temperature using sodium lauryl sulfate as the surfactant. The investigation includes the: (1) nature and source of the free radical for the initiation process; (2) effects of different types of cavitation; and (3) dependence of the polymerization rate, polymer particle number generated, and the polymer molecular weight on acoustic intensity, argon gas flow rate, surfactant concentration, and initial monomer concentration. It was found that the polymerization could be initiated by ultrasound in the emulsion systems containing methyl methacrylate, water, and sodium lauryl sulfate at ambient temperature in the absence of a conventional initiator. The source of the free radical for the initiation process was found to come from the degradation of the sodium lauryl sulfate, presumably in the aqueous phase. The weight average molecular weight of the poly(methyl methacrylate) obtained varied from 2,500,000 to 3,500,000 g mol⁻¹, and the conversion for polymerization was up to 70%. Deviations from the Smith-Ewart kinetics were observed. The polymerization rate was found to be proportional to the acoustic intensity to the 0.98 power; to the argon gas flow rate to the 0.086 power; to the surfactant concentration to the 0.08 power, with the 0.035M-0.139M surfactant concentration range; and to the surfactant concentration to the 0.58 power, with the 0.139M-0.243M surfactant concentration range. The polymerization rate was found to increase with increasing initial monomer concentration up to a point where it became independent of initial monomer concentration. The polymer particle number generated per milliliter of water was found to be proportional to the acoustic intensity to the 1.23 power; to the argon gas flow rate to the 0.16 power; to the surfactant concentration to the 0.3 power, with the 0.035M-0.139M surfactant concentration range; and to the surfactant concentration to the 1.87 power, with the 0.139M - 0.243Msurfactant concentration range. The polymer weight average molecular weight was found to be proportional to the acoustic intensity to the 0.21 power, and to the argon gas flow rate to the 0.02 power. It was found to be inversely proportional to the surfactant concentration to the 0.12 and 0.34 power, with the 0.035M-0.139M and the 0.139M-0.243M surfactant concentration ranges, respectively. The polymer yield and polymerization rate were found to be much larger than those obtained from an ultrasonically initiated bulk polymerization method. The polymerization rates obtained at ambient temperature were found to be similar to or higher than those obtained from the conventional higher temperature thermal emulsion polymerization method. This investigation demonstrated the capability of ultrasound to both initiate and accelerate polymerization in the emulsion system, and to do this at a lower temperature that could offer substantial energy savings. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 797-825, 1999

Key words: emulsion polymerization; ultrasound; acoustic intensity; resonant cavitation; transient cavitation

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INTRODUCTION

In previous publications, we have reported the ultrasonically initiated free radical catalyzed polymerization of methyl methacrylate $(MMA)^1$ in

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1991 and of acrylamide² in 1992. We have also reported the ultrasonically initiated free radicalcatalyzed copolymerization between styrene and maleic anhydride³ in 1992, and a preliminary study of ultrasonically initiated free radical-catalyzed emulsion polymerization of MMA^{4a} in 1993. An emulsion copolymerization study was presented in 1996,^{4b} and a patent^{4c} was issued for the ultrasonically initiated polymerizations in 1995. A thorough study of the initiation of polymerization by ultrasound in an emulsion system containing MMA monomer and sodium lauryl sulfate surfactant is reported herein to show the potential application of this new technique to emulsion polymerizations.

The propagation of intense ultrasonic waves in a liquid leads to cavitation (i.e., the formation and collapse of microbubbles). Small gas bubbles disorganize the structure of the liquid by weakening the intermolecular forces within the liquid. The molecular motion induced by the pressure acoustic waves disrupts the cohesive forces within the liquid, leading to the formation of cavities or microbubbles. Stable microbubbles oscillate about some average size, whereas unstable microbubbles grow to a maximum size at which point they implode. This implosion generates shock waves that may produce luminescent gases and electromagnetic radiation.⁵ It is the unstable microbubbles that account for the unusual effects in certain chemical reactions.⁵ Although the chemical effects of ultrasound in a liquid were originally attributed to an electrical discharge process proposed by Frenkel and others,⁶⁻⁹ the cavitation theory proposed by Noltkingk and Neppiras¹⁰ has become the most widely accepted model. Their model describes the size, the temperature, and the pressure of the bubbles in an acoustic field. It assumes that high temperatures and large pressures develop during the adiabatic collapse of the bubble. Flynn and Mason¹¹ provided a review of the cavitation model in 1964. More recent reviews are available in a series of papers in Ultrason ics^{12-14} and in Shutilov's¹⁵ book.

The cavitation model has been simplified as follows¹⁶⁻¹⁹: (1) The cavitation bubbles grow slowly and isothermally at the bulk temperature (T_i) during the low pressure phase of the ultrasound wave. At the end of this low-pressure phase, the cavitation bubble is assumed to be filled with either the liquid vapor at the equilibrium vapor pressure of the liquid only, or with both sparging gas and the liquid vapor. (2) The bubbles collapse quickly and adiabatically to a pressure (P_f) at the beginning of the high-pres-

sure phase. The collapse of this kind of cavitation bubble results in hot spots.²⁰ The local temperature generated (T_f) on the collapse of cavitation bubbles can be estimated, if one assumes an ideal and reversible adiabatic collapse to be:

$$T_f = T_i [P_f (r-1)/P_i]$$

where T_i represents the temperature before the collapse of the cavitation bubble, most often taken as bulk temperature. T_f is the final temperature after the collapse of the cavitation bubble. P_i and P_f are the pressures that correspond to temperatures T_i and T_f , respectively, and r is the ratio of specific heats of the gas or the gas-vapor mixture in the bubble. Similar theoretical results are obtained from the equation $T_f = T_i[(RP_f)/(C_pP_i)]$ for the irreversible adiabatic collapse of the cavity, where it is noted that (r - 1) can be approximated by (R/C_p) as in the case for polyatomic molecules. The local temperature produced by the collapse of the bubbles is estimated to be several hundred to several thousand degrees Kelvin.^{21–24} This is able to split the organic molecules homolitically, to produce free radicals and to induce free radical reactions.

Over the past few years, ultrasound has been widely used for emulsification, catalysis, homogenization, suspension, disaggregation, scission, dispersion, deagglomeration, and solubilization processes, as well as synthetic organic and organometallic chemistry.^{5,25,26} Ultrasound has been known to: (1) accelerate conventional chemical reactions, (2) induce aqueous redox reactions, (3) cause polymer degradation, and (4) induce decomposition or cause reaction in organic solvents.²⁷ The application of ultrasound in the area of polymer chemistry was first reported by Lindstrom and Lamm²⁸ and Henglelin²⁹ for the polymerization of acrylonitrile in an aqueous medium. Since then, ultrasound has been used in several areas of polymer chemistry. In addition to the works we have reported, $^{1-4}$ Kruus $^{17,18,30-33}$ and others $^{34-39}$ have also reported both polymerization and depolymerization resulting from the use of ultrasound. The aforementioned work shows the potential of the application of ultrasound in the preparation of polymeric materials.

EXPERIMENTAL

Apparatus

A schematic diagram of the apparatus is shown in Figure 1. Ultrasound, with a frequency of 20 kHz,



Figure 1 Schematic diagram of ultrasonic polymerization apparatus.

was produced using a Sonics and Materials Model EC-1500 ultrasonic generator. A 1-inch standard titanium horn was used to couple the piezoelectric transducer to the liquid of interest. The oscillator power was set at various points on a range from 20 to 70 (on a scale of 100), and cooling air was blown over the ultrasonic horn to prevent overheating. Acoustic energy corresponding to oscillator power was measured calorimetrically^{40,41} by cavitating a known amount of water in a Dewar flask, recording the temperature change as a function of time, and calculating the total energy released. The acoustic energies varied between 34-72 W, and this corresponded to a range of acoustic intensity from 6.8 W cm⁻² to 14.4 W cm^{-2} . Ultrasonic irradiation of the monomer emulsion was conducted with the tip of the coupling horn immersed directly in the emulsion.

Reagents and Materials

Reagent-grade MMA was obtained from the Fisher Chemical Company (Pittsburgh, PA) and distilled under vacuum to remove the hydroquinone inhibitor before use. Distilled water was used. Sodium lauryl sulfate [assayed as sodium dodecyl sulfate (SDS), 70% dodecyl sulfate, 25% tetradecyl sulfate, and 5% hexadecyl sulfate sodium salt], bromoform (99%), ammonium persulfate (99%) and poly(MMA) ($M_w = 900,000$) were obtained from Aldrich Chemical Company (Milwaukee, WI) and used as received. Hydroquinone was obtained from Allied Chemical Company and used as received. 1-Propanol suitable for the use

in liquid and gas chromatography was obtained from Omnisolo Chemical Company and used as received.

Polymerization Processes, Latexes, and Polymer Characterizations

Several emulsion systems were polymerized under different conditions to study the nature and source of free radicals for the initiation process of ultrasonically initiated emulsion polymerization. Five parameters that control polymerization rate, polymer particle number, and polymer molecular weight were varied: (1) type of cavitation, (2)acoustic intensity, (3) argon gas flow rate, (4) surfactant concentration, and (5) initial monomer concentration. Concentrations of ingredients were reported in units of moles per liter of aqueous phase. The emulsion volume used for all experiments was fixed because the rate of polymerization was found to vary to the inverse square root of the liquid monomer volume.^{32,33} The emulsion was prepared by adding the distilled monomer to the aqueous surfactant solution at a rate of 2-3 mL min⁻¹, with stirring at room temperature for 15 min. The emulsion was introduced to the reaction container, a 17-cm high \times 6-cm diameter flat-bottomed Pyrex glass tube. It was deoxygenated by bubbling with argon gas for 3 min, 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 a cooling bath mixture of ethylene glycol and water maintained at -10° C. During the ultrasonically initiated polymerization, dry argon was bubbled continuously through the solution to promote cavitation by providing nuclei for the formation of the bubbles. No stirring mechanism was required due to the rapid streaming and efficient mixing caused by ultrasound and by the argon gas flowing through the reactor.

The temperature of the reaction solution was measured as a function of time. A gravimetric method was used to determine the % conversion of MMA. Sonication intervals ranging from 5 to 100 min were used to obtain the time versus % conversion curve needed to calculate the polymerization rate. Each sonication interval was performed three times and the average value of the % yield was used to construct the time versus % conversion curve. The entire sample volume was kept constant throughout the sonication experiments (i.e., no sample was removed during each interval of sonication), because any change to the volume would have changed the ultrasound effective rate. The reaction tube was removed from the bath immediately after ultrasonic irradiation. Latex samples were coagulated with acetone, followed by methanol precipitation, several water washings, and vacuum-drying at 60°C for 24 h. The samples were cooled to room temperature under vacuum, sealed, and weighed to determine the mass of polymer formed. The conventional emulsion polymerization was performed without ultrasound in a 250-mL three-neck round-bottomed flask equipped with a stirrer, a nitrogen inlet, a dropping funnel, and condenser at 75°C to compare with ultrasonically initiated emulsion polymerizations. A radical trapping experiment was also performed with ultrasound to confirm the source of the free radicals involved in the initiation process. This radical trapping experiment was performed by ultrasonically irradiating 4.2 mL of radical trapping agent, bromoform, with 100 mL of water and 1 g of sodium lauryl sulfate at an acoustic intensity of 13.0 W $\rm cm^{-2}$ under an argon flow rate of 0.74 mL/s for 30 min. This was followed by adding 100 mL of 1-propanol to the irradiated solution, then subjecting this solution to gas chromatography/mass spectroscopy (GC/MS) spectrum analysis.

GC/MS analysis was performed by a HP5970 mass selective detector and a HP5890 gas chromatograph. A 0.4- μ L injection volume with a 1 : 40 split ratio, a 280°C injection temperature, and a 260°C transfer line temperature was used. The temperature program was held at 100°C for 2 min and increased to 260°C at a 10°C min⁻¹ rate.

Molecular Weight Analysis

The polymer molecular weights were measured using gel permeation chromatography (Waters Associates model 201A) with a single phenol gel five linear column ($350 \times 78 \text{ mm}, 5 \mu \text{m}, 10^3 \times 10^7$; Phenomenex) and a differential refractometer detector. Tetrahydrofuran was used as the eluting solvent; the flow rate was 1 mL min⁻¹ and the operation temperature was room temperature. The column was calibrated using five low-dispersity polystyrene standards with known molecular weights ranging from 5,000 to 3,000,000. The polymer molecular weights were recorded in comparison with a polystyrene standard by using the Mark–Houwink–Sakurada equation.

Infrared (IR) Spectroscopy Analysis

IR spectra were obtained on a Perkin-Elmer 283 B spectrophotometer.

Nuclear Magnetic Resonance (NMR) Analysis

High-resolution ¹H NMR spectra were obtained at 200 MHz using a JEOL FX-200 Fourier Transform NMR Spectrometer.

Latex Particle Size and Polymer Particles Number Analysis

The volume-average diameters (D_v) of the latex (polymer) particles were measured by dynamic light scattering using a NICOMP particle size analyzer (model 370). The particle number (N_p) generated per milliliter of water was calculated from the following equation: $N_p = 6 \times Y \times 10^{21}/\pi \times (D_v)^3 \times D_p$, where Y is latex solid content, D_v is volume-average diameter of the latex particle, and D_p is polymer density.

RESULTS AND DISCUSSION

Effects of Different Types of Cavitation

Polymerizations were performed with ultrasound in the presence and absence of bubbling argon gas to investigate the effect of different types of cavitation on polymerization rate and polymer molecular weight. Results are reported in Table I.

When there was a substantial flow of argon gas going through the reaction tube, the cavitation noise was soft and polymerization occurred. The % conversion of MMA to poly(MMA) varied from 20 to 61%, and the weight average molecular weight of poly(MMA) varied from 2.1 million g mol⁻¹ to 3.5 million g mol⁻¹, with a sonication time of 30–35 min. When there was no argon gas flowing through the reaction tube, the cavitation noise was loud. A very small amount of black materials formed, but no polymerization occurred. Similar results were reported by Kruus and colleagues^{17,18} on the ultrasonically initiated bulk polymerization of styrene and MMA.

There are two specific types of cavitation that can occur^{13,14,17,27,42}: transient and resonant. Transient (or vapor) cavitation, which occurs when there is no gas flow through the solution, results from the formation and collapse of the bubble within a few cycles. The audible noise from this type of cavitation is loud and harsh, and there are cavitation bubbles only in the immediate vicinity of the ultrasonic probe. The bubbles produced by transient cavitation contain only the vapor of the liquid, and the collapse of the bubble is dominated by internal forces. As a result, the pressure in transient cavitation bubbles can be

| No. | MMA (mL) | Water (mL) | ${f S^b}\ (g)$ | Intensity ^c (W cm ⁻²) | $\begin{array}{c} Argon \ Flow \\ Rate \\ (mL \ s^{-1}) \end{array}$ | Reaction Time (min) | IT ^d (°C) | FT ^e (°C) | Polymer Yield (g) | Wt % Conversion | $M_w 	imes 10^{-6^{ m f}} \ ({ m g mol}^{-1})$ |
|--------|-------------|---------------|----------------|---|--|---------------------------|-------------------------|-------------------------|-------------------------|--------------------|--|
| 1-1 | 6 | 116 | 1 | 9.2 | 0.32 | 35 | 5 | 27 | 3.4 | 61 | 2.47 |
| 1-2 | 6 | 116 | 1 | 9.2 | 0 | 35 | 5 | | 0 | 0 | 0 |
| 1-3 | 12 | 110 | 1 | 9.2 | 0.32 | 32 | 5 | 29 | 4.76 | 42.4 | 2.80 |
| 1-4 | 12 | 110 | 1 | 9.2 | 0 | 32 | 5 | | 0 | 0 | 0 |
| 1-5 | 18 | 104 | 1 | 9.2 | 0.32 | 35 | 5 | 30.5 | 6.05 | 35.9 | 3.06 |
| 1-6 | 18 | 104 | 1 | 9.2 | 0 | 35 | 5 | | 0 | 0 | 0 |
| 1-7 | 22 | 100 | 1 | 9.2 | 0.32 | 35 | 5 | 31 | 6.35 | 30.8 | 3.22 |
| 1-8 | 22 | 100 | 1 | 9.2 | 0 | 35 | 5 | _ | 0 | 0 | 0 |
| 1-9 | 30 | 92 | 1 | 9.2 | 0.32 | 35 | 5 | 32 | 5.88 | 20.9 | 3.24 |
| 1-10 | 30 | 92 | 1 | 9.2 | 0 | 35 | 5 | _ | 0 | 0 | 0 |
| 1-11 | 22 | 100 | 1 | 13.0 | 0.48 | 30 | 5 | 36 | 7.93 | 38.5 | 3.47 |
| 1 - 12 | 22 | 100 | 1 | 13.0 | 0 | 30 | 5 | _ | 0 | 0 | 0 |
| 1 - 13 | 22 | 100 | 1 | 11.0 | 0.48 | 30 | 5 | 34 | 7.06 | 34.3 | 3.37 |
| 1 - 14 | 22 | 100 | 1 | 11.0 | 0 | 30 | 5 | | 0 | 0 | 0 |
| 1 - 15 | 22 | 100 | 1 | 9.2 | 0.48 | 30 | 5 | 31.5 | 6.44 | 31.2 | 3.24 |
| 1 - 16 | 22 | 100 | 1 | 9.2 | 0 | 30 | 5 | | 0 | 0 | 0 |
| 1 - 17 | 22 | 100 | 1 | 7.6 | 0.48 | 30 | 5 | 24 | 4.43 | 21.5 | 3.08 |
| 1 - 18 | 22 | 100 | 1 | 7.6 | 0 | 30 | 5 | _ | 0 | 0 | 0 |
| 1 - 19 | 22 | 100 | 1 | 6.8 | 0.48 | 30 | 5 | 23.5 | 4.31 | 20.9 | 3.04 |
| 1-20 | 22 | 100 | 1 | 6.8 | 0 | 30 | 5 | | 0 | 0 | 0 |
| 1 - 21 | 22 | 100 | 7 | 9.2 | 0.32 | 30 | 5 | 36.5 | 9.44 | 44.2 | 2.14 |
| 1-22 | 22 | 100 | 7 | 9.2 | 0 | 30 | 5 | | 0 | 0 | 0 |
| 1-23 | 22 | 100 | 5 | 9.2 | 0.32 | 35 | 5 | 34.5 | 9.17 | 44.5 | 2.55 |
| 1-24 | 22 | 100 | 5 | 9.2 | 0 | 35 | 5 | _ | 0 | 0 | 0 |
| 1-25 | 22 | 100 | 3 | 9.2 | 0.32 | 35 | 5 | 33.5 | 7.95 | 38.6 | 2.88 |
| 1-26 | 22 | 100 | 3 | 9.2 | 0 | 35 | 5 | | | 0 | 0 |
| 1-27 | 22 | 100 | 1 | 9.2 | 0.32 | 35 | 5 | 30 | 6.35 | 30.8 | 3.22 |
| 1-28 | 22 | 100 | 1 | 9.2 | 0 | 35 | 5 | | | 0 | 0 |
| 1-29 | 22 | 100 | 1 | 9.2 | 0.54 | 35 | 5 | 32.5 | 7.1 | 34.5 | 3.25 |
| 1 - 30 | 22 | 100 | 1 | 9.2 | 0 | 35 | 5 | _ | _ | 0 | 0 |
| 1-31 | 22 | 100 | 1 | 9.2 | 0.78 | 35 | 5 | 35 | 8.16 | 39.6 | 3.28 |
| 1-32 | 22 | 100 | 1 | 9.2 | 0 | 35 | 5 | _ | _ | 0 | 0 |

Table IEffect of Different Types of Cavitation on Polymerization Rate and Polymer MolecularWeight^a

^a Cooling bath temperature = -10° C.

^b S, sodium lauryl sulfate, surfactant.

^c Acoustic intensity.

much higher than the acoustic pressure applied. When sufficient gas is introduced near the horn tip, the ultrasound seems to break the initial bubbles into microbubbles, and the streaming caused by the ultrasound distributes these microbubbles throughout the solution. This type of cavitation is called resonant (stable or gaseous) cavitation. The audible noise from this type of cavitation is hissing and soft, and there are cavitation bubbles dispersed through the reaction vessel. The bubbles produced by stable cavitation contain the sparging gas as well as the liquid vapor. The oscillations of the bubbles are governed primarily by the applied acoustic pressure variations. ^d Initial reaction temperature.

^e Final reaction temperature.

^fWeight average molecular weight.

The magnitude of pressure (P_i) before the cavitation bubble collapses is not the same for transient cavitation as it is for resonant cavitation. In transient cavitation, P_i can be approximated to the vapor pressure of the liquid at the bulk temperature. For resonant cavitation, the cavitation bubble also contains sparging gas; therefore, the magnitude of P_i is near the order of an atmosphere. The net result is that the local temperature reached when a transient cavity collapses is considerably higher than the local temperature attained when a resonant cavity collapses.¹⁷ As a result, the temperature reached by the collapse of resonant cavitation is appropriate to initiate polymerization; but, the temperature reached by the collapse of transient cavitation is so high (>1,000°K) that a pyrolysis-type reaction, which forms colored compounds, rather than polymerization occurs.¹⁷

In summary, data presented herein indicate that ultrasonic initiation of the polymerization in the emulsion systems takes place primarily due to resonant cavitation, which requires the bubbling of substantial gas through the reaction solution. In the absence of this gas, the cavitation is transient, and the local temperature reached is so high (>1,000°K) that it may be excessive for the more controlled reactions needed to initiate polymerization. Therefore, no initiation of polymerization occurs. Instead, depolymerization and the forming of colored compounds due to pyrolysis occur.

Free Radical Nature of the Ultrasonically Initiated Emulsion Polymerization of MMA

As mentioned in the Introduction section, the sonochemical reaction is caused by the free radical generated on the collapse of the cavitation bubbles during the cavitation process. Therefore, one can expect that this reaction can be prohibited by a radical scavenger. In this section of experiments, a free radical scavenger, hydroquinone, was added to a series of polymerization performed with ultrasound to confirm the free radical nature of the ultrasonically initiated emulsion polymerization. Results are shown in Table II.

No polymerization occurred when hydroquinone was present in the reaction system. Without hydroquinone, polymerization occurred; the % conversion of MMA to poly(MMA) varied from 21 to 61%, and the weight average molecular weight of poly(MMA) varied from 2.1 million g mol⁻¹ to 3.5 million g mol⁻¹, with 30–35 min of sonication. These results show that the polymerization can be inhibited by a free radical scavenger. This also demonstrates the free radical nature of the ultrasonically initiated emulsion polymerization of MMA. Other studies^{1–3,28–39,43,44} also show that free radicals can be produced in the cavitating liquid to initiate sonochemical reactions, solution, and bulk polymerization reactions.

Thermally Initiated Polymerization Versus Ultrasonically Initiated Polymerization

Several emulsions were polymerized by both the conventional emulsion polymerization method

and the ultrasonically initiated emulsion polymerization method to investigate the thermal or cavitation nature of the ultrasonically initiated emulsion polymerization. Results are shown in Table III.

No polymerization occurred when the conventional emulsion polymerization was conducted at 75°C for 4 h using different emulsions in the absence of conventional initiator. With the same emulsions using the ultrasonically initiated emulsion polymerization method, the % conversion of MMA to poly(MMA) varied from 21 to 61%, and the weight average molecular weight of poly(MMA) varied from 2.1 million g mol⁻¹ to 3.5 million g mol⁻¹, with 30 to 35 min of sonication and the reaction temperature increasing from an initial temperature of 5°C to a final temperature ranging from 27° – 37° C.

The results indicate that: (1) ultrasonically initiated emulsion polymerization occurs at relatively low temperatures as a result of cavitation process, and (2) polymerization is not caused directly by bulk thermal contributions from the reaction medium. High local temperatures generated during an adiabatic bubble collapse in the cavitation process can produce free radicals by a thermolytic process.^{19,20,45} Shock waves or the shear stress generated on the collapse of the cavitation bubbles can also produce free radicals by a mechanical degradation process.^{34,46} Some of the free radicals thus produced have sufficient lifetime to migrate into the bulk liquid to initiate polymerization.

Source of Free Radicals of the Initiation Process for the Ultrasonically Initiated Emulsion Polymerization of MMA

Several experiments were performed with ultrasound to investigate the possible source of free radicals in the initiation process of this ultrasonically initiated emulsion polymerization, in which no conventional water-soluble initiator was added to initiate the polymerization. Results are shown in Table IV.

No polymerization occurred when pure MMA was irradiated with ultrasound at an acoustic intensity of 13.0 W cm⁻² under an argon gas flow rate of 0.78 mL s⁻¹ for 90 min of sonication. Similar results were observed when mixtures of water plus MMA at various ratios were run under the same conditions. When MMA and sodium lauryl sulfate mixtures were run under the same reaction conditions, some polymerization occurred (<0.1% conversion) after 90 min of sonication.

| No. | MMA (mL) | Water (mL) | ${f S^b}\ (g)$ | Hydro- quinone (g) | Intensity ^c (W cm ⁻²) | $\begin{array}{c} Argon \ Flow \\ Rate \\ (mL \ s^{-1}) \end{array}$ | Reaction Time (min) | Polymer Yield (g) | Wt % Conversion | $M_w	imes 10^{-6^{ m f}} \ ({ m g\ mol}^{-1})$ |
|--------|-------------|---------------|----------------|--------------------------|---|--|---------------------------|----------------------|--------------------|--|
| 2-1 | 6 | 116 | 1 | 1.5 | 9.2 | 0.32 | 35 | 0 | 0 | 0 |
| 1-1 | 6 | 116 | 1 | 0 | 9.2 | 0.32 | 35 | 3.4 | 61.0 | 2.47 |
| 2-2 | 12 | 110 | 1 | 1.5 | 9.2 | 0.32 | 32 | 0 | 0 | 0 |
| 1-3 | 12 | 110 | 1 | 0 | 9.2 | 0.32 | 32 | 4.76 | 42.4 | 2.80 |
| 2-3 | 18 | 104 | 1 | 1.5 | 9.2 | 0.32 | 35 | 0 | 0 | 0 |
| 1-5 | 18 | 104 | 1 | 0 | 9.2 | 0.32 | 35 | 6.05 | 35.9 | 3.06 |
| 2-4 | 22 | 100 | 1 | 1.5 | 9.2 | 0.32 | 35 | 0 | 0 | 0 |
| 1-7 | 22 | 100 | 1 | 0 | 9.2 | 0.32 | 35 | 6.35 | 30.8 | 3.22 |
| 2-5 | 30 | 92 | 1 | 1.5 | 9.2 | 0.32 | 35 | 0 | 0 | 0 |
| 1-9 | 30 | 92 | 1 | 0 | 9.2 | 0.32 | 35 | 5.88 | 20.9 | 3.24 |
| 2-6 | 22 | 100 | 1 | 1.5 | 13.0 | 0.48 | 30 | 0 | 0 | 0 |
| 1-11 | 22 | 100 | 1 | 0 | 13.0 | 0.48 | 30 | 7.93 | 38.5 | 3.47 |
| 2-7 | 22 | 100 | 1 | 1.5 | 11.0 | 0.48 | 30 | 0 | 0 | 0 |
| 1 - 13 | 22 | 100 | 1 | 0 | 11.0 | 0.48 | 30 | 7.06 | 34.3 | 3.37 |
| 2-8 | 22 | 100 | 1 | 1.5 | 9.2 | 0.48 | 35 | 0 | 0 | 0 |
| 1 - 15 | 22 | 100 | 1 | 0 | 9.2 | 0.48 | 30 | 6.44 | 31.2 | 3.24 |
| 2-9 | 22 | 100 | 1 | 1.5 | 7.6 | 0.48 | 30 | 0 | 0 | 0 |
| 1 - 17 | 22 | 100 | 1 | 0 | 7.6 | 0.48 | 30 | 4.43 | 21.5 | 3.08 |
| 2 - 10 | 22 | 100 | 1 | 1.5 | 6.8 | 0.48 | 30 | 0 | 0 | 0 |
| 1-19 | 22 | 100 | 1 | 0 | 6.8 | 0.48 | 30 | 4.31 | 20.9 | 3.04 |
| 2-11 | 22 | 100 | 7 | 1.5 | 9.2 | 0.32 | 30 | 0 | 0 | 0 |
| 1-21 | 22 | 100 | 7 | 0 | 9.2 | 0.32 | 30 | 9.44 | 44.2 | 2.14 |
| 2-12 | 22 | 100 | 5 | 1.5 | 9.2 | 0.32 | 35 | 0 | 0 | 0 |
| 1-23 | 22 | 100 | 5 | 0 | 9.2 | 0.32 | 35 | 9.17 | 44.5 | 2.55 |
| 2-13 | 22 | 100 | 3 | 1.5 | 9.2 | 0.32 | 35 | 0 | 0 | 0 |
| 1-25 | 22 | 100 | 3 | 0 | 9.2 | 0.32 | 35 | 7.95 | 38.6 | 2.88 |
| 2-14 | 22 | 100 | 1 | 1.5 | 9.2 | 0.32 | 35 | 0 | 0 | 0 |
| 1-27 | 22 | 100 | 1 | 0 | 9.2 | 0.32 | 35 | 6.35 | 30.8 | 3.22 |
| 2-15 | 22 | 100 | 1 | 1.5 | 9.2 | 0.54 | 35 | 0 | 0 | 0 |
| 1-29 | 22 | 100 | 1 | 0 | 9.2 | 0.54 | 35 | 7.1 | 34.5 | 3.25 |
| 2-16 | 22 | 100 | 1 | 1.5 | 9.2 | 0.78 | 35 | 0 | 0 | 0 |
| 1-31 | 22 | 100 | 1 | 0 | 9.2 | 0.78 | 35 | 8.16 | 39.6 | 3.28 |

Table II Free Radical Nature of Ultrasonically Initiated Emulsion Polymerization of MMA^a

^a Cooling bath temperature = -10° C.

^b S, sodium lauryl sulfate, surfactant.

The above results imply that free radical polymerization cannot be initiated by ultrasound with pure MMA or MMA in an aqueous phase under the acoustic intensity of 13.0 W cm⁻², and an argon gas flow rate of 0.78 mL s^{-1} . Either no radical species form or possibly the radical formed terminate or recombine so quickly that their life time is insufficient to initiate the polymerization. These phenomena could be attributed to lower cavitation efficiencies in organic liquids³⁹ and a high percentages of radical recombination occurring in water in the presence of argon gas.^{27,47,48} When MMA and sodium lauryl sulfate were ultrasonically irradiated under the same conditions, there must be some radicals generated that survive for a long enough time to initiate the polymerization.

^c Acoustic intensity.

^d Weight average molecular weight.

Further radical trapping experiments—which involved ultrasonically irradiating a radical scavenger, bromoform, with water and sodium lauryl sulfate at an acoustic intensity of 13.0 W cm^{-2} under an argon gas flow rate of 0.74 mL s⁻¹ over 30 min of sonication followed by GC/MS analysis-identified the existence of 1-bromododecane from the GC/MS spectrum (Figure 2). This confirms the source of radicals as coming from the surfactant molecule and that sonication degrades the surfactant into $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, and OSO₃Na radicals—all of which can initiate the polymerization. Results in Tables I, II, and IV show that the radicals generated in the emulsion system (i.e., MMA, water and SDS) with ultrasound produce both a higher yield and a higher molecular weight polymer than those obtained

| | MMA (mL) | Water (mL) | ${\mathop{\rm SDS^b}\limits_{(g)}}$ | Reaction Time (min) | Reaction Temperature (°C) | Stirring Rate (rpm) | Polymer Yield (g) | Wt % Conversion |
|------|--------------|---------------|-------------------------------------|---------------------------|---------------------------------|---------------------------|----------------------|--------------------|
| Ther | mally Initia | ted Polyme | rization ^a | | | | | |
| 3-1 | 6 | 116 | 1 | 240 | 75 | 250 | 0 | 0 |
| 3-2 | 12 | 110 | 1 | 240 | 75 | 250 | 0 | 0 |
| 3-3 | 18 | 104 | 1 | 240 | 75 | 250 | 0 | 0 |
| 3-4 | 22 | 110 | 1 | 240 | 75 | 250 | 0 | 0 |
| 3-5 | 30 | 92 | 1 | 240 | 75 | 250 | 0 | 0 |
| 3-6 | 22 | 100 | 3 | 240 | 75 | 250 | 0 | 0 |
| 3-7 | 22 | 100 | 5 | 240 | 75 | 250 | 0 | 0 |
| 3-8 | 22 | 100 | 7 | 240 | 75 | 250 | 0 | 0 |

Table III Thermally Vs. Ultrasonically Initiated Polymerization^a

^a Conventional emulsion polymerization method was used for all reactions.

^b SDS, sodium lauryl sulfate, surfactant.

| | MMA (mL) | Water (mL) | $\mathop{\mathrm{SDS}^{\mathrm{b}}}_{(\mathrm{g})}$ | Intensity ^c (W cm ⁻²) | $\begin{array}{c} Argon \ Flow \\ Rate \\ (mL \ s^{-1}) \end{array}$ | Reaction Time (min) | Polymer Yield (g) | Wt % Conversion | $M_w 	imes 10^{-6^{ m d}} \ ({ m g\ mol}^{-1})$ | Final Temperature (°C) |
|--------|-------------|---------------|---|---|--|---------------------------|----------------------|--------------------|---|------------------------------|
| Ultra | sonically | Initiated | Polyme | rization ^a | | | | | | |
| 1-1 | 6 | 116 | 1 | 9.2 | 0.32 | 35 | 3.40 | 61.0 | 2.47 | 27.0 |
| 1-3 | 12 | 110 | 1 | 9.2 | 0.32 | 32 | 4.76 | 42.4 | 2.80 | 29.6 |
| 1-5 | 18 | 104 | 1 | 9.2 | 0.32 | 35 | 6.05 | 35.9 | 3.06 | 30.5 |
| 1-7 | 22 | 100 | 1 | 9.2 | 0.32 | 35 | 6.35 | 30.8 | 3.22 | 31.0 |
| 1-9 | 30 | 92 | 1 | 9.2 | 0.32 | 35 | 5.88 | 20.9 | 3.24 | 32.0 |
| 1-25 | 22 | 100 | 3 | 9.2 | 0.32 | 35 | 7.95 | 38.6 | 2.88 | 33.5 |
| 1 - 23 | 22 | 100 | 5 | 9.2 | 0.32 | 35 | 9.17 | 44.5 | 2.55 | 34.5 |
| 1-21 | 22 | 100 | 7 | 9.2 | 0.32 | 30 | 9.44 | 44.2 | 2.14 | 36.5 |

^a Initial reaction temperature was 5°C.

^b SDS, sodium lauryl sulfate, surfactant.

^c Acoustic intensity.

^d Weight average molecular weight.

from bulk (i.e., MMA and SDS) systems. This phenomenon can be attributed to better isolation of growing radicals and better cavitation efficiencies in the emulsion system.

In summary, the sources of the free radicals for the initiation process in this ultrasonically initiated emulsion polymerization comes either from (1) the thermal degradation of the (C—O) bond of sodium lauryl sulfate as a result of high local temperatures generated on the collapse of the cavitation bubble^{19,20,45} or (2) from the mechanical degradation of the (C—O) bond of sodium lauryl sulfate as a result of shock waves or the shear stress generated on the collapse of the cavitation bubble.^{34,46} In either case, the free radicals generated thus initiate free radical polymerization.

Effects of Acoustic Intensity on Polymerization Rate, Polymer Particle Number, and Polymer Molecular Weight

Acoustic intensity is the main parameter influencing the number of cavitation bubbles produced. The effects of acoustic intensity on polymerization rate, polymer particle number, and polymer molecular weight were studied by ultrasonically irradiating a MMA emulsion containing 2.06 mol of MMA and 0.035 mol of SDS (1% based on the aqueous phase) per liter of water at different acoustic intensities under an argon gas flow rate of 0.74 mL s⁻¹ in a -10° C cooling bath. Results are presented in Figures 3–7.

From the temperature profiles obtained in these experiments, the reaction temperatures rose rapidly (roughly 20°C, with initial 5°C reaction temperature) in the first 10 min after ultrasound was turned on, then leveled to a plateau region ($\sim 22^{\circ}-23^{\circ}$ C) and then rose again ($\sim 25^{\circ}-28^{\circ}$ C) within the final 5 min of sonication. During the last 5 min of sonication, polymer layer adhered onto the horn for all acoustic intensity experiments studied, presumably due to the vigorous horn vibration, or due to the temperature generated on the surface of the horn. This caused the reaction temperature to rise from the plateau

| No. | MMA (mL) | Water (mL) | ${f S}^{f a}$ (g) | Intensity (W cm ⁻²) | Argon Flow Rate (mL s ⁻¹) | IT ^b (°C) | Reaction Time (min) | Wt % Conversion |
|-------------------|-------------|---------------|-------------------|------------------------------------|---|-------------------------|---------------------------|--------------------|
| 4-1 | 80 | 0 | 0 | 13.0 | 0.78 | 5 | 30 | 0 |
| 4-2 | 80 | Ő | Ő | 13.0 | 0.78 | 5 | 60 | ů 0 |
| 4-3 | 80 | 0 | 0 0 | 13.0 | 0.78 | 5 | 90 | 0 |
| 4-4 | 90 | 10 | 0 | 13.0 | 0.78 | 5 | 90 | 0 |
| 4-5 | 80 | 20 | 0 | 13.0 | 0.78 | 5 | 90 | 0 |
| 4-6 | 70 | 30 | 0 | 13.0 | 0.78 | 5 | 90 | 0 |
| 4-7 | 60 | 40 | 0 | 13.0 | 0.78 | 5 | 90 | 0 |
| 4-8 | 50 | 50 | 0 | 13.0 | 0.78 | 5 | 90 | 0 |
| 4-9 | 40 | 60 | 0 | 13.0 | 0.78 | 5 | 90 | 0 |
| 4-10 | 30 | 70 | 0 | 13.0 | 0.78 | 5 | 90 | 0 |
| 4-11 | 20 | 80 | 0 | 13.0 | 0.78 | 5 | 90 | 0 |
| 4-12 | 10 | 90 | 0 | 13.0 | 0.78 | 5 | 90 | 0 |
| 4-13 | 80 | 0 | 1 | 13.0 | 0.78 | 5 | 90 | < 0.1% |
| 4-14 | 80 | 0 | 5 | 13.0 | 0.78 | 5 | 90 | $<\!0.1\%$ |
| 4-15 | 80 | 0 | 8 | 13.0 | 0.78 | 5 | 90 | $<\!0.1\%$ |
| 4-16 ^c | 80 | 0 | 1 | 13.0 | 0.78 | 5 | 90 | 0 |
| $4-17^{\circ}$ | 80 | 0 | 5 | 13.0 | 0.78 | 5 | 90 | 0 |
| 4-18 ^c | 80 | 0 | 8 | 13.0 | 0.78 | 5 | 90 | 0 |

Table IV Source of Initiation Process of Ultrasonically Initiated Emulsion Polymerization of MMA

^a S, sodium lauryl sulfate, surfactant.

^b IT, initial reaction temperature.

 $^{\rm c}$ 1.5 g of hydroquinone was added to solution before reaction.

region at the last stage of sonication. It was noticed that cavitation in the solution stopped, shown by a marked change in the sound of the sonication at this time, and no further polymerization occurred thereafter. This demonstrates that cavitation is necessary for the polymerization to occur. There was no sign of any destabilization of poly(MMA) latexes for all experiments during the polymerization of the emulsions. The latexes obtained were completely homogeneous.

The monomer conversion versus time curves shown in Figure 3 were similar in shape to those shown by Zimmt⁴⁹ in his study of conventional emulsion polymerization of MMA. The relatively linear curves observed at lower acoustic intensity indicated that no noticeable gel effect occurs within the conversion range studied. As acoustic intensity increases, nonlinear curves were observed. This indicates a gel effect occurs at higher acoustic intensities. This will be shown in the molecular development curve discussed later. Small induction periods were always recorded in the polymerization process. The length of the induction period varied from 5 to 7 min, depending on the acoustic intensity. The smallest induction period was observed at the highest acoustic intensity. These induction periods are characteristic of most emulsion polymerization whether initiated by radiation or chemical initiators.

The polymerization rates were calculated from the slopes of the relatively linear zones of the monomer conversion *versus* time curves shown in Figure 3 by using the following equation: R_p (mol L^{-1} of water-s) = -d[M]/dt = -[(1/dt) (polymerwt./ M_0)]/[(initial water volume (mL)/1,000)] = 10 slope (monomer wt./water wt.) (1/ M_0) (1/60), where (monomer wt./water wt.) is the initial monomer to initial water weight ratio in the emulsion formula, and M_0 is the molecular weight of monomer.

Over these relatively linear ranges, the reaction temperatures are within plateau regions (varied by $1^{\circ}-2^{\circ}$ C), the polymerization rates are relatively constant, and are proportional to *N*, the number of particles per liter of latex. It is this rate that will be used throughout this article.

Polymerization Rate

From the log-log plot of polymerization rate versus acoustic intensity shown in Figure 4 and temperature profiles obtained from these experiments, the following phenomena were observed: (1) the polymerization rate increased as the 0.98 power of the acoustic intensity, with acoustic intensity increasing from 6.8 to 13.0 W cm⁻², then it decreased beyond the acoustic intensity of 13.0 W cm⁻²; and (2) final reaction temperature in-



Figure 2 Mass spectrum of $C_{12}H_{25}Br$ detected from ultrasonically irradiated solution. (Water = 100 mL, bromoform = 4.2 mL, SDS = 1 g, acoustic intensity = 13.0 W cm⁻², argon gas flow rate = 0.74 mL s⁻¹, sonication time = 30 min, cooling bath temperature = $-10^{\circ}C$.)

creased with increasing acoustic intensity ($\sim 10^{\circ}$ C difference between highest and lowest acoustic intensities). The increase in polymerization rate with increasing acoustic intensity is presumably due to an increase in the radical generation rate, an increase in final reaction temperature, and gel effect as acoustic intensity used in the reaction system is increased. The effect of acoustic intensity on the radical generation rate will be discussed in the companion article. The increase in the final reaction temperature results in increasing propagation rate constant; therefore, the polymerization rate.

This phenomenon is confirmed from the increase of the slope (reaction rate constant) of monomer conversion *versus* time curves, with acoustic intensity as shown in Figure 3. The increase in the final reaction temperature with increasing acoustic intensity is attributed to an increase in the number of cavitation bubbles, an increase of the heat generated from horn vibration, and the heat released from polymerization. Gel effect was observed at higher % conversion as shown in monomer conversion *versus* time curves in Figure 3.

The polymerization rate increased with acoustic intensity only up to a limiting point (13.0 W cm^{-2}). Beyond this point, no further benefit was obtained, as was commonly the case for both sono-

chemical reactions⁵⁰ and ultrasonically initiated bulk polymerizations.^{32,39} This phenomenon indicates a limitation for the assumption that there is a simple linear relationship between acoustic intensity and the number of cavitation bubbles. Sirotyuk⁵⁰ reported that, initially, the number of cavitation bubbles increased with increasing acoustic intensity until a certain peak intensity was reached. Increasing the intensity further produced less cavitation bubbles. He attributed this to an increase in the collapse time for the cavitation bubbles.

Kruus and Patraboy³² clarified this phenomenon by stating that both the maximum radii obtained by the bubbles and the number of bubbles increased with increasing acoustic intensity. Further increases in the maximum radii then resulted in larger collapse times for the bubbles. This increase in maximum radii and collapse time continued until the collapse time exceeded onehalf the period of the ultrasound. At this point, the bubbles could no longer collapse completely in every acoustic period. This increase in time between collapse events allowed a partial coagulation of the cavitation bubbles to occur. These enlarged bubbles then floated to the surface of the liquid or produced the foam in the liquid. The system produced fewer, larger, and more stable



Figure 3 Monomer % conversion *versus* time curve for the ultrasonically initiated emulsion polymerization of MMA at various acoustic intensities. (MMA = 22 mL, water = 100 mL, SDS = 1 g, argon gas flow rate = 0.74 mL s⁻¹, cooling temperature = -10° C.)

cavitation bubbles, and this resulted in a reduction in the number of potential cavitation nuclei.

The applied ultrasonic frequency is also a factor that determines the size of the cavitation bubbles and the time scales for bubble growth and collapse.⁵⁰ Therefore, the limiting intensity and slope for the curve as shown in Figure 4 will probably be different at different frequencies.

According to the Smith–Ewart⁵¹ theory, the rate of an emulsion polymerization at an average number of radicals per particle n = 0.5 (case II) is as follows: $-dM/dt = 0.5 K_p N[M]_p = K'[M]_p (P/\mu)^{0.4} (A_s S)^{0.6}$, where N is the number of particles per liter of water, $[M]_p$ is monomer concentration in the particle, -dM/dt is the rate of polymerization in mol L⁻¹-s⁻¹, K_p is the rate constant for chain propagation, S is the surfactant concentration, A_s is the area covered by one molecule of surfactant, P is the generation rate of free radical, and μ is the rate of increase in volume of a single particle.

Because the rate of radical generation is proportional to the number of cavitation bubbles and the number of cavitation bubbles is proportional to the acoustic intensity,^{32,39} it would be expected from the Smith–Ewart Case II Kinetics that the rate of polymerization would depend on acoustic intensity to the 0.4 power, when all other parameters are kept constant (i.e., -dM/dt = constant $[M]_p$ [Acoustic Intensity]^{0.4}). The rate dependence of acoustic intensity to the 0.98 power found in this study is higher than the 0.4 as predicted from the Smith–Ewart theory.

This indicates the kinetics of this ultrasonically initiated emulsion polymerization system does not follow the prediction of the Smith–Ewart theory. The reason for the high-order dependence of the polymerization rate on the acoustic intensity is a puzzle, but it may be attributed to the increase in reaction temperature or gel effect when the acoustic intensity used in the ultrasonically initiated emulsion polymerization system is increased.

Number of Polymer Particles

The number of polymer particles produced per mL of water after 30 min of sonication was within



Figure 4 Effect of acoustic intensity on polymerization rate for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, SDS = 1 g, argon gas flow rate = 0.74 mL s⁻¹, cooling bath temperature = -10° C.)

 10^{14} and 10^{15} particle/mL range. These values are in the same magnitude typically reported in other investigations of conventional emulsion polymerization of MMA.^{52,53} The log-log plot (Figure 5) of the number of polymer particles produced per milliliter of water after 30 min of sonication versus acoustic intensity shows that the number of polymer particles produced increased as the 1.23 power of the acoustic intensity. It can be seen from Figures 4 and 5 that the number of polymer particles produced and the rate of polymerization both increased with acoustic intensity. This trend implies that the increase of polymerization rate with increasing acoustic intensity is due to the increase of the number of polymer particles generated. An increase in the acoustic intensity results in an increase in the number of cavitation bubbles, as well as an increase in the reaction temperature. These generates more initiator radicals. Therefore, as more polymer particles are nucleated and produced, the resulting polymerization rate is enhanced.

Polymer Molecular Weight

From the monomer conversion *versus* polymer molecular weight curve shown in Figure 6, one

sees a rapid rise in the molecular weight at low monomer % conversion, followed by a relatively constant molecular weight value during the "constant-rate" period. The molecular weight distribution (M_w/M_n) was close to 2, the theoretical "most probable" distribution value. During the early, particle-forming stage of the reaction (interval I), the radical production rate will be larger relative to the number of particles, leading to a lower, but rapidly rising, molecular weight. Then, during the "constant" rate period (interval II), when the number of particles is relatively constant, the molecular weight should be invariant with conversion. However, the molecular weight still showed a slight increase with conversion during interval II, presumably due to gel effect that results from the suppression of the termination reaction as the viscosity in the polymerization locus increases with increasing conversion. This molecular weight development is consistent with the theoretical predictions and it agrees with the results observed by Piirma and Gardon⁵⁴ in their work on conventional emulsion polymerization of MMA.





Figure 5 Effect of acoustic intensity on the number of polymer particles generated for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, SDS = 1 g, argon gas flow rate = 0.74 mL s^{-1} , sonication time = 30 min, cooling bath temperature = -10° C.)

The molecular weight distributions (M_w/M_n) of poly(MMA) produced by the ultrasonically initiated emulsion polymerization method are close to 2. They showed no significant difference from those produced by the conventional emulsion polymerization method.⁵⁴

From the log–log plot of M_w versus acoustic intensity after 30 min of sonication, as shown in Figure 7, it appears that the polymer weight average molecular weight increased as the 0.21 power of the acoustic intensity with the acoustic intensity increasing from 6.8 to 13.0 W cm⁻². The polymer weight average molecular weight then decreased beyond the acoustic intensity of 13.0 W cm⁻².

The increase in the polymer molecular weight with increasing acoustic intensity is attributed to the gel effect that results from the increase of polymer viscosity as the acoustic intensity used in the reaction system is increased.



Figure 6 Weight average molecular weight as a function of monomer % conversion at an acoustic intensity of 9.2 W cm⁻² for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, SDS = 1 g, argon gas flow rate = 0.74 mL s⁻¹, cooling bath temperature = -10° C.)



Figure 7 Effect of acoustic intensity on the weight average molecular weight for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, SDS = 1 g, argon gas flow rate = 0.74 mL s^{-1} , sonication time = 30 min, cooling bath temperature = -10° C.)

In this experimental section dealing with different acoustic intensities, the final yield of the ultrasonically initiated emulsion polymerization of MMA performed with ultrasound at acoustic intensities ranging from 6.8 to 14.4 W cm⁻² under an argon flow rate of 0.74 mL s⁻¹ at ambient temperature (final reaction vessel temperature: 27.5°–38°C) ranged from 31 to 40%, with 30–40 min of sonication. The polymerization rate ranged from 3.5×10^{-4} to 5.9×10^{-4} mol L⁻¹ s⁻¹ and polymer weight average molecular weight ranged from 3.05×10^6 to 3.47×10^6 g mol⁻¹.

By comparison, the final yield of the ultrasonically initiated bulk polymerization of MMA performed by Kruus and Patraboy³² with ultrasound at an acoustic intensity of 20 W cm⁻² under an argon gas flow rate of 20 mL s⁻¹ at ambient temperature (32°-40°C) was ~ 3%, with 120 min of sonication. The polymerization rate ranged from 4.08 × 10⁻⁶ to 4.14 × 10⁻⁶ mol L^{-0.5} s⁻¹, and weight average molecular weight ranged from 5.9 × 10⁵ to 7.2 × 10⁵ g mol⁻¹. The polymerization rate of the conventional emulsion polymerization of MMA performed by Zimmt⁴⁹ at 60°C using Tergital 7 as the surfactant and potassium persulfate as the initiator ranged from 0.8×10^{-4} to 10.3×10^{-4} mol L⁻¹ s⁻¹.

The above results show that ultrasonically (cavitation) induced polymerization is more efficient in the emulsion systems than in bulk organic systems. This is expected because the lower vapor pressure and surface tension of the aqueous emulsion system result in a higher local temperature on collapse of the cavitation bubbles and thus a higher reaction rate. One must also realize that ultrasound is transmitted better in an aqueous phase than an organic phase due to the higher dielectric constant of water. This better transmission of ultrasound in the aqueous phase results in a greater absorption of the ultrasound, a greater cavitation efficiency, and thus net higher reaction rate.

The above results also demonstrate that, by simply using ultrasound, one can achieve a similar or even higher emulsion polymerization rate at ambient temperature, compared with that ob-



Figure 8 Monomer % conversion *versus* time curve for the ultrasonically initiated emulsion polymerization of MMA at various argon gas flow rates. (MMA = 22 mL, water = 100 mL, SDS = 1 g, acoustic intensity = 9.2 W cm⁻², cooling bath temperature = -10° C.)

tained by a higher temperature thermal emulsion polymerization method. The sonication polymerization process thus offers accelerated polymerization rates and greater energy savings.

Finally, when emulsion polymerization was conducted in the presence of 0.1% (based on water) ammonium persulfate with an acoustic intensity of 13.0 W cm⁻² under an argon gas flow rate of 0.74 mL s⁻¹, the final yield increased to 55% with 30 min of sonication, compared with 39% without any initiator. This shows that the rate of the ultrasonically initiated emulsion polymerization of MMA can be enhanced even further by the presence of added initiator. Further experiments with incremental addition of more initiator should give even higher yield.

Effects of Argon Gas Flow Rate on Polymerization Rate, Polymer Particle Number, and Polymer Molecular Weight

The effects of argon gas flow rate on both polymerization rate, polymer particle number, and polymer molecular weight were studied by ultrasonically irradiating an MMA emulsion containing 2.06 mol of MMA and 0.035 mol of SDS (1% based on the aqueous phase) per liter of water at an acoustic intensity of 9.2 W cm⁻² under different argon gas flow rates in a -10° C cooling bath. The results are presented in Figures 8–12.

In these polymerization experiments, small induction periods were recorded. The length of the induction period increased as the argon flow rate decreased. At an argon gas flow rate of 0.25 mL s⁻¹, no polymer adhered onto the horn after 35 min of sonication. At argon gas flow rates ranging from 0.32 to 0.78 mL s⁻¹, polymers adhered onto the horn after 35 min of sonication.

Polymerization Rate

From the log-log plot of polymerization rate versus argon gas flow rate shown in Figure 9 and temperature profiles obtained from these experiments, the following phenomena were observed: (1) the polymerization rate increased as the 0.086 power of the argon gas flow rate, and (2) the final reaction temperature increased slightly with increasing argon gas flow rate (~ 2°C difference between highest and lowest argon gas flow rate). The increase in the polymerization rate with increasing argon gas flow rate is presumably due to an increase in the radical generation rate, a slight increase in the reaction temperature and gel effect. This increase in the radical generation rate and the reaction temperature in turn result from an increase in the number of cavitation bubbles and an increase of the heat generated from polymerization when the argon gas flow rate used in the ultrasonically initiated emulsion polymerization system is increased. The lower dependence of the rate on the argon gas flow rate, compared with the acoustic intensity, shows that the effect



Figure 9 Effect of argon gas flow rate on the polymerization rate for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, SDS = 1 g, acoustic intensity = 9.2 W cm^{-2} , cooling bath temperature = -10° C.)



Log Argon Gas Flow Rate

Figure 10 Effect of argon gas flow rate on the number of polymer particles generated for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, SDS = 1 g, acoustic intensity = 9.2 W cm⁻², sonication time = 35 min, cooling bath temperature = -10° C.)

of argon gas flow rate on polymerization rate is less significant.

Number of Polymer Particles

The log-log plot (Figure 10) of the number of polymer particles produced per mL of water after 35 min of sonication versus argon gas flow rate shows that the number of polymer particles produced increased as the 0.16 power of the argon gas flow rate. Both the number of polymer particles produced and polymerization rate increased with argon gas flow rate as shown in Figures 9 and 10. This trend implies that polymerization rate increases with argon gas flow rate due to the increase of the number of polymer particles generated. Increasing the argon gas flow rate enhances the nucleation of cavitation bubbles, as well as slightly increases reaction temperature. These produce a greater number of cavitation bubbles and, consequently, generating more initiator radicals. Therefore, as more polymer parti-



Figure 11 Weight average molecular weight as a function of monomer % conversion under an argon gas flow rate of 0.32 mL s^{-1} for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, acoustic intensity = 9.2 W cm^{-2} , SDS = 1 g, cooling temperature = -10° C.)



Figure 12 Effect of argon gas flow rate on the weight average molecular weight for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, SDS = 1 g, acoustic intensity = 9.2 W cm⁻², sonication time = 35 min, cooling bath temperature = -10° C.)

cles are nucleated and produced, the resulting polymerization rate is enhanced.

Polymer Molecular Weight

From the plot of monomer conversion *versus* polymer molecular weight curve shown in Figure 11, one sees a rapid rise in the molecular weight at low monomer % conversion followed by a relatively constant molecular weight value during the "constant rate" period. This is consistent with theoretical predictions.

From the log-log plot of M_w versus argon gas flow rate shown in Figure 12, it appears that the polymer weight average molecular weight increased as the 0.02 power of the argon gas flow rate. This increase in the polymer molecular weight with increasing argon gas flow rate is attributed to gel effect, which results from the increase of polymer viscosity as argon gas flow rate used in the reaction system is increased.

Effects of Surfactant Concentration on Polymerization Rate, Polymer Particle Number, and Polymer Molecular Weight

The effects of surfactant concentration on both polymerization rate, polymer particle number, and polymer molecular weight were studied by ultrasonically irradiating MMA emulsions containing 2.06 mol of MMA per liter of water at an acoustic intensity of 9.2 W cm⁻² under an argon

gas flow rate of 0.32 mL s^{-1} in a -10°C cooling bath over a 7-fold surfactant concentration range, [S] = 0.035M to [S] = 0.243M. The experiments dealing with the dependence of conversion (%) over 35 min on sodium lauryl sulfate concentration from below the critical micelle concentration (CMC) to above the CMC were also conducted in the same reaction conditions. The results are presented in Figures 13–18.

In these polymerization experiments, the induction period varied from 5 to 7 min and decreased with increasing surfactant concentration. Coagulation of polymer on the horn occurred after 35 min of sonication for all surfactant concentrations studied.

Polymerization Rate

From the plot of monomer % conversion versus surfactant concentration shown in Figure 14, the log-log plot of polymerization rate versus surfactant concentration shown in Figure 15, and temperature profiles obtained from these experiments, five phenomena were observed: (1) no polymerization occurred in the system containing only water and MMA; (2) polymerization occurred in the system containing water, MMA, and ammonium persulfate; (3) polymerization occurred when the surfactant concentration was below the CMC (0.00839*M*) value, and the transition of the sodium lauryl sulfate concentration from below to



Figure 13 Monomer % conversion *versus* time curve for the ultrasonically initiated emulsion polymerization of MMA at various surfactant concentrations. (MMA = 22 mL, water = 100 mL, argon gas flow rate = 0.32 mL s⁻¹, acoustic intensity = 9.2 W cm⁻², cooling bath temperature = -10° C.)



Surfactant Concentration (mole/ L of Water)

Figure 14 The effect of SDS concentration on % monomer conversion for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, acoustic intensity = 9.2 W cm⁻², argon gas flow rate = 0.32 mL s^{-1} , sonication time = 35 min, cooling bath temperature = -10° C.)

above the CMC affects the extent of polymerization to a lesser extent compared with that of a styrene emulsion polymerization⁵⁵; (4) the polymerization rate above the CMC increased as the 0.08 power of the surfactant concentration in the range of surfactant concentrations from 0.035M to 0.139M, and the polymerization rate increased as the 0.58 power of the surfactant concentration in the range of surfactant concentration from 0.139M to 0.243M; and (5) final reaction temperature increased with increasing surfactant concentration ($\sim 5^{\circ}$ C difference between highest and lowest surfactant concentration). The increase in the polymerization rate with increasing surfactant concentration is presumably due to three phenomena: (1) the increase in the radical generation rate resulting from an increase in the number of surfactant molecules that serve as initiator, (2) the increase in micellar and homogeneous nucleation; and (3) the increase in reaction temperature resulting from an increase of the heat generated from polymerization.





Figure 15 Effect of surfactant concentration on the polymerization rate for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, acoustic intensity = 9.2 W cm⁻², argon gas flow rate = 0.32 mL s⁻¹, cooling bath temperature = -10° C.)



Figure 16 Effect of surfactant concentration on the number of polymer particles generated for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, acoustic intensity = 9.2 W cm⁻², argon gas flow rate = 0.32 mL s⁻¹, sonication time = 35 min, cooling bath temperature = -10° C.)

Number of Polymer Particles

The log-log plot (Figure 16) of the number of polymer particles produced per milliliter of water after 35 min of sonication versus surfactant concentration shows that the number of polymer particles produced increased as the 0.3 power of the surfactant concentration in the range of surfactant concentrations from 0.035M to 0.139M. It also shows that the number of polymer particles produced increased as the 1.87 power of the surfactant concentration in the range of surfactant concentration from 0.139M to 0.243M. Both the number of polymer particles produced and polymerization rate increased with surfactant concentration as shown in Figures 15 and 16. This trend implies that polymerization rate increases with surfactant concentration due to the increase in the number of polymer particles generated. Increased surfactant concentration results in increasing radical generation, homogeneous and micelle nucleation, thus total nucleated polymer particles. These thus increase the polymerization rate.



Figure 17 Weight average molecular weight as a function of monomer % conversion at 0.035*M* surfactant concentration for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, SDS = 1 g, acoustic intensity = 9.2 W cm⁻², argon gas flow rate = 0.32 mL s⁻¹, cooling bath temperature = -10° C.)



Figure 18 Effect of surfactant concentration on the weight average molecular weight for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 22 mL, water = 100 mL, acoustic intensity = 9.2 W cm^{-2} , argon gas flow rate = 0.32 mL s^{-1} , sonication time = 35 min, cooling bath temperature = -10° C.)

Polymer Molecular Weight

From the plot of the conversion versus polymer molecular weight curve shown in Figure 17 and the log-log plot of M_w versus surfactant concentration shown in Figure 18, one sees a rapid rise in the molecular weight at low monomer % conversion, followed by a slight increase in the molecular weight value during the "constant-rate" period (interval II). It can also be seen that the polymer weight average molecular weight decreased as the 0.12 power of the surfactant concentration with the surfactant concentration increasing from 0.035*M* to 0.139*M*, and the polymer weight average molecular weight decreased as the 0.34 power of the surfactant concentration with the surfactant concentration increasing from 0.139M to 0.243M. As previously described, the polymerization rate increases with increasing surfactant concentration because of the increase in radical generation rate, homogeneous and micellar nucleation, and reaction temperature. Therefore, an increase in surfactant concentration in an ultrasonically initiated emulsion polymerization system may result in increasing both the radical generation rate and the polymerization rate. The decrease in the polymer molecular weight with increasing surfactant concentration suggests that the effect of the increase in the radical generation rate that could result in a lower molecular weight is greater than the effect of the increase in the polymerization rate that could result in a higher molecular weight (Xn = Rp/Ri). Therefore, the decrease in the polymer molecular weight with increasing surfactant concentration could be attributed to the increase of radical generation rate resulting from an increase in the number of surfactant molecules that serve as initiator.

The previously described results show that the dependence of the polymerization rate and the polymer molecular weight on the surfactant concentration do not follow the prediction of the Smith-Ewart theory. These deviations from the Smith-Ewart Case II Kinetics may be attributed to two factors: (1) the hydrophilicity of MMA and (2) sodium lauryl sulfate serves as both surfactant and initiator.

MMA is one of the more water-soluble of the "water-immiscible" monomers. Its solubility in water is 1.5% at 45°C.56 Therefore, based on the Harkins' theory, the polymerization of this monomer can be initiated both in the water phase and in the micelles of surfactant. These characteristics lead to an emulsion polymerization mechanism somewhat different from that proposed by the Smith-Ewart theory. Gershberg⁵⁷ and Okamura and Motoyma⁵⁸ have reviewed the emulsion polymerization kinetics of the relatively watersoluble monomers and found that the order of reaction with respect to the concentration of surfactant decreased significantly as the water solubility of the monomer increased. They attributed these deviations from the Smith-Ewart theory to the hydrophilicity of the monomers. Fitch and colleagues⁵⁹ studied the aqueous polymerization of MMA using ammonium persulfate as the initiator and found that the reaction mixture was perfectly homogeneous initially. Then, upon initiation, the free radicals grew in solution until they reached a critical size of insolubility; in this range (interval I), the reaction kinetics followed by that of a typical homogeneous polymerization. The macroradicals continued to grow by the addition of more monomer units, but as a separate phase, the reaction kinetics followed that of an emulsion polymerization.

Atkinson and Cotton⁶⁰ and Guah and Pallit⁶¹ drew similar conclusions, respectively, in their work on the aqueous photopolymerization and aqueous polymerization of MMA by saying that homogeneous polymerization proceeded in the aqueous phase at the early stages of the reaction. Baxendale and colleagues⁶⁰ reported the polymerization of MMA in the absence and presence of a cationic surfactant. They concluded that initiation occurred in the aqueous phase, and that the polymer particles formed by homogeneous nucleation process (i.e., by precipitation and stabilization in the colloidal state by the surfactant) were swollen with monomer, continued to grow, and served as the locus of polymerization.

Trommsdorff and colleagues⁶³ studied the emulsion polymerization by using turkey red oil as the surfactant and potassium persulfate as the initiator, and found that the polymerization rate was not influenced significantly by variation of the surfactant concentration in the range of 0.125-4%. Kanamara and Terasoki⁶⁴ studied the emulsion polymerization of MMA at 70°C by using sodium lauryl sulfate as the surfactant and ammonium persulfate as the initiator. They found that the values of degree of polymerization (DP) varied, not to the -0.6 power of the initiator concentration predicted by the Smith-Ewart Case II Kinetics, but to the -0.46 to -0.3 power. The variation with surfactant concentration was to the 0.17 power rather than to the expected 0.6 power. Lee and Longbottom⁶⁵ studied the emulsion polymerization of MMA at 35°C using sodium lauryl sulfate as the surfactant and Cu^{2+} -N₂H₅OH, Fe³⁺–N₂H₅OH, and Mn³⁺–N₂H₅OH as initiators. They found that the polymerization rate varied not to the 0.6 power of the surfactant concentration predicted by Smith-Ewart Case II Kinetics, but to the 0.18-0.55 power of the surfactant concentration depending on the type of the initiators. Gershberg⁵⁷ has shown that MMA emulsion polymerization kinetics deviated considerably from Smith-Ewart Case II Kinetics. He found that the polymerization rate varied to the 0.3-0.4 power of the surfactant concentration. Piirma and Gardon⁶⁷ also observed deviation from Smith-Ewart Case II Kinetics for emulsion polymerization of MMA and attributed this deviation to: (1) particle formation mechanism (i.e., homogeneous and micellar particle nucleation mechanism occurring simultaneously), (2) radical desorption from the growing polymer particle, and (3) gel effect.

In our ultrasonically initiated emulsion polymerization of MMA, no conventional initiator was used; but, rather, sodium lauryl sulfate served as the surfactant and the initiator. To a small extent, polymerization occurred in the aqueous MMA solution in the presence of ammonium persulfate. The transition of the sodium lauryl sulfate concentration from below to above the CMC affected the extent of polymerization to a lesser extent, compared with that of a nonwater-soluble styrene emulsion polymerization. The polymer-

ization rate was not influenced significantly by variation of surfactant concentration (i.e., $R_n \alpha[S]^{0.08}$) within the 0.035M (1%) to 0.139M (4%) surfactant concentration range. These results suggest that particle formation for this ultrasonically initiated emulsion polymerization of MMA follows both the homogeneous nucleation mechanism and micellar nucleation mechanism. The tendency of the surfactant to form micelles in this surfactant concentration range becomes correspondingly less important, and the effect of the surfactant as a colloid stabilizer becomes more important. This behavior occurs because the oligomers formed in the initial stages of the polymerization tend to precipitate out of the aqueous solution and form potential polymerization loci if the precipitated oligomers could be sufficiently stabilized against massive coagulation.

When the surfactant concentration increased from 0.139M(4%) to 0.243M(7%), the dependence of the polymerization rate on the surfactant concentration increased to the 0.58 power, (i.e., $R_p \alpha[S]^{0.58}$). This increase in the polymerization rate is probably due to (1) the increase in the extent of the micellar nucleation in the particle formation period, and (2) the increased tendency of the surfactant to serve as initiator.

The dependence of the polymerization rate on surfactant concentration is lower than the 0.6 power predicted by the Smith-Ewart theory. There is, however, good agreement in the literature that the surfactant concentration does not affect the rate of polymerization to the same extent in MMA as in an ideal styrene emulsion polymerization.

The polymer weight average molecular weight decreased with the surfactant concentration increasing from 0.035M to 0.243M. This decline in molecular weight associated with increasing surfactant concentration implies that more termination reactions occur between growing polymer radicals and radicals coming from surfactant. These results confirm our suggestion that sodium lauryl sulfate serves as both surfactant and initiator.

Effects of Initial Monomer Concentration on Polymerization Rate and Polymer Molecular Weight

The effects of initial monomer concentration on both polymerization rate and polymer molecular weight were studied by ultrasonically irradiating MMA emulsions containing 1 g of sodium lauryl sulfate or 1 wt % of sodium lauryl sulfate (based



Figure 19 Monomer % conversion *versus* time curve for the ultrasonically initiated emulsion polymerization of MMA at various monomer concentrations. (Acoustic intensity = 9.2 W cm⁻², argon gas flow rate = 0.32 mL s⁻¹, SDS = 1 g, cooling bath temperature = -10° C.)

on water) at an acoustic intensity of 9.2 W cm⁻² under an argon gas flow rate of 0.32 mL s⁻¹ in a -10° C cooling bath over a 9-fold initial monomer concentration range, [M] = 0.48M to [M] = 4.07M. The results are presented in Figures 19–24.

In these polymerization experiments, the induction periods varying from 5 to 10 min were observed and increased with increasing initial monomer concentration. Polymer coagulation occurred on the horn after 35-45 min of sonication for all initial monomer concentrations, except in the case of the 0.48*M* monomer concentration.

Polymerization Rate

From the log-log plots of polymerization rate versus initial monomer concentration shown in Figures 21 and 22, it can be seen that the polymerization rate increased with increasing initial monomer concentration (i.e., $R_p \alpha$ [Monomer]^{0.36} or $R_p \alpha$ [Monomer]^{0.38}) to a point and then became independent of initial monomer concentration. The polymerization rate further dropped at a higher initial monomer concentration. Similar results were observed by Acres and Dalton⁶⁷ in their work on 60 Co γ -ray initiated emulsion polymerization of MMA.

According to the Smith-Ewart theory, a thermodynamic equilibrium of monomer concentration exists between monomer droplets and growing polymer particles in interval I and interval II periods. As a result, the polymerization rate is independent of monomer concentration if sufficient monomer is added to the system to saturate the water and latex particles. When less monomer is added, the rate will be expected to increase with increasing monomer concentration. The variation of the polymerization rate with initial monomer concentration in this study therefore follows the prediction of the Smith-Ewart theory. The drop of the polymerization rate at high mono-



Figure 20 Monomer % conversion *versus* time curve for the ultrasonically initiated emulsion polymerization of MMA at various monomer concentrations. (Acoustic intensity = 9.2 W cm^{-2} , argon gas flow rate = 0.32 mL s^{-1} , SDS = 1 wt % of water, cooling bath temperature = -10° C.)

mer concentrations (i.e., 4.07M) is presumably due to the decrease in cavitation efficiency as the organic phase (MMA) increases.³⁹

Polymer Molecular Weight

From the plots of the conversion versus time curves obtained at 0.48*M* initial monomer concentration shown in Figures 19 and 20, the plot of the conversion versus molecular weight curve obtained at 0.48*M* initial monomer concentration shown in Figure 23 and the log-log plot of M_w versus initial monomer concentration shown in Figure 24, three phenomena were observed: (1) a rapid increase in the molecular weight at low monomer % conversion followed by a slight increase in molecular weight during the "constant-rate" period (interval II), (2) a slight gel effect between 66–70.5% conversion and polymer degradation after 70.5% conversion in the case of an



Figure 21 Effect of monomer concentration on the polymerization rate for the ultrasonically initiated emulsion polymerization of MMA. (Acoustic intensity = 9.2 W cm^{-2} , argon gas flow rate = 0.32 mL s^{-1} , SDS = 1 g, cooling bath temperature = -10° C.)



Figure 22 Effect of monomer concentration on the polymerization rate for the ultrasonically initiated emulsion polymerization of MMA. (Acoustic intensity = 9.2 W cm^{-2} , argon gas flow rate = 0.32 mL s^{-1} , SDS = 1 wt % of water, cooling bath temperature = -10° C.)

emulsion containing 0.48*M* initial monomer concentration, and (3) the weight average molecular weight increased with increasing initial monomer concentration (i.e., $M_w \alpha$ [Monomer]^{0.18}), to a point, then became independent of initial monomer concentration. The gel effect phenomenon was observed by Zimmt,⁴⁹ Trommsdorff and colleagues,⁶³ and Kanamaru and Terasoki⁶⁴ in their works on the emulsion polymerization of MMA. It was attributed to the reduction in termination rates as the viscosity of the medium increased at higher % conversion. Polymer degradation phenomenon was observed by Kruus and colleagues¹⁷ in their work on the ultrasonically initiated bulk polymerization of styrene, and Price and colleagues³⁹ in their wok on the ultrasonically initiated bulk polymerization of MMA. Polymer degradation happened because polymerization and concurrent depolymerization occurred simultaneously when the sonication time was long enough. The polymer molecular weight increased with increasing initial monomer concentration up to a point then leveled off to a relatively constant value. This behavior follows the prediction of the Smith-Ewart theory, and it is consistent with the above study of the effect of initial monomer concentration on polymerization rate.

A possible mechanism of this ultrasonically initiated emulsion polymerization system could be proposed given information from the above studies of the: (1) source of free radical in initiation process, (2) effects of acoustic intensity, (3) effects of surfactant concentration, and (4) effects of initial monomer concentration. In this proposed mechanism, sodium lauryl sulfate degrades into sulfate ion radical and alkyl radicals in aqueous phase under ultrasonic irradiation. These radicals may (1) move into the micelle to proceed with



6.52 6.50 Slope = 0.186.48 Z, 6.46 Log 6.44 6.42 6.40 6.38 -0.2 0.0 0.2 0.4 0.6 0.4 Log Monomer Concentration

Figure 23 Weight average molecular weight as a function of monomer % conversion at 0.035*M* monomer concentration for the ultrasonically initiated emulsion polymerization of MMA. (MMA = 6 mL, water = 112 mL, acoustic intensity = 9.2 W cm⁻², argon gas flow rate = 0.32 mL s^{-1} , SDS = 1 g, cooling bath temperature = -10° C.)

Figure 24 Effect of monomer concentration on the weight average molecular weight for the ultrasonically initiated emulsion polymerization of MMA. (Acoustic intensity = 9.2 W cm^{-2} , argon gas flow rate = $0.32 \text{ mL} \text{ s}^{-1}$, SDS = 1 g, sonication time = 35 min, cooling bath temperature = -10° C.)

micellar nucleation and follow similar emulsion polymerization mechanisms suggested by the Smith-Ewart theory, or (2) begin to polymerize with monomer dissolved in the aqueous phase and proceed with homogeneous nucleation. As the solution polymerization continues in the aqueous phase, the growing oligomeric radicals may move into the monomer droplet, growing polymer particles; they may self-coil to form small primary particles or combine with other aqueous oligomers to form particles or continue to grow. The small primary particles formed through this homogeneous nucleation process will precipitate when they reach their critical size, then adsorb surfactant to become stable colloid monomerswollen polymer particles and serve as polymerization loci for the continuous propagation reaction. As the particle population increases, primary radicals growing in the aqueous phase have a lesser chance to precipitate and nucleate new particles. Particle nucleation will cease when the total number of particles is sufficient to adsorb all the surfactant.

Termination can arise via the following methods as described by Baxendale and colleagues⁶²: (1) chain transfer of the swollen active polymer chains to monomer, dead polymer, or surfactant in the monomer swollen polymer latex; and (2) bimolecular disproportion or coupling between the swollen active polymer chains and primary (oligomeric) radicals or between the swollen active polymer chains and other chains inside the monomer swollen polymer latex. Because, in all cases, the termination involves the migration of the growing chain end toward each other through the reaction medium in the monomer swollen polymer latex, the rate of viscous diffusion will become a rate-determining factor, and K_t will decrease as the viscosity of the medium increases. This leads to a slower termination rate and can cause autoacceleration in polymerization at higher conversion.

Polymer Characterization

A typical IR and proton NMR spectrum of resulting poly(MMA) obtained at an acoustic intensity of 13 W cm⁻² are shown in Figures 25 and 26, respectively, and are representative of the remaining samples obtained at other experimental conditions. The fingerprint comparison of these poly(MMA) spectra with those obtained from commercial sources reveals a direct match-up of the major peaks and fine structure of the spectra for all samples analyzed.

CONCLUSIONS

- 1. The initiation of ultrasonically induced emulsion polymerization of MMA takes place primarily due to resonant cavitation, which requires the bubbling of substantial gas through the reaction solution. In the absence of this gas, the cavitation is transient and no apparent initiation of the emulsion polymerization of MMA occurs.
- 2. The initiation process of the ultrasonically initiated emulsion polymerization of MMA is a free radical process, because it can be retarded by free radical scavengers.
- 3. The ultrasonically initiated emulsion polymerization of MMA is caused by the cavitation process and occurs at relatively low temperatures, compared with the conventional thermal emulsion polymerization processes.
- 4. The mode of polymerization initiation is postulated to result from the ultrasonically induced degradation of surfactant molecules (sodium lauryl sulfate) in the aqueous phase. No conventional water-soluble initiator is necessary to initiate the polymerization in this ultrasonically initiated emulsion polymerization system. The rate ofthisultrasonicallyinitiated emulsion polymerization can be enhanced by the presence of a added conventional initiator.
- 5. Weight average molecular weights ranging from 2.5 million g mol⁻¹ to 3.5 million g mol^{-1} are attained with 30–40 min of sonication. Polymer yields ranging from 30 to 70% are attained within 30-70 min of sonication. The polymer yields and polymerization rates attained are much higher than those attained from the ultrasonically initiated bulk polymerization method. The polymerization rates attained at ambient temperature are similar or higher than those attained from the higher temperature thermal emulsion polymerization method. This shows the capability of ultrasound to accelerate the polymerization and offer substantial energy savings.
- 6. The polymerization rate increases as the 0.98 power of the acoustic intensity with acoustic intensity increasing from 6.8 to 13.0 W cm⁻². It then decreases at the acoustic intensity of 14.4 W cm⁻². The number of polymer particles produced increased as the 1.23 power of the acoustic intensity with acoustic intensity increasing



CM-1

Figure 25 IR spectrum of poly(MMA) obtained at 13.0 W cm⁻² acoustic intensity. (MMA = 22 mL, water = 100 mL, SDS = 1 g, argon gas flow rate = 0.74 mL s⁻¹, sonication time = 30 min, cooling bath temperature = -10° C.)

from 6.8 to 13.0 W cm⁻². The polymer weight average molecular weight increases as the 0.21 power of the acoustic intensity with acoustic intensity increasing from 6.8 to 13.0 W cm⁻². It then decreases at the acoustic intensity of 14.4 W cm⁻². The increase in the polymerization rate with increasing acoustic intensity is presumably due to an increase in the radical generation rate, the reaction temperature, and gel effect resulting from an increase in the number of cavitation bubbles, heat generated from horn vibration and polymerization, and an increase in polymer viscosity. These three phenomena result in increasing the

total polymer particles generated and reaction rate constant, therefore enhancing the polymerization rate. The increase in the polymer molecular weight with increasing acoustic intensity is attributed to gel effect.

7. The polymerization rate increases as the 0.086 power of the argon gas flow rate. The number of polymer particles produced increased as the 0.16 power of the argon gas flow rate. The polymer weight average molecular weight increases as the 0.02 power of the argon gas flow rate. The increase in the polymerization rate with increasing argon gas flow rate is presumably due to an increase in the radical generation rate, a





slight increase in the reaction temperature, and gel effect resulting from an increase in the number of cavitation bubbles, and heat generated from polymerization and polymer viscosity. These three phenomena result in increasing the total polymer particles generated and reaction rate constant, therefore enhancing the polymerization rate. The increase of the polymer molecular weight with increasing argon gas flow rate is attributed to gel effect.

- 8. The polymerization rate increases as the 0.08 power of the surfactant concentration, the number of polymer particles produced increased as the 0.3 power of the surfactant concentration, and the polymer weight average molecular weight decreases as the 0.12 power of the surfactant concentration within the 0.035M - 0.139M surfactant concentration range. The polymerization rate increases as the 0.58 power of the surfactant concentration, the number of polymer particles produced increased as the 1.87 power of the surfactant concentration, and the polymer weight average molecular weight decreases as the 0.34 power of the surfactant concentration within the 0.035M-0.243M surfactant concentration range. The particle formation mechanism of this ultrasonically initiated emulsion polymerization is suggested to follow both homogeneous nucleation and micellar nucleation mechanisms. The increase in the polymerization rate with increasing surfactant concentration is presumably due to an increase in the radical generation rate, the micellar, homogeneous nucleation, and the reaction temperature. These four phenomena result in increasing the total polymer particles generated and reaction rate constant, therefore enhancing the polymerization rate. The decrease in the polymer molecular weight with increasing surfactant concentration is presumably due to an increase in the radical generation rate resulting from an increase in the number of surfactant molecules that serve as initiator.
- 9. The polymerization rate and polymer weight average molecular weight increase with increasing initial monomer concentration to a point, then become independent of initial monomer concentration.
- 10. The kinetics of this ultrasonically initiated emulsion polymerization of MMA show some deviations from the traditional

Smith–Ewart theory. It appears to follow the scheme proposed by Gershberg⁵⁷ rather than the traditional Smith–Ewart theory.

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