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Ultrasonically initiated free radical catalyzed emulsion polymerization of methyl methacrylate

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ULTRASONICALLY INITIATED FREE RADICAL CATALYZED EMULSION POLYMERIZATION OF METHYL METHACRYLATE

by

HSIN-CHIEH JOE CHOU, 1960-

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PUBLICATION DISSERTATION OPTION

This dissertation has been prepared in the form of three papers for publication. The first two papers from page 1 to page 143 have been prepared in the style utilized by the Journal of the Applied Polymer Science and have been accepted for publication. The third paper from page 144 to page 166 has been also prepared in the style utilized by the Journal of the Applied Polymer Science and will be submitted for publication. Another paper in entitled "Analysis of Ultrasonically Induced Free Radicals in the Emulsion Polymerization System by GC/MS" has been published in Journal of the Applied Polymer Science. It was coauthored by Dr. Edward Liu and is included in his dissertation. Five papers have been presented by author in national ACS meetings respectively and are published in Polymer Materials Science and Engineering. Part of thesis work is also included in a U.S. Patent of Dr. Stoffer and Dr. Sitton. This data has also been presented by author in different companies and universities such as 3M, Union Carbide, National Starch and Chemical, Lord Corporation, Cytec Industries, BF Goodrich, Akzo Nobel Inc. and Lehigh University.

ABSTRACT

The emulsion polymerization of methyl methacrylate initiated by ultrasound has been studied at ambient temperature using sodium lauryl sulfate as the surfactant.

The source of the free radical for the initiation process was found to come from the degradation of the sodium lauryl sulfate presumably in aqueous phase. The weight average molecular weight (M_w) of the poly (methyl methacrylate) obtained varied from 2,500,000 to 3,500,000 g mole^{-1} and the conversion for the polymerization was up to 70%.

The polymerization rate, the number of polymer particles generated and the free radical concentration in initiation precess were found to increase with acoustic intensity, argon gas flow, surfactant concentration.

The polymer weight average molecular weight was found to increase with acoustic intensity and argon gas flow rate. It was found to decrease with increasing surfactant concentration. The polymerization rates obtained at ambient temperature were found be similar to or higher than those obtained from the conventional higher temperature thermal emulsion polymerization. Deviations from the Smith-Ewart kinetics were observed.

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

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Keywords: Emulsion Polymerization, Ultrasound, Acoustic Intensity, Resonant Cavitation, Transient Cavitation.

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: (1) the nature and source of the free radical for the initiation process, (2) the effects of different types of cavitation and (3) the 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 aqueous phase. The weight average molecular weight (M_w) of the poly(methyl methacrylate) obtained varied from 2,500,000 to 3,500,000 g mole^{-1} and the conversion for the 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 when within the 0.035 M to 0.139 M surfactant concentration range, and to the surfactant concentration to the 0.58 power when within the 0.139 M to 0.243 M 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 ml 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 when within the 0.035 M to 0.139 M surfactant concentration range, and to the surfactant concentration to the 1.87 power when within the 0.139 M to 0.243 M surfactant 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 when within the 0.035 M to 0.139 M and the 0.139 M to 0.243 M 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 the polymerization in the emulsion system, and to do this at a lower temperature which could offer substantial energy savings.

INTRODUCTION

In previous publications, we have reported the ultrasonically initiated free radical catalyzed polymerization of methyl methacrylate[1] in 1991, and of acrylamide[2] in 1992. We have also reported the ultrasonically initiated free radical catalyzed copolymerization between styrene and maleic anhydride[3] in 1992 and a preliminary study of ultrasonically initiated free radical catalyzed emulsion polymerization of methyl methacrylate[4] in 1993. A thorough study of the initiation of polymerization by ultrasound in an emulsion system containing methyl methacrylate monomer and sodium lauryl sulfate surfactant is reported here 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, while unstable microbubbles grow to a maximum size at which point they implode. This implosion generates shock waves which 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[6-9], the cavitation theory proposed by Noltking and Noppiras[10] 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[11] provided a review of the cavitation model in 1964. More recent reviews are available in a series of papers in Ultrasonics[12-14] and in Shutilov's book[15].

The cavitation model has been simplified as follows[16-19]: (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 pressure 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 which 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 $T_f = T_i\ [(R\ P_f) / (C_p\ P_i)]$ 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 (1) to accelerate conventional chemical reactions, (2) to induce aqueous redox reactions, (3) to cause polymer degradation and (4) to induce decomposition or cause reaction in organic solvents[27]. The application of ultrasound in the area of polymer chemistry was first reported by Lindstrom et. al.[28] and Henglein[29] 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 above 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 was produced using a Sonics and Materials Model EC-1500 ultrasonic generator. A one 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 to 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 carried out with the tip of the coupling horn immersed directly in the emulsion.

Reagents and Materials

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

Polymerization Processes, Latexes and Polymers Characterizations

Several emulsion systems were polymerized under different conditions in order to study the nature and the source of free radicals for the initiation process of ultrasonically initiated emulsion polymerization.

Five parameters which 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 minutes. The emulsion was introduced to the reaction container, a 17 cm high x 6 cm diameter flat bottom pyrex glass tube. It was deoxygenated by bubbling with argon gas for 3 minutes, 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 in order 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 the 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 percent conversion of methyl methacrylate. Sonication intervals ranging from 5 to 100 minutes were used to obtain the time versus percent conversion curve needed to calculate the polymerization rate. Each sonication interval was performed three times and the average value of the percent yield was used to construct the time versus percent 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 hours. 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 3-neck round bottom flask equipped with a stirrer, a nitrogen inlet, a dropping funnel and condenser at 75°C to compare with ultrasonically initiated emulsion polymerizations.

Effects of Different Types of Cavitation: Different emulsions were irradiated by ultrasound with and without argon gas to study the effect of different types of cavitation on polymerization rate and polymer molecular weight. The emulsion recipes and the reaction conditions are shown in Table I.

The Free Radical Nature of the Ultrasonically Initiated Emulsion Polymerization of MMA: A series of polymerization experiments was performed with ultrasound in the presence and absence of the radical scavenger (hydroquinone) to study the nature of the ultrasonically initiated emulsion polymerization of methyl methacrylate. The emulsion recipes and reaction conditions are shown in Table II.

Ultrasonically Initiated Polymerization versus Thermally Initiated Polymerization: A series of polymerization experiments was performed with ultrasound at ambient temperature. The same emulsions were polymerized under conventional emulsion polymerization methods at 75°C without ultrasound to distinguish the cavitation induced and thermal induced emulsion polymerization. The emulsion recipes and reaction conditions are shown in Table III.

The Source of the Free Radical of the Initiation Process for the Ultrasonically Initiated Emulsion Polymerization of MMA, Radical Trapping Experiment and GC/MS Analysis: Polymerization experiments with pure MMA, with MMA plus water, and with MMA plus surfactant were performed with ultrasound to identify the source of the free radicals of the initiation process for the ultrasonically initiated emulsion polymerization of methyl methacrylate.

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 1g of sodium lauryl sulfate at an acoustic intensity of 13.0 W/cm^2 under an argon flow rate of 0.74 ml/sec for 30 minutes. This was followed by adding 100 ml of 1-propanol to the irradiated solution then subjecting this solution to GC/MS spectrum analysis.

GC/MS analysis was performed by a HP5970 mass selective detector and a HP5890 gas chromatograph. A 0.4 µl injection volume with a 1:40 split ratio, a 280°C injection temperature, and a 260°C transfer line temperature were used. The temperature program was held at 100°C for 2 minutes and then increased to 260°C at a 10°C/minute rate. The sample solutions and reaction conditions are shown in Table IV.

The Effects of Acoustic Intensity: A series of polymerization experiments was performed with ultrasound at different acoustic intensities under constant argon gas flow rate, surfactant concentration and initial monomer concentration in order to investigate the effect of acoustic intensity on polymerization rate, polymer particle number and polymer molecular weight. The emulsion recipes and reaction conditions are shown in Table V.

The Effects of Argon Gas Flow Rate: A series of polymerization experiments was performed with ultrasound at different argon gas flow rates under constant acoustic intensity, surfactant concentration, and initial monomer concentration in order to investigate the effect of argon gas flow rate on polymerization rate, polymer particle number and polymer molecular weight. The emulsion recipes and reaction conditions are shown in Table VII.

The Effects of Surfactant Concentration: A series of polymerization experiments was performed with ultrasound at different surfactant concentrations under constant acoustic intensity, argon gas flow rate and initial monomer concentration in order to investigate the effect of surfactant concentration on polymerization rate, polymer particle number and polymer molecular weight. The emulsion recipes and reaction conditions are shown in Table IX.

Effects of Initial Monomer Concentration: A series of polymerization experiments was performed with ultrasound at different initial monomer concentrations under constant acoustic intensity, argon gas flow rate and surfactant concentration in order to investigate the effect of initial monomer concentration on polymerization rate and polymer molecular weight. The emulsion recipes and reaction conditions are shown in Table XI.

Molecular Weight Analysis: The polymer molecular weights were measured using gel permeation chromatography (Waters Associates model 201A) with a single phenol gel 5 linear column (350 x 78 mm, 5 micron, 10^3 x 10^7, phenomenex) and a differential refractometer detector. Polymer solutions of 0.1 - 0.2% concentration were filtered to remove any gelled material or insoluble particles. Approximately 40 μl of this solution was injected into the column. Tetrahydrofuran was used as the eluting solvent, the flow rate was 1ml 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 to a polystyrene standard by using the Mark-Houwink-Sakurada equation in which log M_w of sample = [1 / (1 + a of sample)] [log (K of polystyrene / K of sample)] + [(1 + a of polystyrene) / (1 + a of sample)] [log (M_w of polystyrene)], where K and a are Mark-Houwink constants. A correction for instrument spreading was also made to obtain better results.

Infrared Spectroscopy Analysis: Infrared (IR) spectra were obtained on a Perkin Elmer 283 B spectrophotometer. The PMMA solutions (in THF) were cast as films, air dried, and placed under vacuum at room temperature for 12 hours. Infrared spectra were taken in the usual manner.

Nuclear Magnetic Resonance (NMR) Analysis: High resolution ^1H nuclear magnetic resonance spectra were obtained at 100 MHz and 25 MHz using a JEOL FX-100 Fourier Transform NMR Spectrometer. A switchable carbon and proton probe was employed. The spectrometer was locked on an internal deuterochloroform signal during operation. A 5% (w/w) poly(methyl methacrylate) in deuterochloroform solution was prepared and transferred to 5 mm NMR sample tubes. Two drops of TMS were added to the sample tube. Proton NMR spectra were accumulated at 100 MHz. Quadrature detection was employed with a 1000 Hz spectral window using 4096 data points. The deuterated solvent served as the internal lock.

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 ml of water was calculated from the following equation: $N_p = 6 \times Y \times 10^{21} / \pi \times$

$(D_v)^3$ x D_p, with Y = latex solid content; D_v = volume-average diameter of the latex particle; D_p = polymer density.

RESULTS AND DISCUSSION

The Effects of Different Types of Cavitation

Polymerization 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. The 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 percent conversion of methyl methacrylate to poly(methyl methacrylate) varied from 20 to 61% and the weight average molecular weight of poly(methyl methacrylate) varied from 2.1 million g $mole^{-1}$ to 3.5 million g $mole^{-1}$ with a sonication time of 30 to 35 minutes. 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 et. al. on the ultrasonically initiated bulk polymerization of styrene and methyl methacrylate[17,18].

There are two specific types of cavitation which 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 much higher than the acoustic pressure applied. When sufficient gas is introduced near the horn tip, the ultrasound appears 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.

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 (> 1000°K) that a pyrolysis type reaction, which forms colored compounds, rather than polymerization occurs[17].

In summary, the data presented above 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 (>1000°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 occurs.

Free Radical Nature of the Ultrasonically Initiated Emulsion Polymerization of MMA

As was 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. The results are shown in Table II.

No polymerization occurred when hydroquinone was present in the reaction system. Without hydroquinone, polymerization occurred, the percent conversion of methyl methacrylate to poly(methyl methacrylate) varied from 21 to 61%, and the weight average molecular weight of poly(methyl methacrylate) varied from 2.1 million g mole^{-1} to 3.5 million g mole^{-1} with 30 to 35 minutes 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 methyl methacrylate. 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. The results are shown in Table III.

No polymerization occurred when the conventional emulsion polymerization was conducted at 75°C for 4 hours using different emulsions in the absence of conventional initiator. With the same emulsions using the ultrasonically initiated emulsion polymerization method, the percent conversion of methyl methacrylate to poly(methyl methacrylate) varied from 21 to 61% and the weight average molecular weight of poly(methyl methacrylate) varied from 2.1 million g $mole^{-1}$ to 3.5 million g $mole^{-1}$ with 30 to 35 minutes of sonication and the reaction temperature increasing from an initial temperature of 5°C to a final temperature ranging from 27°C to 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.

The 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. The results are shown in Table IV.

No polymerization occurred when pure methyl methacrylate was irradiated with ultrasound at an acoustic intensity of 13.0 W/cm^2 under an argon gas flow rate of 0.78 ml/sec for 90 minutes of sonication. Similar results were observed when mixtures of water plus methyl methacrylate at various ratios were run under the same conditions. When methyl methacrylate and sodium lauryl sulfate mixtures were run under the same reaction conditions, some polymerization occurred (less than 0.1% conversion) after 90 minutes of sonication.

The above results imply that free radical polymerization cannot be initiated by ultrasound with pure methyl methacrylate or methyl methacrylate in an aqueous phase under the acoustic intensity of 13.0 W/cm^2, and an argon gas flow rate of 0.78 ml/sec. 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 liquids[39] and a high percentages of radical recombination occurring in water in the presence of argon gas[27,47,48]. When methyl methacrylate and sodium lauryl sulfate were ultrasonically irradiated under the same conditions, there must be some radicals generated which survive for a long enough time to initiate the polymerization.

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/sec over 30 minutes 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 OSO_3Na radicals all of which can initiate the polymerization. The results in Tables 1, 2, and 4 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 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 the free radical polymerization.

The 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 methyl methacrylate emulsion containing 2.06 moles of MMA and 0.035 moles 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/sec in a -10°C cooling bath.

The results are presented in Tables V and VI. The monomer conversion versus time curves obtained at various acoustic intensities are shown in Figure 3 and the monomer conversion versus weight average molecular weight curve obtained at an acoustic intensity of 9.2 W/cm^2 is shown in Figure 6. The log-log plot of polymerization rate versus acoustic intensity is shown in Figure 4. The log-log plot of number of polymer particles produced per ml of water after 30 minutes of sonication versus acoustic intensity is shown in Figure 5. The log-log plot of M_w versus acoustic intensity after 30 minutes of sonication is shown in Figure 7.

From the temperature profiles given in Table V, it can be seen that the reaction temperatures rose rapidly (roughly 20°C) in the first 10 minutes after the ultrasound was turned on, then levelled to a plateau region and then rose again within the final 5 minutes of sonication. During the last 5 minutes 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 plateau 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 destablization of poly(methyl methacrylate) 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 Zimm[49] in his study of conventional emulsion polymerization of methyl methacrylate. 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 minutes depending upon 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 by 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 (moles/liter of water-sec) = - d[M] / dt = - [(1 / dt) (polymer Wt / M_o)] / [(initial water volume (ml) / 1000)] = 10 slope (monomer Wt / water Wt) (1 / M_o) (1 / 60), where (monomer Wt / water Wt) is the initial monomer to initial water weight ratio in the emulsion formula, and M_o is the molecular weight of monomer.

Over these relatively linear ranges, the reaction temperatures are within plateau regions, the polymerization rate are relatively constant and are proportional to N, the number of particles per liter of latex. It is this rate which will be used throughout this communication.

Polymerization Rate: From the data given in Tables V, VI and the log-log plot of polymerization rate versus acoustic intensity shown in Figure 4, it can be seen that (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 increased with increasing acoustic intensity.

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 following paper. 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. The gel effect was observed at higher percent 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 sonochemical reactions[50] 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. Sirotyuk reported[50] 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[32] 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 one-half 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 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-Ewart theory[51], the rate of an emulsion polymerization at an average number of radicals per particle n = 0.5 (Case II) is as follows: $- dM/dt = 0.5\ K_p\ N\ [M]_p = K'\ [M]_p\ (P/\mu)^{0.4}\ (A_sS)^{0.6}$, 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 moles/L-sec, 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.

Since 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., $- dM/dt = \text{constant } [M]_p \text{ [Acoustic Intensity]}^{0.4}$). 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 minutes of sonication was within 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 methyl methacrylate[52,53]. The log-log plot (Figure 5) of number of polymer particles produced per ml of water after 30 minutes 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 data given in the Table V and monomer conversion versus polymer molecular weight curve shown in Figure 6, one sees a rapid rise in the molecular weight at low monomer percent 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 which 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 Howard et. al.[54] in their work on conventional emulsion polymerization of methyl methacrylate.

The molecular weight distributions (M_w/M_n) of poly(methyl methacrylate) produced by the ultrasonically initiated emulsion polymerization method given in Table V showed no significant difference from those produced by the conventional emulsion polymerization method[54].

From the data given in Table V and the log-log plot of M_w versus acoustic intensity after 30 minutes 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 which results from the increase of polymer viscosity as the acoustic intensity used in the reaction system is increased.

In this experimental section dealing with different acoustic intensities, the final yield of the ultrasonically initiated emulsion polymerization of methyl methacrylate 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/sec at ambient temperature (final reaction vessel temperature 27.5 to 38°C) ranged from 31 to 40% with 30 to 40 minutes of sonication. The polymerization rate ranged from 3.5×10^{-4} to 5.9×10^{-4} mole $L^{-1}S^{-1}$ and polymer weight average molecular weight ranged from 3.05×10^6 to 3.47×10^6 g mole^{-1}.

By comparison, the final yield of the ultrasonically initiated bulk polymerization of methyl methacrylate performed by Kruus et. al.[32] with ultrasound at an acoustic intensity of 20 W/cm^2 under an argon gas flow rate of 20 ml sec^{-1} at ambient temperature (32°C to 40°C) was around 3 % with 120 minutes of sonication. The polymerization rate ranged from 4.08

x 10^{-6} to 4.14 x 10^{-6} mole $L^{0.5}S^{-1}$ and weight average molecular weight ranged from 5.9 x 10^5 to 7.2 x 10^5 g $mole^{-1}$. The polymerization rate of the conventional emulsion polymerization of methyl methacrylate performed by Zimmt[49] at 60°C using Tergital 7 as the surfactant and potassium persulfate as the initiator ranged from 0.8 x 10^{-4} to 10.3 x 10^{-4} mole $L^{-1}S^{-1}$.

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 realizes 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 as compared to that obtained 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 carried out 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/sec, the final yield increased to 55% with 30 minutes of sonication as compared to 39% without any initiator. This shows that the rate of the ultrasonically initiated emulsion polymerization of methyl methacrylate can be enhanced even further by the presence of added initiator. Further experiments with incremental addition of more initiator should give even higher yield.

The 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 a methyl methacrylate emulsion containing 2.06 moles of MMA and 0.035 moles 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 Tables VII and VIII. The monomer conversion versus time curves obtained at various argon gas flow rates are shown in Figure 8 and monomer conversion versus weight average molecular weight curve obtained at 0.32 ml sec^{-1} argon gas flow rate is shown in Figure 11. The log-log plot of polymerization rate versus argon gas flow rate is shown in Figure 9. The log-log plot of number of polymer particles produced per ml of water after 35 minutes of sonication versus argon gas flow rate is shown in Figure 10. The log-log plot of M_w versus argon gas flow rate after 35 minutes of sonication is shown in Figure 12.

The monomer conversion versus time curves shown in Figure 8 again were similar in shape to those shown by Zimmt[49]. Small induction periods were recorded. The length of the induction period varied from 5 to 13 minutes depending on the argon gas flow rate. It increased as the argon flow rate decreased. There was no sign of any destablization of poly(methyl methacrylate) latexes for all experiments during the polymerization of the emulsions. The latexes obtained were completely homogeneous. At an argon gas flow rate of 0.25 ml sec^{-1}, no polymer adhered onto the horn after 35 minutes of sonication. At argon gas flow rates ranging from 0.32 to 0.78 ml sec^{-1}, polymers adhered onto the horn after 35 minutes of sonication.

Polymerization Rate: From the data given in Tables VII, VIII and the log-log plot of polymerization rate versus argon gas flow rate shown in Figure 9, it can be seen that (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. 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, as compared to the acoustic intensity, shows that the effect of argon gas flow rate on polymerization rate is less significant.

Number of Polymer Particles: The log-log plot (Figure 10) of number of polymer particles produced per ml of water after 35 minutes 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 particles are nucleated and produced, the resulting polymerization rate is enhanced.

Polymer Molecular Weight: From the data given in Table VII and 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 percent conversion followed by a relatively constant molecular weight value during the "constant-rate" period. This is consistent with theoretical predictions.

From the data given in Table VII and 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.

In this experimental section dealing with different argon gas flow rates, the final yield of the ultrasonically initiated emulsion polymerization of methyl methacrylate performed with ultrasound at an acoustic intensity of 9.2 W/cm^2 under argon flow rates ranging from 0.25 to 0.78 ml sec^{-1} at ambient temperature (final reaction vessel temperature 28 to 35°C) ranged from 28 to 40% with 35 to 40 minutes of sonication. The polymerization rate ranged from 3.8×10^{-4} to 4.6×10^{-4} mole $L^{-1}S^{-1}$ and the polymer weight average molecular weight ranged from 3.02×10^{6} to 3.28×10^{6} g $mole^{-1}$. These results again show that ultrasonically (cavitation) induced polymerization is more efficient in an emulsion system than in a bulk organic system and lower temperature ultrasonically initiated emulsion polymerization results in a similar or a higher polymerization rate as compared to that obtained from a higher temperature thermal emulsion polymerization method.

The 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 methyl methacrylate emulsions containing 2.06

moles 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 sec^{-1} in a -10°C cooling bath over a seven fold surfactant concentration range, [S] = 0.035 M to [S] = 0.243 M. The experiments dealing with the dependence of conversion (%) over 35 minutes on sodium lauryl sulfate concentration from below the CMC to above the CMC were also conducted in the same reaction conditions.

The results are presented in Tables IX and X. The monomer conversion versus time curves obtained at various surfactant concentrations are shown in Figure 13 and the conversion versus molecular weight curve obtained at 0.035 M surfactant concentration is shown in Figure 17. The plot of monomer percent conversion versus surfactant concentration after 35 minutes of sonication is shown in Figure14. The log-log plot of polymerization rate versus surfactant concentration is shown in Figure 15. The log-log plot of number of polymer particles produced per ml of water after 35 minutes of sonication versus surfactant concentration is shown in Figure 16. The log-log plot of M_w versus surfactant concentration after 35 minutes of sonication is shown in Figure 18.

The monomer conversion versus time curves shown in Figure 13 were similar in shape to those shown by Zimmt[49]. The induction period varied from 5 to 7 minutes and decreased with increasing surfactant concentration. There was no sign of any destablization of poly(methyl methacrylate) latexes for all experiments during the polymerization of the emulsions. The latexes obtained were completely homogeneous. Coagulation of polymer on the horn occurred after 35 minutes of sonication for all surfactant concentrations studied.

Polymerization Rate: From the data given in Tables IX and X, the plot of monomer percent conversion versus surfactant concentration shown in Figure 14 and the log-log plot of polymerization rate versus surfactant concentration shown in Figure 15, four phenomena were observed: (1) no polymerization occurred in the system containing only water and methyl methacrylate; (2) polymerization occurred in the system containing water, methyl methacrylate and ammonium persulfate; (3) polymerization occurred when the surfactant concentration was below the CMC (critical micelle concentration, 0.00839 M) value and the transition of the sodium lauryl sulfate concentration from below to above the CMC affects the extent of polymerization to a lesser extent as compared to that of a styrene emulsion polymerization[55]; (4) the polymerization rate above the CMC increased as the 0.08 power of the surfactant concentration in the range of surfactant concentrations from 0.035 M to 0.139 M and the polymerization rate increased as the 0.58 power of the surfactant concentration in the range of surfactant concentration from 0.139 M to 0.243 M. 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 .

Number of Polymer Particles: The log-log plot (Figure 16) of number of polymer particles produced per ml of water after 35 minutes 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 0.035 M to 0.139 M. 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 0.139 M to 0.243 M. 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.

Polymer Molecular Weight: From the data given in Table IX, 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 monomer percent 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 0.139 M to 0.243 M. As was mentioned in the above paragraph, 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 which could result in a lower molecular weight is greater than the effect of the increase in the polymerization rate which could result in a higher molecular weight ($X_n = R_p / R_i$). 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 above 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 methyl methacrylate, (2) sodium lauryl sulfate serves as both surfactant and initiator.

Methyl methacrylate 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. Gershberg[57] and Okamura[58] have reviewed the emulsion polymerization kinetics of the relatively water-soluble 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 et. al.[59] studied the aqueous polymerization of methyl methacrylate 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[60] and Guah[61] drew similar conclusions respectively in their work on the aqueous photopolymerization and aqueous polymerization of methyl methacrylate by saying that homogeneous polymerization proceeded in the aqueous phase at the early stages of the reaction. Baxendale et. al.[62] reported the polymerization of methyl methacrylate 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 et. al.[63] 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 to 4 %. Kanamara et. al.[64] studied the emulsion polymerization of methyl methacrylate at 70°C by using sodium lauryl sulfate as the surfactant and ammonium persulfate as the initiator. They found that the values of 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. P. I. Lee et al.[65] studied the emulsion polymerization of methyl methacrylate at 35 °C using sodium lauryl sulfate as the surfactant and, Cu^{++}–N_2H_5OH, Fe^{+++}–N_2H_5OH and Mn^{+++}–N_2H_5OH 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 to 0.55 power of the surfactant concentration depending on the type of the initiators. Gershberg[57] has shown that methyl methacrylate emulsion polymerization kinetics deviated considerably from Smith-Ewart Case II Kinetics. He found that the polymerization rate varied to the 0.3 to 0.4 power of the surfactant concentration. R. K. Greenes[66] 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 methyl methacrylate, 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 methyl methacrylate 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 as compared to that of a non-water soluble styrene emulsion polymerization. The polymerization rate was not influenced significantly by variation of surfactant concentration, (i.e., $R_p \alpha [S]^{0.08}$) within the 0.035 M (1%) to 0.139 M (4%) surfactant concentration range. These results suggest that particle formation for this ultrasonically initiated emulsion polymerization of methyl methacrylate 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 0.139 M (4 %) to 0.243 M (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.

Although the dependence of polymerization rate on surfactant concentration is lower than the 0.6 power predicted by 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 methyl methacrylate as in an ideal styrene emulsion polymerization.

The polymer weight average molecular weight decreased with the surfactant concentration increasing from 0.035 M to 0.243 M. 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.

In this experimental section dealing with different surfactant concentrations, the final yield of the ultrasonically initiated emulsion polymerization of methyl methacrylate performed with ultrasound at an acoustic intensity of 9.2 W/cm^2 using emulsions containing 0.035 M to 0.243 M of SDS under an argon flow rate of 0.32 ml sec^{-1} at ambient temperature (final reaction vessel temperature 31 to 36°C) ranged from 31 to 47% with 30 to 35 minutes of sonication. The polymerization rate ranged from 4.2×10^{-4} to 6.5×10^{-4} mole $L^{-1}S^{-1}$ and polymer weight average molecular weight ranged from 2.14×10^{6} to 3.22×10^{6} g $mole^{-1}$. These results again show that ultrasonically (cavitation) induced polymerization is more efficient in an emulsion system than in a bulk organic system and the lower temperature ultrasonically initiated emulsion polymerization results in a similar or a higher polymerization rate as compared to that obtained from a higher temperature thermal emulsion polymerization method.

The 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 methyl methacrylate emulsions containing 1 g of sodium lauryl sulfate or 1 weight % of sodium lauryl sulfate (based on water) at an acoustic intensity of 9.2 W/cm^2 under an argon gas flow rate of 0.32 ml sec^{-1} in a -10°C cooling bath over a 9 fold initial monomer concentration range, [M] = 0.48 M to [M] = 4.07 M.

The results are presented in Tables XI and XII. The plots of the conversion versus time curves obtained at various initial monomer concentrations are shown in Figures 19 and 20. The plot of the monomer conversion versus the molecular weight curve obtained at 0.48 M initial monomer concentration is shown in Figure 23. The log-log plots of polymerization rate versus initial monomer concentration are shown in

Figures 21 and 22. The log-log plot of M_w versus initial monomer concentration is shown in Figure 24.

The monomer conversion versus time curves were similar in shape to those shown by Zimmt[49]. The induction periods varied from 5 to 10 minutes were observed and increased with increasing initial monomer concentration. No destablization of poly(methyl methacrylate) latexes was observed for any experiment during the polymerization of the emulsion. The latexes obtained were completely homogeneous. Polymer coagulation occurred on the horn after 35 to 45 minutes of sonication for all initial monomer concentrations except in the case of the 0.48 M monomer concentration.

Polymerization Rate: From the data given in Table XII, 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., $R_p \alpha [\text{Monomer}]^{0.36}$ or $R_p \alpha [\text{Monomer}]^{0.38}$), to a point and then became independent of initial monomer concentration. The polymerization rate further dropped at higher initial monomer concentration. Similar results were observed by Acres et. al.[67] in their work on ^{60}Co gamma ray initiated emulsion polymerization of methyl methacrylate.

According to the Smith-Ewart theory, a thermodynamic equilibrium of monomer concentration exists between monomer droplets and growing polymer particles in interval I and 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 the 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 monomer concentrations (i.e., 4.07 M) is presumably due to the decrease in cavitation efficiency as the organic phase (MMA) increases[39].

Polymer Molecular Weight: From the data given in Table XI, 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 percent conversion followed by a slight increase in molecular weight during the "constant-rate" period (interval II) (2) a slight gel effect between 66 to 70.5 percent conversion and polymer degradation after 70.5 percent conversion in the case of an emulsion containing 0.48 M initial monomer concentration, and (3) the weight average molecular weight increased with increasing initial monomer concentration, (i.e., $M_w \alpha [\text{Monomer}]^{0.18}$), to a point, then became independent of initial monomer concentration. The gel effect phenomenon was observed by Zimmt[49], R. K. Green[64] and Trommdcorff[61] in their works on the emulsion polymerization of methyl methacrylate. It was attributed to the reduction in termination rates as the viscosity of the medium increased at higher percent conversion. Polymer degradation phenomenon was observed by Kruus et. al.[17] in their work on the ultrasonically initiated bulk polymerization of styrene and Price et. al.[39] in their work on the ultrasonically initiated bulk polymerization of methyl methacrylate. 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.

In this experimental section dealing with different initial monomer concentrations, the final yield of the ultrasonically initiated emulsion polymerization of methyl methacrylate performed with ultrasound using emulsions containing 0.48 M to 4.07 M monomer at an acoustic intensity of 9.2 W/cm^2 under an argon gas flow rate of 0.32 ml sec^{-1} at ambient temperature (final reaction vessel temperature 29 to 35°C) ranged from 19 to 74% with 30 to 70 minutes of sonication. The polymerization rate ranged from 2.5 to 4.3 x 10^{-4} mole L^{-1}S^{-1} and polymer weight average molecular weight ranged from 2.5 to 3.24 x 10^6 g mole^{-1}. These results again show that ultrasonically (cavitation) induced polymerization is more efficient in an emulsion system than in a bulk organic system and lower temperature ultrasonically initiated emulsion polymerization results in a similar or higher polymerization rate as compared to that obtained from a higher temperature thermal emulsion polymerization method.

A possible mechanism of this ultrasonically initiated emulsion polymerization system could be proposed given information from the above studies of (1) the source of free radical in initiation process, (2) the effects of acoustic intensity, (3) the effects of surfactant concentration and

(4) the 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 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 monomer-swollen 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 J. H. Baxendale[62]: (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. Since 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 PMMA obtained at an acoustic intensity of 13 W/cm^2 are shown in Figure 25 and 26 respectively and are representative of the remaining samples obtained at other experimental conditions. The fingerprint comparison of these PMMA 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 methyl methacrylate 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 methyl methacrylate occurs.

(2) The initiation process of the ultrasonically initiated emulsion polymerization of methyl methacrylate is a free radical process as it can be retarded by free radical scavengers.

(3) The ultrasonically initiated emulsion polymerization of methyl methacrylate is caused by the cavitation process and occurs at relatively low temperatures as compared to 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 of this ultrasonically initiated emulsion polymerization can be enhanced by the presence of a added conventional initiator.

(5) Weight average molecular weights ranging form 2.5 million g/mole to 3.5 million g/mole are attained with 30 to 40 minutes of sonication. Polymer yields ranging from 30 to 70% are attained within 30 to 70 minutes 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 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 enhance 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, heat generated from polymerization and polymer viscosity. These three phenomena result in increasing the total polymer particles generated and reaction rate constant, therefore enhance 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 0.035 M to 0.139 M 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 0.035 M to 0.243 M 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 enhance 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 methyl methacrylate show some deviations from the traditional Smith-Ewart theory. It appear to follow the scheme proposed by Genshberg[57] rather than the traditional Smith-Ewart theory.

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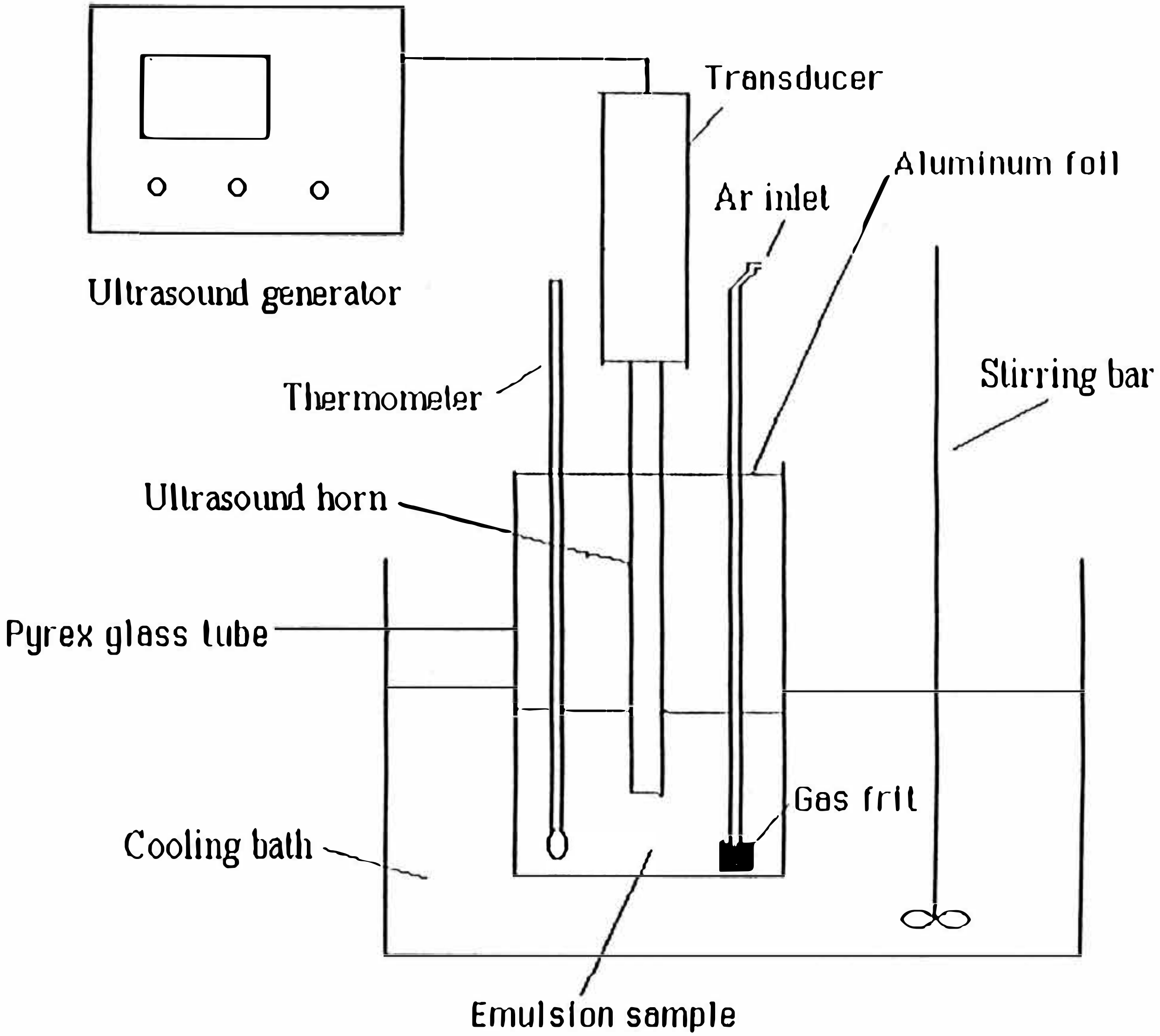


Figure 1. Schematic diagram of ultrasonic polymerization apparatus

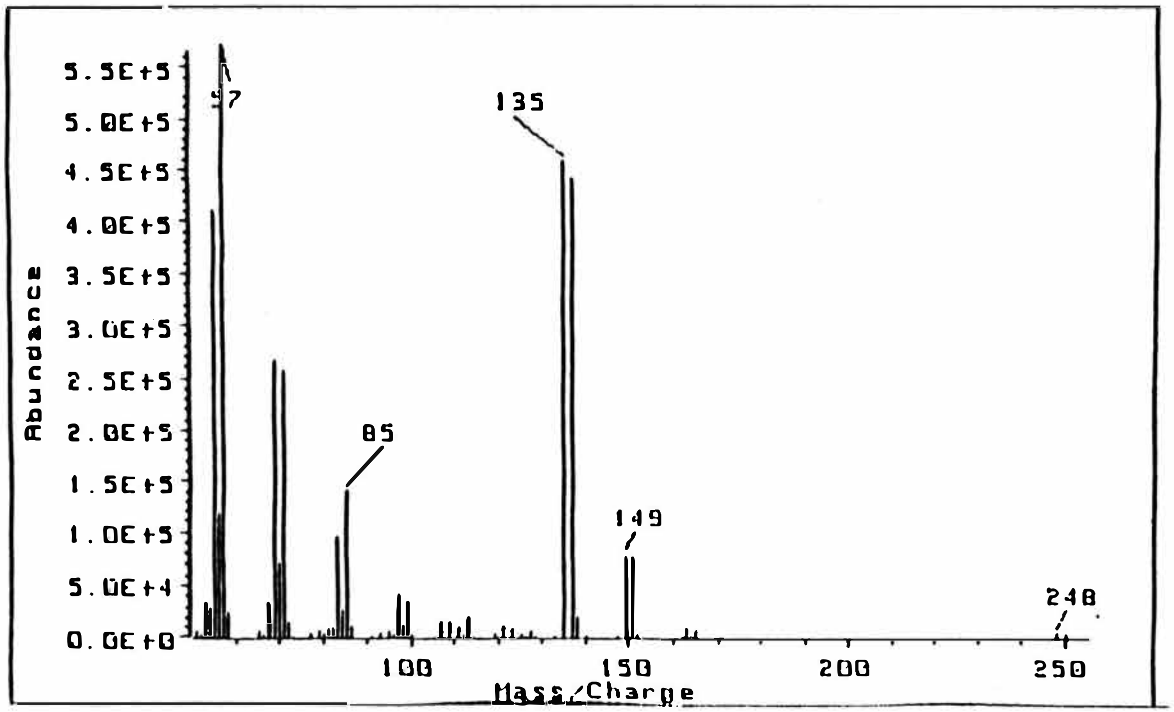


Figure 2. The mass spectrum of $C_{12}H_{25}Br$ detected from ultrasonically irradiated solution. (water = 100 ml, bromoform = 4.2 ml, SDS = 1g, acoustic intensity = 13.0 Wcm-2, argon gas flow rate = 0.74 ml/sec, sonication time = 30 minutes, cooling bath temp. = -10°C)

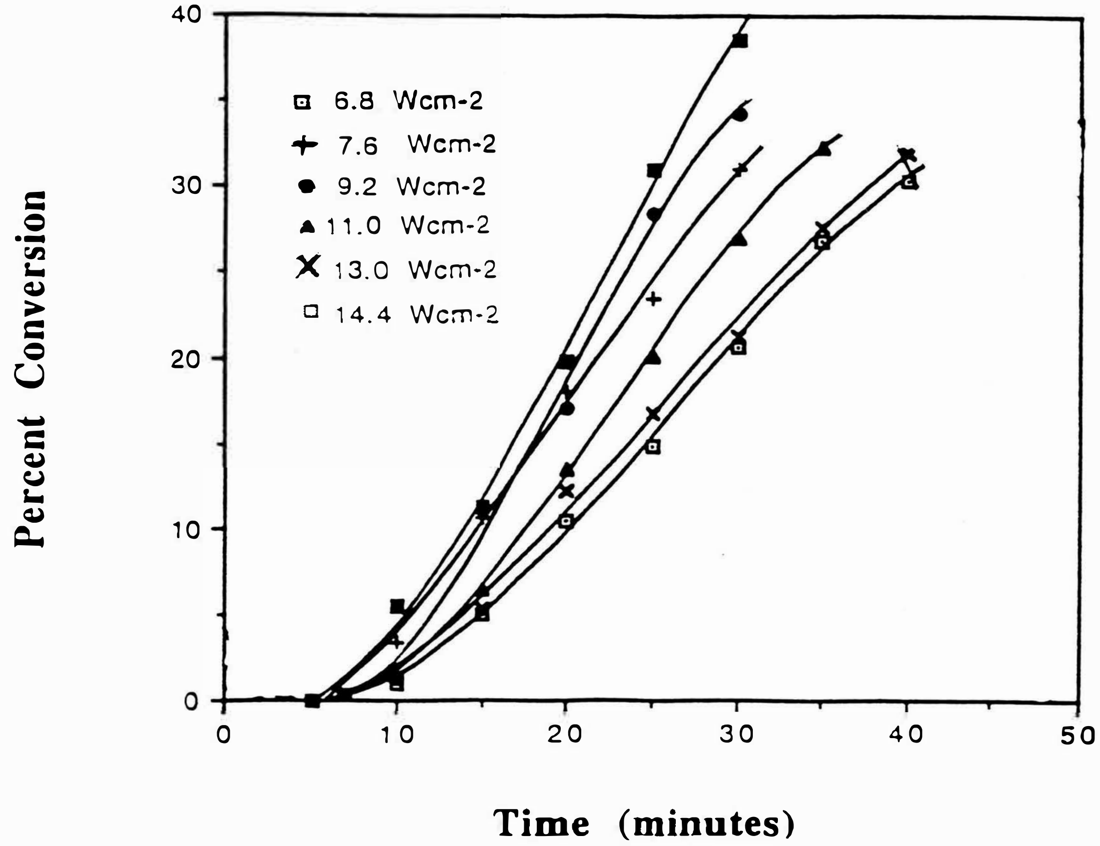


Figure 3. Monomer percent conversion vs. time curve for the ultrasonically initiated emulsion polymerization of methyl methacrylate at various acoustic intensities. (MMA= 22 ml, water=100 ml, SDS =1g, argon gas flow rate= 0.74 ml/sec, cooling temp. = -10°C)

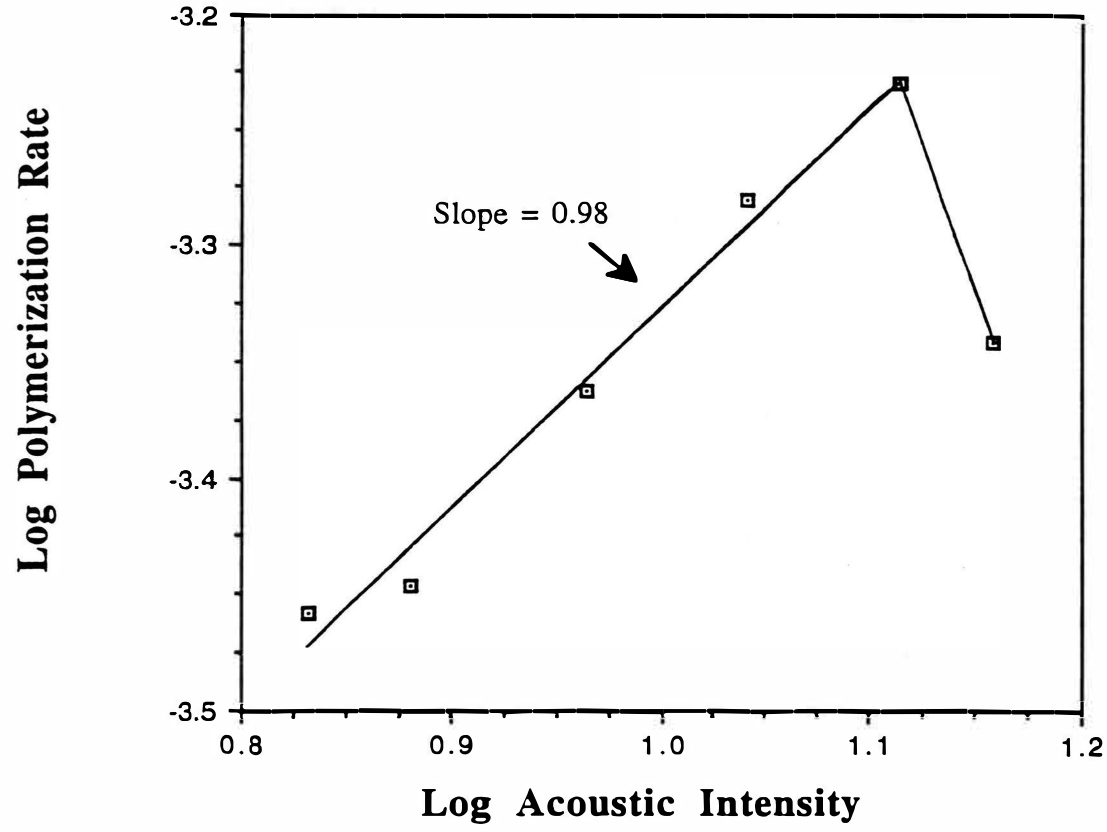


Figure 4. Effect of acoustic intensity on polymerization rate for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA = 22 ml, water = 100 ml, SDS = 1 g, argon gas flow rate = 0.74 ml/sec, cooling bath temp. = -10°C)

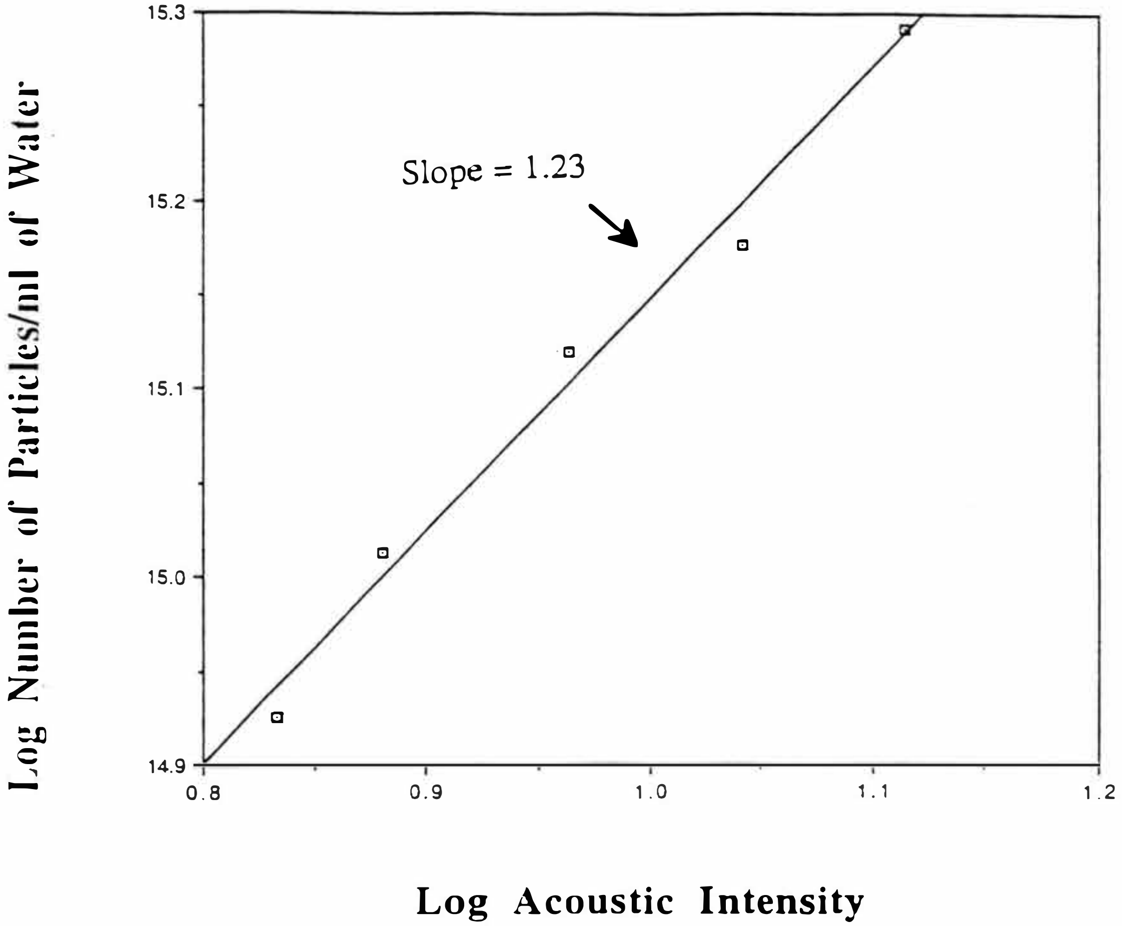


Figure 5. Effect of acoustic intensity on the number of polymer particles generated for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA = 22 ml, water = 100 ml, SDS =1 g, argon gas flow rate = 0.74 ml/sec, sonication time = 30 minutes, cooling bath temp.= -10°C)

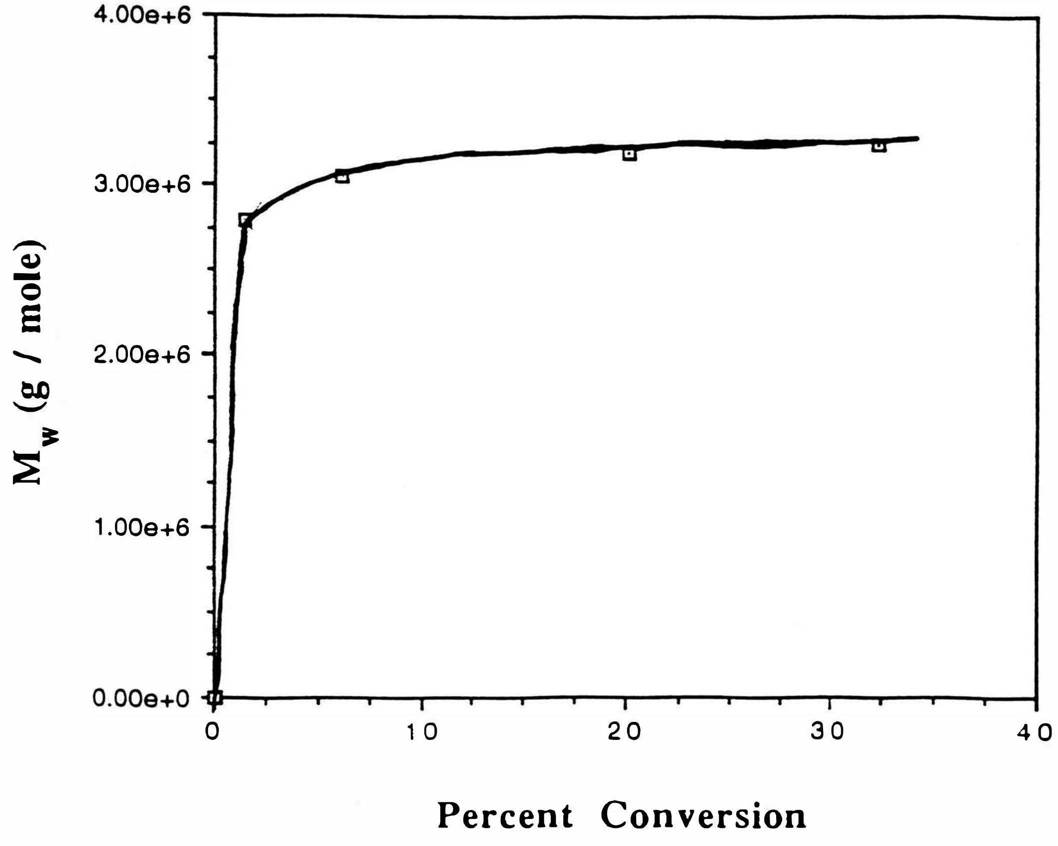


Figure 6. Weight average molecular weight as a function of monomer percent conversion at an acoustic intensity of 9.2 Wcm-2 for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA = 22 ml, water = 100 ml, SDS = 1 g, argon gas flow rate = 0.74 ml/sec, cooling bath temp. = -10°C)

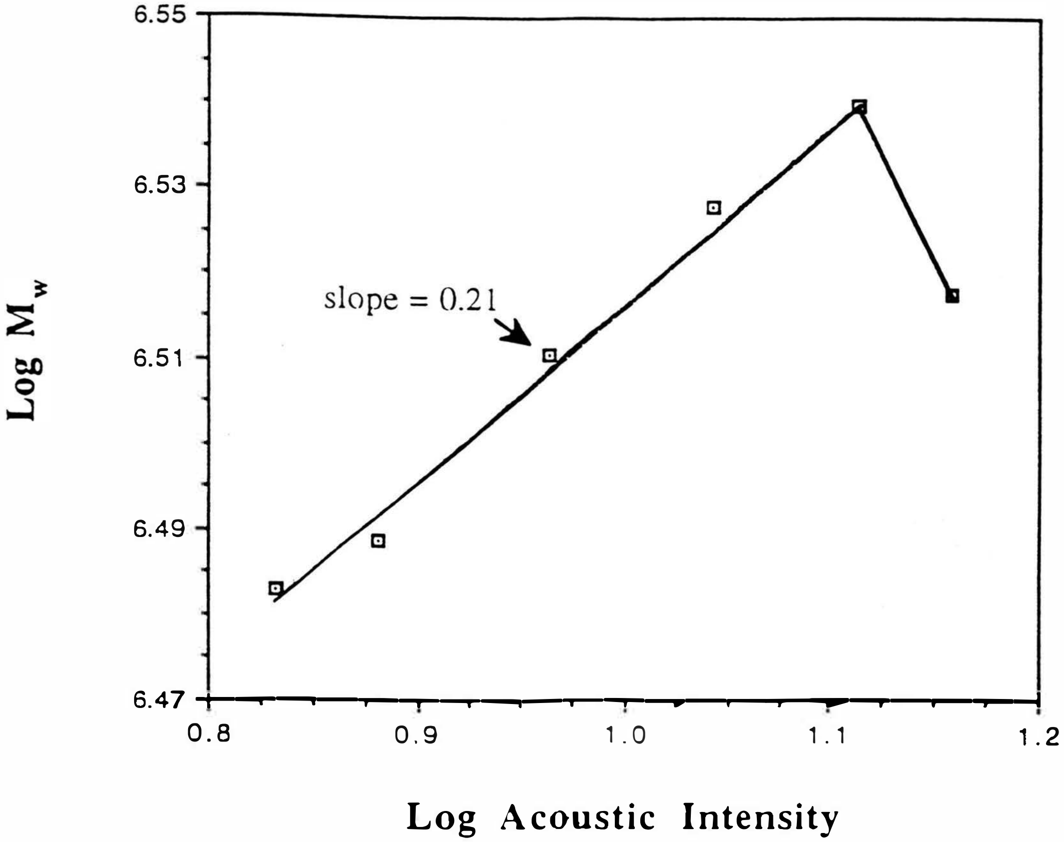


Figure 7. Effect of acoustic intensity on the weight average molecular weight for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA = 22 ml, water = 100 ml, SDS =1 g, argon gas flow rate = 0.74 ml/sec, sonication time = 30 minutes, cooling bath temp.= -10°C)

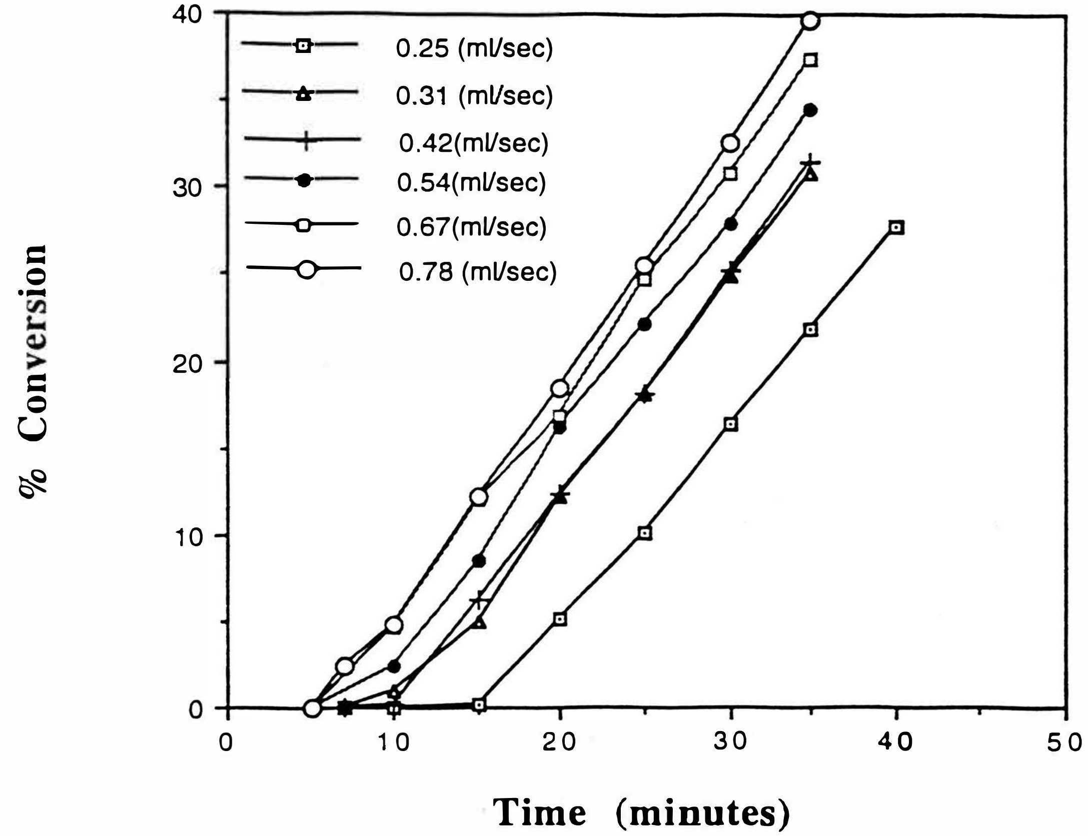


Figure 8. Monomer percent conversion vs. time curve for the ultrasonically initiated emulsion polymerization of methyl methacrylate at various argon gas flow rates. (MMA = 22 ml, water = 100 ml, SDS = 1 g, acoustic intensity = 9.2 Wcm-2, cooling bath temp. = -10°C)

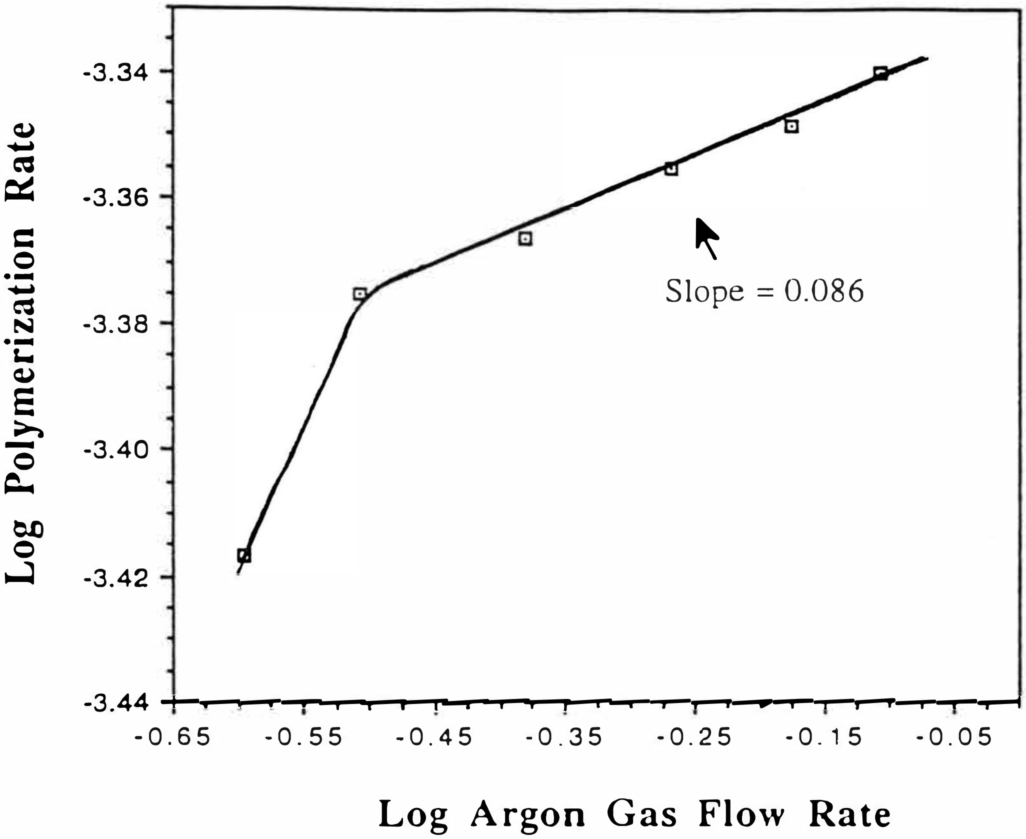


Figure 9. Effect of argon gas flow rate on the polymerization rate for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA= 22 ml, water= 100 ml, SDS = 1 g, acoustic intensity = 9.2 Wcm^{-2}, cooling bath temp.= -10°C)

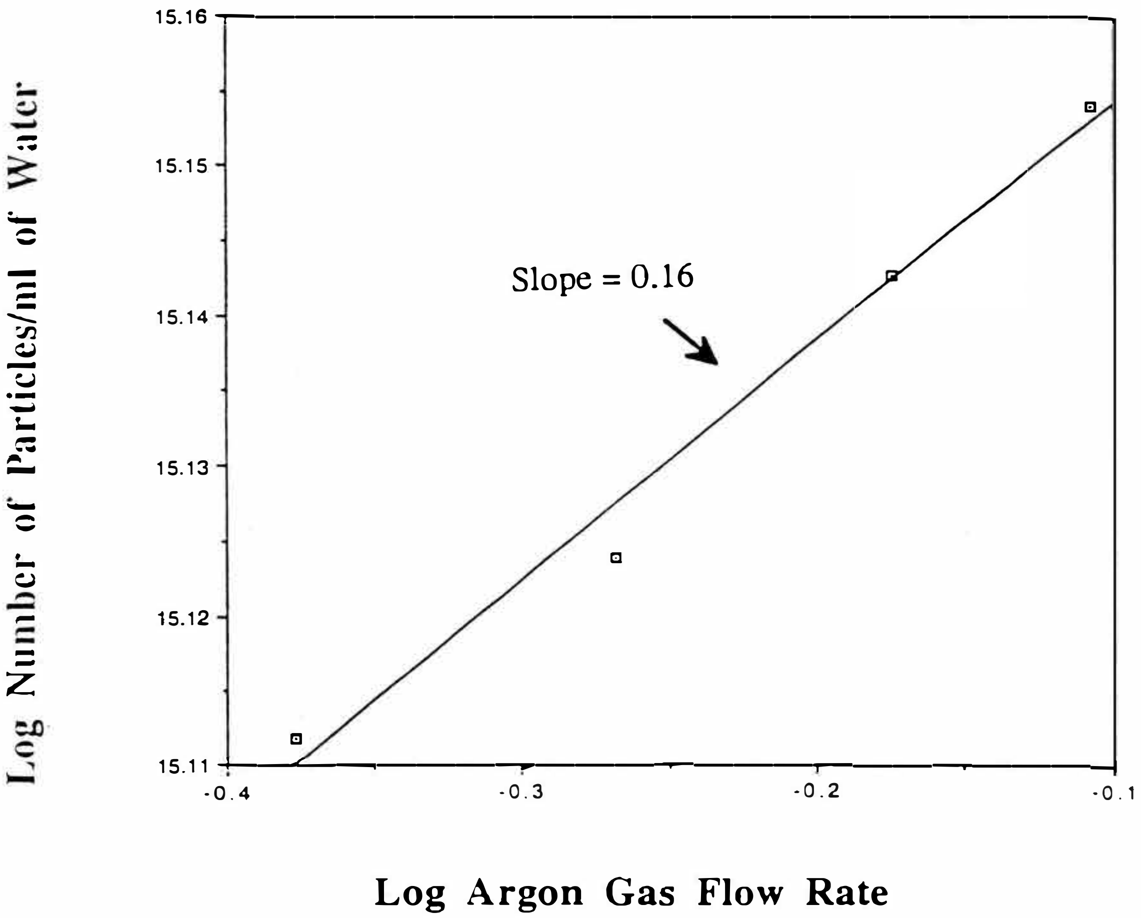


Figure 10. Effect of argon gas flow rate on the number of polymer particles generated for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA = 22 ml, water = 100 ml, SDS =1 g, acoustic intensity = 9.2 Wcm-2, sonication time = 35 minutes, cooling bath temp. = -10 °C)

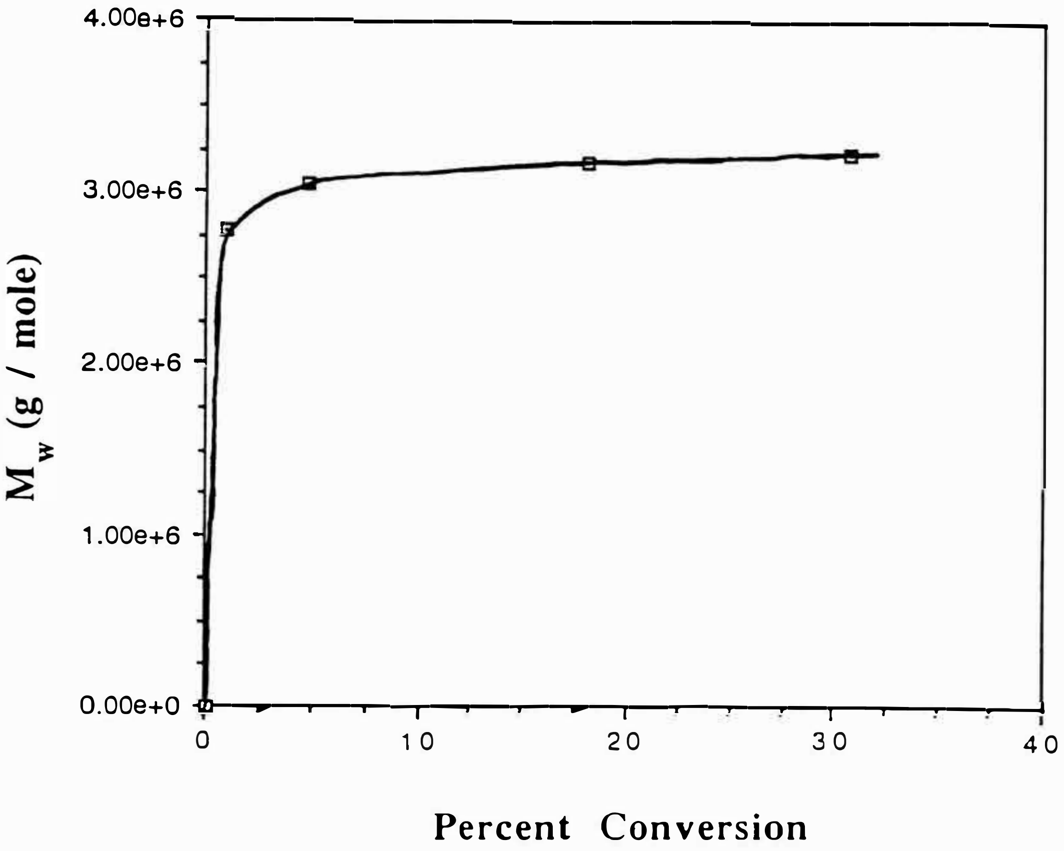
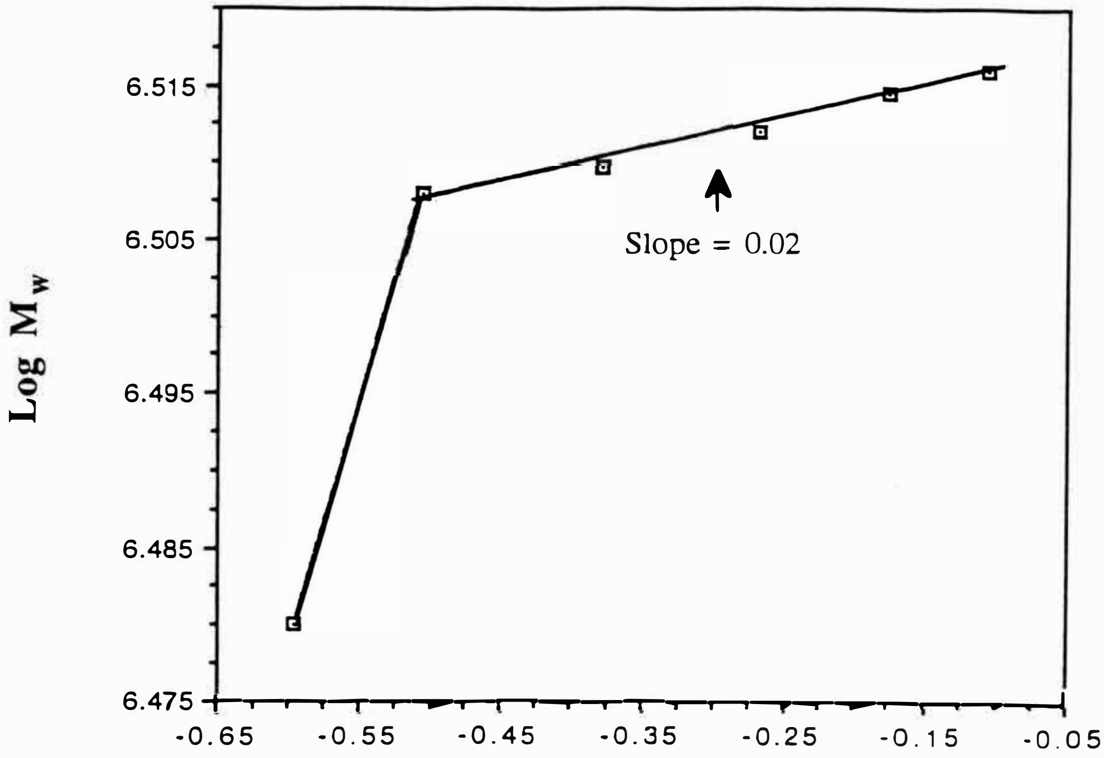


Figure 11. Weight average molecular weight as a function of monomer percent conversion under an argon gas flow rate of 0.32 ml/sec for the ultrasonically initiated emulsion polymerization of methyl methacrylate.
(MMA = 22 ml, water = 100 ml, acoustic intensity = 9.2 Wcm^{-2}, SDS = 1g, cooling temp. = -10°C)



Log Argon Gas Flow Rate

Figure 12. Effect of argon gas flow rate on the weight average molecular weight for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA = 22 ml, water = 100 ml, SDS =1 g, acoustic intensity = 9.2 Wcm^{-2}, sonication time = 35 minutes, cooling bath temp. = -10 °C)

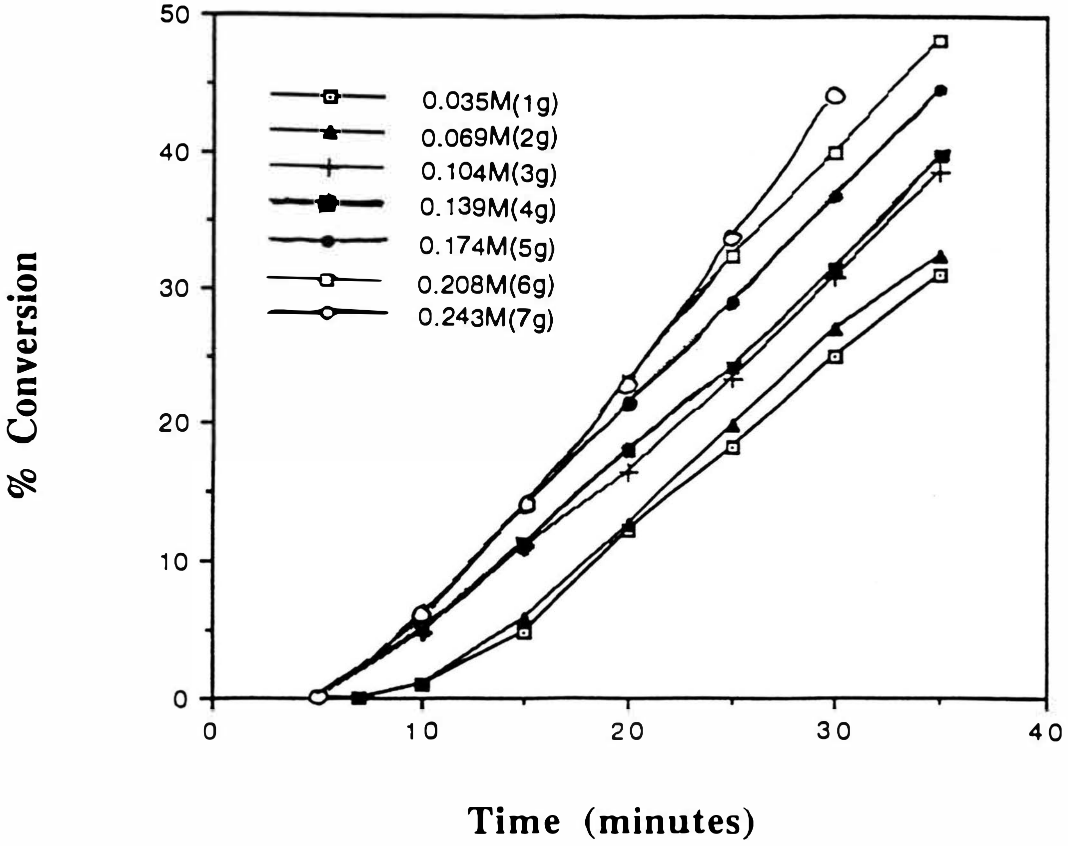


Figure 13. Monomer percent conversion vs. time curve for the ultrasonically initiated emulsion polymerization of methyl methacrylate at various surfactant concentrations.
(MMA = 22 ml, water = 100 ml, argon gas flow rate = 0.32 ml/sec, acoustic intensity= 9.2 Wcm-2, cooling bath temp. = -10°C)

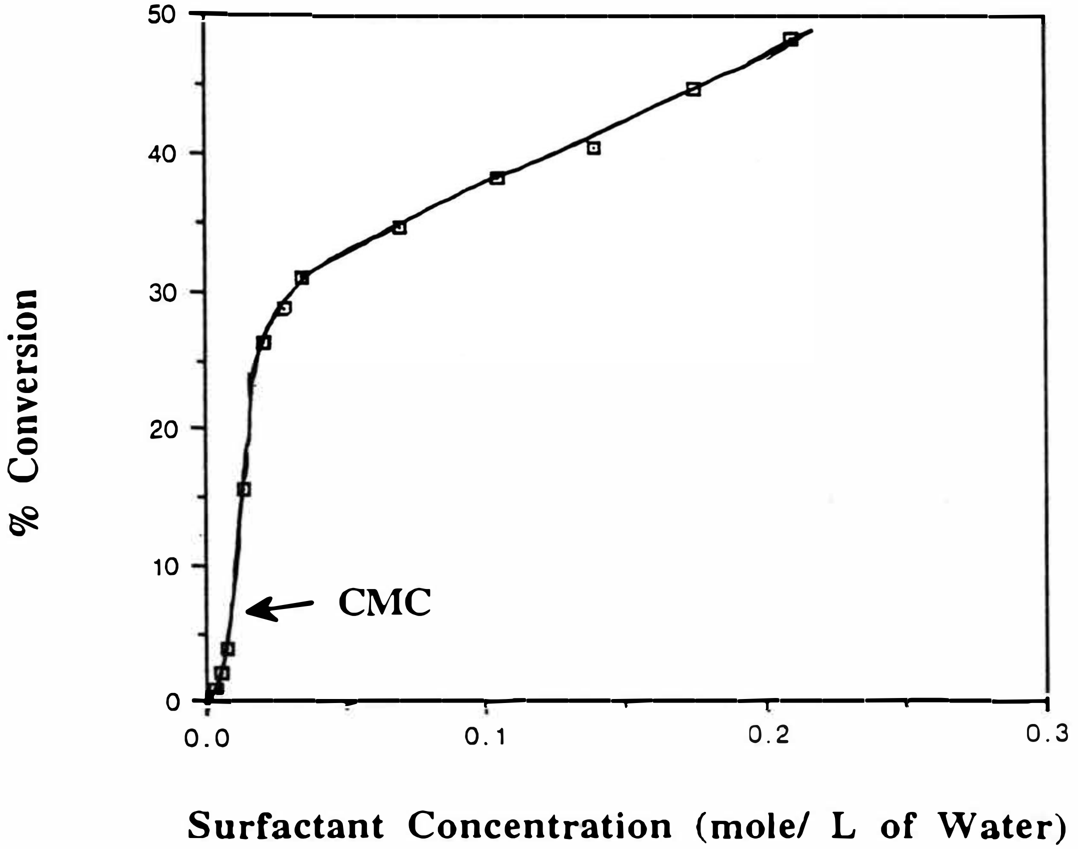


Figure 14. The effect of SDS concentration on % monomer conversion for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA = 22 ml, water = 100 ml, acoustic intensity = 9.2 Wcm-2, argon gas flow rate = 0.32 ml/sec, sonication time = 35 minutes,cooling bath temp. = -10 °C)

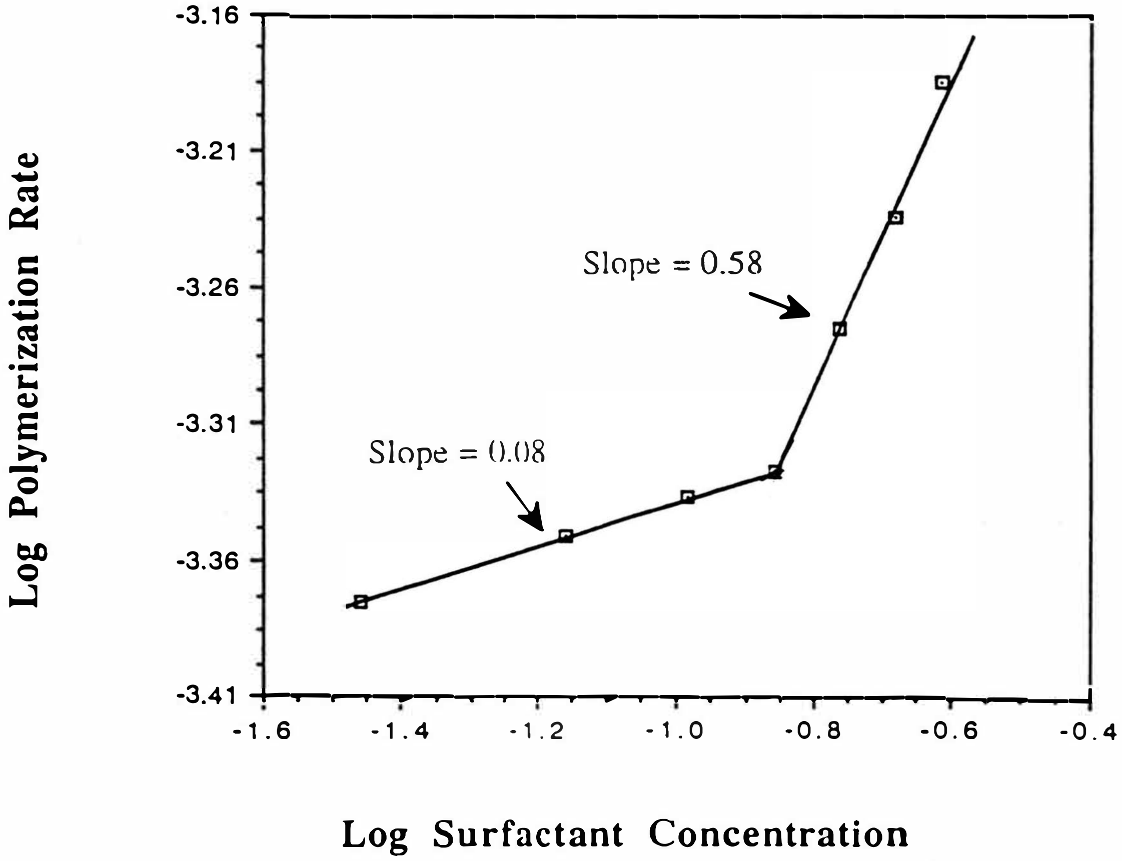


Figure 15. Effect of surfactant concentration on the polymerization rate for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MM = 22 ml, water = 100 ml, acoustic intensity = 9.2 Wcm^{-2}, argon gas flow rate = 0.32 ml/sec, cooling bath temp. = -10°C)

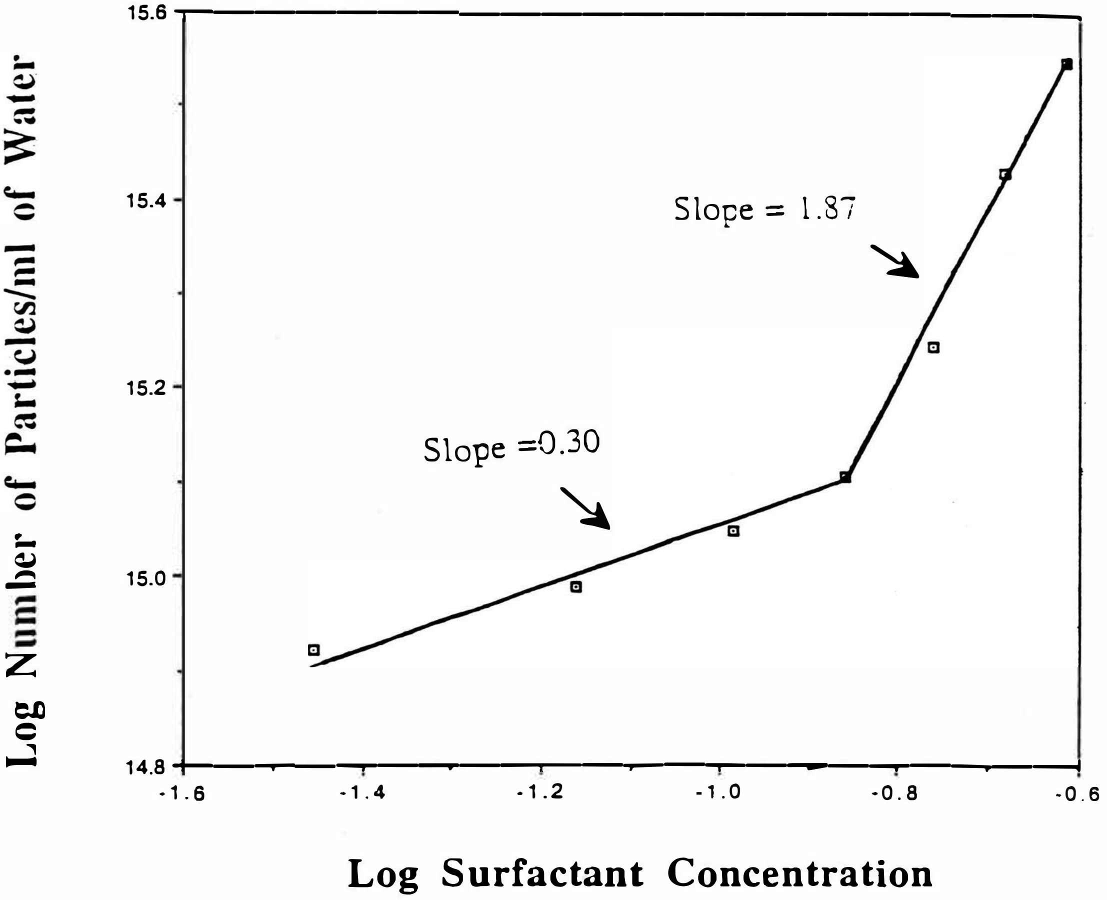


Figure 16. Effect of surfactant concentration on the number of polymer particles generated for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA = 22 ml, water = 100 ml, acoustic intensity = 9.2 Wcm^{-2}, argon gas flow rate = 0.32 ml/sec, sonication time = 35 minutes, cooling bath temp. = -10°C)

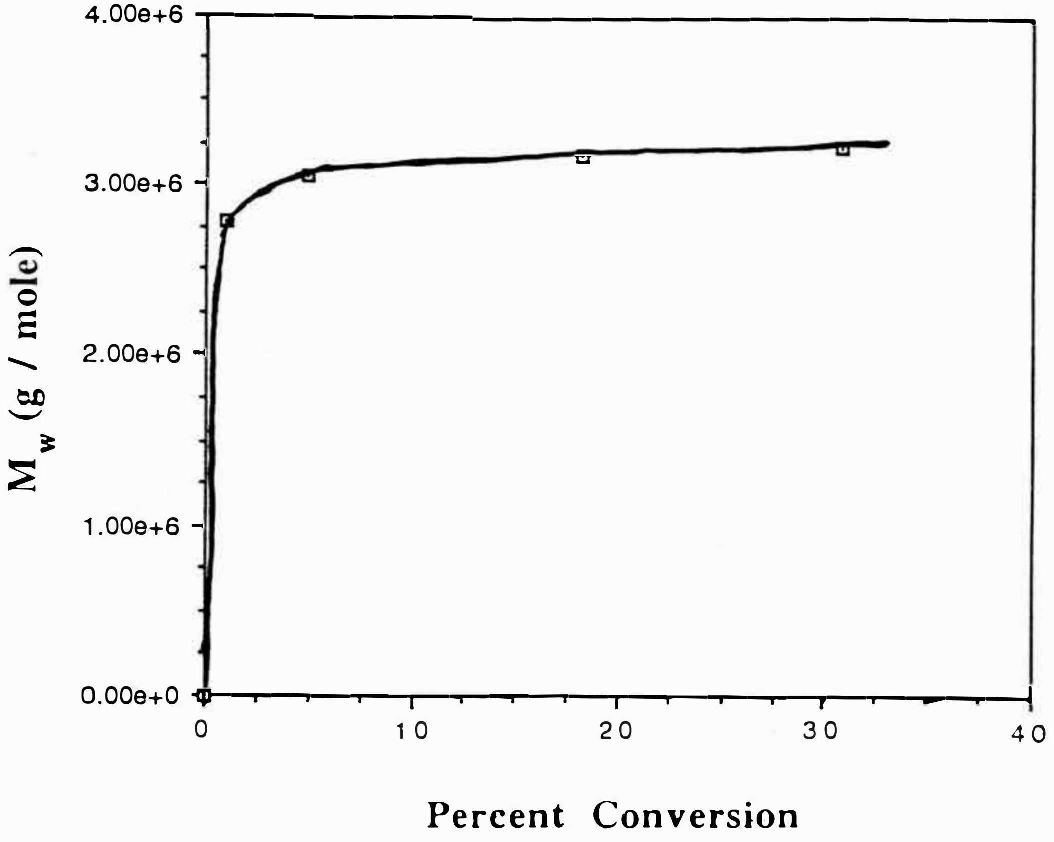


Figure 17. Weight average molecular weight as a function of monomer percent conversion at 0.035 M surfactant concentration for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA = 22 ml, water = 100 ml, SDS = 1 g, acoustic intensity = 9.2 Wcm-2, argon gas flow rate = 0.32 ml/sec, cooling bath temp. = -10°C)

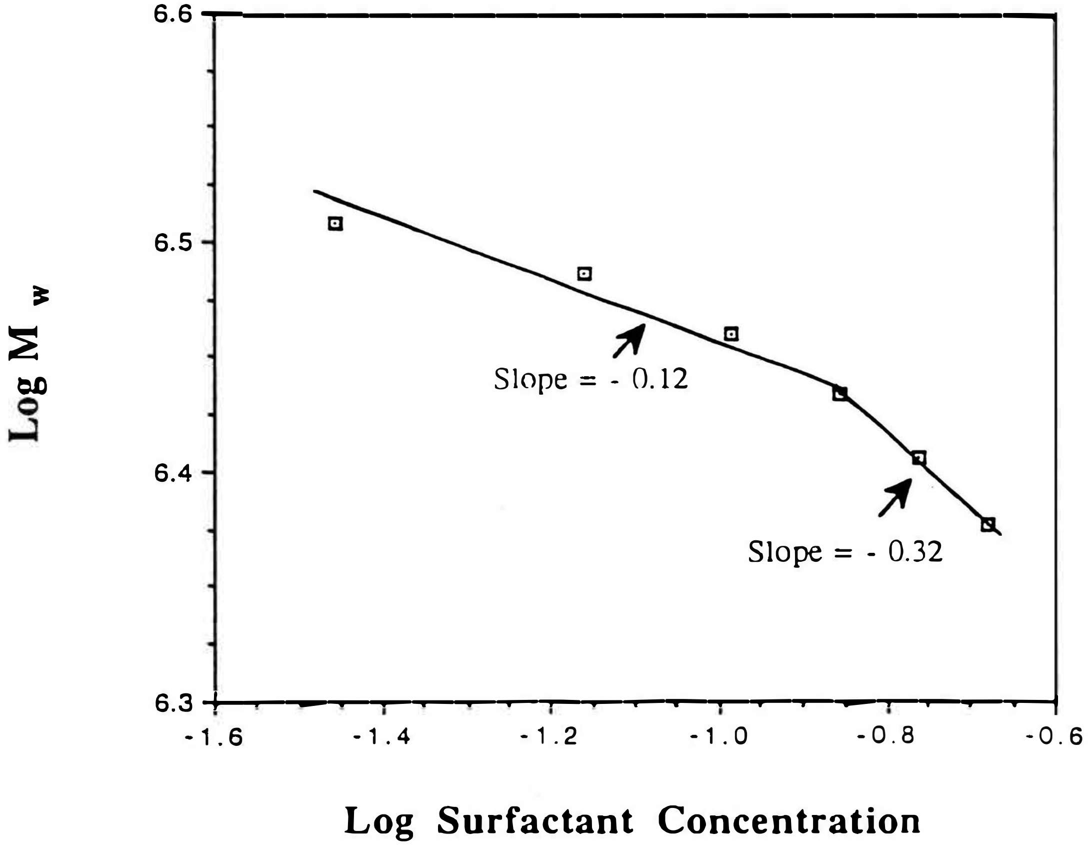


Figure 18. Effect of surfactant concentration on the weight average molecular weight for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA = 22 ml, water = 100 ml, acoustic intensity = 9.2 Wcm^{-2}, argon gas flow rate = 0.32 ml/sec , sonication time = 35 minutes, cooling bath temp. = -10°C)

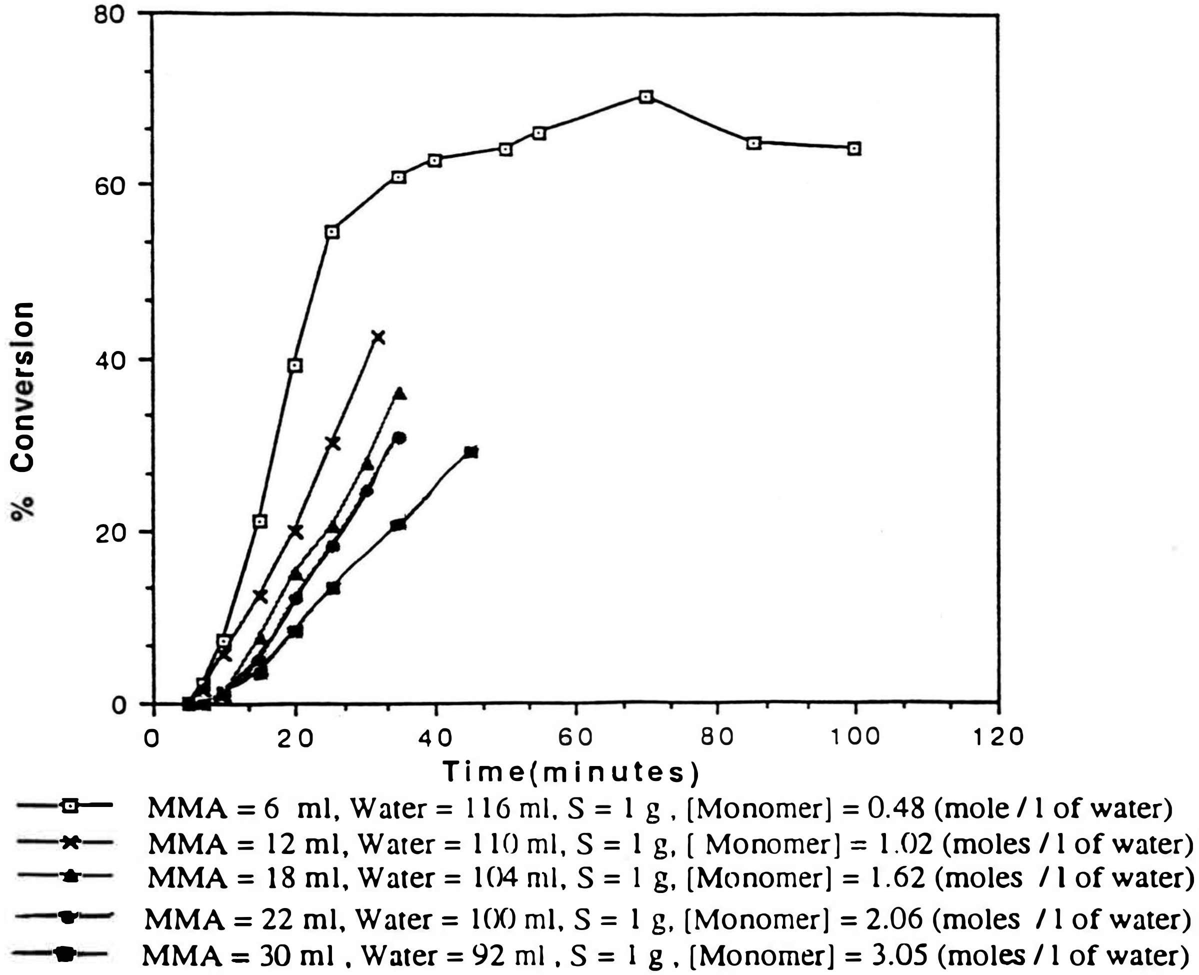


Figure 19. Monomer percent conversion vs. time curve for the ultrasonically initiated emulsion polymerization of methyl methacrylate at various monomer concentrations. (acoustic intensity = 9.2 Wcm^{-2}, argon gas flow rate = 0.32 ml/sec, SDS = 1 g, cooling bath temp.= -10°C)

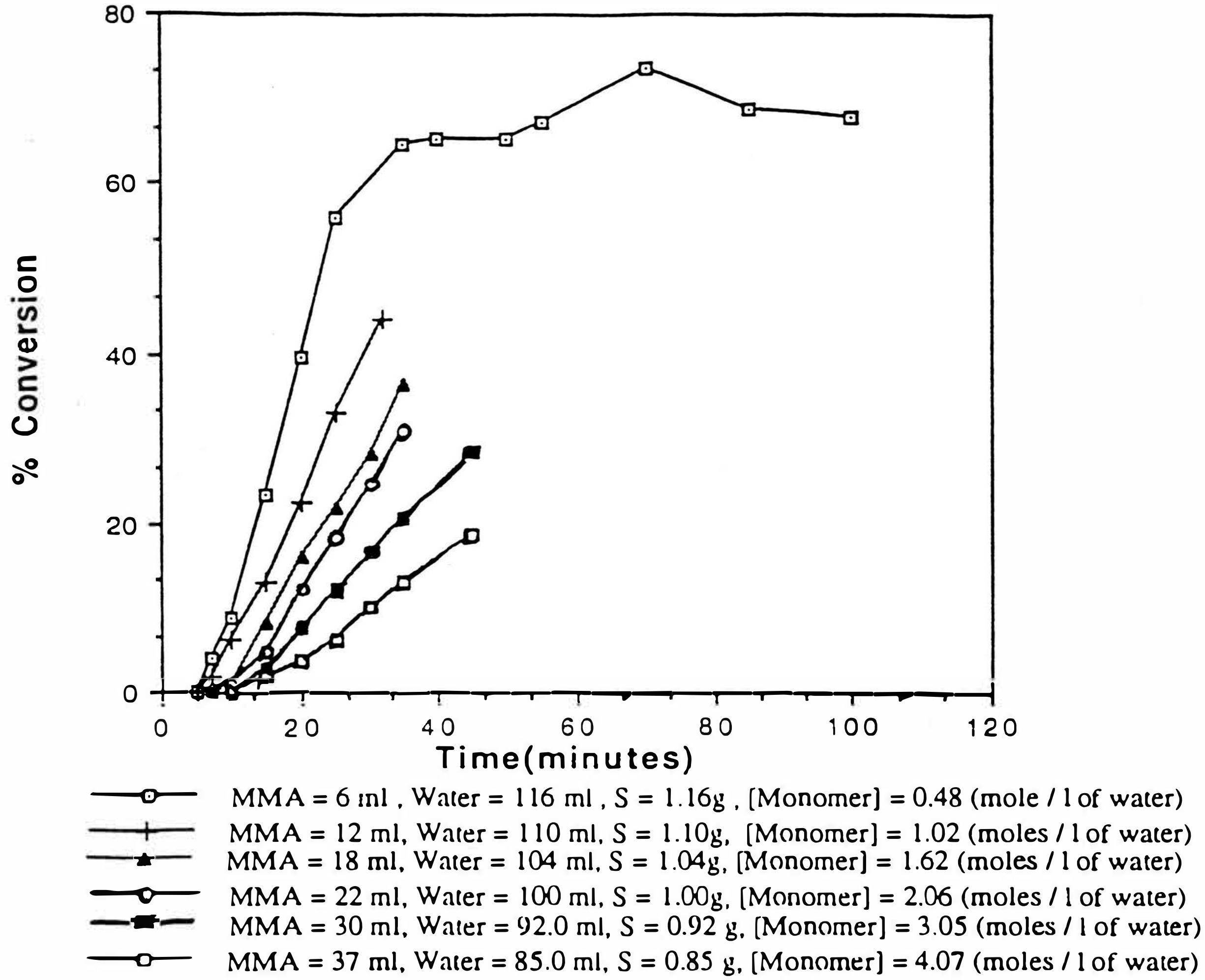


Figure 20. Monomer percent conversion vs. time curve for the ultrasonically initiated emulsion polymerization of methyl methacrylate at various monomer concentrations.
(acoustic intensity = 9.2 Wcm^{-2}, argon gas flow rate = 0.32 ml/sec, SDS = 1 wt % of water, cooling bath temp. = -10°C)

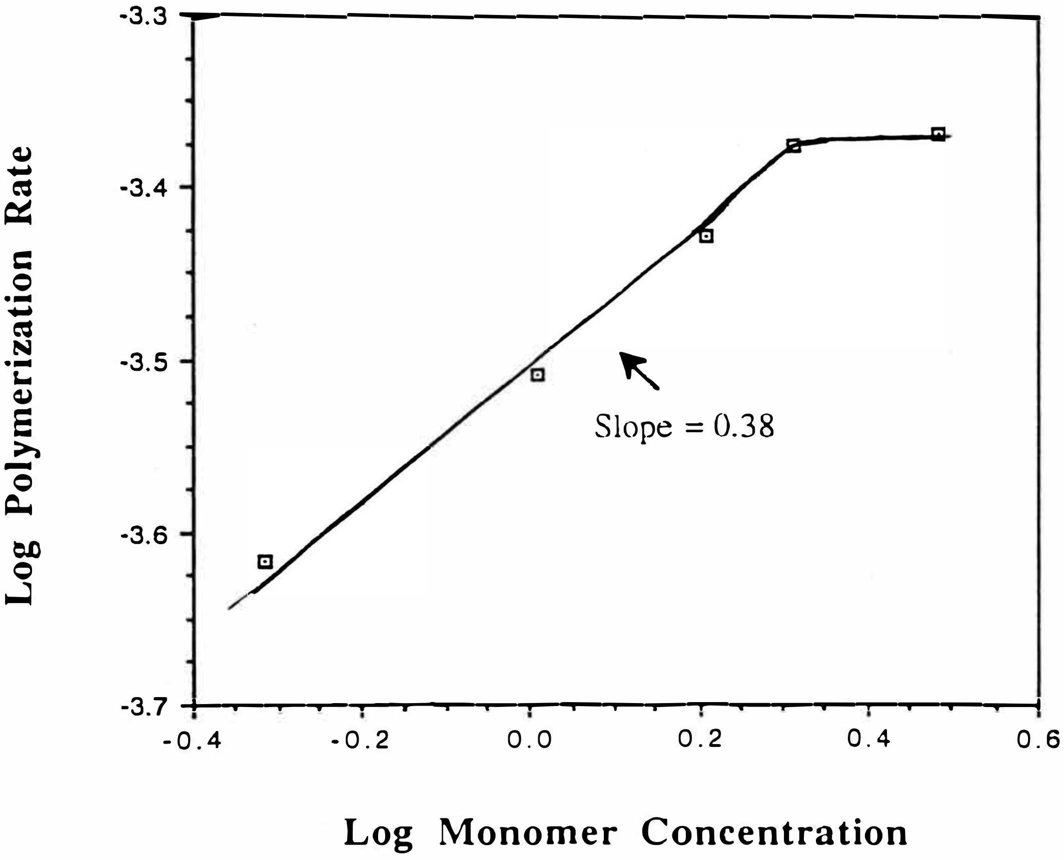


Figure 21. Effect of monomer concentration on the polymerization rate for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (acoustic intensity = 9.2 Wcm^{-2}, argon gas flow rate = 0.32 ml/sec, SDS = 1 g , cooling bath temp. = - 10°C)

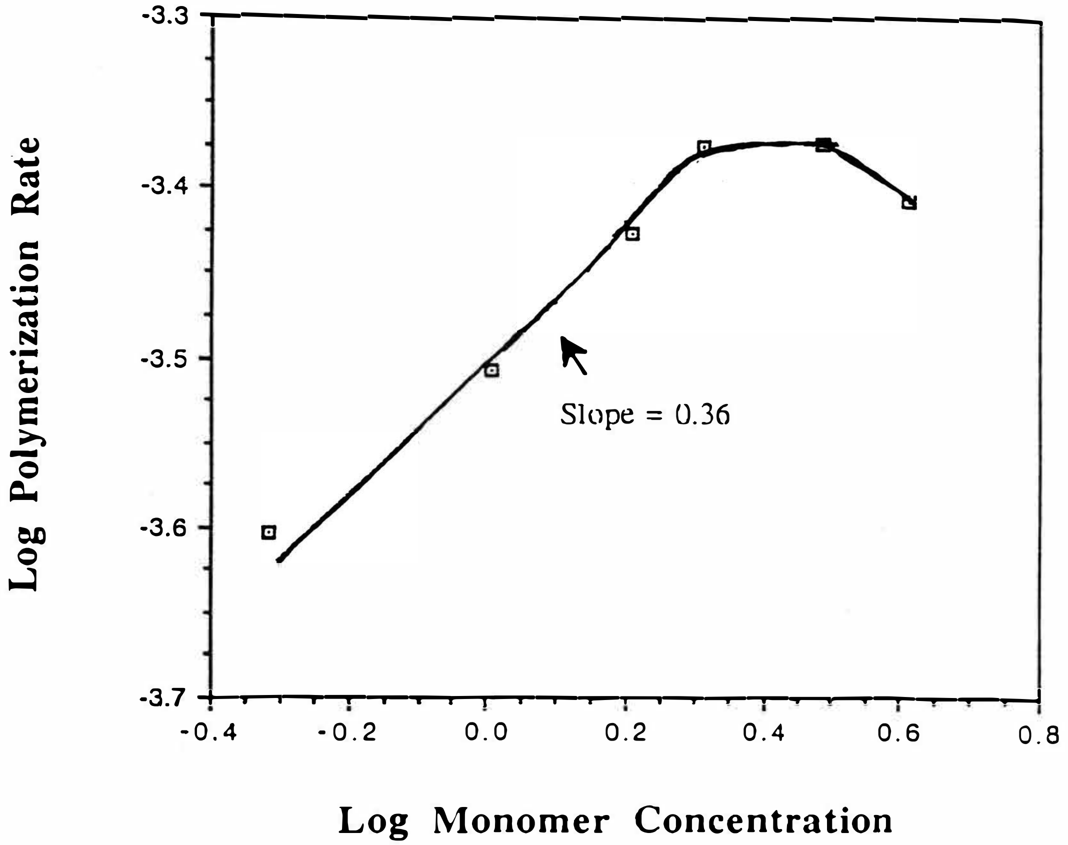


Figure 22. Effect of monomer concentration on the polymerization rate for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (acoustic intensity = 9.2 Wcm-2, argon gas flow rate = 0.32 ml/sec, SDS = 1 wt % of water, cooling bath temp. = -10 °C)

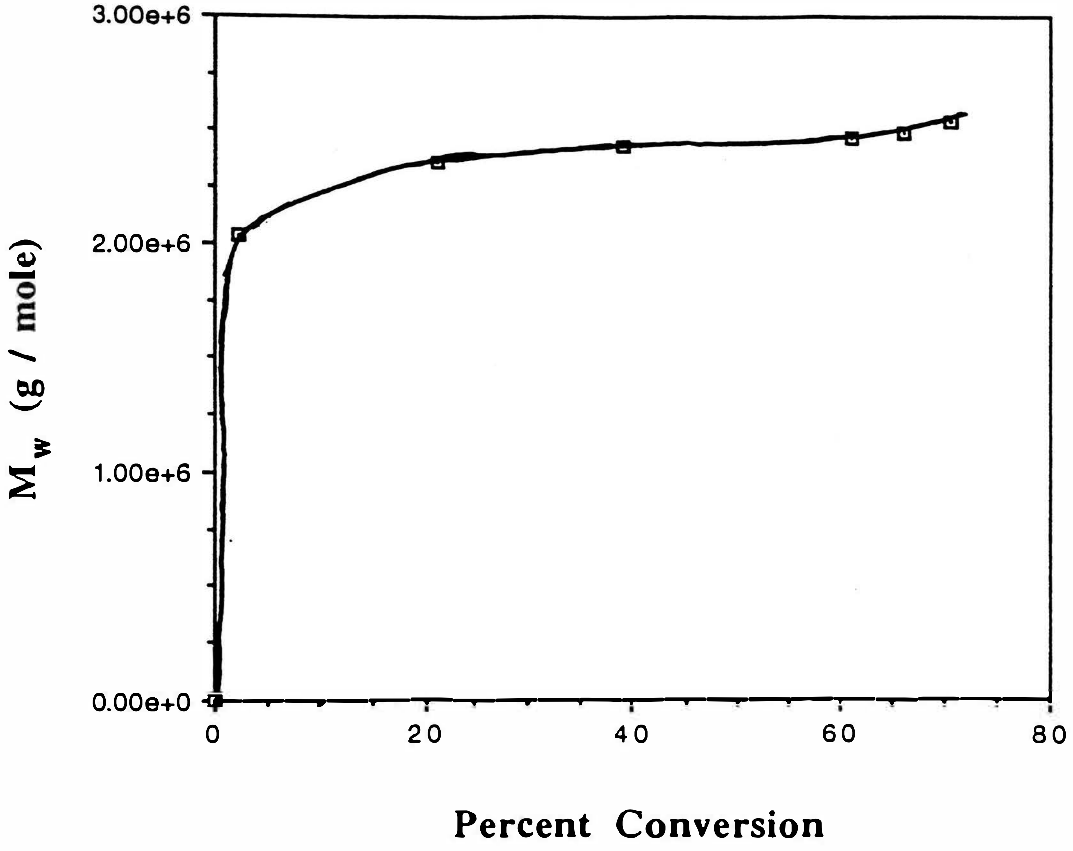


Figure 23. Weight average molecular weight as a function of monomer percent conversion at 0.035 M monomer concentration for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (MMA = 6 ml, water = 112 ml, acoustic intensity = 9.2 Wcm^{-2}, argon gas flow rate = 0.32 ml/sec, SDS = 1 g, cooling bath temp. = -10°C)

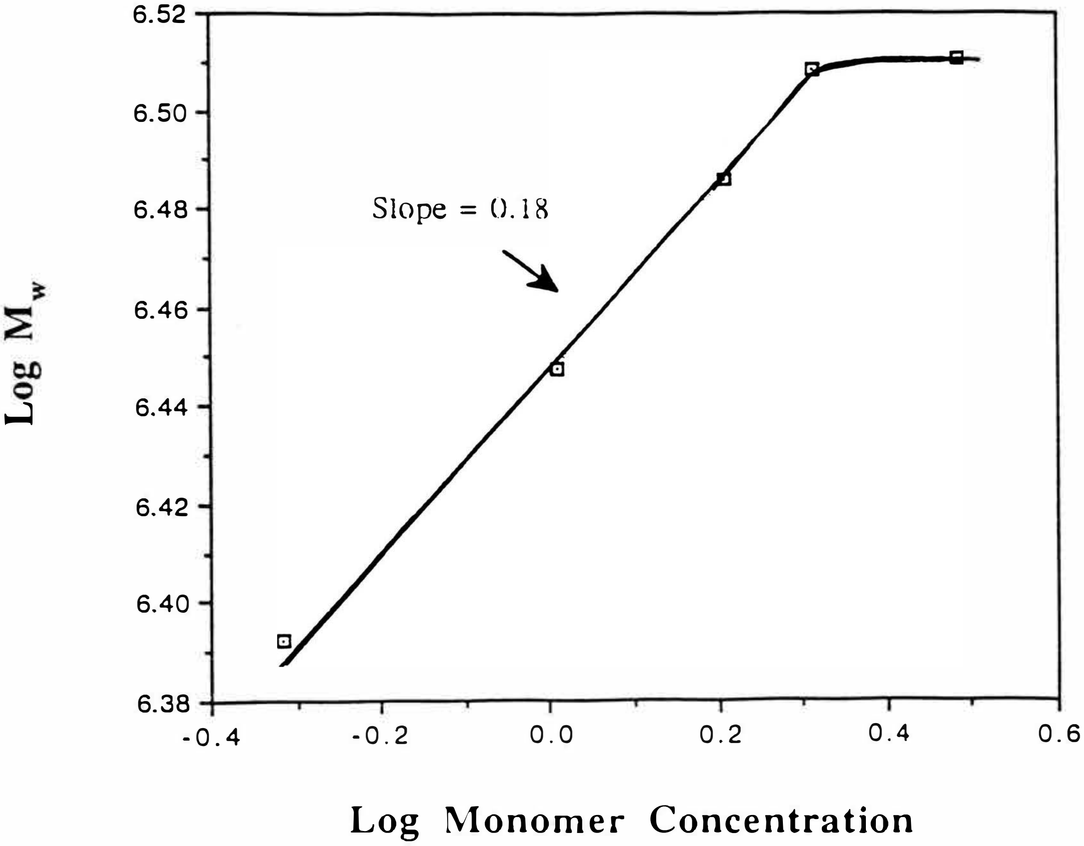


Figure 24. Effect of monomer concentration on the weight average molecular weight for the ultrasonically initiated emulsion polymerization of methyl methacrylate. (acoustic intensity = 9.2 Wcm-2, argon gas flow rate = 0.32 ml/sec, SDS = 1g, sonication time = 35 minutes, cooling bath temp. = -10° C)

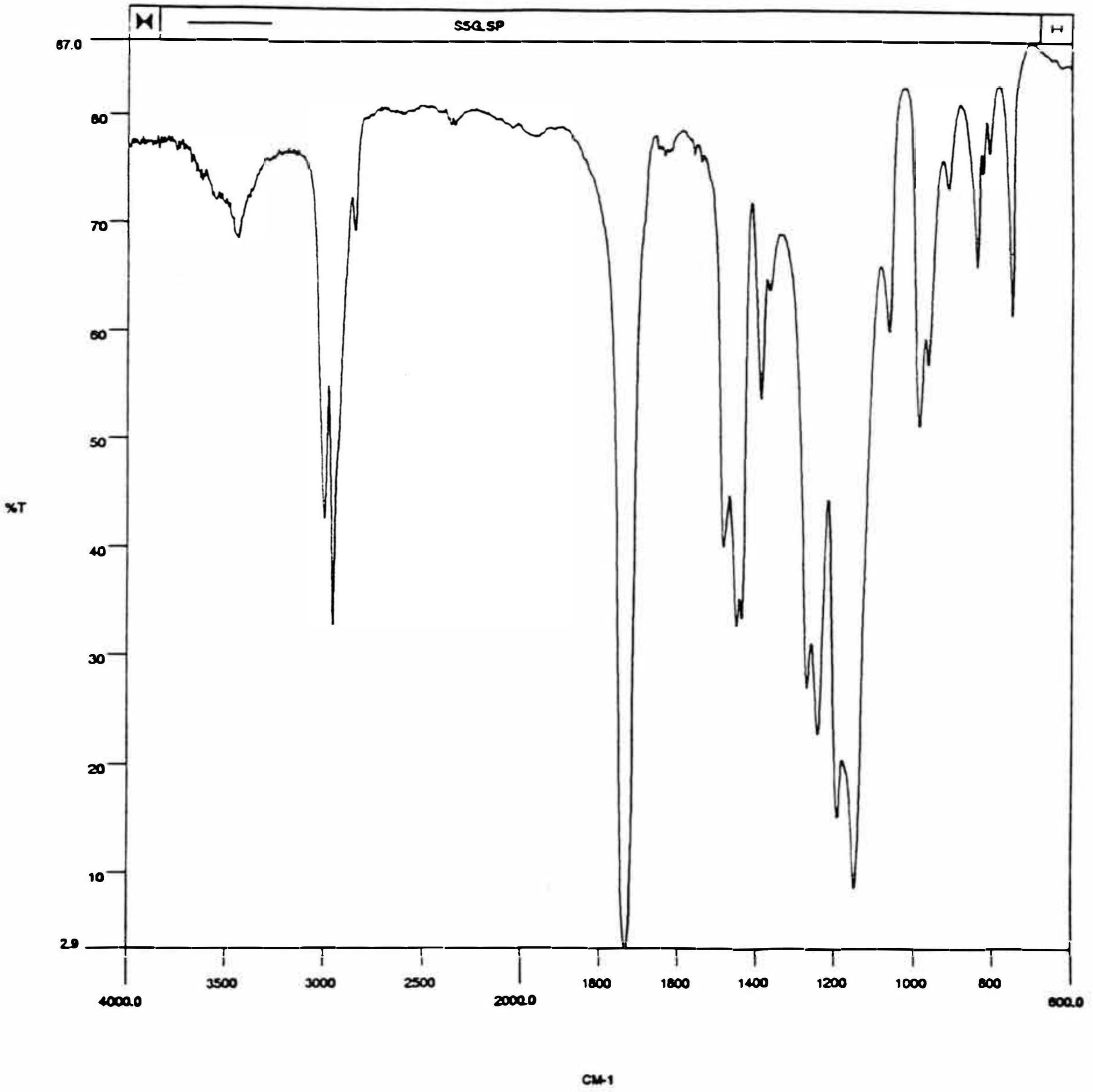


Figure 25. IR spectrum of PMMA obtained at 13.0 Wcm-2 acoustic intensity. (MMA = 22 ml, water = 100 ml, SDS =1 g, argon gas flow rate = 0.74 ml/sec, sonication time = 30 minutes, cooling bath temp.= -10°C)

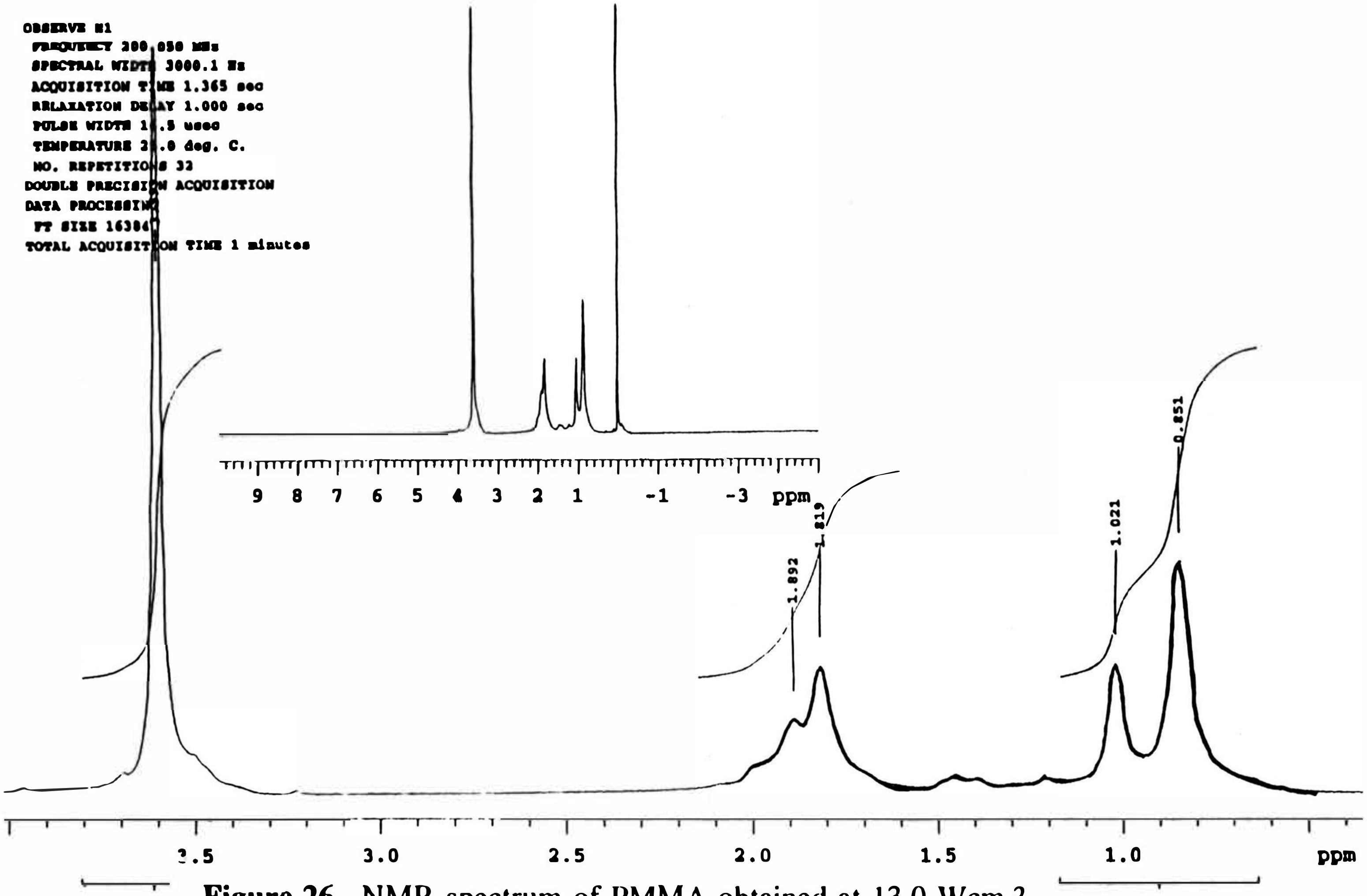


Figure 26. NMR spectrum of PMMA obtained at 13.0 Wcm^{-2} acoustic intensity. (MMA = 22 ml, water = 100 ml, SDS =1 g, argon gas flow rate = 0.74 ml/sec, sonication time = 30 minutes, cooling bath temp.= -10°C)

Table I Effect of Different Types of Cavitation on Polymerization Rate and Polymer Molecular Weight[a]

#	MMA (ml)	Water (ml)	S[b] (g)	Intensity[c] (Wcm^{-2})	Ar flow Rate (ml/sec)	Reaction time (min)	IT[d] (°C)	FT[e] (°C)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6}[f] (g/mole)
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

Table I (Continued)

#	MMA (ml)	Water (ml)	S[b] (g)	Intensity[c] (Wcm^{-2})	Ar flow Rate (ml/sec)	Reaction time (min)	IT[d] (°C)	FT[e] (°C)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6} [f] (g/mole)
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

[a] Cooling bath temperature = -10°C
[b] Sodium lauryl sulfate, surfactant
[c] Acoustic intensity
[d] Initial reaction temperature
[e] Final reaction temperature
[f] Weight average molecular weight

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

#	MMA (ml)	Water (ml)	S[b] (g)	Hydro-quinone (g)	Intensity[c] (Wcm^{-2})	Ar Flow Rate (ml/sec)	Reaction Time (min)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6}[d] (g/mole)
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

Table II (Continued)

#	MMA (ml)	Water (ml)	S[b] (g)	Hydro-quinone (g)	Intensity[c] (Wcm^{-2})	Ar Flow Rate (ml/sec)	Reaction Time (min)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6}[d] (g/mole)
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

[a] Cooling bath temperature = -10°C

[b] Sodium lauryl sulfate, surfactant

[c] Acoustic intensity

[d] Weight average molecular weight

Table III Ultrasonically vs. Thermally Initiated Polymerization[a]

#	MMA (ml)	Water (ml)	S[b] (g)	Reaction Time (min)	Reaction Temperature (°C)	Stirring Rate (rpm)	Polymer Yield (g)	Wt% Conversion
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

[a] Conventional emulsion polymerization method was used for all reactions.

[b] Sodium lauryl sulfate, surfactant

#	MMA (ml)	Water (ml)	S[b] (g)	Intensity[c] (W cm^{-2})	Ar flow Rate (ml/sec)	Reaction Time (min)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6} [d] (g/mole)	FT[e] (°C)
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	29.0
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] Ultrasonically-initiated polymerization method was used for all reactions. Initial reaction temperature was 5°C.

[b] Sodium lauryl sulfate, surfatant

[c] Acoustic intensity

[d] Weight average molecular weight

[e] Final reaction temperature

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

#	MMA (ml)	Water (ml)	S[a] (g)	Intensity (Wcm^{-2})	Ar flow Rate (ml/sec)	IT[b] (°C)	Reaction Time (min)	Wt% Conversion
4-1	80	0	0	13.0	0.78	5	30	0
4-2	80	0	0	13.0	0.78	5	60	0
4-3	80	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[c]	80	0	5	13.0	0.78	5	90	0
4-18[c]	80	0	8	13.0	0.78	5	90	0

[a] Sodium lauryl sulfate, surfactant

[b] Initial reaction temperature

[c] 1.5g hydroquinone was added to solution before reaction.

Table V Effect of the Acoustic Intensity on Polymer Yield and Polymer Molecular Weight[a]

#	Acoustic Intensity (Wcm^{-2})	Reaction Time (min)	Initial Reaction Temperature (°C)	Final Reaction Temperature (°C)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6} [b] (g/mole)	Mn x 10^{-6} [c] (g/mole)	Mw/Mn
5-20-1	6.8	5	5	-	0	0	-	-	-
5-20-2	6.8	10	5	20.5	0.19	0.9	-	-	-
5-20-3	6.8	15	5	22.0	1.02	5.0	-	-	-
5-20-4	6.8	20	5	22.5	2.16	10.5	-	-	-
5-20-5	6.8	25	5	23.0	3.03	14.7	-	-	-
5-20-6	6.8	30	5	23.5	4.31	20.6	3.04	1.68	1.81
5-20-7	6.8	35	5	25.0	5.53	26.8	-	-	-
5-20-8	6.8	40	5	27.5	6.27	30.4	-	-	-
5-30-1	7.6	5	5	-	0	0	-	-	-
5-30-2	7.6	10	5	20.5	0.27	1.3	-	-	-
5-30-3	7.6	15	5	22.5	1.08	5.2	-	-	-
5-30-4	7.6	20	5	23.0	2.52	12.2	-	-	-
5-30-5	7.6	25	5	23.5	3.45	16.7	-	-	-
5-30-6	7.6	30	5	24.0	4.37	21.2	3.08	1.77	1.74
5-30-7	7.6	35	5	25.5	5.69	27.6	-	-	-
5-30-8	7.6	40	5	28.5	6.60	32.0	-	-	-
5-40-1	9.2	5	5	-	0	0	0	-	-
5-40-2	9.2	10	5	21.5	0.28	1.4	2.80	-	-
5-40-3	9.2	15	5	23.0	1.16	6.1	3.06	-	-
5-40-4	9.2	20	5	24.5	2.78	13.5	-	-	-
5-40-5	9.2	25	5	26.5	4.12	20.1	3.19	-	-
5-40-6	9.2	30	5	28.5	5.56	27.0	3.24	1.81	1.79
5-40-7	9.2	35	5	32.3	6.76	32.3	-	-	-

Table V (Continued)

#	Acoustic Intensity (Wcm^{-2})	Reaction Time (min)	Initial Reaction Temperature (°C)	Final Reaction Temperature (°C)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6} [b] (g/mole)	Mn x 10^{-6} [c] (g/mole)	Mw/Mn
5-50-1	11.0	5	5	-	0	0	-	-	-
5-50-2	11.0	10	5	26.0	0.28	1.4	-	-	-
5-50-3	11.0	15	5	28.0	2.28	11.1	-	-	-
5-50-4	11.0	20	5	29.5	3.50	17.0	-	-	-
5-50-5	11.0	25	5	31.5	5.85	28.4	-	-	-
5-50-6	11.0	30	5	34.0	7.06	34.3	3.37	1.97	1.71
5-60-1	13.0	5	5	-	0	0	-	-	-
5-60-2	13.0	7	5	-	0.08	0.4	-	-	-
5-60-3	13.0	10	5	28.5	1.11	5.4	-	-	-
5-60-4	13.0	15	5	30.0	2.32	11.3	-	-	-
5-60-5	13.0	20	5	31.5	4.06	19.7	-	-	-
5-60-6	13.0	25	5	32.5	6.38	31.0	-	-	-
5-60-7	13.0	30	5	36.0	7.93	38.5	3.47	2.08	1.66
5-70-1	14.4	5	5	-	0	0	-	-	-
5-70-2	14.4	7	5	-	0.06	0.3	-	-	-
5-70-3	14.4	10	5	32.5	0.81	3.4	-	-	-
5-70-4	14.4	15	5	33.5	2.20	10.7	-	-	-
5-70-5	14.4	20	5	34.0	3.70	18.0	-	-	-
5-70-6	14.4	25	5	36.5	4.83	23.5	-	-	-
5-70-7	14.4	30	5	38.0	6.39	31.0	3.3	1.96	1.68

[a] MMA = 22 ml, water = 100 ml, sodium lauryl sulfate = 1 g, argon gas flow rate = 0.74 (ml/sec), cooling bath temperature = -10°C for all reactions.

[b] Weight average molecular weight

[c] Number average molecular weight

Table VI Effect of Acoustic Intensity on **Polymerization Rate**[a]

Power Setting Reading	Acoustic Power (W)	Acoustic Intensity (Wcm^{-2})	Conversion Curve Slope[b]	R_p (moles/ℓ-sec) **Polymerization Rate**
20	34	6.8	1.03	0.00035
30	38	7.6	1.06	0.00037
40	46	9.2	1.35	0.00046
50	55	11.0	1.62	0.00056
60	65	13.0	1.86	0.00064
70	72	14.4	1.33	0.00046

[a] R_p = Conversion curve slope x 10 x $\left(\frac{initial \quad wt \ of \ monomer}{initial \quad wt \ of \ water}\right)\left(\frac{1}{monomer \ molecular \ weight}\right) x \ \frac{1}{60}$,

MMA = 22 ml, water = 100 ml, sodium lauryl sulfate = 1 g, argon flow rate = 0.74 ml/sec, cooling bath temperature = -10°C.

[b] Conversion curve slope is taken by linear portion of time-% conversion curve.

Table VII Effect of Argon Gas Flow Rate on Polymer Yield and Polymer Molecular Weight [a]

#	Ar Flow Rate (ml/sec)	Reaction Time (min)	Initial Reaction Temperature (°C)	Final Reaction Temperature (°C)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6} [b] (g/mole)
6-0-1	0	5	5	-	0	0	0
6-0-2	0	10	5	-	0	0	0
6-0-3	0	15	5	-	0	0	0
6-0-4	0	20	5	-	0	0	0
6-0-5	0	25	5	-	0	0	0
6-0-6	0	30	5	-	0	0	0
6-0-7	0	35	5	-	0	0	0
6-0.25-1	0.25	10	5	-	0	0	-
6-0.25-2	0.25	15	5	20.5	0.34	1.6	-
6-0.25-3	0.25	20	5	22.5	1.3	6.3	-
6-0.25-4	0.25	25	5	23.5	2.58	12.5	-
6-0.25-5	0.25	30	5	24.5	3.71	18.1	-
6-0.25-6	0.25	35	5	26.0	4.76	23.1	3.02
6.0-25-7	0.25	40	5	28.0	5.74	27.8	-
6-0.32-1	0.32	7	5	-	0	0	0
6-0.32-2	0.32	10	5	20.0	0.2	1.0	2.78
6-0.32-3	0.32	15	5	21.5	1.01	4.9	3.05
6-0.32-4	0.32	20	5	23.0	2.52	12.2	-
6-0.32-5	0.32	25	5	25.5	3.61	17.5	3.18
6-0.32-6	0.32	30	5	28.0	4.86	23.6	-
6-0.32-7	0.32	35	5	31.0	6.35	30.8	3.18
6-0.42-1	0.42	7	5	-	0	0	-
6-0.42-2	0.42	10	5	20.0	0.04	0.2	-
6-0.42-3	0.42	15	5	21.5	1.28	6.2	-
6-0.42-4	0.42	20	5	22.5	2.54	12.4	-
6-0.42-5	0.42	25	5	25.5	3.75	18.2	-
6-0.42-6	0.42	30	5	29.0	5.20	25.2	-
6-0.42-7	0.42	35	5	32.0	6.49	31.5	3.23

Table VII (Continued)

#	Ar Flow Rate (ml/sec)	Reaction Time (min)	Initial Reaction Temperature (°C)	Final Reaction Temperature (°C)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6} [b] (g/mole)
6-0.54-1	0.54	5	5	-	0	0	-
6-0.54-2	0.54	10	5	20.0	0.49	2.4	-
6-0.54-3	0.54	15	5	21.5	1.75	8.5	-
6-0.54-4	0.54	20	5	23.0	3.34	16.2	-
6-0.54-5	0.54	25	5	26.0	4.55	22.1	-
6-0.54-6	0.54	30	5	29.5	5.77	28.0	-
6-0.54-7	0.54	35	5	32.5	7.10	34.5	3.252
6-0.67-1	0.67	5	5	-	0	0	-
6-0.67-2	0.67	10	5	22.0	0.95	4.6	-
6-0.67-3	0.67	15	5	24.0	2.48	12.0	-
6-0.67-4	0.67	20	5	25.0	3.48	17.0	-
6-0.67-5	0.67	25	5	27.0	5.11	24.8	-
6-0.67-6	0.67	30	5	30.0	6.41	31.1	-
6-0.67-7	0.67	35	5	33.0	7.70	37.4	3.270
6-0.78-1	0.78	5	5	-	0	0	-
6-0.78-2	0.78	8	5	24.0	0.49	2.4	-
6-0.78-3	0.78	10	5	24.5	1.00	4.9	-
6-0.78-4	0.78	15	5	25.5	2.52	12.2	-
6-0.78-5	0.78	20	5	26.5	3.82	18.5	-
6-0.78-6	0.78	25	5	27.5	5.25	25.5	-
6-0.78-7	0.78	30	5	31.0	6.90	33.5	-
6-0.78-8	0.78	35	5	33.5	8.49	41.2	3.281

[a] MMA = 22 ml, water = 100 ml, sodium lauryl sulfate = 1 g, acoustic intensity = 9.2 Wcm^{-2}, cooling bath temperature = -10°C for all reactions.

[b] Weight average molecular weight

Table VIII Effect of Argon Gas Flow Rate on Polymerization Rate[a]

Argon Gas Flow Rate (ml/sec)	Conversion Curve Slope[b]	R_p(moles/ℓ-sec) Polymerization Rate
0	0	0
0.25	1.12	0.00038
0.31	1.23	0.00042
0.42	1.25	0.00043
0.54	1.29	0.00044
0.67	1.31	0.00045
0.78	1.33	0.00046

[a] R_p = Conversion curve slope x 10 x $\left(\frac{\textit{initial wt of monomer}}{\textit{initial wt of water}}\right)\left(\frac{1}{\textit{monomer molecular weight}}\right) x \frac{1}{60}$,

MMA = 22 ml, water = 100 ml, sodium lauryl sulfate = 1 g,
acoustic intensity = 9.2 Wcm^{-2}, cooling bath temperature = -10°C.

[b] Conversion curve slope is taken by linear portion of time-% conversion curve.

Table IX Effect of Surfactant Concentration on Polymer Yield and Polymer Molecular Weight[a]

#	S[b] (g)	Reaction Time (min)	Initial Reaction Temperature (°C)	Final Reaction Temperature (°C)	Polymer Yield (g)	Wt% Conversion	$M_w \times 10^{-6}$[c] (g/mole)
7-0-1	0	35	5	-	0	0	0
7-0-2[d]	0	35	5	-	0.21	1.00	-
7-0.1-1	0.1	35	5	20.0	0.22	1.1	-
7-0.15-1	0.15	35	5	20.5	0.45	2.2	-
7-0.2-1	0.2	35	5	21.0	0.84	4.1	-
7-0.4-1	0.4	35	5	21.5	3.24	15.7	-
7-0.6-1	0.6	35	5	23.5	5.44	26.4	-
7-0.8-1	0.8	35	5	30.0	5.90	28.6	-
7-1-1	1	7	5	-	0	0	0
7-1-2	1	10	5	20.0	0.20	1.0	2.78
7-1-3	1	15	5	21.5	1.01	4.9	3.05
7-1-4	1	20	5	23.0	2.25	12.2	-
7-1-5	1	25	5	25.5	3.75	18.2	3.18
7-1-6	1	30	5	28.0	5.12	25.0	-
7-1-7	1	35	5	31.0	6.35	30.8	3.22
7-2-1	2	7	5	-	0	0	-
7-2-2	2	10	5	20.0	0.21	1.0	-
7-2-3	2	15	5	21.0	1.18	5.7	-
7-2-4	2	20	5	22.0	2.60	12.6	-
7-2-5	2	25	5	25.5	4.08	19.8	-
7-2-6	2	30	5	29.0	5.72	27.8	-
7-2-7	2	35	5	32.0	7.10	34.5	3.07

Table IX (Continued)

#	S^b (g)	Reaction Time (min)	Initial Reaction Temperature (°C)	Final Reaction Temperature (°C)	Polymer Yield (g)	Wt% Conversion	$Mw \times 10^{-6}$ [c] (g/mole)
7-3-1	3	5	5	-	0	0	-
7-3-2	3	10	5	21.0	0.994	4.8	-
7-3-3	3	15	5	22.0	2.260	11.0	-
7-3-4	3	20	5	24.5	3.380	16.4	-
7-3-5	3	25	5	26.0	4.210	23.2	-
7-3-6	3	30	5	30.5	6.310	30.7	-
7-3-7	3	35	5	33.5	7.950	38.6	2.882
7-4-1	4	5	5	-	0	0	-
7-4-2	4	10	5	22.5	1.05	5.1	-
7-4-3	4	15	5	23.5	2.30	11.2	-
7-4-4	4	20	5	24.5	3.73	18.1	-
7-4-5	4	25	5	26.0	4.95	24.0	-
7-4-6	4	30	5	31.0	6.46	31.3	-
7-4-7	4	35	5	34.0	8.33	40.4	2.714
7-5-1	5	5	5	-	0	0	-
7-5-2	5	10	5	23.5	1.16	5.6	-
7-5-3	5	15	5	24.5	2.87	14.0	-
7-5-4	5	20	5	25.5	4.43	21.5	-
7-5-5	5	25	5	26.5	5.97	29.0	-
7-5-6	5	30	5	31.0	7.58	36.8	-
7-5-7	5	35	5	34.5	9.17	44.5	2.548
7-6-1	6	5	5	-	0	0	-
7-6-2	6	10	5	24.5	1.26	6.1	-
7-6-3	6	15	5	25.5	2.90	14.1	-
7-6-4	6	20	5	26.5	4.75	23.0	-
7-6-5	6	25	5	27.5	6.65	32.3	-
7-6-6	6	30	5	32.0	8.24	40.0	-
7-6-7	6	35	5	35.0	9.93	48.2	2.383

Table IX (Continued)

#	S[b] (g)	Reaction Time (min)	Initial Reaction Temperature (°C)	Final Reaction Temperature (°C)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6} [c] (g/mole)
7-7-1	7	5	5	-	0	0	-
7-7-2	7	10	5	26.0	1.27	6.2	-
7-7-3	7	15	5	27.0	2.97	14.4	-
7-7-4	7	20	5	30.0	4.73	22.9	-
7-7-5	7	25	5	32.5	6.30	33.7	-
7-7-6	7	30	5	36.5	9.44	45.8	2.14

[a] MMA = 22 ml, water = 100 ml, intensity = 9.2 Wcm^{-2}, argon gas flow rate = 0.32 ml/sec, cooling bath temperature = -10°C for all reactions.

[b] Sodium lauryl sulfate, surfactant

[c] Weight average molecular weight

[d] 0.1% ammonium persulfate (based on water) was added.

Table X Effect of Surfactant Concentration on Polymerization Rate[a]

(S)[b] Wt (g)	[S][c] (mole/ℓ of Water)	Conversion Curve Slope[d]	R_p (moles/ℓ-sec) Polymerization Rate
1	0.035	1.23	0.00042
2	0.069	1.30	0.00045
3	0.104	1.34	0.00046
4	0.139	1.37	0.00047
5	0.174	1.55	0.00053
6	0.208	1.70	0.00058
7	0.243	1.91	0.00065

[a] R_p = conversion curve slope x 10 x $\left(\frac{\text{initial wt of monomer}}{\text{initial wt of water}}\right)\left(\frac{1}{\text{monomer molecular weight}}\right) x \frac{1}{60}$,

MMA = 22 ml, water = 100 ml, acoustic intensity = 9.2 W cm^{-2}, argon flow rate = 0.32 ml/sec, cooling bath temperature = -10°C.

[b] Sodium lauryl sulfate, surfactant

[c] Surfactant concentration

[d] Conversion curve slope is taken by linear portion of time-% conversion curve.

Table XI Effect of Initial Monomer Concentration on Polymer Yield and Polymer Molecular Weight[a]

#	MMA (ml)	Water (ml)	[M][b]	S[c] (g)	Reaction Time (min)	IT[d] (°C)	FT[e] (°C)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-4} [f] (g/mole)
8-a-1	6	116	0.48	1.16	7	5	-	0.24	4.2	-
8-a-2	6	116	0.48	1.16	10	5	18.5	0.51	9.0	-
8-a-3	6	116	0.48	1.16	15	5	20.0	1.32	22.0	-
8-a-4	6	116	0.48	1.16	20	5	21.0	2.22	39.6	-
8-a-5	6	116	0.48	1.16	25	5	24.0	3.13	55.8	-
8-a-6	6	116	0.48	1.16	35	5	27.5	3.63	64.7	-
8-a-7	6	116	0.48	1.16	40	5	28.0	3.65	65.1	-
8-a-8	6	116	0.48	1.16	50	5	29.0	3.66	65.2	-
8-a-9	6	116	0.48	1.16	55	5	30.0	3.76	67.0	-
8-a-10	6	116	0.48	1.16	70	5	31.5	4.14	73.6	-
8-a-11	6	116	0.48	1.16	85	5	32.5	3.87	68.8	-
8-a-12	6	116	0.48	1.16	100	5	34.0	3.81	67.8	-
8-b-1	6	116	0.48	1	7	5	-	0.13	2.3	2.04
8-b-2	6	116	0.48	1	10	5	18.0	0.41	7.4	-
8-b-3	6	116	0.48	1	15	5	19.5	1.20	21.2	2.36
8-b-4	6	116	0.48	1	20	5	21.0	2.20	39.3	2.43
8-b-5	6	116	0.48	1	25	5	23.5	3.07	54.7	-
8-b-6	6	116	0.48	1	35	5	27.0	3.40	61.0	2.47
8-b-7	6	116	0.48	1	40	5	27.5	3.53	63.0	-
8-b-8	6	116	0.48	1	50	5	28.5	3.61	64.3	-
8-b-9	6	116	0.48	1	55	5	29.5	3.71	66.1	2.49
8-b-10	6	116	0.48	1	70	5	31.0	3.96	70.5	2.54
8-b-11	6	116	0.48	1	85	5	32.0	3.65	65.0	2.38
8-b-12	6	116	0.48	1	100	5	33.5	3.61	64.3	2.36
8-c-1	12	110	1.02	1.1	7	5	-	0.21	1.9	-
8-c-2	12	110	1.02	1.1	10	5	19.0	0.73	6.5	-
8-c-3	12	110	1.02	1.1	15	5	21.5	1.47	13.1	-
8-c-4	12	110	1.02	1.1	20	5	24.0	2.27	22.5	-
8-c-5	12	110	1.02	1.1	25	5	26.5	3.71	33.0	-
8-c-6	12	110	1.02	1.1	32	5	29.5	4.94	44.0	-

Table XI (Continued)

#	MMA (ml)	Water (ml)	[M]^{b}	S^{c} (g)	Reaction Time (min)	IT^{d} (°C)	FT^{e} (°C)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6} ^{f} (g/mole)
8-d-1	12	110	1.02	1	7	5	-	0.195	1.7	-
8-d-2	12	110	1.02	1	10	5	18.5	0.650	5.8	-
8-d-3	12	110	1.02	1	15	5	20.5	1.410	12.6	-
8-d-4	12	110	1.02	1	20	5	23.5	2.240	20.0	-
8-d-5	12	110	1.02	1	25	5	26.0	3.390	30.0	-
8-d-6	12	110	1.02	1	32	5	29.0	4.760	42.4	2.80
8-e-1	18	104	1.62	1.04	7	5	-	0	0	-
8-e-2	18	104	1.62	1.04	10	5	20.0	0.175	1.0	-
8-e-3	18	104	1.62	1.04	15	5	21.5	1.390	8.3	-
8-e-4	18	104	1.62	1.04	20	5	23.0	2.700	16.0	-
8-e-5	18	104	1.62	1.04	25	5	25.5	3.680	21.9	-
8-e-6	18	104	1.62	1.04	30	5	28.0	4.770	28.3	-
8-e-7	18	104	1.62	1.04	35	5	31.0	6.120	36.4	-
8-f-1	18	104	1.62	1	7	5	-	0	0	-
8-f-2	18	104	1.62	1	10	5	19.5	0.155	9.9	-
8-f-3	18	104	1.62	1	15	5	20.5	1.290	7.7	-
8-f-4	18	104	1.62	1	20	5	22.0	2.540	15.1	-
8-f-5	18	104	1.62	1	25	5	25.0	3.470	20.6	-
8-f-6	18	104	1.62	1	30	5	27.5	4.720	28.0	-
8-f-7	18	104	1.62	1	35	5	30.5	6.060	35.9	3.06
8-g-1	22	100	2.06	1	7	5	-	0	0	-
8-g-2	22	100	2.06	1	10	5	20.0	0.20	1.0	-
8-g-3	22	100	2.06	1	15	5	21.5	1.01	4.9	-
8-g-4	22	100	2.06	1	20	5	23.0	2.52	12.2	-
8-g-5	22	100	2.06	1	25	5	25.5	3.75	18.2	-
8-g-6	22	100	2.06	1	30	5	28.5	5.12	24.8	-
8-g-7	22	100	2.06	1	35	5	31.0	6.35	30.8	3.22

Table XI (Continued)

#	MMA (ml)	Water (ml)	[M][b]	S[c] (g)	Reaction Time (min)	IT[d] (°C)	FT[e] (°C)	Polymer Yield (g)	Wt% Conversion	Mw x 10^{-6} [f] (g/mole)
8-h-1	30	92	3.05	0.92	7	5	-	0	0	-
8-h-2	30	92	3.05	0.92	10	5	22.5	0.04	0.1	-
8-h-3	30	92	3.05	0.92	15	5	24.0	0.85	3.0	-
8-h-4	30	92	3.05	0.92	20	5	25.5	2.14	7.6	-
8-h-5	30	92	3.05	0.92	25	5	27.5	3.55	12.2	-
8-h-6	30	92	3.05	0.92	30	5	30.5	4.87	16.6	-
8-h-7	30	92	3.05	0.92	35	5	31.0	5.77	20.6	-
8-h-8	30	92	3.05	0.92	45	5	34.0	7.51	28.5	-
8-i-1	30	92	3.05	1	7	5	-	0	0	-
8-i-2	30	92	3.05	1	11.5	5	23.0	0.38	1.4	-
8-i-3	30	92	3.05	1	15	5	24.5	1.03	3.7	-
8-i-4	30	92	3.05	1	20	5	26.5	2.35	8.4	-
8-i-5	30	92	3.05	1	25	5	28.5	3.76	13.4	-
8-i-6	30	92	3.05	1	35	5	32.0	5.88	21.0	3.24
8-i-7	30	92	3.05	1	45	5	35.0	8.22	29.3	-
8-j-1	37	85	4.07	0.85	10	5	-	0	0	-
8-j-2	37	85	4.07	0.85	13	5	24.0	0.06	0.2	-
8-j-3	37	85	4.07	0.85	15	5	25.5	0.86	1.8	-
8-j-4	37	85	4.07	0.85	20	5	27.0	1.32	3.8	-
8-j-5	37	85	4.07	0.85	25	5	28.5	2.27	6.6	-
8-j-6	37	85	4.07	0.85	30	5	30.0	4.07	10.4	-
8-j-7	37	85	4.07	0.85	35	5	30.5	4.99	13.2	-
8-j-8	37	85	4.07	0.85	45	5	31.0	6.40	18.5	-
8-k-1	48	73.5	6.11	0.74	35	5	28.0	2.28	5.1	
8-k-2	61	61	9.36	0.61	35	5	28.5	1.28	2.2	

[a] Acoustic intensity = 9.2 Wcm^{-2}, argon gas flow rate = 0.32 ml/sec, cooling bath temperature = -10°C for all reactions.
[b] Initial monomer concentration (moles/ℓ of water)
[c] Sodium lauryl sulfate, surfactant
[d] Initial reaction temperature
[e] Final reaction temperature
[f] Weight average molecular weight

Table XII Effect of Initial Monomer Concentration on Polymerization Rate[a]

[S][b] (g)	MMA (ml)	Water (ml)	Monomer/Water (Wt Ratio)	[Monomer] (mole/ℓ of water)	Conversion Curve Slope[c]	R_p(moles/ℓ-sec) **Polymerization Rate**
1.16	6	116	0.048	0.48	3.09	0.00025
1.00	6	116	0.048	0.48	2.99	0.00024
1.10	12	110	0.102	1.02	1.83	0.00031
1.00	12	110	0.102	1.02	1.82	0.00031
1.04	18	104	0.162	1.62	1.39	0.00037
1.00	18	104	0.162	1.62	1.38	0.00037
1.00	22	100	0.206	2.06	1.23	0.00042
0.92	30	92	0.306	3.05	0.83	0.00042
1.00	30	92	0.306	3.05	0.84	0.00043
0.85	37	85	0.407	4.07	0.58	0.00039

[a] R_p = conversion curve slope x $\left(\frac{initial \quad wt\ of\ monomer}{initial \quad wt\ of\ water}\right)\left(\frac{1}{monomer \quad molecular \quad weight}\right) x \frac{1}{60}$, acoustic intensity = 9.2 Wcm^{-2}, argon gas flow rate = 0.32 ml/sec, cooling bath temperature = -10°C.

[b] Sodium lauryl sulfate, surfactant

[c] Conversion slope is taken by linear portion of time-% conversion curve.

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

Radical Generation Process Studies and Kinetic Data Interpretation

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Keywords: Ultrasound, Radical Traps, Radical Scavenger, GC/MS.

SYNOPSIS

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 SDS 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 0.035 M to 0.139 M surfactant concentration range and (3b) the 1.09 power of the surfactant concentration within the 0.139 to 0.243 M surfactant concentration range. The generated free radical concentration, the number of polymer particles produced and 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.

INTRODUCTION

In the previous paper[1], we have reported the ultrasonically initiated emulsion polymerization of methyl methacrylate at ambient temperature using sodium lauryl sulfate as the surfactant in the absence of a conventional initiator. We have also reported the preliminary radical generation process study[2] and a specially designed GC-MS analytical method to identify the source of free radicals that served as initiators[3] in this ultrasonically initiated emulsion polymerization of methyl methacrylate.

Ultrasound was shown to be a useful tool for initiating the radical emulsion polymerization of methyl methacrylate 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 to 0.243 M surfactant concentration range.

In order to have a better understanding of the kinetics of the ultrasonically initiated emulsion polymerization of methyl methacrylate, 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 methyl methacrylate.

EXPERIMENTAL

Apparatus

The apparatus used was described in the previous papers[1,2,3].

Materials and Reagents

Sodium lauryl sulfate (assayed as SDS, 70% dodecyl sulfate, 25% tetradecyl sulfate and 5% hexadecyl sulfate sodium salt) and bromoform (99%) were obtained from the Aldrich Chemical Company and used as received. n-Propanol suitable for the use in liquid and gas chromatography was obtained from the Omnisolv Chemical Company 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 minutes. This solution was then introduced to the reactor, a 17 cm high x 6 cm diameter flat bottom pyrex glass tube. It was deoxygenated with argon gas for 3 minutes 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°C. During ultrasonic irradiation, dry argon was bubbled continuously through the solution in order to promote cavitation by providing nuclei for the formation of the bubbles. The reactor was ultrasonically irradiated for 30 minutes 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[3]. In the quantitative analysis procedure, the 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 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 in order 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 ± 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 gram of SDS, 100 ml of water and 100 ml of n-propanol.

RESULTS AND DISCUSSION

The 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 mole of SDS (1% based on the aqueous phase) and 0.48 mole of bromoform per liter of water at different acoustic intensities under an argon gas flow rate of 0.74 ml sec^{-1} in a -10°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^2 under a 0.74 ml /sec argon flow rate were shown in Figure 2 in the previous paper[1]. 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[1] and are summarized in Table I.

The total concentration of alkylbromide (C_a) and alkane free radical concentration (C_b) were reported in units of mg per ml 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 were shown in Figures 4, 5, 7 in the previous paper[1]. 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[1,3] 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[3].

In the previous paper[1], 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^2. These values then decreased at an acoustic intensity of 14.4 W/cm^2. The increase in polymerization rate with increasing acoustic intensity was attributed to an increase in total polymer particles generated assuming resulting from an increase in radical generation rate. It was also attributed to reaction rate constant increase as reaction temperature increase with acoustic intensity. The increase in polymer molecular weight with increasing acoustic intensity was attributed to gel effect[1].

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^2. This decrease in the extent of radical generation is attributed to a decrease in the number of cavitation bubbles after a maximum intensity peak[1]. 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[1] that an increase in the acoustic intensity resulting in increasing radical generation, thus produce more polymer particles and enhance polymerization rate.

The rate of emulsion polymerization per liter of water and number average degree of polymerization can be expressed as follows[4-6] :

$$R_p = n\ N\ K_p\ [\ M\ ]_p \qquad \text{-------(1)}$$

$$X_n = R_p\ /\ R_i = n\ N\ K_p\ [\ M\ ]_p\ /\ R_i \qquad \text{-------(2)}$$

where n is the average number of radicals per particle, $[M]_p$ is the monomer concentration in a polymer particle in moles/L, K_p is the propagation constant in L/mole-sec, N is the number of polymer particles per liter of water and R_i is initiation rate in moles/L-sec.

Since 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 N due 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, (3) gel effect. As a result, the polymerization 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 increase 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 lowering molecular weight. This gel effect phenomenon was observed at higher acoustic intensity based on the molecular development curve shown in previous paper[1].

The 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 mole of SDS (1% based on the aqueous phase) and 0.48 mole of bromoform 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 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[1] 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 Figure 9, 10, 12 in the previous paper[1]. 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[1], 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[1]to an increase in total polymer particles generated assuming resulting from an increase in radical generation rate. It was also attributed to slightly reaction rate constant increase as reaction temperature slightly increase with argon gas flow rate. The increase in polymer molecular weight with increasing argon gas flow rate was attributed to gel effect[1].

From the data given in Table II and Figure 3, it appears 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[1] that increasing argon gas flow rate resulting in increasing radical generation, thus produce more polymer particles and enhance polymerization rate.

Since 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 N due to the increase in radical generation rate resulting from an increase in the number of cavitation bubbles, (2) an slightly increase in the propagation rate constant due to the slightly 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 apparent 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 increasing the initiation rate and lowering molecular weight.

The 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 different amount of surfactant and 0.48 mole of bromoform per liter of water at an acoustic intensity of 9.2 W/cm^2 under an argon gas flow rate of 0.32 ml/sec in a -10°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[1] and are summarized in Table III. The log-log 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 Figure 15, 16, 18 in the previous paper[1]. 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[1], the polymerization rate and polymer particle number were shown to increase as the 0.08 and 0.3 power of the surfactant concentration respectively with the surfactant concentration increasing from 0.035 M to 0.139 M. The polymerization rate and polymer particle number then increased as the 0.58 and 1.87 power of the surfactant concentration respectively with the surfactant concentration increasing from 0.139 M to 0.243 M. This increase in polymerization rate with increasing surfactant concentration was assumed[1] to be due to the increase in radical generation rate, micellar, homogeneous nucleation and reaction temperature. The polymer weight average molecular weight was shown to decrease as the 0.12 power of the surfactant concentration with the surfactant concentration increasing from 0.035 M to 0.139 M. The polymer weight average molecular weight then decreased as the 0.34 power of the surfactant concentration with the surfactant concentration increasing from 0.139 M to 0.243 M. This decrease in polymer molecular weight with increasing surfactant concentration was assumed[1] 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 appears that the free radical concentration generated in the SDS aqueous solution increased as the 0.35 power of the surfactant concentration with the surfactant concentration increasing from 0.035 M to 0.139 M. The free radical concentration generated then increased as the 1.09 power of the surfactant concentration with the surfactant concentration increasing from 0.139 M to 0.243 M. 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[1] that increasing surfactant concentration resulting in increasing radical generation, thus produce more polymer particles and enhance polymerization rate.

Since 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 N due to the increase in radical generation rate resulting from an increase in the number of surfactant molecules that serve as initiators, and (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, (3) an increase in micelle and homogeneous nucleation. As a result, the polymerization rate will increase with increasing surfactant concentration due to the increases in radical generation rate, micellar, homogeneous nucleation and reaction temperature. Figure 6 summaries 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 x K_p, which leads to higher molecular weight. This explains our assumption[1] 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.

CONCLUSION

1. The radical generation rate, the polymer particles number generated and the polymerization rate all increase with increasing acoustic intensity from 6.8 to 13.0 W/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/sec. 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 0.035 M to 0.243 M. The increase in polymerization rate with increasing surfactant concentration is attributed to an increase in the radical generation rate, micellar, homogeneous nucleation and reaction temperature. Polymer molecular weight decreases with increasing surfactant concentration from 0.035 M to 0.243 M. 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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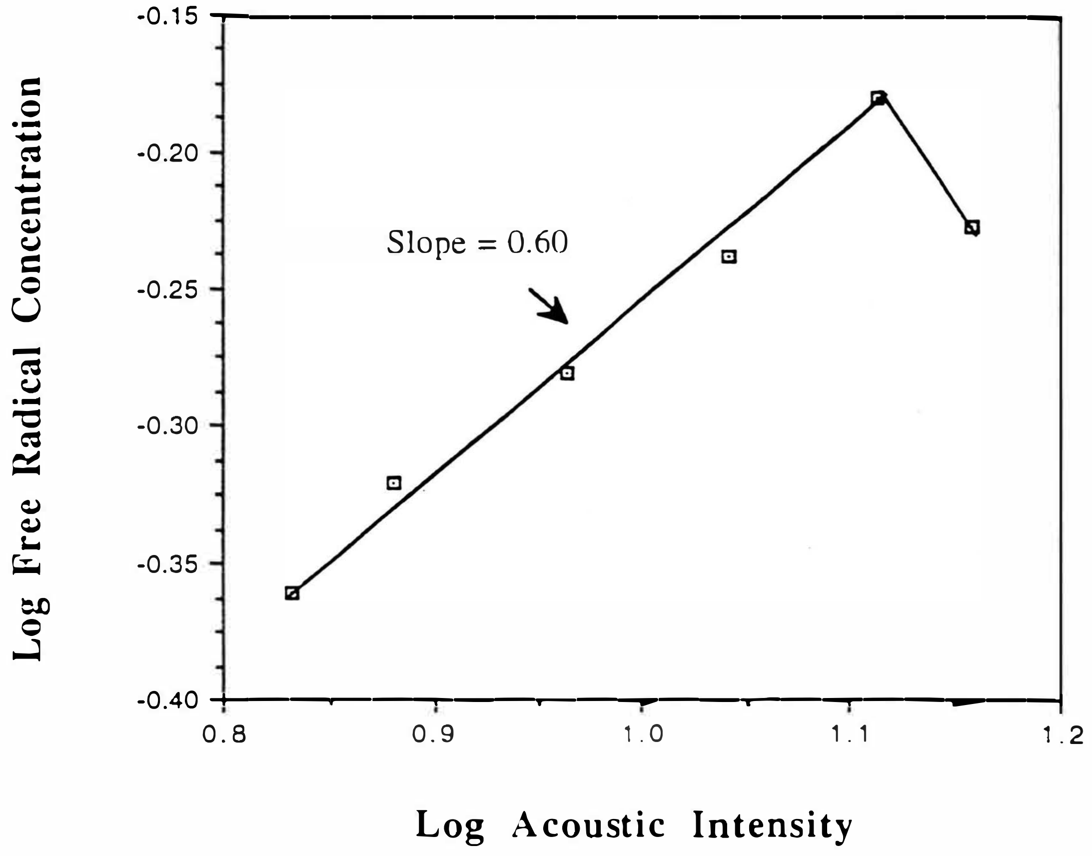

Figure 1. Effect of acoustic intensity on radical concentration in SDS aqueous solution. (water =100 ml, bromoform = 4.2 ml, SDS =1 g, argon gas flow rate = 0.74 ml/sec, sonication time = 30 minutes, cooling bath temperature = -10°C)

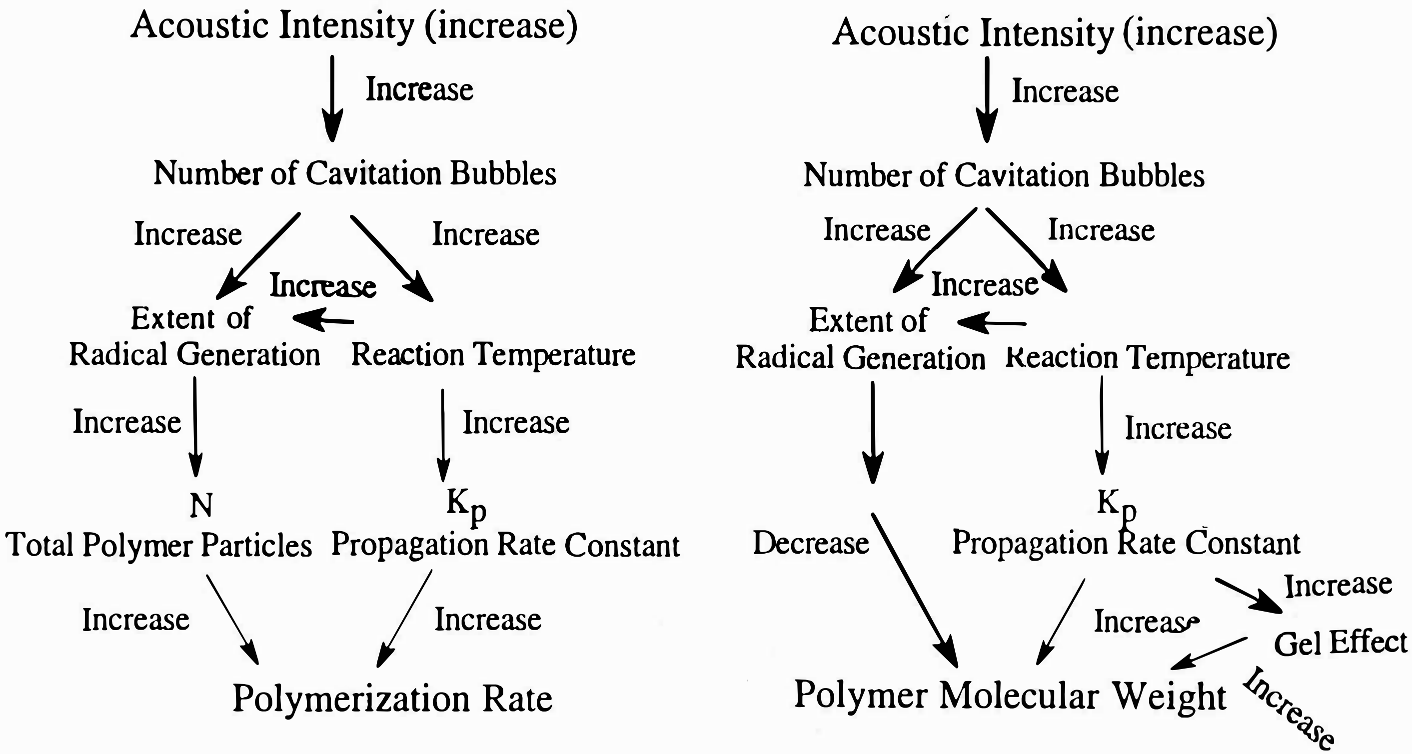

Figure 2. Summaries of relationship between acoustic intensity, extent of radical generation, apparent polymerization rate and polymer molecular weight.

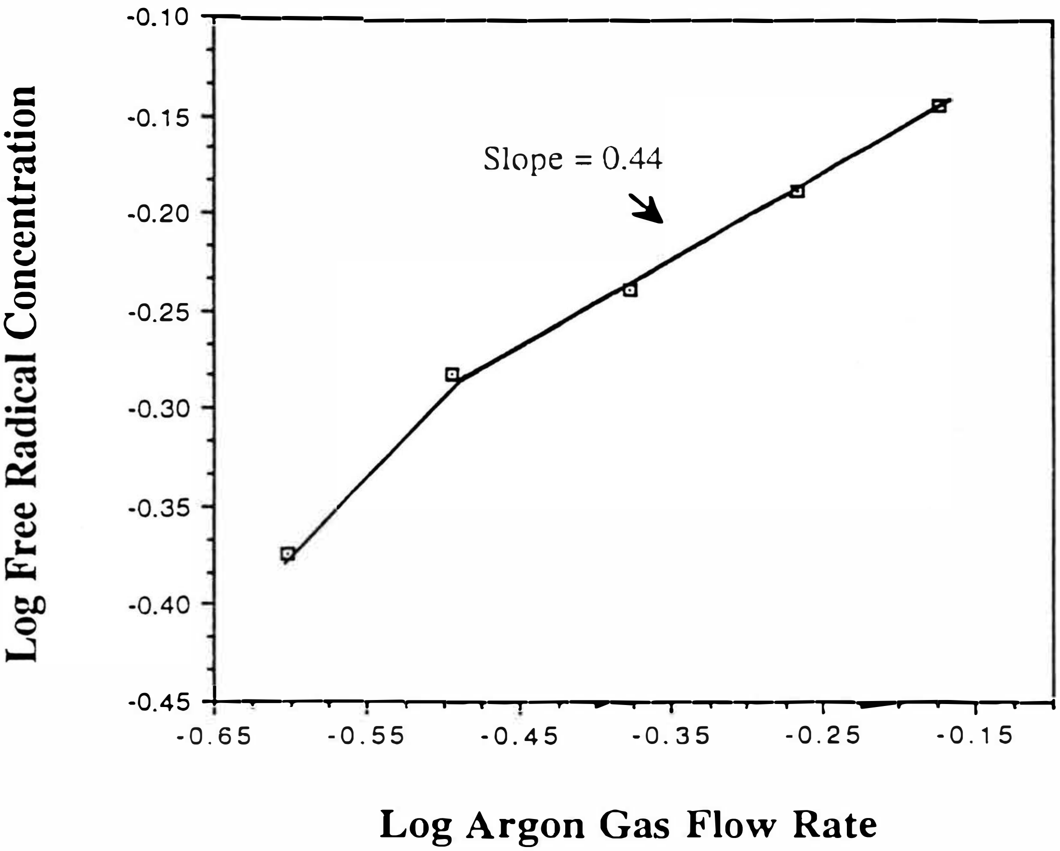

Figure 3. Effect of argon gas flow rate on radical concentration in SDS aqueous solution. (water = 100 ml, SDS = 1 g, bromofrom = 4.2 ml, acoustic intensity = 9.2 Wcm-2, sonication time = 30 minutes, cooling bath temp. = -10°C)

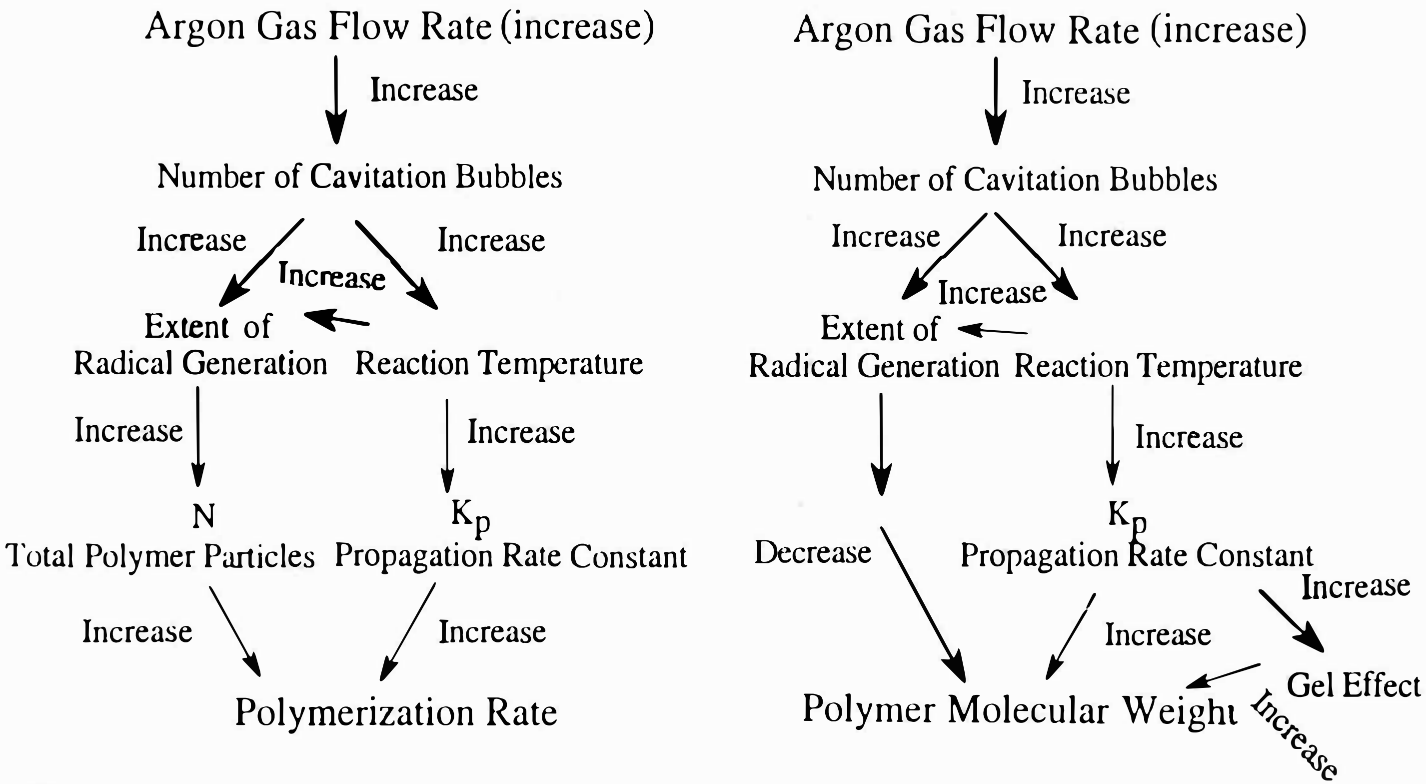

Figure 4. Summaries of relationship between argon gas flow rate, extent of radical generation, apparent polymerization rate and polymer molecular weight.

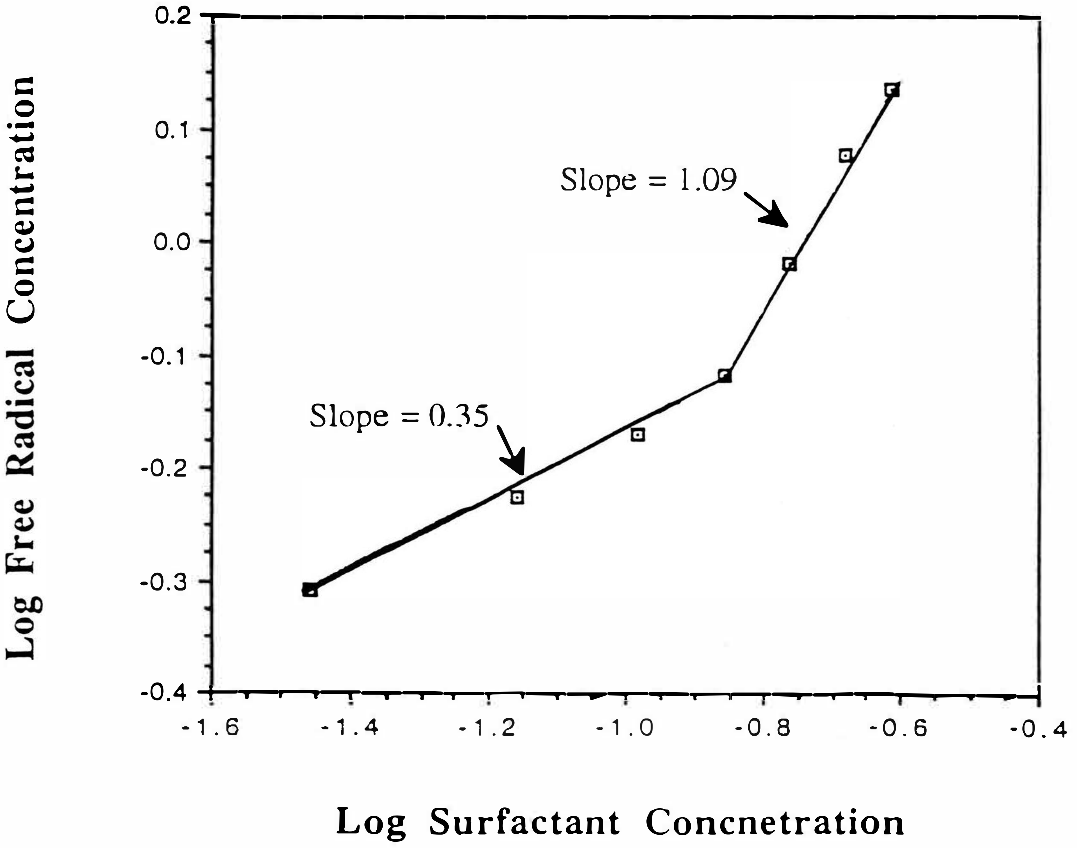

Figure 5. Effect of surfactant concentration on radical concentration in SDS aqueous solution. (water = 100 ml, bromoform = 4.2 ml, acoustic intensity = 9.2 Wcm^{-2},argon gas flow rate = 0.32 ml/sec, sonication time = 30 minutes, cooling bath temp. = -10°C)

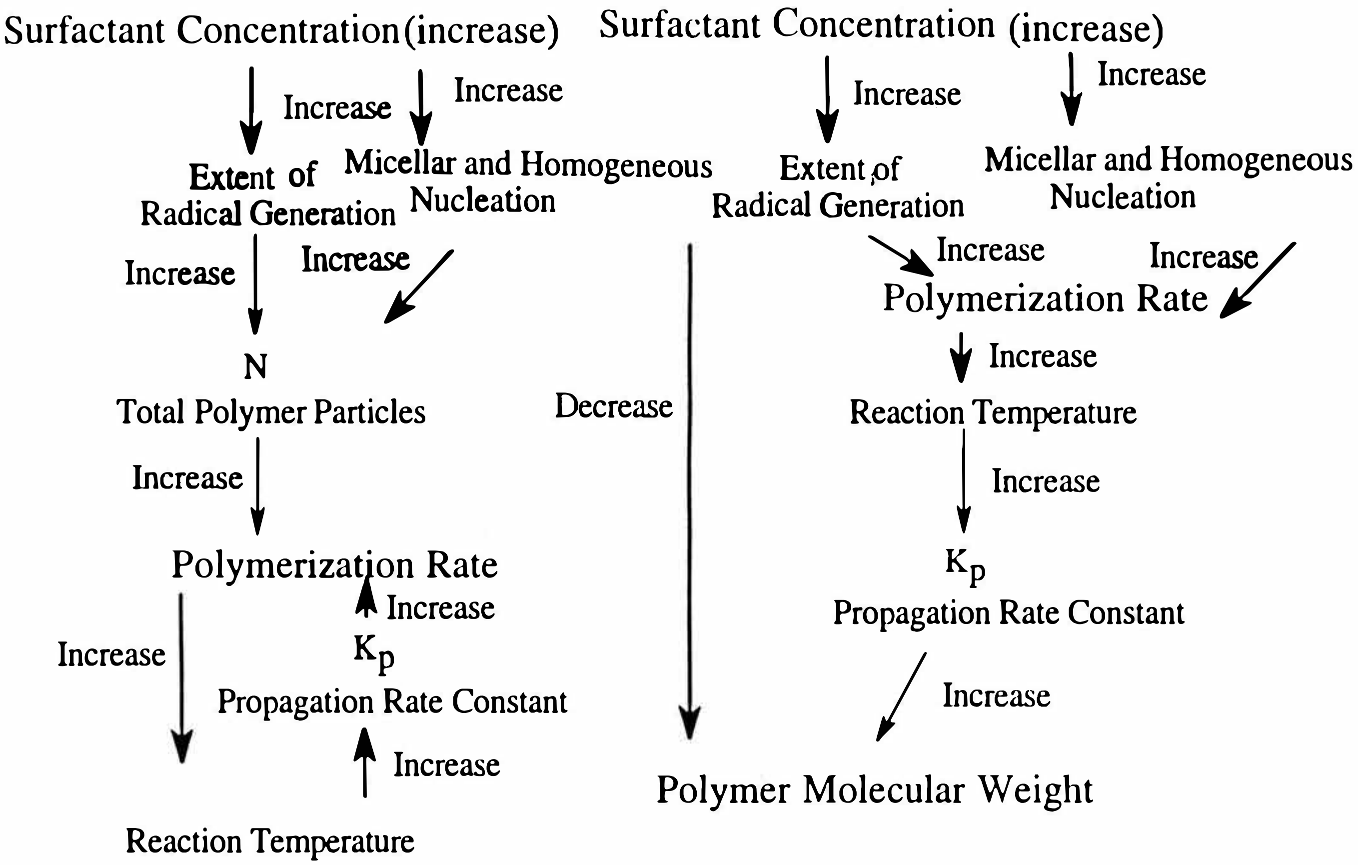

Figure 6. Summaries of relationship between surfactant concentration, extent of radical generation rate, apparent polymerization rate, polymer molecular weight.

Table I Effect of Acoustic Intensity on Radical Concentration, Polymerization Rate and Polymer Molecular Weight for the Ultrasonically Initiated Emulsion Polymerization of Methyl methacrylate[a]

No	Acoustic Intensity (Wcm^{-2})	C_a[b] (mg / ml)	C_b[c] (mg / ml)	R_p[d] x 10^4 (moles / l-sec)	M_w[e] x 10^{-6} (g / mole)
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

[a] Sample solution used for radical concentration studies was prepared by 100 ml of water, 4.2 ml of bromoform and 1g of SDS. Argon gas flow rate used was 0.74 ml/sec, sonication time was 30 min. and cooling bath temp. was -10 °C.

[b] C_a is total concentration in mg per ml of water of 1-bromododecane, 1-bromotetradecane and1-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 reference 1.

[e] M_w is weight average molecular weight cited from reference 1.

Table II Effect of Argon Gas Flow Rate on Radical Concentration, Polymerization Rate and Polymer Molecular Weight for the Ultrasonically Initiated Emulsion Polymerization of Methyl methacrylate[a]

No	Ar Flow Rate (ml / sec)	C_a[b] (mg / ml)	C_b[c] (mg / ml)	R_p[d] x 10^4 (moles / l-sec)	M_w[e] x 10^{-6} (g / mole)
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

[a] Sample solution used for radical concentration studies was prepared by 100 ml of water, 4.2 ml of bromoform, and 1g of SDS. Acoustic intensity used was 9.2 Wcm^{-2}, sonication time was 30 min. and cooling bath temp. was -10 °C.

[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 reference 1.

[e] M_w is weight average molecular weight cited from reference 1.

Table III Effect of Surfactant Concentration on Radical Concentration, Polymerization Rate and Polymer Molecular Weight for the Ultrasonically Initiated Emulsion Polymerization of Methyl methacrylate[a]

No	[SLS] (moles / l)	C_a[b] (mg / ml)	C_b[c] (mg / ml)	R_p[d] x 10^4 (moles / l-sec)	M_w[e] x 10^{-6} (g / mole)
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

[a] 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 Wcm^{-2}, argon gas flow rate was 0.32 ml/sec, sonication time was 30 min. and cooling bath temp. was -10 °C.

[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 reference 1.

[e] M_w is weight average molecular weight cited from reference 1.

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

Tacticity and T_g Investigation

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Keywords: Tacticity, Glass Transition Temperature, IR, NMR.

SYNOPSIS

In this paper, we investigate the effect of changes in acoustic intensity, argon gas flow rate and surfactant concentration on tacticity and T_g of the resulting poly(methyl methacrylate), PMMA, from the ultrasonically initiated free radical catalyzed emulsion polymerization. The tacticities of the resulting polymers were compared with those obtained by the conventional radically initiated polymerization method and ultrasonically initiated bulk polymerization method to see whether there is any effect on the propagation reaction under the ultrasonically initiated emulsion polymerization. The effects of acoustic intensity, argon gas flow rate and surfactant concentration on tacticity, T_g, R_p (polymerization rate), and M_w (weight average molecular weight) are compared in order to gain a

better understanding of ways to control these variables in ultrasonically initiated free radical catalyzed emulsion polymerization. The resulting PMMA polymers produced from ultrasonically initiated free radical catalyzed emulsion polymerization are predominantly syndiotactic polymers. Changing any of these variables had little effect on the microstructure of propagation reaction when compared to conventional radically initiated and ultrasonically initiated bulk polymerization methods.

INTRODUCTION

It is well recognized that polymer tacticity (or stereoregularity) has a significant influence on the physical and mechanical properties of a polymer. For example, atactic polypropylene is a soft, tacky substance, while both isotactic and sydiotactic polypropylene are high crystalline. Isotactic poly(methyl methacrylate) (PMMA) has a crystalline melting point (T_m) of 160°C, whereas the T_m of sydiotactic PMMA is 200°C. The glass transition temperature (T_g) occurs at about 43°C for isotactic PMMA and at 160°C for sydiotactic PMMA because of an increase in the stiffness of the polymer chains. The conventional radical initiation polymerization and ultrasonically initiated bulk polymerization of methyl methacrylate were both found to produce predominantly sydiotactic PMMA chains. In this paper, we investigate the effect of acoustic intensity, argon gas flow rate and surfactant concentration on tacticity and T_g of resulting PMMA from the ultrasonically initiated free radical catalyzed emulsion polymerization. The tacticities of the resulting polymers were compared with those obtained by the conventional radical initiation polymerization method and ultrasonically initiated bulk polymerization method to see whether there is any effect on the propagation reaction under the ultrasonically initiated emulsion polymerization.

The effects of acoustic intensity, argon gas flow rate and surfactant concentration on tacticity, T_g, R_p (polymerization rate), and M_w (weight average molecular weight) are compared in order to gain a better understanding of ways to control these variables in ultrasonically initiated free radical catalyzed emulsion polymerization.

EXPERIMENTAL

Reagents and Materials

Poly(methyl methacrylate) (PMMA) was obtained from previous work[1-3]. Tetrahydrofuran (THF), deuterated chloroform, and tetramethylsilane (TMS) were obtained from the Aldrich Chemical Company and used as received.

Ultrasonic Polymerization, Polymer Separation and Purification

The ultrasonically initiated emulsion polymerization procedure, reaction apparatus, emulsion recipes used for acoustic intensity, argon gas flow rate and surfactant concentration studies, polymer separation, and polymer purification are described in previous work[1,2,3]. In this system[2] the surfactant also acts as the free radical initiator.

IR Analysis

Infrared (IR) spectra were obtained on a perkein Elmer 283 spectrophotometer. The PMMA films for analysis were casted from THF solution at room temperature.

NMR Analyses and Tacticity Determination

^{1}H-NMR spectra of the polymer samples were determined by the use of an FT-NMR spectrometer (JEOL, 200MHz) at ambient temperature. The polymers were dissolved (10wt%) in deuterated chloroform with TMS as an internal standard.

Syndiotactic (S), atactic (A) and isotactic (I) triads were determined from peak areas of α methyl proton at chemical shift[4] of 0.9, 1.03 and 1.2 ppm respectively, in NMR spectra of PMMA. The probability of generating a meso sequence, P_m or (σ) , for Bernoullian statistics during propagation can be calculated by eq. (1), (2) and (3) derived from Bovey and Tiers[5,6] :

$$(I) = P_m^2 \text{ or } (I) = \sigma^2 \qquad \text{--------(1)}$$

$$(A) = 2\,P_m\,(1-P_m) \text{ or } (A) = 2\,\sigma\,(1-\sigma) \qquad \text{--------(2)}$$

$$(S) = (1-P_m)^2 \text{ or } (S) = (1-\sigma)^2 \qquad \text{--------(3)}$$

where (I), (A) and (S) show the probability of forming isotactic, atactic and syndiotactic triads, respectively. A parameter indicating a deviation from Bernoullian statistics was obtained[7] using eq. (4):

$$U = 4\,(I)\,(S)/(A)^2 \qquad \text{--------(4)}$$

Glass Transition Temperature (T_g) Determination

The T_g of PMMA was determined with a Differential Scanning Calorimeter (DSC-4, Perkin Elmer) which is repeatedly calibrated with an indium standard. Samples were heated to 180°C for 2.5 minutes under nitrogen and quenched to 50°C. After 3 minutes, samples were reheated from 50°C to 180°C under nitrogen at 20°C /min heating rate. T_g was identified as the midpoint of the endothermic displacement between linear baselines. The Fox equation[8] was used to predict the T_g of resulting PMMA as follows:

$$1/T_{gr} = W_i / T_{gi} + W_a / T_{ga} + W_s / T_{gs}$$

where T_{gr} is T_g of resulting PMMA. T_{gi} (43°C), T_{ga} (105°C), and T_{gs} (160°C) is T_g of isotactic, atactic and syndiotactic PMMA, respectively[9]; while W_i, W_a and W_s is weight fraction of isotactic, atactic and syndiotactic chains in the resulting PMMA, respectively. Weight fraction in this case could be replaced by mole fraction because isotactic, atactic and syndiotactic PMMA have same molecular weight.

RESULTS AND DISCUSSION

IR Analysis

The IR spectrum of atactic and isotactic PMMA from the literature[10] are presented in Figure 1. A typical IR spectrum obtained at an acoustic intensity of 13 W/cm^2 is shown in Figure 2 and is representative of the remaining samples obtained at other experimental conditions.

As shown in Figure 1, the atactic PMMA has a strong doublet in the 1200-1300 cm^{-1} region, but the isotactic PMMA has a single absorption band in this region. All PMMA spectra obtained from our study possess a strong doublet in the 1200-1300 cm^{-1} region. This rules out the possibility of obtaining predominantly isotactic PMMA in our ultrasonically initiated emulsion polymerization system. Commercial sydidotactic PMMA has an IR spectrum identical with atactic PMMA. Thus Proton NMR analysis is further used to quantitatively determine the tacticity of the resulting polymers.

The Effect of Acoustic Intensity on T_g , R_p and M_w

A typical proton NMR spectrum obtained at an acoustic intensity of 13 W/cm^2 is shown in Figure 3 and is representative of the remaining samples obtained at other acoustic intensities. Triad tacticity of the PMMA polymers calculated from the NMR spectra, along with T_g calculated by the Fox equation, polymerization rate and weight average molecular weight from previous work,[1,2,3] are summarized in Table I. The Triad tacticity of the PMMA polymers obtained from Bovey's[5,11] and Price's[12] work in conventional radical initiated polymerization and ultrasonically initiated bulk polymerization are summarized in Table II. As can be seen from Table I, the P_m value increases from 0.188 to 0.233 as acoustic intensity used in ultrasonically initiated emulsion polymerization system increases from 6.8 to 14.4 W/cm^2. All φ values are close to unity, indicating that the polymers conform to Bernoullian statistics. These P_m values are similar to those P_m values shown in Table II which were obtained from the conventional free radical initiated polymerization and the ultrasonically initiated bulk polymerization methods. It confirms that sonication with different acoustic intensities in the emulsion polymerization system leads to predominantly syndiotactic polymers and has little effect on the microstructure of propagation reaction. However, lowering the acoustic intensity used in ultrasonically initiated emulsion polymerization system lowers the final reaction temperature of the polymerization system. This raises the proportion of syndiotacticity along the polymer chain and lowers the P_m value. There is additional energy required for isotactic placement[11] because the repulsive forces required for the bulky ester groups in isotactic polymer chains. Therefore, as the reaction temperature is lowered, more thermodynamically favored syndiotactic addition occurs.

The glass transition temperature of a polymer is mainly determined by the polymer's M_w and microstructure[13]. In our ultrasonically initiated emulsion polymerization system, M_w ranged from 2.5 to 3.5 million g/mole. Therefore, the effect of M_w on T_g is limited (i.e., $T_g = T_g^{\infty} - k / M)^{13}$ and the microstructure of polymer becomes the major factor in determining the T_g of the PMMA.

As can be seen from Table I, the T_g values calculated by the Fox equation match well with the T_g values obtained from DSC measurement. T_g decreases from 128.7°C to 121.2°C as the acoustic intensity used in ultrasonically initiated emulsion polymerization system increases from 6.8 to 14.4 W/cm^2· This can be explained by the factor of final reaction temperature. As the acoustic intensity increases, the final reaction temperature of the polymerization increases. This lowers the proportion of syndiotacticity in polymer chains which lowers the T_g of the polymers.

According to Table I, the M_w of PMMA increases from 3.04×10^6 to 3.47×10^6 and the R_p increases from 3.49×10^{-4} to 5.90×10^{-4} mole/L-sec, when the acoustic intensity used in ultrasonically initiated emulsion polymerization increases from 6.8 to 13.0 W/cm^2. The effect of acoustic intensity on R_p and M_w evidentially is more significant than the effect of acoustic intensity on tacticity and T_g. Therefore, acoustic intensity is a parameter in the ultrasonically initiated emulsion polymerization which could be used to control R_p and M_w. Like conventional radical initiated polymerizations[5,11] and ultrasonically initiated bulk polymerization[12], the reaction temperature of ultrasonically initiated emulsion polymerization system remains the main parameter which could be used to control T_g and microstructure of the resulting polymer.

The Effect of Argon Gas Flow Rate on Tacticity, T_g, R_p and M_w

Triad tacticity and T_g of the PMMA polymers along with polymerization rate and weight average molecular weight are summarized in Table III. As can be seen from Table III, the P_m value increases from 0.192 to 0.209 as argon gas flow rate used in ultrasonically initiated emulsion polymerization system increases from 0.25 to 0.78 ml/sec. This shows that sonication with different argon gas flow rates in the emulsion polymerization system leads to predominantly syndiotactic polymers and has little effect on the microstructure of the propagation reaction. At an argon gas flow rate of 0.25 ml/sec, the final reaction temperature is 26°C,which produced a slightly higher proportion of sydiotactic chains (64.7%). For the rest of argon gas flow rate studied, the final temperature reached in the polymerization reaction system is similar, therefore no difference of the proportion of sydiotactic chains was observed in the resulting polymers. All P_m values obtained are close to 0.2.

As can be seen from Table III, the T_g values calculated by the Fox equation match well with the T_g values obtained from DSC measurement. T_g decreases from 127.3°C to 123.4°C when the argon gas flow rate used in ultrasonically initiated emulsion polymerization system increases from 0.25 to 0.78 ml/sec. The lowest final reaction temperature was observed at the lowest argon flow rate. This resulted in a higher proportion of sydiotactic chains being formed, thus a higher T_g polymer. For the rest of argon gas flow rates studied, a smaller proportion of sydiotactic chains are produced. Thus, very little difference in T_g of the resulting polymer was observed for the rest of the polymerization.

From the data in Table III, one can see that M_w of PMMA increases from 3.02×10^6 to 3.28×10^6 and R_p increases from 3.83×10^{-4} to 4.57×10^{-4} mole/L-sec, when argon gas flow rate used in ultrasonically initiated emulsion polymerization system increases from 0.25 to 0.78 ml/sec. There is little effect of changing the argon gas flow rate on the R_p, M_w, tacticity and T_g of the resulting polymer. Therefore, argon gas flow rate is not a significant parameter which could be used in the ultrasonically initiated emulsion polymerization system to control the R_p, M_w, T_g and microstructure of the resulting polymer.

The Effect of Surfactant Concentration (Initiator) on Tacticity, T_g , R_p and M_w

Triad tacticity and T_g of the PMMA along with polymerization rate and weight average molecular weight are summarized in Table IV. As can be seen from the table, the P_m value increases from 0.199 to 0.226 when the surfactant concentration used in ultrasonically initiated emulsion polymerization system increases from 0.04 to 0.24 M. In this case the surfactant also serves as the initiator. This result shows that sonication with different surfactant concentrations in emulsion polymerization system leads to predominantly syndiotactic polymers and has little effect on the microstructure of propagation reaction. The final reaction temperature in the polymerization system increases from 31°C to 36.5°C when the surfactant concentration used in ultrasonically initiated emulsion polymerization system increases from 0.04 to 0.24 M due to the heat released from increased the polymerization rate. As a result, less proportion of syndiotactic chains were produced and a higher P_m value was obtained when the surfactant concentration used in ultrasonically initiated emulsion polymerization system is increased.

As can be seen from Table IV, the T_g values calculated by the Fox equation again match well with the T_g values obtained from DSC measurement. The value of T_g decreases from 126.0°C to 120.0°C when surfactant concentration, which is also the initiator, used in ultrasonically initiated emulsion polymerization system increases from 0.04 to 0.24 M. Higher surfactant concentration used in ultrasonically initiated emulsion polymerization system results in a higher final reaction temperature in polymerization system and produces less fraction of syndiotactic chains, therefore a lower T_g for the polymer.

From the data shown in Table IV, it can be seen that M_w of PMMA decreases from 3.22×10^6 to 2.14×10^6 and R_p increases from 4.22×10^{-4} to 6.54×10^{-4} mole/L-sec, when surfactant concentration used in ultrasonically initiated emulsion polymerization system increases from 0.04 to 0.24 M. The effect of surfactant concentration on R_p and M_w is obviously more significant than the effect of surfactant concentration on tacticity and $T_{g.}$ Therefore, surfactant concentration, which is also the initiator, is a parameter in ultrasonically initiated emulsion polymerization system which could be used to control R_p and $M_{w.}$

CONCLUSION

Ultrasonically initiated free radical polymerization were studied at different acoustic intensities, argon gas flow rates, surfactant concentrations and with one variable changed at a time. The P_m value increased from 0.188 to 0.233 and T_g of the PMMA decreased from 128.7°C to 121.2°C when acoustic intensity used in ultrasonically initiated emulsion polymerization system increases from 6.8 to 14.4 W/cm^2. The P_m value increased from 0.192 to 0.209 and T_g of PMMA decreased from

127.3°C to 123.4°C when argon gas flow rate increased from 0.25 to 0.67 ml/sec. The P_m value increased from 0.199 to 0.226 and T_g of PMMA decreased from 126°C to 120.0°C when surfactant concentration increased from 0.04 to 0.24 M.

The resulting PMMA polymers produced are predominantly syndiotactic polymers. Changing any of these variables had little effect on the microstructure of propagation reaction when compared to conventional radically initiated and ultrasonically initiated bulk polymerization methods. Acoustic intensity and surfactant concentration are the parameters which could be used to control R_p and M_w. However, they are not significant parameters which could be used to control T_g and microstructure of the resulting polymer. Changing the argon gas flow rate caused a slight change in the R_p, M_w, T_g and microstructure of the resulting polymer. Therefore, the argon gas flow rate is not a significant parameter which could be used to control R_p, M_w, T_g and microstructure of the resulting polymer.

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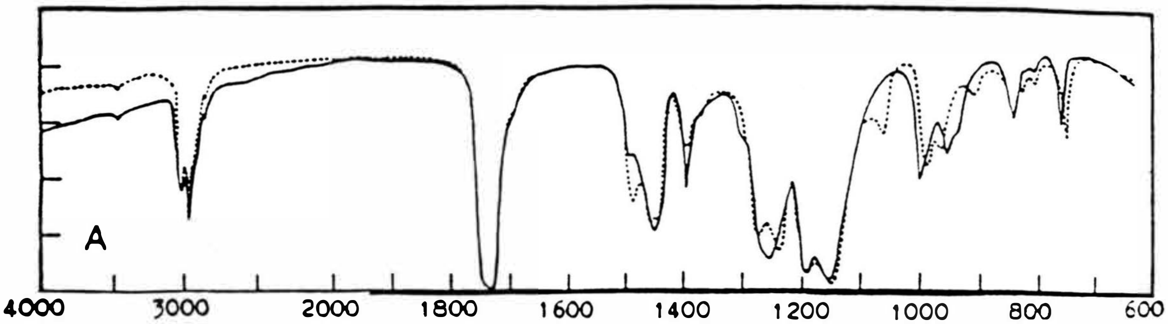

Figure 1. IR spectra of PMMA from reference 10.
(——) isotactic polymer
(------) atactic polymer

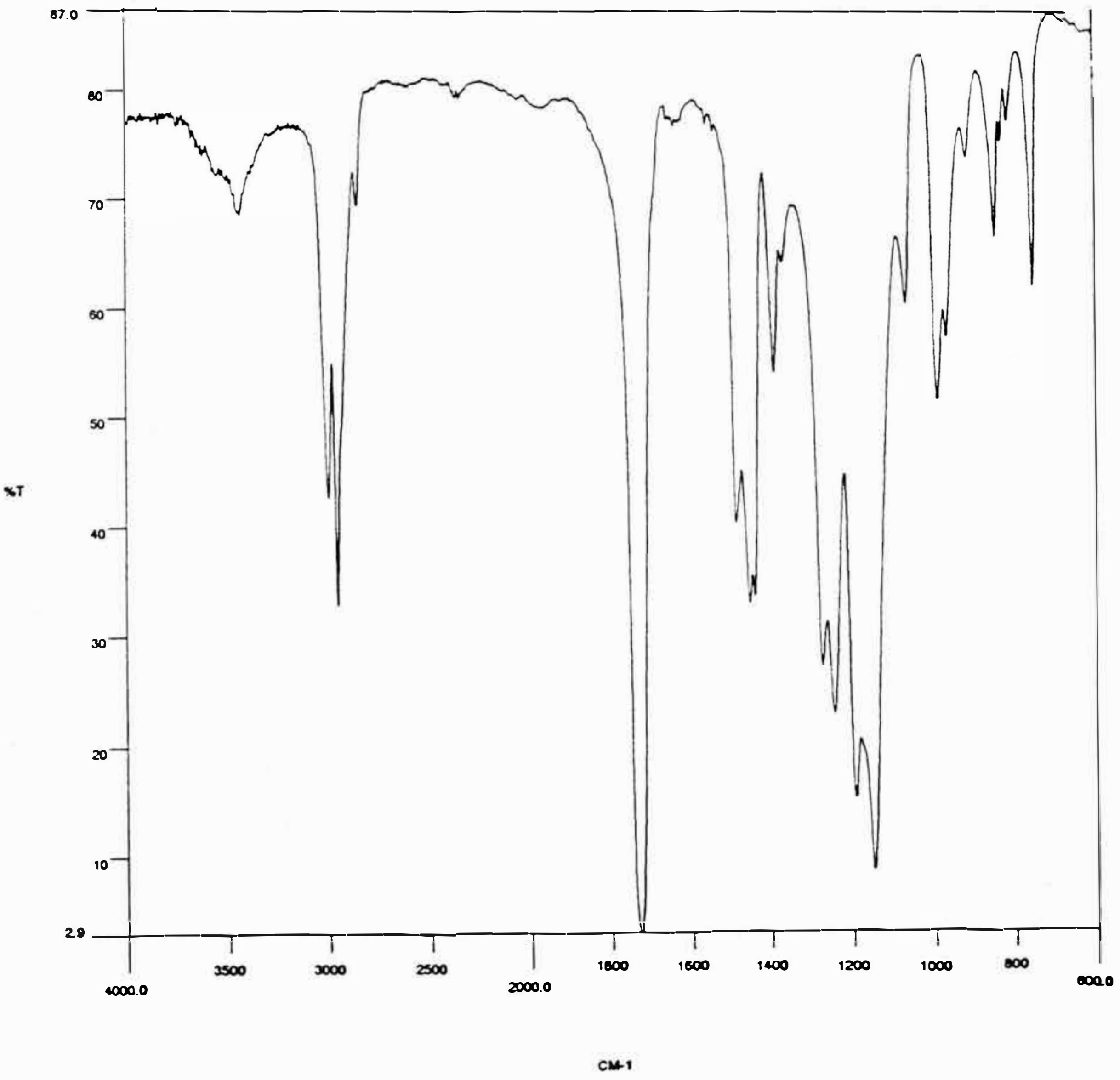

Figure 2. IR spectrum of PMMA obtained at 13.0 Wcm-2 acoustic intensity. (MMA = 22 ml, water = 100 ml, SDS =1 g, argon gas flow rate = 0.74 ml/sec, sonication time = 30 minutes, cooling bath temp.= -10°C)

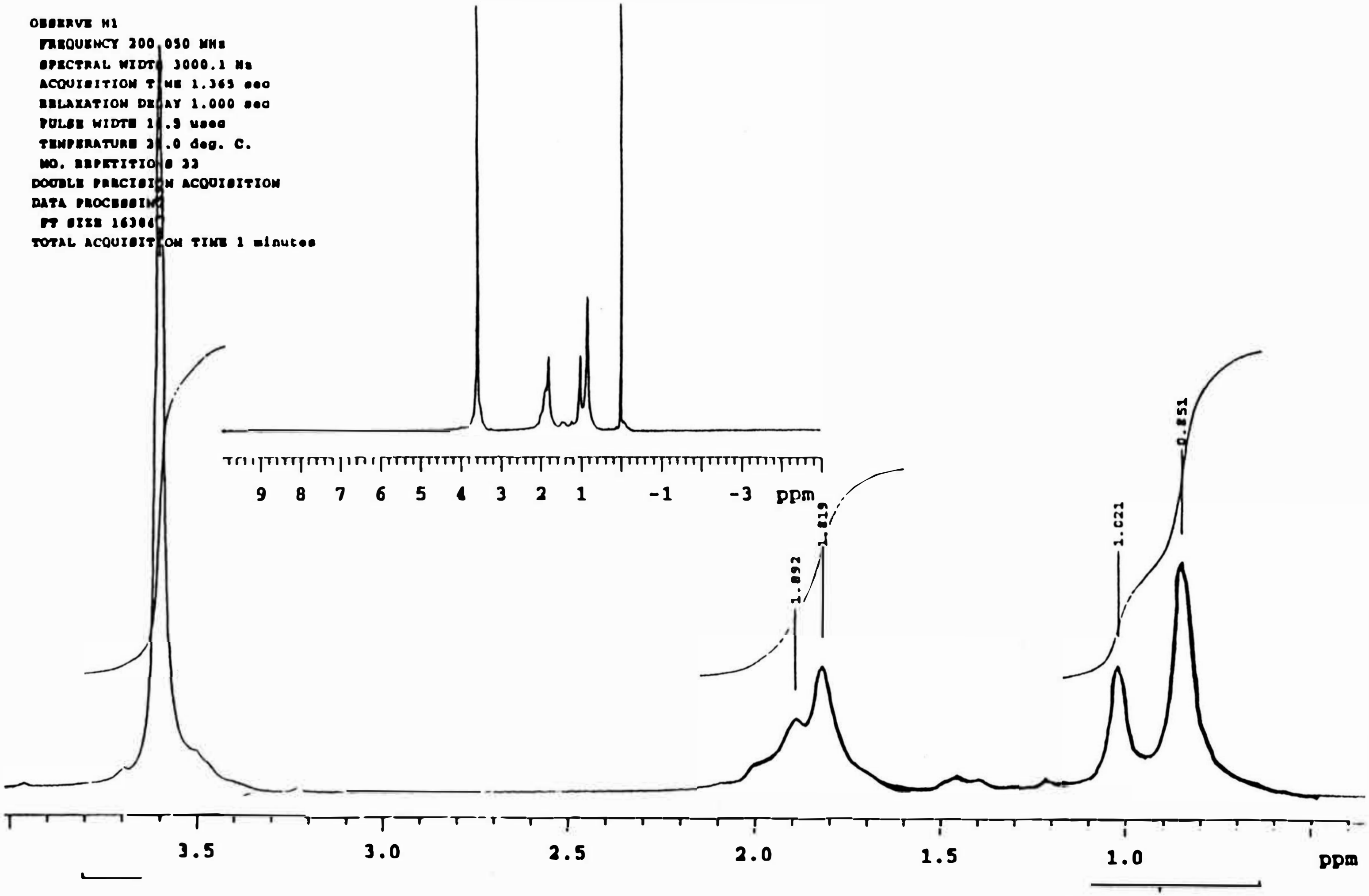

Figure 3. NMR spectrum of PMMA obtained at 13.0 Wcm^{-2} acoustic intensity.
(MMA = 22 ml, water = 100 ml, SDS =1 g, argon gas flow rate = 0.74 ml/sec, sonication time = 30 minutes, cooling bath temp.= -10°C)

Table I Tacticity and T_g of PMMA Prepared by Ultrasonically Initiated Emulsion Polymerization Method with Various Acoustic Intensities[a]

No	Acoustic Intensity (Wcm^{-2})	FT[b] (°C)	Triad Ratio (%)			av P_m[c]	φ[c]	T_{g1}[d] (°C)	T_{g2}[d] (°C)	R_p[e] x 10^4 (moles/l-sec)	M_w[f] x 10^{-6} (g/mole)
			I	A	S						
1	6.80	23.5	3.4	31.2	65.4	0.188	0.93	127.4	128.7	3.49	3.04
2	7.60	24.0	3.6	31.9	64.5	0.194	0.92	126.4	126.9	3.58	3.08
3	9.20	32.3	3.9	32.6	63.6	0.200	0.93	124.9	125.2	4.34	3.24
4	11.00	34.0	4.3	33.1	62.6	0.208	0.97	124.0	124.2	5.25	3.37
5	13.00	36.0	5.2	34.5	60.3	0.225	1.04	121.0	123.1	5.90	3.47
6	14.40	38.0	5.6	35.2	59.3	0.233	1.06	119.8	121.2	4.57	3.29

[a] MMA = 22 ml, water = 100 ml, SDS = 1g, argon gas flow rate = 0.74 ml/sec, sonication time = 30 min, cooling bath temp.= -10 °C, initial reaction temp. = 5 °C. [b] Final reaction temperature. [c] P_m and φ were calculating using eqs. (1), (3), and (4), respectively and av P_m is average value of Pm obtained from eqs. (1) and (3). [d] T_{g1} was calculating using Fox eq. and T_{g2} was measured from DSC. [e] R_p is polymerization rate cited from reference 1. [f] M_w is weight average molecular weight cited from reference 1.

Table II Tacticity of PMMA Prepared by Coventional Initiation, Gamma Irradiation, ultrasound initiated bulk Polymerization Method

No	Polymerization Conditions	Triad Ratio (%)			P_m[c]
		I	A	S	
1	Irradiation in bulk[a], 0 °C	7.5	30.0	62.5	0.21
2	B_2O_2 in bulk[b], 50 °C	8.5	31.5	60.0	0.23
3	AIBN in 10% toluene solution[a], 50 °C	6.3	37.6	56.0	0.25
4	Lauroyl peroxide in 10 % hexane solution[a], 50 °C	10.5	35.8	53.8	0.26
5	B_2O_2 in bulk[a], 100 °C[a]	8.9	37.5	53.9	0.27
6	ultrousound[c] -10 °C	0.8	25.6	73.6	0.13
7	ultrousound[c] 0 °C	1.7	33.8	64.6	0.18
8	ultrousound[c] 25 °C	2.8	34.3	62.9	0.20
9	ultrousound[c] 40 °C	4.0	40.4	56.4	0.24
10	ultrousound[c] 60 °C	4.3	41.0	54.7	0.25

[a] Reference 5.
[b] Reference 11.
[c] Reference 12.

Table III Tacticity and T_g of PMMA Prepared by Ultrasonically Initiated Emulsion Polymerization Method with Various Argon Gas Flow Rates[a]

No	Argon Flow Rate (ml/sec)	FT[b] (°C)	Triad Ratio (%) I	Triad Ratio (%) A	Triad Ratio (%) S	av P_m[c]	φ[c]	T_{g1}[d] (°C)	T_{g2}[d] (°C)	R_p[e] x 10^4 (moles/l-sec)	M_w[f] x 10^{-6} (g/mole)
1	0.25	26.0	3.5	31.8	64.7	0.192	0.91	126.7	127.3	3.83	3.02
2	0.32	31.0	3.9	32.4	63.7	0.199	0.96	125.5	126.0	4.22	3.22
3	0.42	32.0	3.9	32.5	63.6	0.200	0.94	125.4	124.5	4.30	3.23
4	0.54	32.5	4.0	32.6	63.4	0.202	0.96	125.1	124.0	4.42	3.25
5	0.67	33.0	4.2	32.9	63.0	0.206	0.98	124.3	123.5	4.48	3.27
6	0.78	33.5	4.3	33.5	62.2	0.209	0.96	123.8	123.4	4.57	3.28

[a] MMA = 22 ml, water = 100 ml, SDS = 1g, acoustic intensity = 9.2 Wcm-2, sonication time = 35 min, cooling bath temp.= -10 °C, initial reaction temp. = 5 °C. [b] Final reaction temperature. [c] P_m and φ were calculating using eqs. (1), (3), and (4), respectively and av P_m is average value of Pm obtained from eqs. (1) and (3). [d] T_{g1} was calculating using Fox eq. and T_{g2} was measured from DSC. [e] R_p is polymerization rate cited from reference 1. [f] M_w is weight average molecular weight cited from reference 1.

Table IV Tacticity and T_g of PMMA Prepared by Ultrasonically Initiated Emulsion Polymerization Method with Various Surfactant Concentrations

No	[SDS] (mole/l)	FT^b (°C)	Triad Ratio (%) I	A	S	av $P_m{}^c$	φ^c	$T_{g1}{}^d$ (°C)	$T_{g2}{}^d$ (°C)	$R_p{}^e$ x 10^4 (moles/l-sec)	$M_w{}^f$ x 10^{-6} (g/mole)
1	0.04	31.0	3.9	32.4	63.7	0.199	0.96	125.5	126.0	4.22	3.22
2	0.07	32.0	4.1	32.7	63.3	0.203	0.97	124.8	124.7	4.45	3.07
3	0.10	33.5	4.2	33.0	62.8	0.206	0.98	124.2	124.3	4.61	2.88
4	0.14	34.0	4.6	33.0	62.4	0.213	1.05	123.2	123.4	4.71	2.71
5	0.17	34.5	4.7	34.3	61.0	0.218	0.92	122.4	122.2	5.30	2.55
6	0.21	35.0	4.7	34.7	60.6	0.219	0.95	122.1	121.7	5.84	2.38
7[g]	0.24	36.5	5.0	35.4	59.6	0.226	0.96	121.0	120.0	6.54	2.14

[a] MMA = 22 ml, water = 100 ml, acoustic intensity = 9.2 Wcm-2, argon flow rate = 0.32 ml/sec, sonication time = 35 min, cooling bath temp.= -10 °C, initial reaction temp. = 5 °C. [b] Final reaction temperature. [c] P_m and φ were calculating using eqs. (1), (3), and (4), respectively and av Pm is average value of Pm obtained from eqs. (1) and (3). [d] T_{g1} was calculating using Fox eq. and T_{g2} was measured from DSC. [e] R_p is polymerization rate cited from reference 3. [f] M_w is weight average molecular weight cited from reference 1.

[g] Sonication time = 30 min.

VITA

Hsin-Chieh Joe Chou was born on November 17, 1959 in Koushung, Taiwan. He received his primary and secondary education in Koushung, Taiwan and received his B.S degree from National Taiwan University in Taipei in June, 1984. He worked a few years then came to U.S. for higher education. In August 1988, he enrolled in M.S. program in Polymer and Fiber Science of College of Textile at North Carolina State University. During his study at NCSU, he was selected as a member of Phi Lambda Epsilon Honor Chemical Society due to his good performance in his academic work. He also served as President and Vice president for Taiwanese Graduate Student Association and was heavily involved in extraordinary curriculum activity.

In June 1991, he received his M.S. degree and enrolled in the Ph.D. Program of Polymer and Coating Science in Chemistry Department at the University of Missouri-Rolla. He worked for Dr. Stoffer as a research graduate student in the area of polymer and coating Chemistry. He was involved in five different research projects and had a couple of publications in the Journal of Applied Polymer Science. He currently served as a research associate in the Emulsion Polymer Institute of the Chemistry and Chemical Engineering Departments at Lehigh University.