

Analysis of Ultrasonically Induced Free Radicals in the Emulsion Polymerization System by GC-MS

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SYNOPSIS

A specially designed gas chromatography-mass spectrometry (GC-MS) analytical method has been developed and applied to identify the source of free radicals that served as initiators in a new ultrasonically induced emulsion polymerization system with monomer methyl methacrylate (MMA), surfactant sodium dodecylsulfate (SDS) and water. The results showed the radicals came from the dissociation of SDS under ultrasonic irradiation. A quantitative determination procedure has been also developed and utilized to investigate the effects of the polymerization parameters, such as the surfactant concentration, the acoustic intensity of ultrasound, and the argon flow rate on the concentration of the generated free radicals in the emulsion system under ultrasonic irradiation. The results were helpful to understand the mechanism and kinetics of the system. © 1994 John Wiley & Sons, Inc.

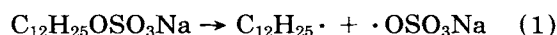
INTRODUCTION

Ultrasonically induced polymerization is a relatively seldom studied and less understood area in polymer science. We have reported the ultrasonically induced free radical polymerization of methyl methacrylate (MMA) and acrylamide, and copolymerization of styrene and maleic anhydride.¹⁻⁴ Earlier, polymerization induced by ultrasound was first reported by Lindstrom and Lamm⁵ in 1951 for acrylonitrile in an aqueous medium. Kurr⁶⁻⁸ and others^{9,10} have reported the polymerization procedures by ultrasonic irradiation.

Usually, the free radical initiators such as peroxides, hydroperoxides, or azo compounds were needed for the polymerization of vinyl monomers. The initiators were induced by ultrasound to produce the free radicals and then the polymerization of vinyl monomers was initiated. However, a very interesting phenomenon was observed in our first study of emulsion polymerization by ultrasonic irradiation with MMA as monomer and sodium dodecylsulfate (SDS) as an emulsifier. The high yield of polymethyl

methacrylate (PMMA, $M_w = 2,000,000$) was obtained even without the conventional free radical initiators.⁴ It was also observed that no polymerization occurred after 90 min of irradiation time when pure MMA (no water and SDS) or MMA with water (no SDS) at various ratios was subjected to a 13-W cm^{-2} of acoustic intensity of ultrasound and a 0.78 mL/s argon flow rate. However, small amounts of polymer were formed after 90 min under ultrasonic irradiation when SDS was included with MMA (no water). Our assumption was that the surfactant SDS was dissociated into free radicals under ultrasonic irradiation with a half time long enough to initiate the polymerization and served as the initiator for the initiation procedure.

In this study, a method development on indirect qualitative and quantitative analysis of ultrasonic initiated free radicals in the emulsion polymerization system by gas chromatography-mass spectrometry (GC-MS) is reported. First, a specially designed experimental procedure was developed to identify the free radicals in the system. It is proposed that SDS, $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$, is decomposed into free radicals under ultrasonic irradiation as in the following equation:



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When bromoform is mixed together with SDS and water (no MMA monomer, otherwise the polymerization would occur) and the mixture is irradiated by ultrasound, the generated free radicals $C_{12}H_{25}\cdot$ then react with $CHBr_3$ to give $C_{12}H_{25}Br$, 1-bromododecane. Therefore, if the 1-bromododecane could be found in the above ultrasound irradiated emulsion system, it would be a strong support for our assumption. The result of GC-MS analysis showed the 1-bromododecane was indeed found in the ultrasound irradiated solution. The details will be given in the results and discussion section. A sample pretreatment procedure and selective ion monitoring (SIM) method were used to determine the free radicals quantitatively. The effects of polymerization parameters of the surfactant concentration, acoustic intensity, and argon flow rate on the generated amount of free radicals were investigated by the developed method.

EXPERIMENTAL

Reagents

Sodium dodecylsulfate (98%), bromoform (99%) and 1-bromododecane (97%) were purchased from Aldrich. The *n*-propanol was purchased from Omnisolv Chemical. All were used as received and distilled water was used for preparation of all emulsion systems.

Apparatus

The polymerization reaction vessel was designed and set up with a 20-kHz ultrasonic generator (Sonic and Materials), model EC-1500, and a standard titanium horn, which is shown schematically in Figure 1. The different runs were made with output of the oscillator power set from 20 to 70 (on a scale of 100) with the cooling air passed through the ultrasonic horn. Ultrasonic irradiation was carried out with the tip of the ultrasonic horn immersed directly in the emulsion system.

Gas chromatography-mass spectrometry analysis was performed on a Hewlett-Packard Model 5970 mass selective detector interfaced to a Hewlett-Packard Model 5890 gas chromatograph. Helium was used as a carrier gas at a linear flow velocity of 20 cm/s at room temperature. A crosslinked methyl silicone capillary column, 12 m \times 0.2 mm \times 0.33 μ m film thickness (Hewlett-Packard), was utilized in all GC-MS analyses. The 0.4–0.8 μ L sample was injected into GC-MS using a 1.0- μ L microsyringe.

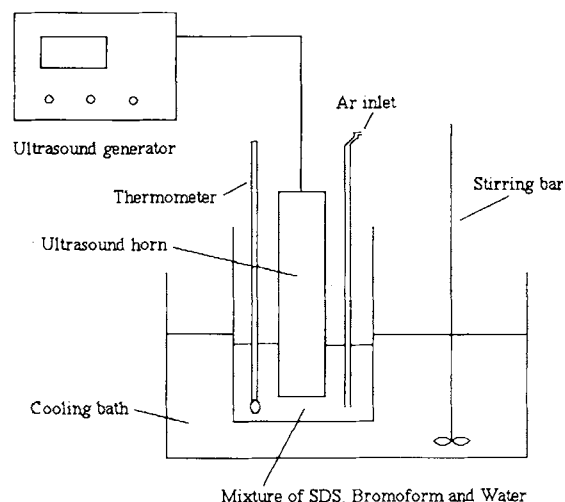


Figure 1 Schematic diagram of ultrasonic reaction apparatus.

A 280°C injector temperature and 260°C transfer line temperature were used. The column temperature was programmed as follows: 100°C, 2 min isothermal, 10°C/min to 260°C, followed by a 5 min isothermal hold at this temperature for qualitative analysis, and 150°C, 2 min isothermal, 10°C/min to 260°C for quantitative analysis. The characteristic ions of the long-chain alkylbromides with m/z 135, 137, 149, and 151 were chosen to build the total ion chromatogram in quantitative analysis procedure. The Chem Station data system was used for data acquisition and editing.

Ultrasonic Irradiation

Various emulsion systems with sodium dodecylsulfate, bromoform, and distilled water were irradiated by ultrasound at the certain acoustic intensity, argon gas flow rate, and surfactant concentration in a cooling bath, which was used to minimize the thermal effect. The emulsion systems were prepared by first adding the certain amount of SDS and then 4.2 mL of bromoform to 100 mL of water, with constant stirring at room temperature for 15 min. The emulsion system was then introduced to the reactor, a 17-cm height \times 6-cm i.d. flat bottom Pyrex glass tube. It was deoxygenated with argon gas for 3 min, then subjected to the ultrasonic irradiation. The horn was always placed 3 cm from the bottom of the reaction vessel. The glass tube was surrounded by a cooling medium ethylene glycol maintained at -10°C . During ultrasonic irradiation, dry argon was bubbled continuously through the emulsion system

in order to promote cavitation by providing nuclei for the formation of the bubbles.

Analysis Procedures

The emulsions irradiated by ultrasound were directly injected into GC-MS to identify the 1-bromododecane resulted from the reaction of radical $C_{12}H_{25}\cdot$, which was assumed from the dissociation of SDS, $C_{12}H_{25}OSO_3Na$, and bromoform, $CHBr_3$. The library search of mass spectrum and standard 1-bromododecane were used for qualitative analysis.

For quantitative analysis of the free radicals, the 100 mL of *n*-propanol was added to each resulted emulsion system irradiated by ultrasound to make the generated 1-bromododecane evenly distributed in the emulsion. The reproducibility of quantitative analysis was not good without this pretreatment. The SIM data acquisition model was chosen in quantitative detection to shorten the analytical time. Each value for calibration curve was taken from the average of the five data, and each measured free radical concentration was obtained from the average of five data, both with the relative error less than $\pm 5.0\%$.

The standard samples used for quantitative analysis was prepared by dissolving the 1-bromododecane in a stock solution, which was made by mixing 1.0 g of SDS, 100 mL of water, and 100 mL of *n*-propanol.

RESULTS AND DISCUSSION

Identification of Free Radical

The GC-MS analysis was carried out for the emulsion with SDS, bromoform, and water irradiated by ultrasound. The gas chromatogram of the emulsion is shown in Figure 2. The three large peaks A, B, and C are 1-dodecene, 1-tetradecene, and 1-hexadecene, respectively, which are unreacted raw material from the surfactant production. These peaks can also be observed in the emulsion system without ultrasonic irradiation. The small peak I is 1-bromododecane, which resulted from the radical reaction of $C_{12}H_{25}\cdot$ (SDS) and bromoform during ultrasonic irradiation. The corresponding mass spectrum is shown in Figure 3. The peak at m/z 248 is the molecular ion and the peak at m/z 250 is very typical

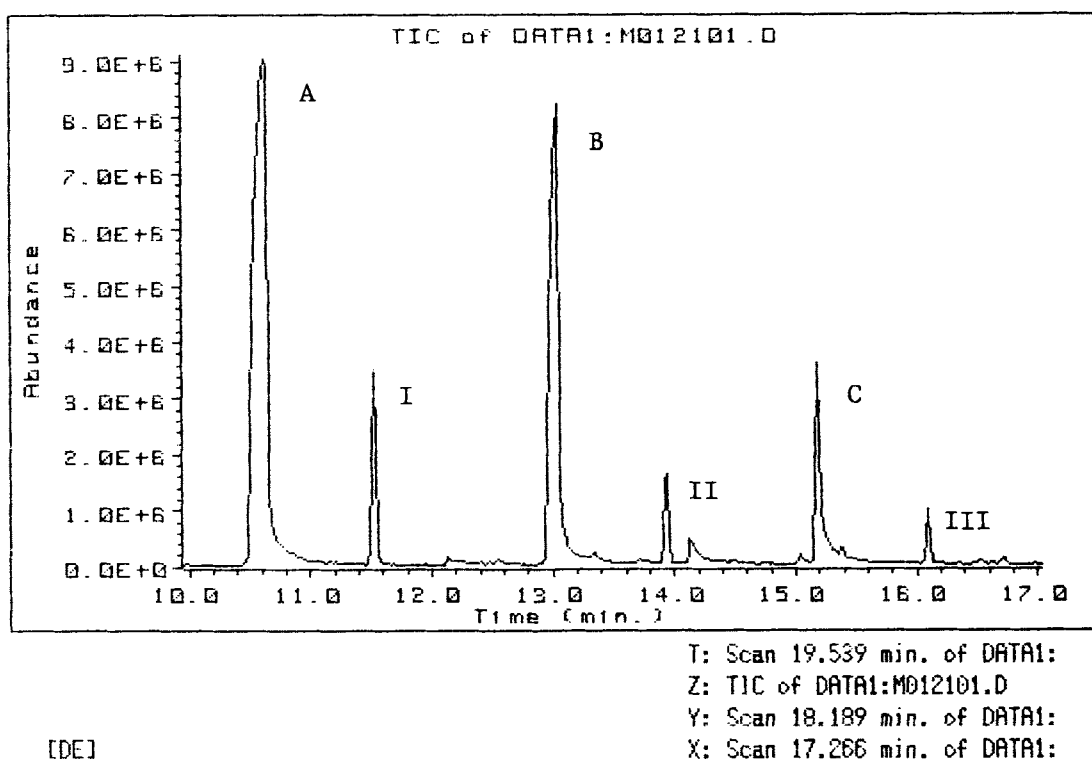
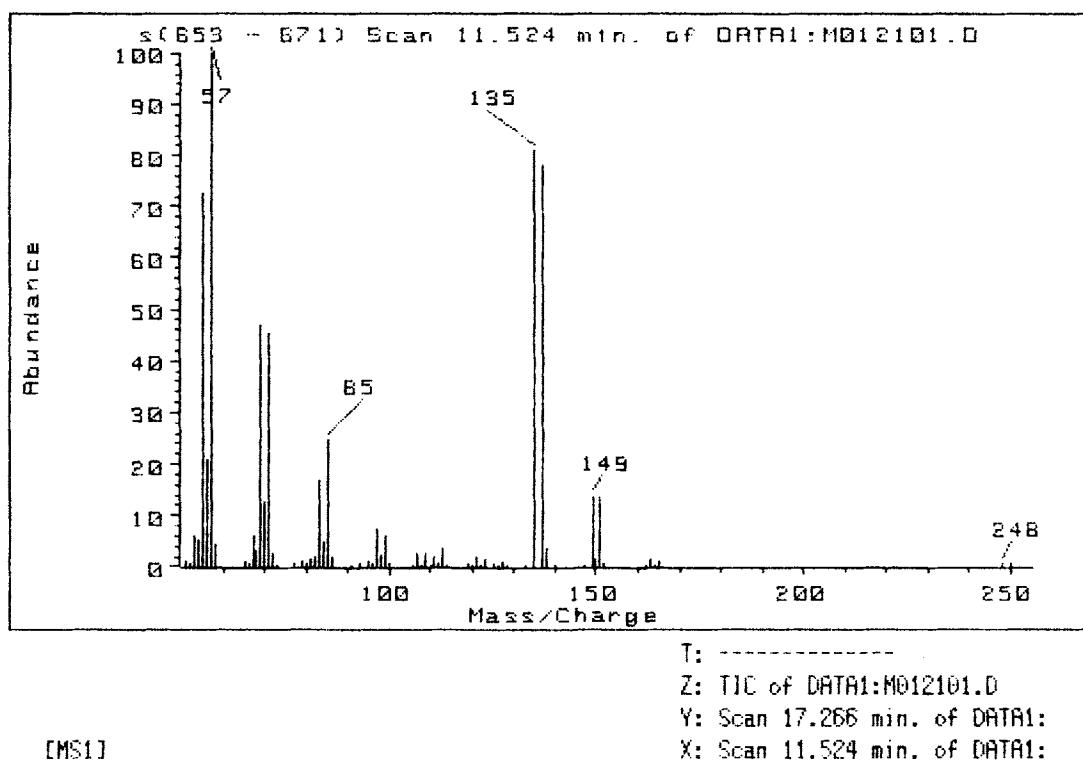


Figure 2 The total ion chromatogram of the emulsion sample (I) 1-bromododecane, (II) 1-bromotetradecane, (III) 1-bromohexadecane, (A) 1-dodecene, (B) 1-tetradecene, (C) 1-hexadecene.



[MS1]

Figure 3 Mass spectrum of 1-bromododecane in the emulsion sample (peak I in Fig. 2).

Br^{81} isotopic ion. The peaks at m/z 135 and 149 are assigned to the fragment ions $[\text{C}_4\text{H}_8\text{Br}]^+$ and $[\text{C}_5\text{H}_{10}\text{Br}]^+$, respectively. The Br^{81} isotopic peaks are also seen at m/z 137 and 151. The library search gave 98% fit with the standard mass spectrum. The standard sample 1-bromododecane was run GC-MS under the same chromatographic conditions and the retention time of the standard was obtained identically with the peak I in Figure 2.

Because the surfactant SDS was actually not pure but a mixture of sodium dodecylsulfate (SDS, major), sodium tetradecylsulfate (STS), and sodium hexadecylsulfate (SHS), the corresponding 1-bromotetradecane and 1-bromohexadecane were also found in the emulsion system of SDS, bromoform, and water irradiated by ultrasound (small peaks II and III in Fig. 2). Similarly, they came from the radical reactions of $\text{C}_{14}\text{H}_{29}\cdot$ and $\text{C}_{16}\text{H}_{33}\cdot$ with bromoform during the ultrasonic irradiation. Their mass spectra are shown in Figure 4, (a) for 1-bromotetradecane and (b) for 1-bromohexadecane. The analogous explanation for 1-bromododecane can also be applied for them. Although no molecular ion peak is observed in Figure 4 (b) due to the low concentration, the characteristic fragment ion peaks and the chromatographic retention time indicate it should be 1-bromohexadecane. The emulsion mixed by SDS, bromoform, and water

without ultrasonic irradiation was also analyzed by GC-MS at the same instrumental condition but no significant 1-bromododecane was found.

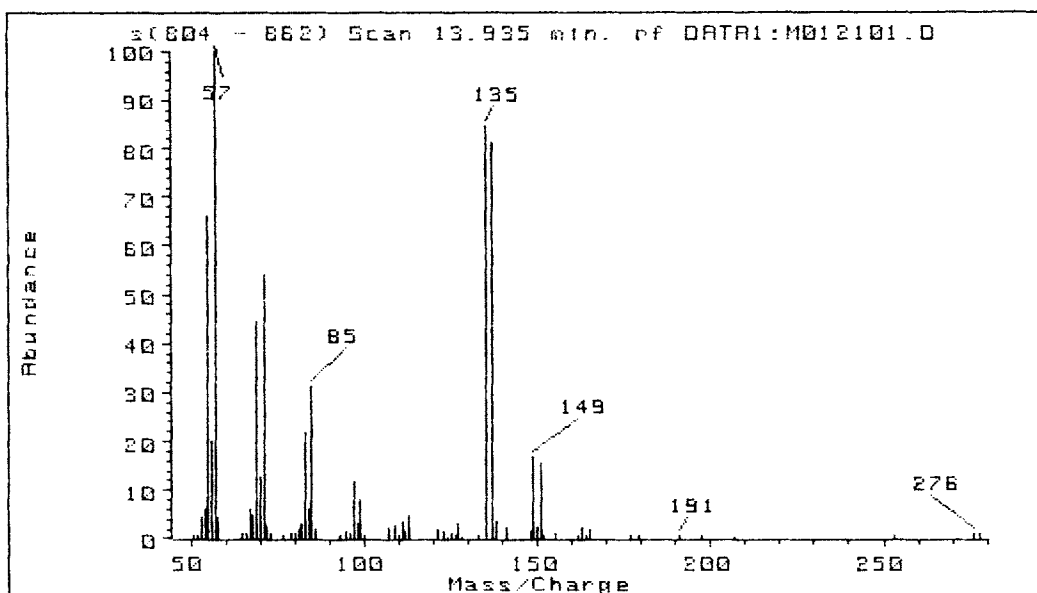
The results of qualitative analysis for the emulsion with SDS, bromoform, and water irradiated by ultrasound provided a strong support for the assumption that the surfactant SDS could produce free radicals that could serve as initiators to initiate the polymerization of MMA in an emulsion system.

Quantitative Analysis of Free Radical

In emulsion polymerization system, the rate of polymerization can be presented as the following equation:¹¹

$$R_p = 1000NK_p[M]n/N_A \quad (2)$$

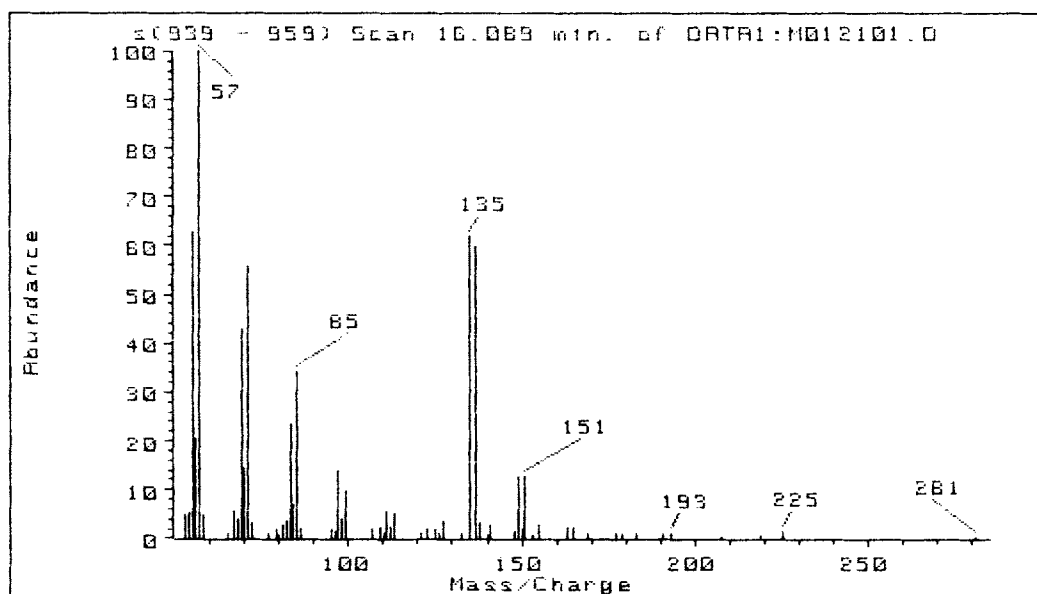
where R_p is the rate of polymerization, N is the total particle numbers per milliliter of reaction medium that increase with the initiator concentration and initiation rate. The effects of the surfactant concentration, acoustic intensity of ultrasound, and argon flow rate on the rate of polymerization were investigated in our previous work.⁴ The quantitative determination of the concentration of initiator free radicals (in this case, resulted from SDS) generated under different experimental conditions would help



a

T: -----
 Z: TIC of DATA1:M012101.D
 Y: Scan 16.089 min. of DATA1:
 X: Scan 13.935 min. of DATA1:

[MS1]



b

T: -----
 Z: TIC of DATA1:M012101.D
 Y: Scan 13.935 min. of DATA1:
 X: Scan 16.089 min. of DATA1:

[MS1]

Figure 4 Mass spectrum of 1-bromotetradecane and 1-bromohexadecane in the emulsion sample. (a) 1-bromotetradecane (peak II in Fig. 2), (b) 1-bromohexadecane (peak III in Fig. 2).

to understand the kinetics of this polymerization system.

Analytical Conditions and Calibration Curve

Besides 1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane, there were some other components shown on the chromatogram of the emulsion with SDS, bromoform, and water irradiated by ultrasound (Fig. 2). Since 1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane had the same characteristic fragment ions with m/z 135, 137, 149, and 151, the selective ion detection method was chosen to shorten the analytical time and increase the accuracy of quantitative determination. The corresponding selective ion chromatogram is shown in Figure 5; the three peaks are 1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane successively. The analysis was finished in 8 min and might be even quicker.

Since 1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane are homologues, they should have very close response factor to mass spectrometer. Thus only standard 1-bromododecane was used to make the calibration curve. The free radical concentration in samples was measured by the sum of the peak areas of three components on chromatogram.

Because all of the three alkyl bromides were hydrophobic, they were not evenly distributed in the emulsion system of SDS and water. The direct injection of these samples gave the results with about $\pm 15.0\%$ error. In order to solve this problem, *n*-propanol was added into the emulsion system to make the three alkyl bromides evenly distributed. Experimental results showed the reproducibility of the quantitative determination was improved with the increase of *n*-propanol added. When the ratio of emulsion and *n*-propanol reach to about 1 : 1 (100 mL *n*-propanol added), the relative error was less than $\pm 5.0\%$. It conforms to the requirement of quantitative analysis.

The calibration curve made by plotting the concentration of 1-bromododecane versus its corresponding chromatographic area is shown in Figure 6. The correlation coefficient (r) equals 0.997. Five different concentration of 0.10, 0.25, 0.50, 0.75, and 1.00 mg/mL 1-bromododecane was used.

The Effects of the Surfactant Amount on the Concentration of Radicals

The seven different amounts of surfactant 1.0–7.0 g were used to investigate the effects of the surfactant amount used in emulsions on the concentration of radicals at the constant acoustic intensity of ul-

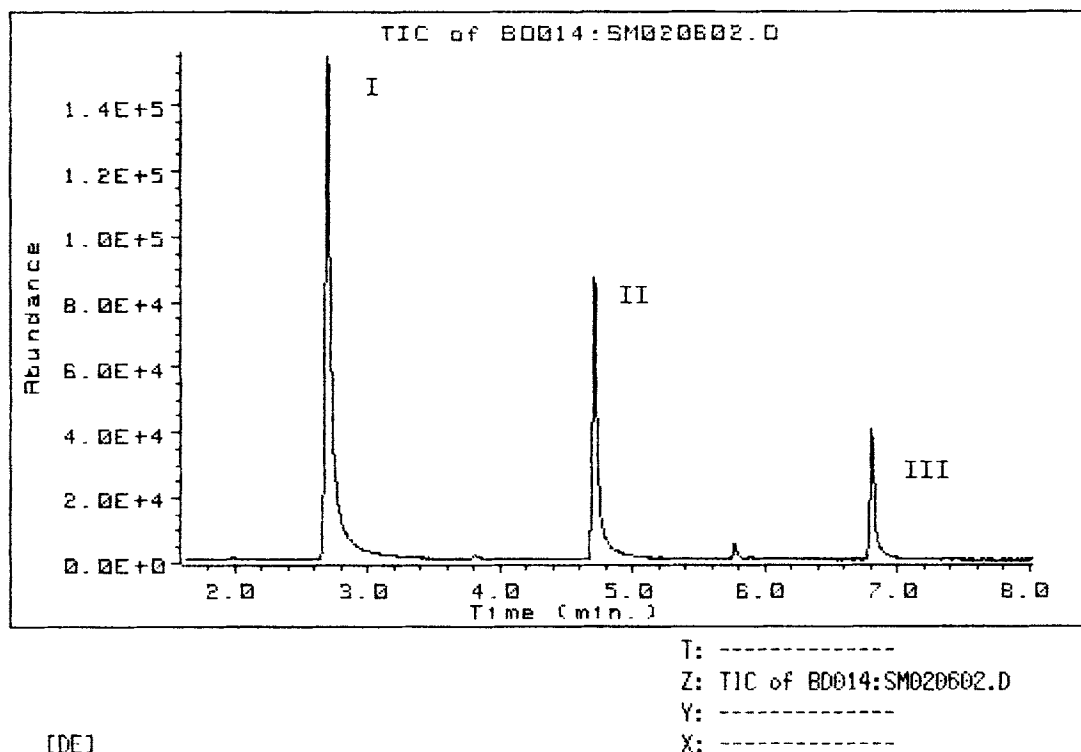


Figure 5 The selective ion chromatogram of the emulsion sample (I) 1-bromododecane, (II) 1-bromotetradecane, (III) 1-bromohexadecane.

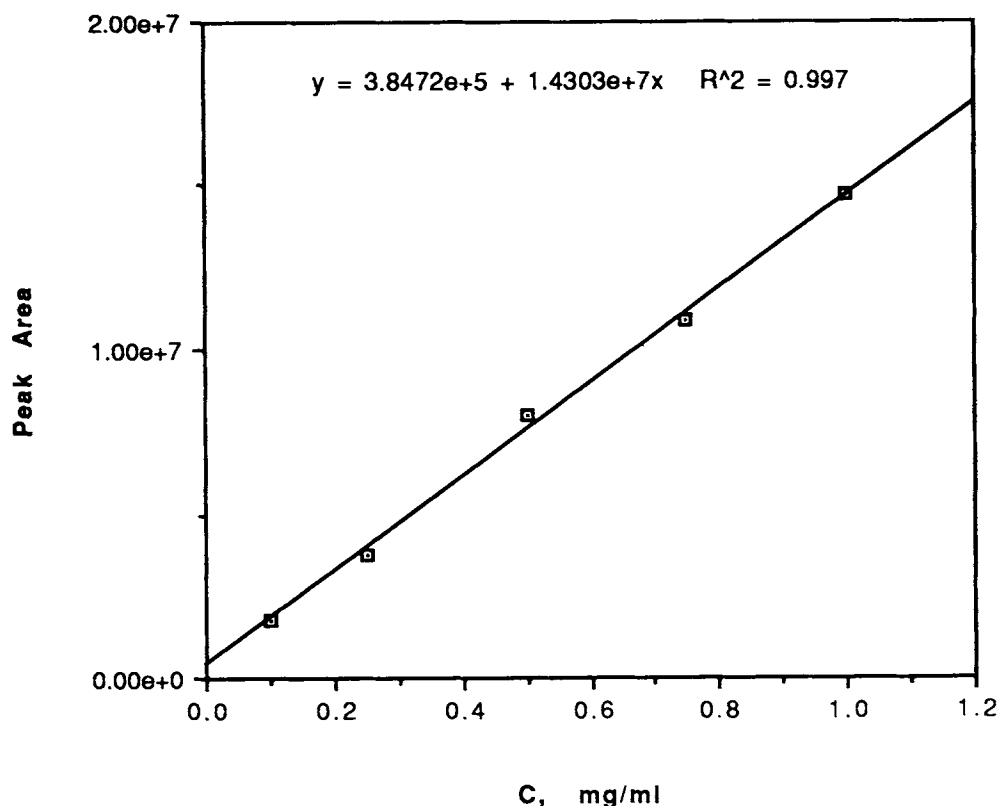


Figure 6 The calibration curve for quantitative analysis.

trasound (9.2 W cm^{-2}) and argon flow rate (0.32 mL/s). The results are summarized in Table I. The concentration of radicals increased with the increase of surfactant amount used. The reason we suggested is that the higher surfactant concentration provides the higher reaction probability under the ultrasonic irradiation, so the more surfactant molecules can dissociate into the free radicals. The trend is very similar to the change of polymerization rate with the surfactant amount.

Effects of the Acoustic Intensity on the Concentration of Radicals

The effects of the acoustic intensity of ultrasound on the concentration of radicals at constant surfactant amount (1.0 g) and argon flow rate (0.48 mL/s) are presented in Table II. The concentration of radicals increased with the increase of the acoustic intensity of ultrasound but dropped at the last point with the acoustic intensity 14.4 W cm^{-2} . This increase is due to the increase of cavitation bubbles, and the decrease at the last point is due to the decrease of cavitation bubbles after the maximum.⁴ This tendency is consistent with the relationship between polymerization rate and the acoustic inten-

sity of ultrasound except the last point at which the radical concentration is just lower than point 5, but the polymerization rate is lower than point 4.

Table I Effects of the Surfactant Amount on the Radical Concentration^a

| No | SDS (g) | C_1^b (mg/mL) | C_2^c (mg/mL) | R_P^d (mol/L s) |
|----|---------|-----------------|-----------------|-----------------------|
| 1 | 1.00 | 0.35 | 0.69 | 3.46×10^{-4} |
| 2 | 2.00 | 0.42 | 0.82 | 3.65×10^{-4} |
| 3 | 3.00 | 0.48 | 0.94 | 3.77×10^{-4} |
| 4 | 4.00 | 0.54 | 1.06 | 3.86×10^{-4} |
| 5 | 5.00 | 0.68 | 1.33 | 4.35×10^{-4} |
| 6 | 6.00 | 0.85 | 1.67 | 4.78×10^{-4} |
| 7 | 7.00 | 0.97 | 1.90 | 5.36×10^{-4} |

^a The emulsion system was prepared by 100 mL of water, 4.2 mL of bromoform, and various amount of SDS. The acoustic intensity of ultrasound was 9.2 W cm^{-2} and the argon flow rate was 0.32 mL/s .

^b C_1 is the determined concentration of the sum of 1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane in the emulsion with 100 mL of *n*-propanol.

^c C_2 is the converted concentration of these alkylbromides in the original emulsion system.

^d R_P is the polymerization rate cited from the Ref. 4.

Effects of Argon Flow Rate on the Concentration of Radicals

The effects of argon flow rate on the concentration of radicals at constant surfactant amount (1.00 g) and the acoustic intensity of ultrasound is listed in Table III. The concentration of radicals increased with the increase of the argon flow rate, which is also caused by the increase of cavitation bubbles. This relationship is analogous to that of polymerization rate and argon flow rate.

On the basis of the above results, we could assume that the contribution of the surfactant amount, the acoustic intensity of ultrasound, and the argon flow rate on the polymerization rate were at least partially from the concentration of radicals generated from surfactant SDS, served as initiator and contributed to N factor in Eq. (2). Although the radical concentration was not determined *in situ* during polymerization (no MMA added), the results were still helpful to understand the mechanism and kinetics of the polymerization in this emulsion system. This part is discussed in a separate paper in detail.¹²

CONCLUSION

The free radicals that initiated the polymerization in an emulsion system with MMA, SDS, and water under ultrasonic irradiation was confirmed from the dissociation of surfactant SDS, which were $C_{12}H_{25}\cdot$, $C_{14}H_{29}\cdot$, and $C_{16}H_{33}\cdot$. The quantitative determination procedure developed for radicals was applicable to the emulsion system. The results showed the tendency of the radical concentration change

Table II Effects of the Acoustic Intensity of Ultrasound on the Radical Concentration^a

| No | I_A^b (W cm ⁻²) | C_1 (mg/mL) | C_2 (mg/mL) | R_p (mol/L s) |
|----|----------------------------------|------------------|------------------|-----------------------|
| 1 | 6.8 | 0.31 | 0.61 | 2.86×10^{-4} |
| 2 | 7.6 | 0.34 | 0.67 | 2.94×10^{-4} |
| 3 | 9.2 | 0.37 | 0.73 | 3.56×10^{-4} |
| 4 | 11.0 | 0.41 | 0.80 | 4.30×10^{-4} |
| 5 | 13.0 | 0.47 | 0.92 | 4.84×10^{-4} |
| 6 | 14.4 | 0.42 | 0.82 | 3.74×10^{-4} |

^a The emulsion system was prepared by 100 mL of water, 4.2 mL of bromoform, and 1.00 g of SDS. The argon flow rate was 0.48 mL/s.

^b I_A is the acoustic intensity of the ultrasound. C_1 , C_2 , and R_p have the same meaning as in Table I.

Table III Effects of the Argon Flow Rate on the Radical Concentration^a

| No | F_A^b (mL/s) | C_1 (mg/mL) | C_2 (mg/mL) | R_p (mol/L s) |
|----|-------------------|------------------|------------------|-----------------------|
| 1 | 0.25 | 0.30 | 0.59 | 3.14×10^{-4} |
| 2 | 0.32 | 0.37 | 0.73 | 3.46×10^{-4} |
| 3 | 0.42 | 0.41 | 0.80 | 3.57×10^{-4} |
| 4 | 0.54 | 0.46 | 0.90 | 3.62×10^{-4} |
| 5 | 0.67 | 0.51 | 1.00 | 3.67×10^{-4} |

^a The emulsion system was prepared by 100 mL of water, 4.2 mL of bromoform, and 1.00 g of SDS. The acoustic intensity of ultrasound was 9.2 W cm⁻².

^b F_A is the argon flow rate. C_1 , C_2 , and R_p have the same meaning as in Table I.

with the surfactant amount used, the acoustic intensity of ultrasound and the argon flow rate was consistent with the change of polymerization rate with the above polymerization parameters. These results were helpful to understand the mechanism and kinetics of this ultrasonic induced emulsion polymerization system.

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