

Bulk Polymerization of Methyl Methacrylate Initiated by High Intensity Ultrasonic Irradiation and ESR Study

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ABSTRACT: High-intensity ultrasound was used to initiate the bulk polymerization of methyl methacrylate. The polymerization rate varied with the sonication time, the intensity of the ultrasound, and the initiator concentration of poly (methyl methacrylate) in the monomer. Electron spin resonance (ESR) spectra, obtained by the spin trapping tech-

nique, testified that free radicals were produced during the sonication process, and the concentration of radicals also changed with the sonication condition. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1731–1735, 2002

Key words: radical polymerization; kinetics (polym.); ESR

INTRODUCTION

Ultrasound has been widely applied in the chemical field, especially in organic synthesis and polymer chemistry. The utilization of ultrasound in polymers includes polymer degradation and polymeric reaction. Schmid et al.¹ and Melville et al.² have made a detailed investigation on polystyrene decomposition in benzene and toluene solution induced by ultrasonic treatment. Tabata et al. also discovered that poly (methyl methacrylate) (PMMA) would be degraded with high ultrasonic irradiation in solution.³ Recently, researches on ultrasonic degradation of several kinds of polymer and some theoretical analysis have been made.^{4–6} With regard to ultrasonic polymerization, a series of block-graft polymer and polymer composite for particular use have been fabricated with ultrasound.^{7–15} Kruus and his coworkers^{16,17} have prepared a small quantity of PMMA and polystyrene by ultrasonically irradiating the pure methyl methacrylate (MMA) and styrene monomer with ultrasound of 20.6 W/cm² intensity for 2 h, respectively. Chou and Stoffer made a very elaborate study of ultrasonically initiated free radical-catalyzed emulsion polymerization of methyl methacrylate.^{18,19} However, much of the research demonstrated that polymer can be fabricated only at low productivity with low-intensity ultrasound even for long times of irradiation. Through our experiments we have found that high-intensity ultrasonic irradiation, even at short sonication times, can produce abundant radicals and thereby induce bulk polymerization of MMA monomer and give a

high yield of the polymer after removing the ultrasound. This implies that the ultrasound technique can be practically utilized for bulk polymerization of MMA monomer at high polymer yield. For this article, we employed short-time superhigh ultrasonic irradiation to initiate the polymerization of MMA monomer and the kinetics of polymerization after sonication was studied for the first time. In addition, ESR investigation of MMA monomer after different ultrasonic irradiation exposure was made to further validate the proposed kinetics and mechanism of the polymerization, which have not been reported previously.

EXPERIMENTAL

Apparatus

A schematic diagram of the ultrasonic chemical reactor is shown as Figure 1. Ultrasound, with a frequency of 25 kHz, was introduced into the reactive liquid with a titanic alloy horn with power output adjustable between 0–1000 W, corresponding to a range of acoustic intensity from 0–500 W/cm².

The ESR spectra were obtained from Varian-E109 ESR spectrometer with 100 kHz modulation.

Reagents

Analytic grade MMA was further purified according to the procedure below. MMA was washed three times with 10 wt % sodium hydroxide aqueous solution to remove the hydroquinone inhibitor and then washed three times with distilled water. The residual water was eliminated through drying with anhydrous magnesium sulfate.

PMMA was dissolved in acetone and then precipitated with the addition of excessive methanol. Purified

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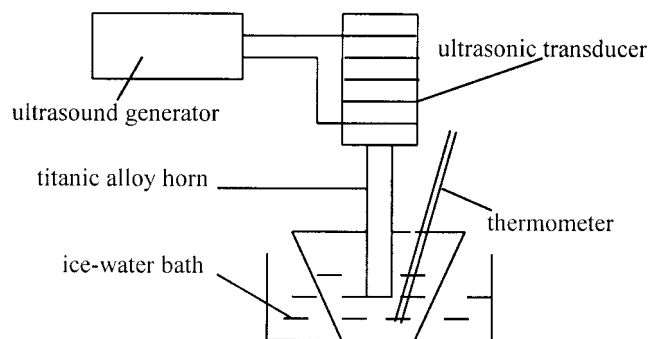


Figure 1 Schematic diagram of Sonochemical reactor.

PMMA was obtained by repeating these procedures three times and then drying.

Reagent grade α -phenyl-*N*-*tert*-butylnitrone (PBN) was used as the spin trap after being recrystallized.

Method

Twenty-five milliliters of purified MMA and the same volume of MMA containing 5 wt % PMMA was introduced into the ultrasonic reactor and irradiated with high-intensity ultrasound, respectively. During irradiation, the temperature of the reactor was maintained at about 10°C with an ice-water bath. Bulk polymerization of MMA was carried out at 60°C after ultrasonic irradiation and the conversion of the monomer, as a function of time, was measured.

Twenty-five milliliters of MMA, containing approximately 0.02 M PBN, was placed into the reactor and irradiated with ultrasound for a certain time. After outgassing with high-purity nitrogen for 20 min, the solution was sampled with a quartz capillary to detect the ESR signal with a spectrometer. Measurements were made on spectra obtained at 200 G in 4 min at a chart speed of 10 cm per minute.

ESR spectrum of the same volume monomer containing 5 wt % PMMA after sonication was also measured using the same procedure as above.

RESULTS AND DISCUSSION

Polymerization kinetics

Sonication time dependence

To determine the relationship between the polymerization rate and the time of ultrasonic pretreatment, the acoustic intensity was kept at 300 W/cm². No MMA monomer polymerized observably when heated at 60°C after 10 min of ultrasonic irradiation and very slow polymerization occurred after 15 min of sonication. Figure 2 shows a plot of MMA conversion vs. time after different times of irradiation with the same intensity ultrasound. It can be concluded that the bulk polymerization rate of MMA monomer increases

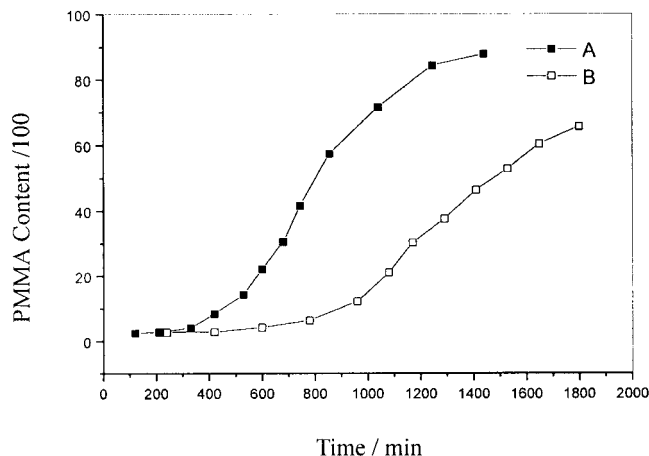


Figure 2 Plots of MMA monomer conversion vs. time after ultrasonic irradiation. (A) Irradiated for 30 min; (B) irradiated for 20 min.

with the ultrasound irradiation time. This indicates that more radicals would be produced by longer sonication times.

Acoustic intensity dependence

No apparent polymerization occurred when MMA monomer was heated at 60°C after 20 min of sonication with ultrasound of 200 W/cm² acoustic intensity in our experiments, and quite slow polymerization was observed after ultrasonic irradiation with an acoustic intensity of 225 W/cm² for 20 min. Weissler et al.²⁰ considered that high-intensity ultrasonic irradiation produced too many cavitation bubbles, which would reflect ultrasound wave confining the energy delivered in the liquid phase. Figure 3 displays the plot of MMA monomer conversion vs. time after different intensities of ultrasonic irradiation for 30 min. There is no evident difference between the polymer-

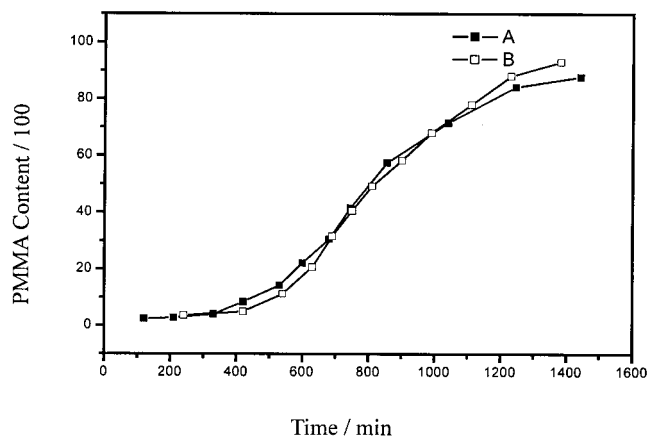


Figure 3 Plots of MMA monomer conversion vs. time after ultrasonic irradiation. (A) Irradiated with 300 W/cm² intensity ultrasound; (B) irradiated with 400 W/cm² intensity ultrasound.

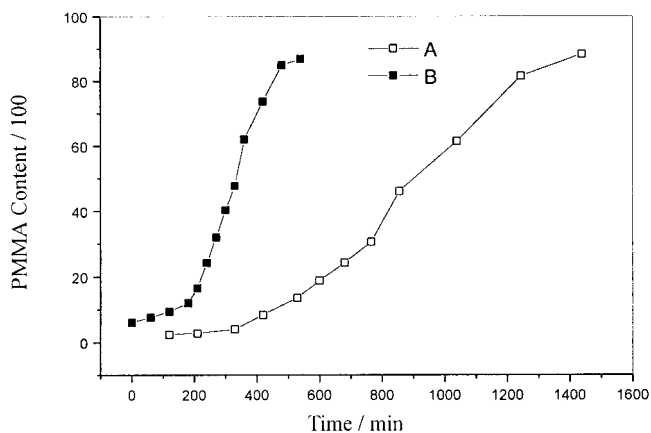


Figure 4 Plots of polymer content as a function of time. (A) Pure MMA monomer after ultrasonic irradiation; (B) MMA monomer containing 5% PMMA after ultrasonic irradiation.

ization rates of reaction system after sonication with ultrasound of 300 W/cm^2 and 400 W/cm^2 intensity, respectively. These indicate that there must be a threshold value and an optimal value of the acoustic intensity for a certain sonochemical system. In our experiments, the minimal and the most appropriate acoustic intensity may be approximately 225 W/cm^2 and 300 W/cm^2 , respectively.

Polymer content dependence

The decomposition of polymer in solution by ultrasonic treatment has been investigated widely. Polymers are more prone to degrade than the monomer molecules after sonication because their large volume and long chains make them undergo more action from the cavitation bubbles. Figure 4 shows the difference of polymerization rate between pure MMA monomer and PMMA MMA solution at the same sonication conditions. The ultrasonic intensity was 300 W/cm^2 , and the time of irradiation was 30 min. This demonstrates that a monomer containing PMMA a has much greater bulk polymerization rate than pure monomer after equal ultrasonic irradiation, possibly due to the large amount of radicals produced by the cleavage of polymer chains.

ESR evidence

Electron spin resonance (ESR) is the most commonly used technique to measure free radicals. Because radicals are generally very reactive and have very short lives, a spin trap is employed to detect the fugacious radical. In our work, α -phenyl-*N*-*tert*-butylnitron was used as the spin trap, which can scavenge the free radicals and form relatively stable nitroxide (eq. (1)).²¹

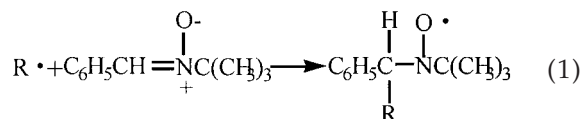


Figure 5 shows the ESR spectra obtained from MMA monomer after ultrasound irradiation with the spin trapping technique. The identification of the free radical trapped can be derived from the value of the nitrogen hyperfine coupling constant (hfsc) and the β -H hyperfine coupling constant. The average spacing of three doublets was measured and gave a corresponding value of β -H hfsc that is about 2.25 G. The spacings between the first and the fifth peak, and the second and the sixth peak were averaged and divided by 2 to give the nitrogen hfsc value about 13.7 G. ESR spectra obtained through different conditions of sonication have the same nitrogen hfsc and β -H hfsc. This indicates that the same kinds of free radical were generated after MMA monomer had undergone ultrasonic irradiation even at different times and intensities. Forrester et al.²² studied the ESR signal of the radical polymerization course of MMA in THF solution by employing PBN as radical scavenger and obtained the β -H hfsc and nitrogen hfsc values consistent with the values from our experiment. We can deduce that the primary

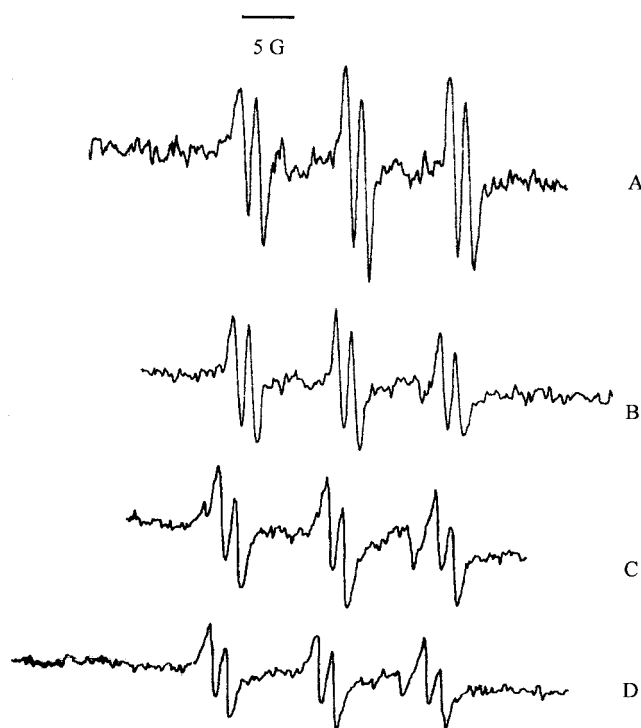
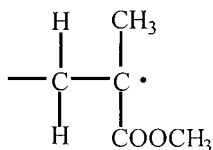


Figure 5 ESR spectra observed from MMA monomer after sonication with a spin trap technique. (A) Monomer containing 5 wt % PMMA irradiated with 300 W/cm^2 ultrasound for 30 min; (B) irradiated with 400 W/cm^2 ultrasound for 30 min; (C) irradiated with 300 W/cm^2 ultrasound for 30 min; (D) irradiated with 300 W/cm^2 ultrasound for 20 min.

radical generated in MMA bulk during the ultrasonic irradiation is



It is known that the ESR peak height is in direct proportion to the relative concentration of unpaired electrons when line width and other experimental condition are uniform, which is expressed as eq. (2). C_s is the radical concentration and h_s is the height of peak of the ESR spectrum of the sample being measured, while C_r and h_r are the radical concentration and the corresponding peak height of ESR spectrum of the referential specimen respectively.

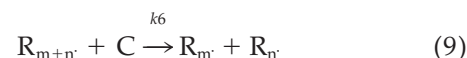
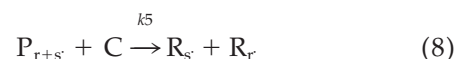
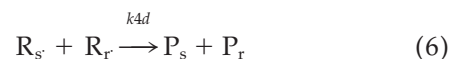
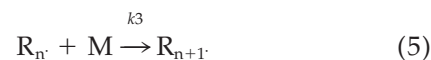
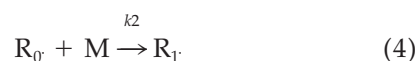
$$\frac{C_s}{C_r} = \frac{h_s}{h_r} \quad (2)$$

Figure 5 shows that the radical concentration of the system increases with sonication time and the intensity of ultrasound, monomer containing a certain content of polymer also generates more radicals after ultrasonic irradiation than pure monomer.

It clearly suggests that the more radicals are generated during the sonication process, the greater is the reaction rate of consequent polymerization.

Mechanism

Much work is needed to thoroughly elucidate the mechanism of the chemical reaction caused by the ultrasonic effect. A common viewpoint is that cavitation produced by the ultrasound in the liquid plays the most important role of the reaction. Suslick et al. pointed out that the high temperature (above 3000 K), attributed to the collapsing of the cavitation bubbles can lead to the degradation of the molecules at the bubble/liquid interface, which creates free radicals.²³ Some of the radicals have life times sufficiently long to migrate into the bulk liquid and induce the chemical reaction. Our experimental results agree with the mechanism¹⁶ of MMA polymerization initiated by the ultrasonic sonication is described in eqs. (3)–(9), where M is monomer, C is cavitation bubble, $R_i\cdot$ are radical species, P_i are dead polymer chains, and k_i are rate constants.



Researches of Kruus and his coworkers have revealed that a certain quantity of PMMA can be prepared during the sonication by the relatively low intensity ultrasound. Free radicals generated from ultrasonic irradiation will react with the monomer molecule and initiate the polymerization according to eqs. (3)–(7). However, polymers also will be decomposed when acting with the cavitation bubbles, as described by eqs. (8) and (9). Furthermore, with increasing irradiation time and ultrasonic intensity, the effect of competitive depolymerization becomes more apparent. Mason et al.²⁴ have pointed out that, when a monomer solution is kept sonicated, there is maximal productivity of the polymer corresponding with the most apropos irradiation time at certain intensity. Moreover, the optimal productivity decreases with the increasing of ultrasound intensity. One concludes that little polymer can be prepared during the sonication of a monomer, but more free radicals would be generated by an intensive ultrasound treatment, and thus it may be an effective method to initiate the bulk polymerization.

CONCLUSION

Bulk polymerization of methyl methacrylate may be initiated by short times of high-intensity ultrasonic irradiation with the monomer, which implies that the ultrasound technique can be effectively applied in polymer preparation. The polymerization rate after irradiation is positively proportional with the concentration of radicals generated by degradation of the monomer molecular and the polymer, which is the essential reason for polymeric reaction. The sonication time and the intensity of ultrasound both are important factors controlling the polymerization rate. A long time of sonication with the monomer leads to a rapid

reaction rate for the following polymerization. However, there must be a basic value for the intensity, and an optimal value for a certain sonochemical system. Addition of a certain content of PMMA to the pure MMA monomer may increase the polymerization rate following the ultrasound treatment.

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