

Study on Bulk Polymerization of Methyl Methacrylate Initiated by Low Intensity Ultrasonic Irradiation

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ABSTRACT: Methyl methacrylate (MMA) was polymerized in bulk solutions using low intensity ultrasonic radiation of 0.25 W/cm². The polymerization occurred after 1 h of irradiation time was applied. The polymerization rate was greatly accelerated either by increasing the amount of poly(methyl methacrylate) (PMMA) granular added into the system or by elongating the irradiation time. However, it was found that the reaction rate increased with the decreasing of the ultrasonic frequencies when the exposure time of the polymerization under the irradiation was less than 3 h. Experimental results verified that the polymerization was initiated by free radicals, which were mainly generated from the

degradation of PMMA macromolecular chains, the friction between the polymer macromolecular chains and the solvent monomer. These findings were obviously different from those obtained when high intensity ultrasonic irradiation was used. The polymers fabricated in this study by using ultrasound irradiation have a narrower molecular weight distribution compared to those obtained from the polymerizations induced by the conventional initiators. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3127–3133, 2010

Key words: bulk polymerization; low intensity; ultrasonic irradiation

INTRODUCTION

The chemical effect of ultrasound in a reaction was reported by Richards and Loomis¹ initially in 1920s, since then it has been widely studied on two major areas, which are degradation and polymerization of monomers.

The ultrasonic degradation of poly(vinyl alcohol) has been explored by Vijayalakshmi et al.² in terms of varying the pH conditions of the solvent, diversifying the compositions of water/solvent binary mixtures, and altering the polymer concentrations. Mohammad et al.³ studied the ultrasonic degradation of poly(vinyl acetate) (PVAc) solutions in tetrahydrofuran (THF) at different temperatures and solution concentrations. The ultrasonic degradation of poly(bisphenol A carbonate), poly(ϵ -caprolactone), and poly(vinyl acetate) were investigated by Sivalingam⁴ using various solvents, such as benzene, monochlorobenzene, and dichlorobenzene. The degradation of many other polymers, such as chitosan and starch,⁵ rhodamine,⁶ various aliphatic polyesters,⁷ dye,^{8–13} pluronic micelles,¹⁴ dextran,¹⁵ poly(vinylpyrrolidone),¹⁶ poly(acrylic acid),¹⁷ and insecticides,¹⁸ etc were also studied already.

In addition, a lot has been reported in literature in the field of the ultrasound initiated polymerizations. Ai et al.¹⁹ prepared a stable emulsion of polystyrene-g-poly(butyl acrylate) with the help of ultrasonic radiation. The effects of various factors on the coagulum ratio were analyzed, such as the strength and time of the ultrasonic radiation, the type and dosage of the emulsifier, the concentrations of the initiator and butyl acrylate, the amount of acrylic acid, and the reaction temperature. Delos et al.²⁰ studied the mechano-chemical reaction for modifying the polypropylene (PP) with maleic anhydride (MAH) by ultrasonic irradiation at 60°C. Through 2³ factorial experimental designs, three factors (variables) and two levels (high and low), the correlations between the percentage of MAH, the percentage of benzoyl peroxide (BPO) and ultrasonic irradiation intensity (Watts) were obtained. Bahattab²¹ investigated on the redox emulsion polymerization of vinyl acetate (VAc) in the absence of an inert gas and with sodium dodecyl sulfate as a surfactant and with ultrasonic energy and they concluded that the use of ultrasound during the polymerization gave a positive effect on the particle size distribution and average molecular weight of VAc polymer, and resulted in obtaining a stable, milky white, opaque latex. The synthesis of polymer composites,^{22–25} copolymers,²⁶ gels,^{27,28} and emulsion polymerization^{29–33} under ultrasonic irradiation were also reported. However, the bulk polymerization initiated by ultrasonic

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irradiation has been reported few and the study of Gu et al.³⁴ is a typical one.

The polymer such as poly(methyl methacrylate) (PMMA) prepared by ultrasonic is considerable pure because it can be gained without the attendance of initiator, so the polymer has many potential use. For example, the PMMA of high purity are used widely on the polymer optical fibers.³⁵ Gu et al.³⁴ studied the bulk polymerization of methyl methacrylate (MMA) initiated by ultrasonic irradiation with high intensity. They concluded that, for a specific sonochemical system, a minimum acoustic intensity was required to initiate the polymerization. Such a threshold value for the MMA system was recommended at approximately 225 W/cm². While a sonochemical system with acoustic intensity of hundreds of watts per square centimeter is expensive and difficult to be obtained, the study of bulk polymerization under low acoustic intensity is important. As we know, there is little research available on such studies. In this article, the bulk polymerization of MMA initiated by the ultrasonic irradiation with an acoustic intensity of 0.25 W/cm² was investigated. The results indicated that even the acoustic intensity was much lower than 1 W/cm² it could also initiate the bulk polymerization of MMA, and the product had a much narrower polydispersity index. The polymerization rate was correlated with the irradiation duration time, ultrasonic frequency and the amount of PMMA granules added into the reactants.

EXPERIMENTAL

Materials and methods

The original MMA was obtained from Forth Organic Chemical Co. (Shandong Zibo, China). Analytic grade sodium hydroxide (NaOH), anhydrous sodium sulfite (Na₂SO₃), azobisisobutyronitrile (AIBN), *n*-dodecyl mercaptan (*n*-DM), and hydroquinone were products of Xi'an Chemical Reagent factory. MMA was further purified by washing it three times using 10 wt % NaOH liquor to eliminate the polymerization inhibitor. Deionized water was used to wash the MMA until the pH condition of the monomer reached neutral (i.e. 6.5–7.5), and the water residuals within MMA was absorbed by Na₂SO₃. The original MMA was finally distilled under the vacuum condition of 0.086 MPa at 55°C twice to obtain the MMA monomer for the studies.

Polymethyl methacrylate (PMMA) granular was prepared using fast bulk polymerization³⁵ initiated by azobisisobutyronitrile (AIBN).

An ultrasonic reactor having four different frequencies (i.e. 20, 30, 40, and 50 kHz) and an outgoing acoustic power of 0.25 W/cm², supplied by Elec-

tronics Institute of Tongda Shaanxi China, was used for the polymerization of PMMA during this study.

Analysis

Molecular weight and molecular weight distribution

The molecular weight distribution of the polymer fabricated by using ultrasonic irradiation was determined using gel permeation chromatography technique (GPC150c, Waters Co., USA) with three ultra-styragel columns from Waters (10³, 10⁴, and 10⁵) with THF as a solvent at 25°C. These columns were calibrated with six narrow polydispersity index PS samples of known molecular weight. THF was pumped at a flow rate of 1.0 mL/min at 35°C.

Conversion rates

A refractometer made by ATAGO Co. Japan was used to monitor the conversion rate during the polymerization process of PMMA based on the well-known theory that the conversion was linearly affected by the refractive indices of the reactant.³⁶

FTIR

The Fourier transform infrared (FTIR) spectroscopic analyses of the samples were performed on a KBr disk by using a FTIR instrument (VERTEX 70, BRUKER, Germany).

Viscosity

The viscosities of the samples were measured using a Programmable DV-II Digital Viscometer supplied by Brookfield Engineering Laboratories (United Kingdom).

Polymerization of MMA initiated by ultrasonic irradiation

Method 1. Mixed solution (20 mL) containing MMA and PMMA granules were added into a 100-mL conical flask. The flask was placed at the center of the ultrasonic bath, which was filled with tap water (which acted as the coupling liquid) in an attempt to constantly control the ambient temperature of the reactor (i.e. 0–5°C). The immersed level of the reactor within the ultrasonic bath was adjusted at the appropriate depth to facilitate obtaining the intensive cavitations bubbles in the reactant. The reaction was initiated using ultrasonic irradiation at a specific frequency for a certain period of time in the ultrasonic bath. The bulk polymerization process of MMA was carried out at 70°C, and its monomer conversion status was hourly measured and evaluated during the polymerization.

Method 2. Identical procedure described in Method 1 was used in Method 2 but in this case there was no PMMA granular involved in the reactants.

Method 3. Identical procedure described in Method 1 was used in Method 3 except that there was no ultrasonic irradiation being employed for the initiation.

Method 4. Identical procedure described in Method 1 was used in Method 4, but in addition, 0.04 g hydroquinone was added into the flask after irradiation.

Method 5. Identical procedure described in Method 1 was used in Method 5, and pure nitrogen gas was bubbled into the reactant with a flow rate of 0.5 L/min during the irradiation.

Polymerization of MMA by traditional initiator

AIBN (0.2 wt %, 0.04 g) and 60 μ L *n*-DM (0.3 wt %) were added to 20 mL MMA monomer. The solution was heated at 85°C for the polymerization until the conversion of monomer reached 20%. The temperature was then reduced and kept at 50°C for 8 h. The polymerization occurring at a lower temperature can reduce the rate of reaction heat releasing and weaken the self-accelerating effect. Finally, the reactant was heated up to 115°C gradually within 3 h and the PMMA was polymerized.³⁷

RESULTS AND DISCUSSIONS

Influence of the PMMA concentrations on the polymerization of MMA

Method 1 was employed to determine the relationship between the PMMA concentration within the reactant solution and the polymerization rate. The

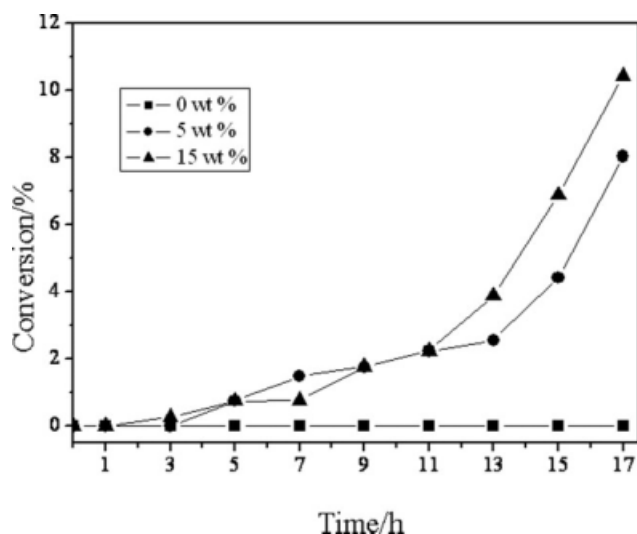


Figure 1 Time dependence of monomer conversion during the bulk polymerization at 70°C after irradiation. The PMMA granular in the MMA solution was 0 wt %, 5 wt %, and 15 wt %, respectively, and the reactant solution was irradiated by the ultrasonic of 30 kHz for 2 h.

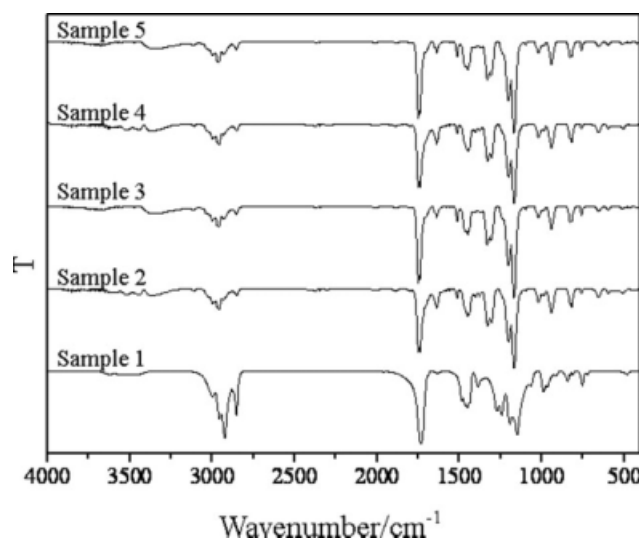


Figure 2 FTIR spectra for samples 1–5, these samples obtained from Method 1–5, respectively.

concentrations of PMMA granular within the MMA solution used in this study were 5 and 15 wt %. Figure 1 shows a plot of the % conversion versus time under the different concentrations (i.e. 5 and 15 wt %) of PMMA in the monomer solution. It can be concluded from Figure 1 that the monomer conversion increased with the concentration of PMMA at the same reaction time. The experimental results obtained from Method 2 (in the absence of PMMA) verified that the conversion of monomers was still 0% even after 3 h of irradiation and 36 h of heating at 70°C. Such phenomena implied that no apparent polymerization occurred without the presence of PMMA in the MMA monomer. In Figure 2, the spectrum of sample prepared via Method 1, the strong peaks at 1149 and 1732 cm^{-1} indicate the ester group. These two peaks can also be found from the spectrum of sample obtained from Method 2. In the former spectrum, the peak at 2924 cm^{-1} , which can be assigned to the stretching vibration of methylene, is as strong as the peaks at 1149 and 1732 cm^{-1} . However, such a peak is relatively weaker in the spectrum of sample from Method 2. On the other hand, the moderate peak at 1377 cm^{-1} indicates the symmetric vibration of " $\text{CH}_2=\text{C}-$ "³⁸ in the spectrum of sample from Method 2, and the peak can not be found in the spectrum of sample from Method 1. Thus, the FTIR results imply that there is no PMMA gained in Method 2 without the addition of PMMA granular. In contrast, large amount of PMMA was produced in method 1.

Influence of irradiation time on the polymerization of MMA

By using Method 1, 1 g PMMA granular was dissolved in 20 mL of MMA monomer solution. The

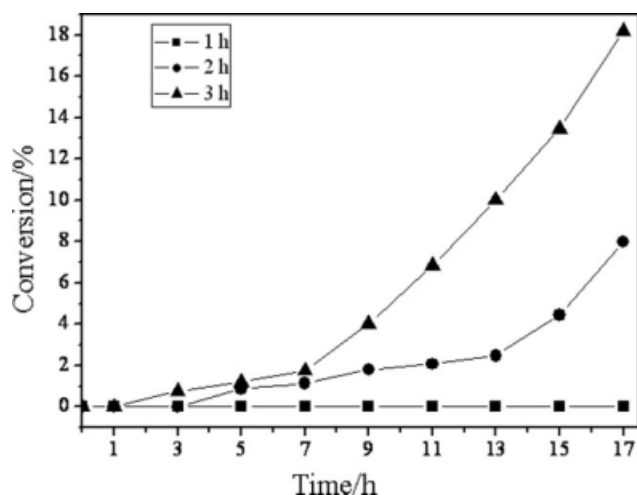


Figure 3 Time dependence of monomer conversion during the bulk polymerization at 70°C after irradiation. The irradiation time was 1, 2, and 3 h, respectively for the same ultrasonic irradiation of 30 kHz, and the PMMA granular in the MMA solution was 5 wt %.

reaction was initiated using the ultrasonic irradiation at the frequency of 30 kHz for 1, 2, and 3 h. The bulk polymerization was carried out at 70°C after the irradiation. The relationship between the conversion of the monomer and the reaction time of the polymerization processes under the different durations (i.e. 1, 2, and 3 h) of ultrasonic irradiation treatment are shown in Figure 3. Figure 3 shows that no apparent polymerization occurred with 1 h ultrasonic irradiation treatment. While 3 h ultrasonic irradiation treatment before the bulk polymerization of MMA resulted in a greater conversion of monomer

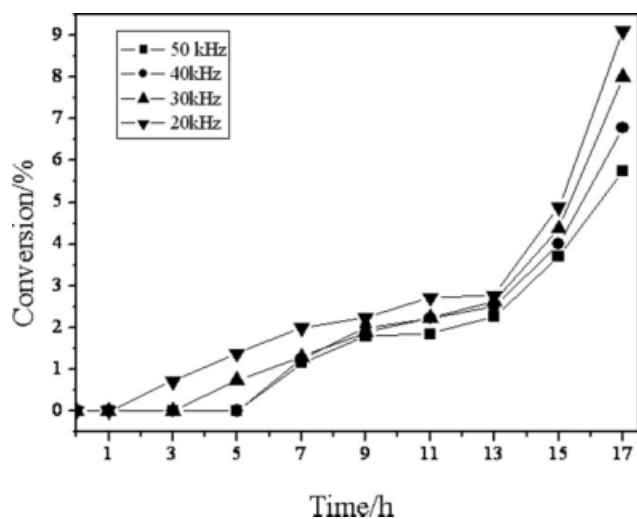


Figure 4 Time dependence of monomer conversion during the bulk polymerization at 70°C after irradiation. The irradiation time was 2 h for different ultrasonic frequencies of 20, 30, 40, and 50 kHz, respectively, and the PMMA granular in the MMA solution was 5 wt %.

compared to the 2 h one at the same reaction time of the polymerization.

Ultrasonic frequencies dependence

By using Method 1, 1 g PMMA granular was dissolved in 20 mL of MMA monomer solution, the obtained mixture was subjected to the ultrasonic irradiation for 2 h at different frequencies, i.e. 20, 30, 40, and 50 kHz. The relationship between conversion and time of the polymerization process is shown in Figure 4. It can be concluded from this figure that with the same ultrasonic treatment duration (i.e. 2 h) the reaction rate of polymerization for PMMA was increased with the decreasing of ultrasonic frequencies.

However, when the time of ultrasound irradiation was extended to 3 h, the reaction rate was similar to each other for the different frequencies of ultrasound (as shown in Fig. 5). In other words, the reaction rate became independent of the frequencies of ultrasound when the duration of ultrasonic treatment reached 3 h.

GPC analysis results of polymers

The gel permeation chromatography (GPC) analysis result of the three types of PMMA is shown in Figure 6, in which: (A) indicates PMMA fabricated by the ultrasonic irradiation initiation, (B) indicates PMMA fabricated by traditional initiator initiation, and (C) indicates PMMA granular added in (A). The detailed results of GPC analysis can also be found in Table I. From the GPC analysis of PMMA the

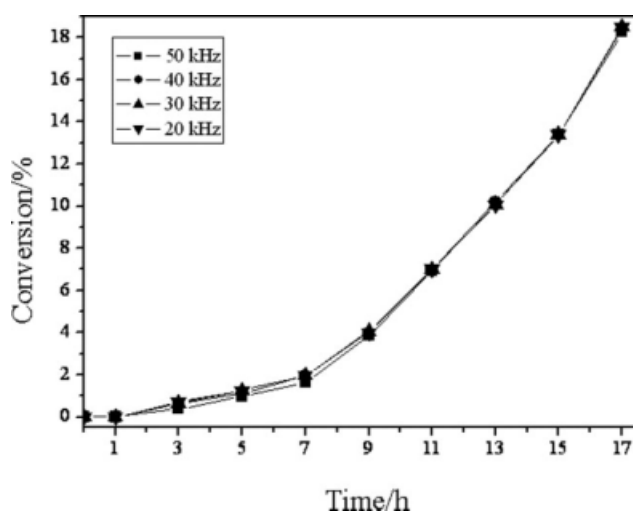


Figure 5 Time dependence of monomer conversion during the bulk polymerization at 70°C after irradiation. The irradiation time was 3 h for different ultrasonic frequencies of 20, 30, 40, and 50 kHz, respectively, and the PMMA granular in the MMA solution was 5 wt %.

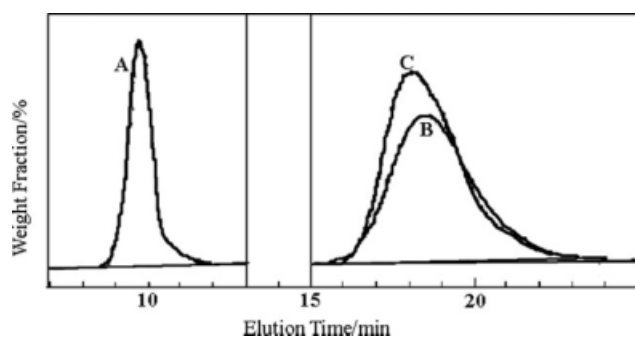


Figure 6 GPC comparison of PMMA initiated by (A) the ultrasonic of 30 kHz irradiated a solution of 1 g PMMA granular and 20 mL MMA monomer for 2 h and heated at 70°C, (B) traditional initiator, and (C) PMMA granular used in (A).

molecular weights of the three polymers were calculated from the elution time. The M_w of PMMA (A), (B), and (C) were 219,510, 71,666, and 96,346 g/mol respectively; and the M_n were 175,865, 40,664, and 63,951 g/mol accordingly. Although the molecular weight of (A) was much larger than that of (B), the polydispersity index (i.e. M_w/M_n) of (A) was much narrower than (B) by 1.25 versus 1.76. The M_w of PMMA (A) was larger than that of (C), and the polydispersity of (A) was much narrower than that of (C) by 1.25 versus 1.51. Such results indicate that most of the PMMA granular macromolecular chain used in (A) was degraded by the ultrasound and did not result in any negative effects on the molecular weight distribution of (A). Comparing with the polymer fabricated by traditional initiator, the polymer fabricated by the ultrasonic irradiation has a more regular molecular weight distribution, which is an outstanding advantage of the method for preparing PMMA stated in the current study. From this prospective, the polymerization initiated by ultrasonic irradiation is a better method.

Reaction mechanism

To probe the mechanism of the polymerization, further experiments were performed using Methods 2, 3, 4, and 5.

The previous observations obtained from the experiments conducted by following Methods 1 and 3 showed that no obvious polymerization of MMA could occur without ultrasonic irradiation treatment even under the relative severe conditions (i.e. at 70°C for 36 h). The FTIR comparison between samples obtained from Methods 1 and 3 also affirmed that no PMMA fabricated under Method 3 (Fig. 2). These results imply that the ultrasonic irradiation was a key factor for the bulk polymerization of MMA monomers. The most possible explanations to this phenomena is that the high energy created from

the ultrasonic irradiations could facilitate the generation of the free radicals, which commonly initiate the polymerization of MMA monomers.

It is well known that the hydroquinone was an excellent inhibitor for free radical polymerization. It could cause the deactivation of free radicals easily. In the experiment carried out by following Method 4, with the presence of hydroquinone in the reactant solution, no polymerization was notified even by heating at 70°C for 36 h with ultrasonic treatment (e.g. 30 kHz) for 2 h. Such a result was also confirmed by the FTIR spectrum of sample prepared using method 4 (Fig. 2). By comparing such results with those obtained from the experiment conducted using Method 3, it can be confirmed that the reactions were based on the free radical polymerization mechanism.

Two obvious effects were obtained when a polymer solution was irradiated by the ultrasound: cavitation bubbles formed and collapsed, and friction between the solvent and polymer was produced due to the variations of the movement speed of each species in the system,³⁹ both outcomes could induce free radicals in the reaction system. No polymerization was observed in the experiment carried out by using Method 2, whilst the reactant polymerized by employing Method 1. The only difference between the experiments by using Methods 1 and 2 was the presence and absence of PMMA granular dissolved in the reactant solution, respectively. In the case of the absence of PMMA macromolecules into the MMA monomer solution, the particles (i.e. MMA molecules) moved at an appreciatively equal velocity, that was not able to generate friction among the reactant molecules, thus no free radicals could be formed. If the cavitation was the main factor that induced the free radicals, the generation of free radicals should be independent on the presence of other substances within the reaction system. In other words, free radicals should be still producible even with only MMA monomers existing in the reaction system. Therefore, the fact that no polymerization occurred in the experiment using Method 2

TABLE I
GPC Analysis of Three Kinds of PMMA

PMMA No.	M_w (g/mol)	M_n (g/mol)	Polydispersity (M_w/M_n)
A	219,510	175,865	1.25
B	71,666	40,664	1.76
C	96,346	63,951	1.51

Note: M_w = Weight average molecular weight, M_n = Number average molecular weight, (A) indicates PMMA fabricated by the ultrasonic irradiation initiation, (B) indicates PMMA fabricated by traditional initiator initiation, (C) indicates PMMA granular added in (A).

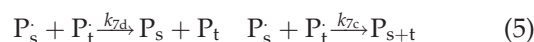
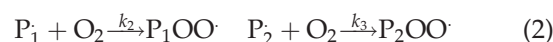
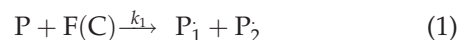
indicated that the friction was the driven-force for the formation of the free radicals, whilst the cavitation was not strong enough to create free radicals in the current study. Gu et al.³⁴ reported that there was a threshold value of 225 W/cm² for the bulk polymerization of MMA, if the intensity of ultrasonic irradiation was lower than the threshold value the reaction could not take place, while the present investigation showed that even a power of 0.25 W/cm² initiated polymerization. It can be concluded that the free radicals came from the cavitation in Gu et al.³⁴ study, while in this study, the free radicals came mainly from the friction.

It can therefore be concluded that the bulk polymerization was initiated by free radicals in this study. The ultrasound resulted in friction between the macromolecular long chain and the monomer molecule, and the free radicals were formed by the friction mainly. However, the free radicals were very active and it was much abnormal for them to live for a long time of 2–3 h. To investigate the phenomenon of long lifetime of free radicals Method 5 was used.

There was no polymerization observed using Method 5, and the FTIR analysis of sample obtained in Method 5 also confirmed the outcome, whilst the reactant polymerized using Method 1. Compared to Method 1, nitrogen gas was introduced in the reactant solution during the ultrasonic initiation process in Method 5. Thus, it can be concluded that the nitrogen air bubbling was an important factor for the polymerization. The reactant solution was irradiated with the presence of air (oxygen and nitrogen) in the flask. After the active free radicals were formed by the ultrasonic irradiation, some of them were easily stabilized by the reaction with oxygen (i.e. by forming the peroxide free radicals), and the stabilized free radicals had a lifetime of several hours at a low temperature (0–5°C). Then the peroxide free radicals initiated the bulk polymerization at 70°C.

According to the experimental results mentioned previously, the reaction mechanism of MMA polymerization in this investigation could be expressed by eqs. (1)–(5). Equation (1) is the chain initiation mechanism, where 'P' is the macromolecular chain of PMMA granular, 'F' is the friction between the macromolecular chain and the molecule of MMA, 'C' the cavitation—it is a secondary factor so it was placed into a bracket; K_1 to K_7 are the rate constants; P_1 and P_2 were the radicals generated from the degradation of the PMMA macromolecule chain. Equations (2) represents the formation of peroxide free radicals. Equations (3) and (4) show the chain growths, where M is the monomer molecule of MMA. Equation (5) represents chain termination. P_s , Pt, and P_{s+t} are dead polymer chains. A small quan-

tity of polymer of P_s , Pt, and P_{s+t} might be degraded by the ultrasonic but which might be neglected because of low temperature and slow reaction rate when the solution was irradiated. Thus it is not specified in the following reaction mechanism equations.



Explanation

On the basis of the reaction mechanism earlier, the phenomenon in Figures 1–5 can be explained completely.

In the case of Figure 1, the more PMMA added to the MMA monomer, the more free radicals are generated in the equal irradiation time, as most of the free radicals are produced by degradation of the PMMA macromolecular chains. Furthermore, as the content of PMMA in the MMA monomer increased, the reactant solution became more viscous (the viscosities of the reactant solution with addition of 0, 5, and 15% PMMA granular in the MMA monomer were 0.56, 1.55, and 3.62 mPa·s, respectively), which could facilitate the active radicals maintaining activity. Both factors together led to the observation obtained in Figure 1 that concentration of free radicals positively depended on the content of PMMA in the MMA monomer solution, and the same applies to the reaction rate.

In the case of Figure 3, with a longer irradiation time a larger concentration of free radicals could be produced (before reaching its saturation level), and the larger concentration of free radicals could lead to a faster reaction rate.

$$\overline{W} = \frac{1}{2} \rho A^2 \omega^2 \quad (6)$$

The energy of sound wave can be expressed by eq. (6), where \overline{W} is the average energy density of sound wave, A the amplitude, and ω the angular frequency of the wave.³⁹ With the same energy density, its amplitude decreased with increasing frequency and the cavitation and friction induced by the ultrasonic also decreased. After the same irradiation time, the lower frequency of ultrasonic irradiation produced more free radicals and induced a faster reaction rate, which agreed with the results in Figure 4.

At the initial stage of the irradiation, the concentration of free radicals increased with the duration time of ultrasonic treatment, while the amount of the deactivated free radicals increased with the content (i.e. the concentration) of the free radicals obtained. There was a dynamic equilibrium process between the formation and deactivation of the active free radicals. When such a balance process was stable the concentration of free radicals was a definite value and was only associated with the power of the ultrasonic.³⁹ In this article, the power of the ultrasound irradiation applied throughout the whole study was 0.25 W/cm^2 . Therefore, the concentration of the free radical was treated as a constant, which resulted in an almost equal reaction rate for each experiment carried out in this study (as shown in Fig. 5).

In this research, it was found that the bulk polymerization of MMA can be initiated by the ultrasonic irradiation with a low acoustic density. Even the power of the ultrasonic is as low as 0.25 W/cm^2 . Most former researchers needed an ultrasonic reactor with much higher acoustic intensity (i.e. 225 W/cm^2 more) to fabricate the bulk polymerization of MMA³⁴ and the reactor was expensive and complex. These shortcomings limit its extensive application. The ultrasonic reactor used in this study costs less and, simple and easy to be provided. The product gained by the ultrasonic irradiation contains scarcely any initiator and has potential applications in some areas, such as polymer optical fibers.³⁴ The method of low power ultrasonic irradiation initiated the bulk polymerization of MMA has obvious merits, and can be extended to prepare other similar polymers (e.g. acrylic acid, butyl acrylate, and methyl acrylate etc).

CONCLUSIONS

Poly(methyl methacrylate) (PMMA) was successfully synthesized via bulk polymerization using low intensity ultrasound irradiation of 0.25 W/cm^2 for a certain time period (e.g. commonly over 1 h) in this study. The reaction was initiated by the free radicals, which mainly came from the friction (induced by the ultrasonic irradiation) between the polymer macromolecular chains and solvent of MMA monomer molecules. The active free radicals were stabilized by forming the peroxide free radical in the presence of oxygen (from air). Consequently, the relatively stable peroxide free radicals initiated the polymerization of MMA at 70°C . The PMMA fabricated by the ultrasonic irradiation gave a narrower molecular weight distribution compared to that fabricated by the conventional modifying approaches using the commercial initiators.

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