Synthesis and Characterization of Poly-(Methyl Methacrylate) Nanoparticles with Ultrasound Assistance

by

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Author's Declaration

I hereby declare that I am the solo author of this thesis. This is the true copy of the thesis; include any required final revisions, as accepted by my committee members.

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Abstract

Nano-sized poly-(methyl methacrylate) (PMMA) is synthesized by employing three different methods with various techniques of emulsifying. This research is aimed at finding more effective and simpler ways to synthesize PMMA nano particles with acceptable particle size and conversion rate. Because of this, particle size and conversion rate are two main indicies for every sample of every different combination of synthesis methods and ways of emulsifying, and those two indicies are tested and calculated most commonly among all experiments. For certain experiments, other aspects of the polymerization process like temperature, initiator type, length of reaction time, and monomer/water ratio are also changed to study their influence on the polymerization. Ultrasound, one type of powerful emulsifying methods, is widely used among most of the experiments, and the intensity of ultrasound is different for every specific experiment.

Three main methods are the batch reaction method, pre-mixing separation method, and differential addition method. There are also five main emulsifying techniques, magnetic stirring, bath ultrasound, probe ultrasonic dismembrator, combination of magnetic stirring and probe ultrasonic dismembrator, and combination of bath ultrasound and probe ultrasonic dismembrator.

For the batch reaction method, results have shown that appropriate intensity of ultrasound can help to lower the particle size to 20nm with narrow distribution. At the same, the traditional

magnetic stirring method cannot even convert all monomers into nano particles, which means there is always a part of MMA monomers being consumed to form rigid floating subjects during the reaction. However, experiments also reveal that a too powerful emulsifying force will lead to implosion, which significantly increases the reaction rate and the particle size. The combined emulsifying methods are much easier to cause implosion than an individual emulsifying method. The increase of particle size should be avoided, but the increase of reaction rate may have advantages in massive production.

The pre-mixing separation method can help to make particle size even smaller and the distribution even narrower than the batch reaction method, but a too-powerful emulsifying method will have greater side effects on this type of reaction method.

Experiments of the differential addition method are designed to synthesize fine polymer particles with narrow distribution, and to achieve a high conversion rate.

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1. Outline of Thesis

Synthesis of nano-sized polymer particles has attracted a vast amount of attention of researchers all over the world. Poly-(methyl methacrylate) (PMMA) is one type of polymer that has been extensively studied because of its application in drug delivery, agriculture, environment, and so on. Experiments done on PMMA can also provide a reference for synthesis of other organic nano particles like poly-methacrylate, polystyrene, and nitrile-butadiene rubber.

To obtain PMMA nano particles, various types of methods have been applied, and every one of them has its own features. The most common way is emulsion polymerization initiated by thermal initiators at high temperature (70-80 ℃) or a redox initiation system at low temperature (30-40 ℃). Differential micro-emulsion polymerization is also used for synthesis, and has proven to be successful in producing small particles. Ultrasound assisted emulsion polymerization is another series of methods that has been tested. The details of all synthesis methods are illustrated in Chapter 2, the Literature Review.

The experiments carried out in this study aim at producing fine PMMA particles with narrow distribution, and making the synthesis process simpler so that it could be applied for mass production. For uniform and small particles synthesis, the particle size and distribution are the most important characteristics. For a mass production synthesis process, the polymerization rate and conversion are more important. In order to reach the objective, various types of synthesis methods were used, and many of them were assisted by ultrasound. The

experimental methods will be introduced in Chapter 3. The details of methods used and results obtained are described in Chapter 4, Results and Discussion.

Since various types of methods were applied, the results are categorized by the methods used in synthesis, and further study was done for those methods that provide significant results. As for the synthesis of small and uniform particles, results obtained by the pre-mixing separation method are reasonable, while results obtained by ultrasound assisted batch reaction appear more suitable for a mass production process. Further experiments were carried out for those two methods with more parameters like temperature, monomer concentration, and initiator types being considered.

The main achievements of this thesis can be concluded as 1) uniform PMMA particles with a diameter of less than 20 nm can be synthesized by the pre-mixing separation method; 2) PMMA particle size of 20-30 nm are synthesized by the ultrasound assisted batch emulsion polymerization method with high conversion, high polymerization rate and a relative simple operation; 3) It is discovered that appropriate intensity of ultrasound irradiation has positive effects on fine particles synthesis, while a overpower ultrasound irradiation source will have negative effects. The detailed information of the achievements and analysis is illustrated in Chapter 4, Results & Discussion.

2. Literature Review

The objectives of this thesis are: 1) synthesize small and uniform PMMA nano particles; 2) discover a reasonable method for mass production of PMMA nano particles. Therefore, methods used to synthesize PMMA nano particles are reviewed in this chapter, which include 1) conventional micro-emulsion polymerization method with thermal initiators or a redox initiation system; 2) differential micro emulsion polymerization with thermal initiators; 3) ultrasound initiated emulsion polymerization without chemical initiators.

Ever since ultrasound was introduced to organic nano particle synthesis, much work has been done on the study of results and mechanism. Dispersion of monomers and initiation of polymerization are two key effects of ultrasound for organic nano particle synthesis. Experiments of ultrasound used for synthesis of other types of polymers could be indirect reference for the study in this thesis, while ultrasound used for PMMA synthesis could be direct reference, and they will be illustrated separately. The studies on the mechanism and various parameters of synthesis are also important in guiding experimental design and phenomenon explanation.

2.1 Synthesis of PMMA nano particles via a conventional method

Nanosized polymer particles are expected to be applied and play a significant role in various fields including medical, environment, agriculture and catalysts due to the advantages of high

surface area and percentage of molecules or atoms on the surface (He et al., 2003). Thus, synthesis of nano polymer particles has attracted a great amount of attention from researchers all over the world, and the study of poly (methyl methacrylate) (PMMA) nano particles is a representative work in this research field. Unlike inorganic nano materials, nano polymer particles like PMMA are usually synthesized by mini emulsion or micro-emulsion polymerization. Micro-emulsion is a thermodynamic system containing solvent, monomer, emulsifier and sometimes co-emulsifier. As reported in previous papers, micro-emulsion polymerization can produce very small particles with particle diameters being less than 20nm. However, in conventional micro-emulsion polymerization of nano particles, the required amount of surfactant is quite large. Surfactants like SDS are quite expensive and have negative effects on polymer nano particles. To avoid the problem, Fu et al. (1998) and Ming et al. (1999) developed their own ways of synthesis using lesser amounts of surfactant. A small part of MMA monomers is added to the reaction system first, and the remaining amount is fed dropwise (Fu et al., 1998). Redox initiation is used and a stirring speed of 600rpm is applied. Sodium dodecyl sulfate is used as surfactant and the temperature of the reaction was 40℃. In this way, the particle size could be lowered to around 13nm, and the surfactant/monomer ratio is over 1:10. In the study of Ming et al. (1999), the surfactant was changed to dodecyl tri-methyl ammonium bromide, and potassium persulfate (PPS) was used as initiator. The reaction temperature was increased to 60℃ and magnetic stirring was applied in these experiments.

2.2 Synthesis of PMMA nano particles by differential micro-emulsion polymerization

He et al. (2003) and Norakankorn et al. (2007) investigated a new method of polymerization of nanosized particles, the differential micro-emulsion polymerization. In their experiments, methyl methacrylate monomers are added into the reaction system continuously as small droplets. In the work of He et al. (2003), water (solvent, polymerization medium), sodium dodecyl sulfate (SDS, surfactant), ammonium persulfate (APS, initiator) and 1-pentanol (co-surfactant) are mixed and heated up to 75 ℃. After that, MMA monomers are introduced continuously into the reaction system as small droplets. The time of monomer addition is 1 h, and then, the reaction was kept at a temperature of 80 ℃ - 85 ℃ before applying a cooling operation. Through this method, PMMA nano particles with z-average diameter of 14.5nm and number-average diameter of 10 nm were obtained (Figure 1). Similar to emulsion polymerization, increased concentration of surfactant results in a decrease of particle size in the experiments.

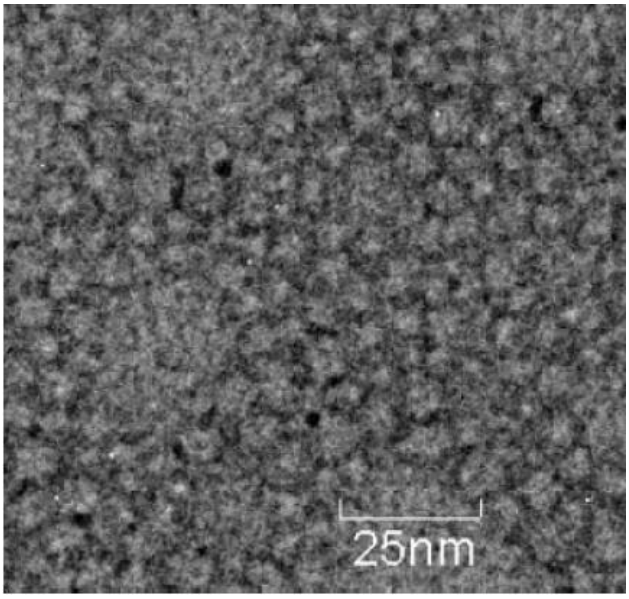

Figure 1. Transmission electron microscope image of nanoparticles obtained by differential micro-emulsion polymerization. (He et al., 2003)

In the paper of Norakankorn et al. (2007), another type of differential micro-emulsion polymerization was carried out. Oil-soluble initiator, 2, 2'-azoisobutyronitrile (AIBN), was used instead of a water-soluble initiator, ammonium persulfate (APS). Co-surfactant, 1-pentanol, is not used in these experiments. The addition time of monomer was extended to one and a half hours, and the reaction temperature was 70 ℃. Nano particles with a number-average diameter of around 20nm were synthesized successfully, and the size was a bit larger than those particles obtained by the method of using a water soluble initiator. It is also reported in the study that the monomer/water ratio has less effect on particle size in this method than in the method investigated by He et al. (2003). This phenomenon can be attributed to the usage of the oil-soluble initiator (AIBN) instead of the water-soluble initiator (APS), which tends to cause particle nucleation to occur in the micelles rather than in the aqueous phase. Both of

these two methods of differential micro-emulsion polymerization showed that the particle size can be controlled by the concentration of surfactant for real application, and usually a high concentration of surfactant leads to small particle size.

Mini emulsion polymerization, which uses water-insoluble monomers to form fine particles, is another way of synthesizing nano particles with less surfactant requirement than micro-emulsion polymerization. In such a reaction system, agglomeration of polymer particles is prevented by hydrophobic reagents. However, the diameter of particles obtained by mini emulsion polymerization is usually over 50nm, which is much larger than the diameter of particles obtained by micro-emulsion polymerization (He et al., 2003).

2.3 Usage of ultrasound in nanosized polymer particle synthesis

In recent years, ultrasound has been widely used in polymer particle synthesis due to its outstanding contributions in blending, dispersing, homogenizing, de-agglomerating and emulsifying. Ultrasound of high intensity can even dissociate the molecules of the surfactant, monomer and solvent to continuously provide free radical species. On this occasion, free radical polymerization can be initiated, and external initiator addition is unnecessary (Chou et al., 1998). The experiments of high intensity ultrasound initiated free radical polymerization can be carried out at ambient temperature because addition of a conventional initiator is not required so that the temperature of reaction system does not have to be raised up to the initiator decomposition temperature.

Micro-emulsion polymerization of butyl acrylate initiated by oil-soluble initiators like dibenzoyl peroxide (DBP) and lauroyl peroxide has been studied using a conventional polymerization method under ultrasound irradiation (Capek et al., 2006). DI water was used as the polymerization reaction medium and sodium dodecyl sulfate was the surfactant. The reaction temperature was set to be 50℃-80 ℃. The surfactant/monomer ratio (by weight) is 1:1 or 4:3, and the monomer/water ratio (by weight) was 3:20 or 1:5, respectively. The research involved a kinetic study, and the experiments were carried out to determine the polymerization rate *vs*. conversion. Results have shown that such methods of polymerization result in a high conversion rate of over 90%, and both a conventional polymerization process (without ultrasound irradiation) and unconventional polymerization process (with ultrasound irradiation) have similar particle size ranging from 60nm to 90nm. An equation for the emulsion polymerization rate (R_p) was formulated by Harkins (1947) and Smith-Ewart (1948):

$$R_p = k_p[M]_p \bar{n} N_p / N_A \quad (1)$$

where, k_p represents the propagation rate constant, $[M]_p$ is the equilibrium monomer concentration in the polymer particles, $\bar{n}$ is average number of radicals per particle, N_p is the number of particles per unit volume of the aqueous phase and N_A represents Avogardo's constant. Evidence obtained from experiments haven shown that the conversion rate increases sharply during the first 40 minutes for all these reactions carried out. The rate for such methods of micro-emulsion polymerization *vs.* conversion rate can be divided roughly into four intervals. For the first interval, where the conversion rate is from 0% to 20%, the polymerization rate increases sharply to a maximum value. In the following second interval, where the conversion

rate is between 20% and 40%, the rate of polymerization decreases. Within the third interval where the conversion rate is between 40%-50%, the polymerization rate is observed to go through another accelerating period, which can be attributed to a gel effective. After the conversion rate exceeds 50%, the polymerization rate decreases continuously until the end of polymerization reaction (Capek et al., 2006). Both types of polymerization reactions, with or without ultrasound irradiation, achieve very high conversion rates (over 80%) during the first 40 minutes of the entire length of reaction time. Comparing with conventional methods of micro-emulsion polymerization, experiments with ultrasound irradiation have a more rapid change of polymerization rate no matter whether in an increasing or decreasing region. On the other hand, ultrasound irradiation reactions are much less sensitive to the temperature of the reaction system. Since R_p varies with mechanistic events like desorption of monomeric radicals and re-retry of exited monomeric radicals, $k_{des,}$ the desorption rate constant, is estimated. The value of k_{des} is shown to be larger under ultrasound irradiation, which means that degradation of micelle aggregates is increased under ultrasound irradiation (Capeket al., 2006). As illustrated above, de-aggregation is one of the advantages of ultrasound applied in micro-emulsion polymerization, and it helps decrease the size of polymer particles. On the other hand, researchers also find that the activation energy is much lower under ultrasound irradiation (=20kJ/mol) than that under the conventional method of micro-emulsion polymerization (=84kJ/mol) (Capek et al.). All the work done above by Capek et al. has clearly shown us some differences between ultrasound assisted micro-emulsion polymerization and conventional conditions, and those differences could become advantages for usage of ultrasound in nano-sized polymer particles synthesis.

Reducing or eliminating use of emulsifier for emulsion or micro-emulsion polymerization is one big advantage for real application since surfactants are expensive and might have negative effects on the properties of nano polymer particles. Zheng et al. (2007) introduced ultrasound for the emulsion copolymerization of styrene a cationic surfactant which could be a copolymer in the reaction. In the reaction, $C_{12}N^+$ (methacryloxyethyl dodecydimethyl ammonium bromide) is used as a surfactant, a monomer, and an initiator. The molecular structure of $C_{12}N^+$ is shown in Figure 2, and the structure of the copolymer, poly-(styrene- $C_{12}N^+$), is shown in Figure 3.

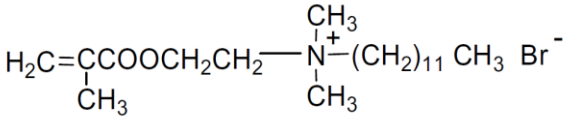

Figure 2. The Molecular Structure of $C_{12}N^+$ (Zheng et al., 2007)

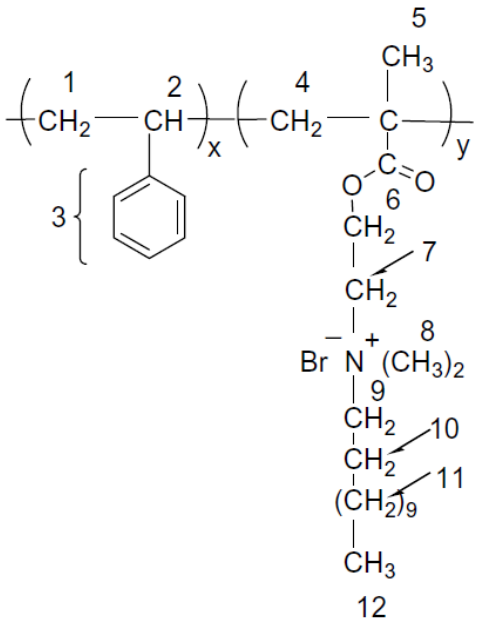

Figure 3. Structure of poly-(Styrene-$C_{12}N^+$) (Zheng et al., 2007)

The numbers in Figure 3 represent different hydrogen signals of different positions obtained from NMR, which is an important characterization technique for the existence of copolymers. In the experiments (Zheng et al., 2007), styrene (monomer), DI water (medium, solvent), and $C_{12}N^+$ (emulsifier, co-monomer, initiator) are mixed in a reaction vessel immersed in a water bath for heating. The total volume is 80 ml with 10% styrene (by volume) and a concentration of $C_{12}N^+$ ranging from 0.015g/ml to 0.035g/ml. The surfactant/monomer ratio (by weight) is calculated to be 1:6 to 1: 2.6. Probe ultrasound with a frequency of 20 kHz and adjustable power output was applied to the reaction system after N_2 bubbling for 10 minutes, and the reaction time was 60min. The power of ultrasound is recorded to be 14.4W to 56.6 W so that the corresponding intensity of ultrasound is 3.0W/cm^2 to 11.8 W/cm^2. Nano particles of poly-(styrene-$C_{12}N^+$) with an average diameter of 40nm are obtained under this condition as shown in Figure 4.

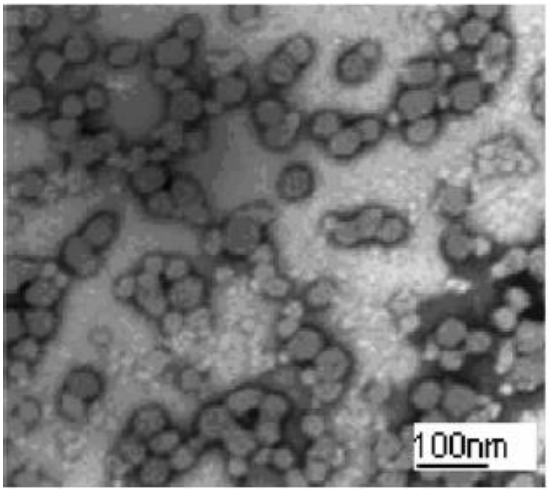

Figure 4. TEM pictures of nanosized poly-(styrene-$C_{12}N^+$) particles obtained by ultrasound irradiated emulsion polymerization (Zheng et al., 2007)

Results have shown that $C_{12}N^+$ is split into radicals and act as conventional initiators under ultrasound irradiation (Zheng et al., 2007). The conversion rate of styrene is as high as 95%, and most of the $C_{12}N^+$ is eliminated because it is consumed in the process of initiation and polymerization, and has become part of the copolymer. Therefore, the purity of such copolymer latex is quite high, and such latex does have numerous potential applications.

Ultrasound has also been applied for the free radical polymerization of acrylonitrile, and has shown its effects of accelerating the polymerization (Selvaraj et al., 2014).

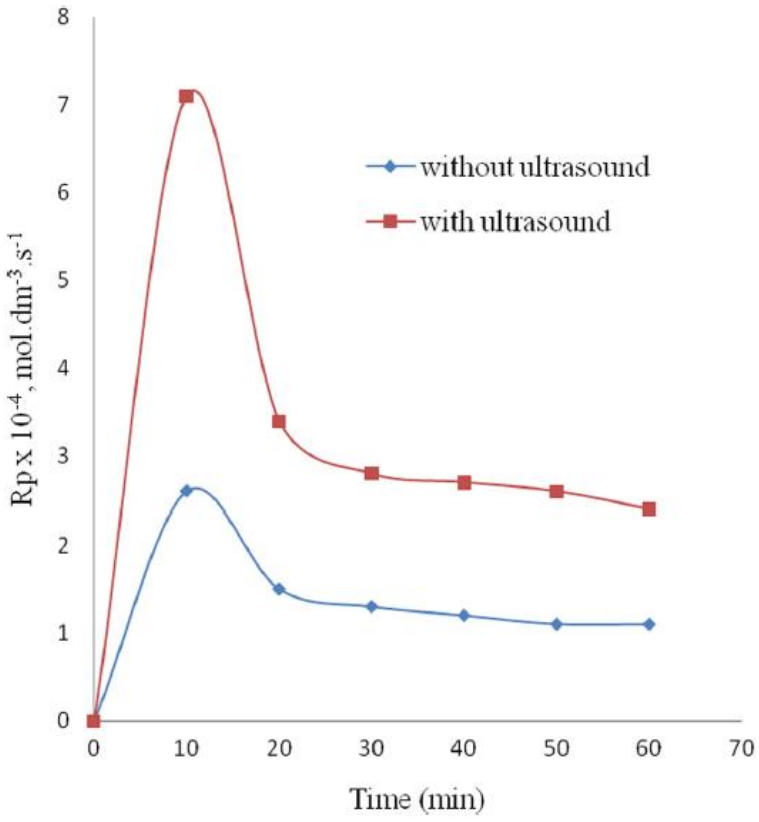

Figure 5. Polymerization rate of acrylonitrile, with or without ultrasound (40 kHz) (Selvaraj et al., 2014)

In this case, poly-acrylonitrile is synthesized with a new multi-site phase-transfer catalyst, and bath ultrasound is applied to the reaction system. The ultrasound device has two different frequencies of 28 kHz and 40 kHz both with the same power output of 300W. The reaction vessel is immersed in the center of the liquid medium (water) in the tank of the ultrasound device, and the ultrasound wave is generated at the bottom of the tank and transmits through the medium to the reactor (bath ultrasound). Unlike the rate of polymerization ($\boldsymbol{R_p}$) obtained from Equation (1), $\boldsymbol{R_p}$ here is calculated via a gravimetrical method as shown in Equation (2).

$$R_{\mathrm{p}} = \frac{1000 \times m_m}{V \times t \times M_m} \tag{2}$$

where, $\boldsymbol{V}$ is the total volume of the reaction mixture (ml), $\boldsymbol{t}$ is the reaction time (s), $\boldsymbol{M_m}$ is the molecular weight of acrylonitrile, and $\boldsymbol{m_m}$ is the weight of poly-acrylonitrile (g). As can be clearly seen from Figure 5, the rate of polymerization under ultrasound (40 kHz, 300W) is much higher than that of a conventional method without ultrasound in all three intervals including increasing, decreasing and final steady intervals. It is reported in the paper that the polymerization rate is enhanced 3 fold under 28 kHz compared to those reactions without ultrasound. For ultrasound with 40 kHz, the polymerization rate is enhanced 8 fold (Selvaraj et al., 2014).

In a paper of Cass et al. (2010), ultrasound was also introduced for the polymerization of water soluble monomers to produce hydrogels.

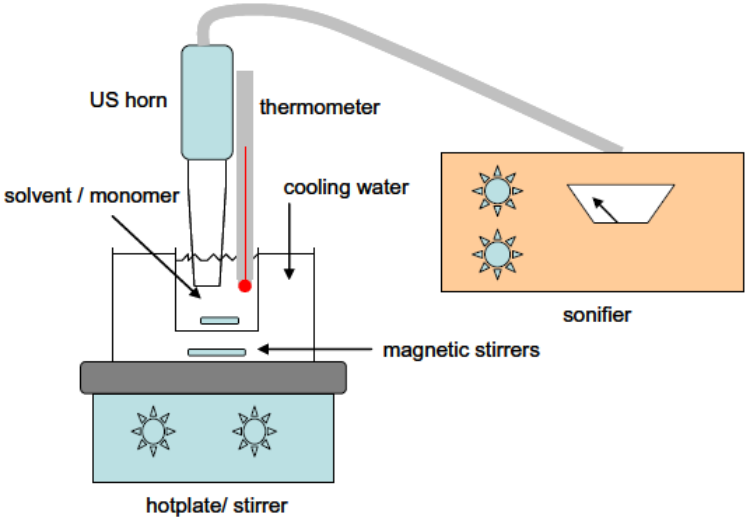

Figure 6. Set-up diagram of ultrasound device applied for hydrogels preparation (Cass et al., 2010)

Monomers of 2-hydroxyethyl methacrylate, poly-(ethylene glycol) dimethacrylate, dextran methacrylate, acrylic acid/ethylene glycol dimethacrylate and acrylamide/bis-acrylamide are used for preparation of hydrogels. The diagram of the device is shown in Figure 6, and it is a type of typical setup for applying probe ultrasound to a conventional reactor equipped with magnetic stirring. Dextran methacrylate is synthesized separately before the preparation of hydrogels. Initiators are usually not welcomed in the synthesis of biomaterials, especially cytotoxic initiators. Under such circumstances, ultrasound of high intensity has shown its advantages for the continuous production of free radicals so that external initiator addition can be avoided.

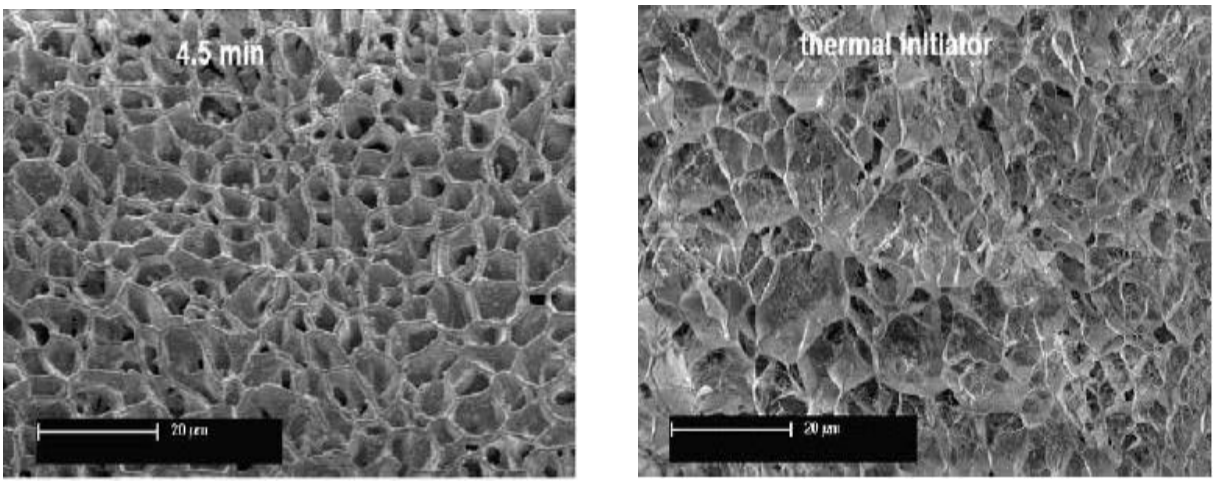

Figure 7. SEM image of ultrasound initiated Dex-MA hydrogels with polymerization time of 4.5min, compared to thermal initiation hydrogels (Cass et al., 2010)

Moreover, it is found that ultrasound initiated hydrogels have more uniform structures than those without ultrasound so that they have a lower swelling ratio than hydrogel obtained from thermal free radical initiation reaction systems (Figure 7). The cause for the result is likely to be attributed to the micro bubbles generated by probe ultrasound and stabilized by the viscous solution (Cass et al., 2010).

High intensity focused ultrasound (HIFU) was used in triggering shape recovery of shape memory copolymers (SMPs) by Li et al. (2014). Cross-linked copolymer samples were prepared in advance by free radical polymerization reaction within a mixture of methyl methacrylate (MMA), butyl acrylate (BA), ethylene dimethacrylate (EGDMA, crosslinker), and AIBN. Samples were made to be of the same shape but with different thickness. Ultrasound with high frequency and high intensity (1.1 MHz, 300W) was used as a heat source for the copolymers, as heating is the key to shape recovery.

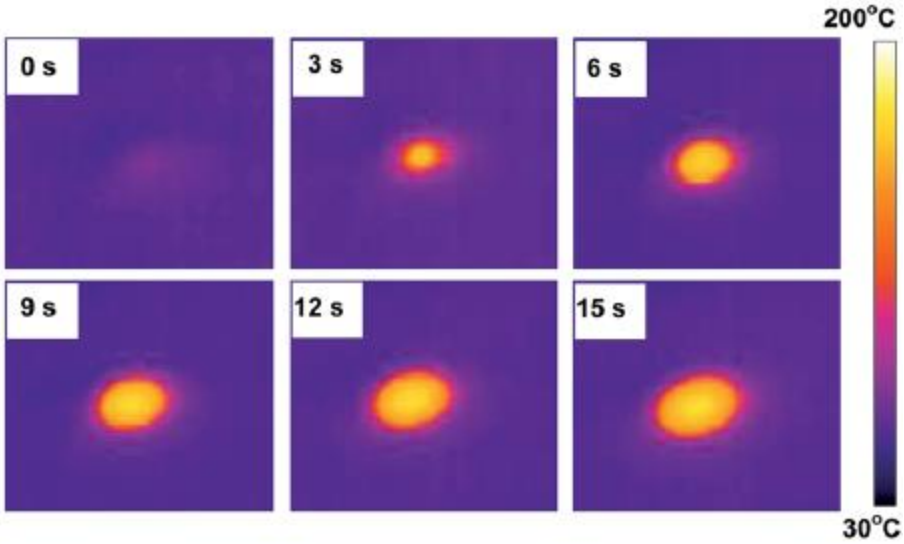

Figure 8. Temperature changes of a copolymer sample under HIFU within 15 seconds, recorded by infrared camera (Li et al., 2014)

As illustrated in this paper, HIFU is a reliable heating resource, and has advantages of quick heating and accurate localization. The temperature of samples can reach as high as 120°C in 15 seconds, and concentrate the heat on the samples without heating the surroundings (Figure 8). Power of heating depends on the intensity of ultrasound so that it can be controlled by adjusting the frequency or amplitude of the ultrasound wave. In addition, ultrasound of the same intensity will have different thermal effects on copolymer sheets of different thickness. Every sample heated by HIFU will have a different process of temperature rising and different equilibrium temperatures, so that optimum thickness of samples for maximum thermal effect can be studied, which is quite different than for conventional heated samples (Li et al., 2014).

Effects of high frequency (213 kHz) ultrasound on micro-emulsion polymerization of *n*-butyl methacrylate (BMA) were studied by Teo et al. (2008), as well as the effects of type and

concentration of surfactants on rate of polymerization, latex size, and molecular weight. The total volume of the reaction was 50ml, the concentration of monomers 0.3M, and the surfactant concentration was varied from 0.5% to 10.5% (by weight). The monomer/surfactant ratio was approximately from 8:1 to 2:5 (by weight). The temperature is maintained at 30℃，which could be ranked as low temperature micro-emulsion polymerization; input of power is 0.1W/ml, and all the reactions are chemical initiator free. Results of high frequency ultrasound initiated PBMA have shown that the conversion rate reaches over 90% percent in 15 minutes while an ionic surfactant is used as a stabilizer, but for non-ionic surfactants, the conversion rate cannot exceed 60%. The particle size of latex with an ionic surfactant is smaller than those with non-ionic ones, and the distribution is also much narrower (Teo et al., 2008).

Corresponding to high frequency ultrasound, high intensity ultrasound initiated mini emulsion and micro-emulsion polymerization of butyl methacrylate was studied by Teo et al. (2009). The difference between high intensity ultrasound and high frequency ultrasound is that the intensity of sound wave is controlled by both frequency and amplitude, so that high intensity ultrasound could be ultrasound with high frequency, high amplitude, or both high frequency and high amplitude. Monomer of butyl methacrylate is mixed with DI water after removing inhibitors with the concentration of ionic surfactant, sodium dodecylsulfate (SDS), ranging from 0.1% to 10.5% (by weight). The reaction system is kept at a temperature of 30 ℃, and ultrasound with frequency of 20 kHz and horn of 19mm is applied to the mixture. The intensity of the input ultrasound wave is estimated to be 8W/cm^2. The total volume for the reaction is 80ml. Since there are no external chemical initiators used for the experiments, the most likely mechanism of such a micro-emulsion polymerization is shown in Figure 9.

Initiation:			
	)))		
H_2O	→	•H + •OH	1
•OH/ •H + M_s	→	HOM_s•/ HM_s•	2
Propagation:			
M_s•	→	M_b•	3
M_b• + M_b	→	M_{ib}•	4
M_b•/ M_{ib}• + D	→	D•	5
M_b•/ M_{ib}• + micelle	→	M_{micib}•/M_{micb}•	6
D•	→	D_p•	7
Termination:			
M_b•/ M_{ib}• + D_p•	→	Polymer particle	8
M_{micib}• + M_b•/ M_{ib}•	→	Oligomer	9
D_p• + SDS	→	Polymer particle + SDS•	10

Figure 9. Mechanism of high intensity ultrasound initiated micro-emulsion polymerization (Teo et al., 2009)

In Figure 9, **)))** represents the ultrasound wave, ***M*** represents monomer, ***s*** is the symbol of the surface of cavitation bubbles, ***b*** is the symbol of bulk solution monomer, ***D*** represents the droplets, ***i*** for more than two molecules per particle, and ***mic*** is the symbol of micelles (Teo et al., 2009).

In the ultrasound initiated polymerization, besides the monomers, molecules of the medium and surfactants can also take part in the polymerization. The results of the experiments indicate that the kinetics of the ultrasound initiated micro-emulsion polymerization follow linear first order plots, and it is an effective and controllable method of synthesizing polymer nano particles with small size and narrow distribution. Experimental samples with high concentration of surfactant appear to have a high rate of polymerization and high conversion rate. High

concentration of surfactant refers to high concentration of micelles and monomer drops and larger surface area. More micelles and drops can provide more sites for polymerization reaction, and larger surface area will enhance the interactions between free radicals and micelles and droplets, which are two important reasons for the high polymerization rate. It also revealed that ultrasound initiated micro-emulsion polymerization follows the mechanism of continuous nucleation where the initiation of reaction is likely to occur in the droplets (Teo et al., 2009).

2.4 Usage of ultrasound in polymerization of methyl methacrylate (MMA)

Ultrasound irradiation was first applied to the emulsion polymerization of MMA by Chou et al. (1998). The effects of ultrasound irradiation, cavitation, and dependence of molecular weight and polymerization rate on various parameters were systematically studied. MMA monomers with a monomer/water ratio (by volume) of 1:19 to 1:5 are mixed with surfactant (SDS) with concentration ranging from 0.035M to 0.243M slowly and with continuous stirring. Reaction time was set to be 30-35 minutes, and the reaction took place at ambient temperature without conventional initiators. The input power of ultrasound is 34W-72W so that the corresponding intensity is 6.8W/cm^2 to 14.4W/cm^2. Under such conditions, the rate of polymerization is high, and the conversion rate can reach as high as 70% (Chou et al., 1998). Results are close to those experiments done with a conventional thermal initiator, but the rate of polymerization and conversion rate are enhanced. It is found that the occurrence of ultrasonic initiation is highly relative to the resonant cavitation, and requires continuous bubbling in the reaction system, without which, no significant polymerization reaction of MMA can be observed. The rate of

polymerization increases with the power of ultrasound, and such a phenomenon can be attributed to more free radicals generated by ultrasound, rising temperature due to the heat from ultrasound vibration and polymerization and gel effect due to increasing cavitation bubbling. The gel effect is also the main reason for the molecular weight increasing with higher ultrasonic intensity. It also revealed that a flow rate of argon, which is introduced into the reaction system for bubbling, also has effects on the polymerization rate. The rate slightly increases with increasing flow rate mainly because of the enhanced gel effect (Chou et al., 1998). Higher concentration of surfactant and initial monomer will also increase the polymerization rate as illustrated above.

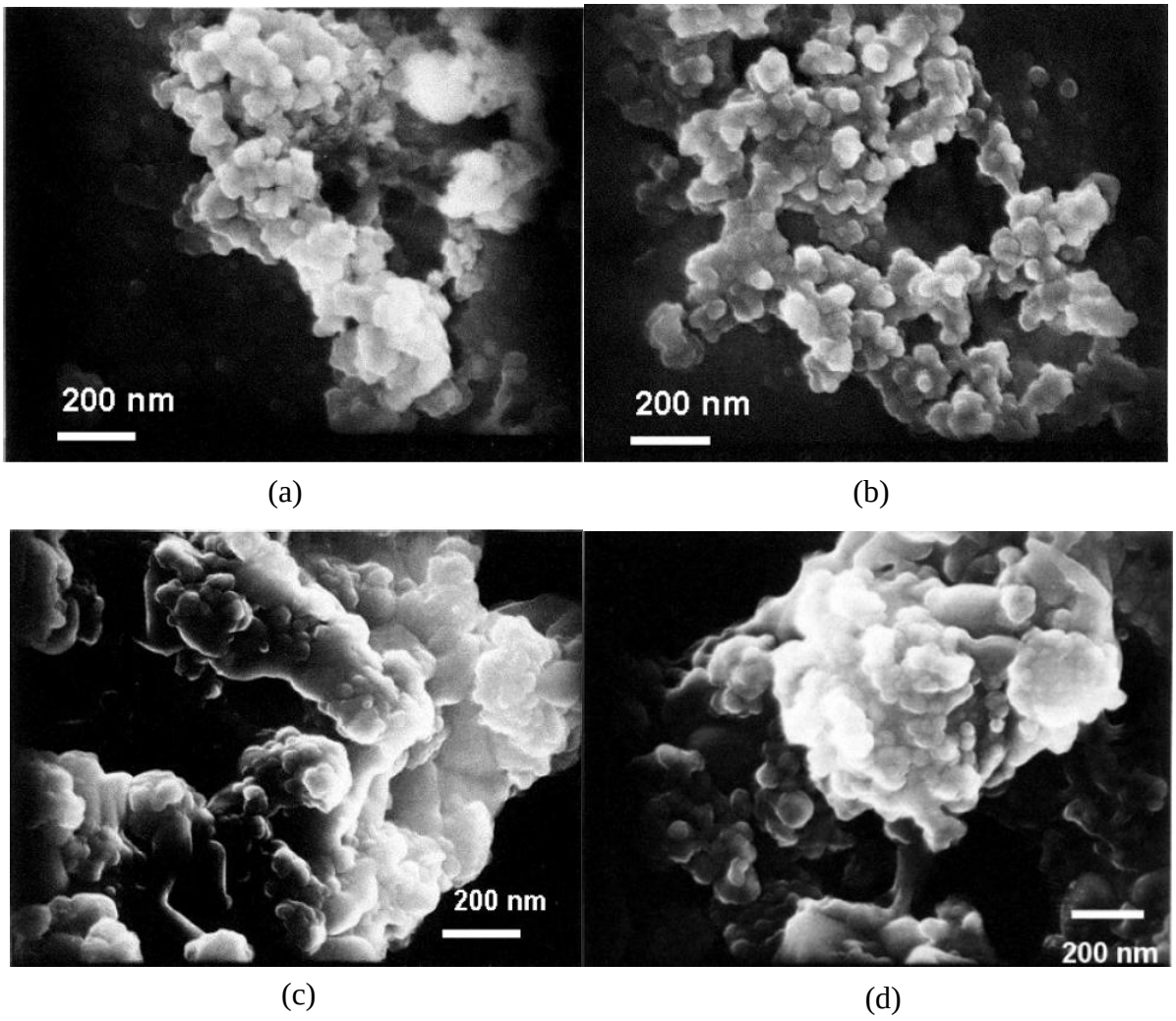

Figure 10. Image of PMMA synthesized with 10% (v/v) MMA and 0.5% (a), 1.5% (b) (w/v) SLS, 0.5% (c), 1.5% (d) CTAB (Parra et al., 2005)

Characterization of PMMA synthesized with ultrasound irradiation (20 kHz, 150W) was carried out by Parra et al. (2005). Various types of data were collected, especially SEM images for PMMA particles synthesized with 10% (v/v) MMA and different types and concentrations of surfactants such as SLS (Sodium laurylsulfate, anionic surfactant) and CTAB (cetyltrimethylammonium bromide, cationic surfactant). As Figure 10 shows, PMMA particles

synthesized with SLS yield and smaller particle size than those synthesized with CTAB, which indicates that the anionic surfactant is better than the cationic surfactant in producing smaller ultrasound irradiated PMMA particles. Besides, it is illustrated above that ionic surfactants are also better than non-ionic surfactants. While within the same type of surfactant, the size of PMMA particles synthesized with SLS does not seem to vary with the concentration of surfactant, in other words, the concentration of surfactant has little effect on particle size. In contrast, the concentration of CTAB has more effect on particle size of PMMA. As can be seen in Figure 10 (c) and (d), higher concentration of CTAB will result in larger particle size. The figures also show that PMMA particles are embedded in the matrix, which may contribute to the surfactant molecules remaining occluded between the polymer chains during the process of polymerization (Parra et al., 2005), and it might be evidence for another form of participation of the surfactant in high intensity ultrasound irradiated emulsion polymerization.

Besides surfactant, other parameters for ultrasound irradiated emulsion polymerization of MMA such as ultrasonic power, ultrasound pulse, and diameter of probe for probe ultrasound were investigated by Korkut et al. (2013). Experiments were carried out on two main values, the conversion of MMA monomers and energy consumption of ultrasound for unity weight of PMMA produced. There were two types of probes used in reaction, diameter of 13mm and 19mm, and different types of probe ultrasound irradiation, continuous and pulse, were also applied to the experiments. The frequency of ultrasound was 20 kHz, and the maximum amplitude is usually determined by the diameter of ultrasound probe. A probe with a diameter of 19mm has a higher maximum amplitude value than that of 13mm, which also consumes more electronic energy, providing higher ultrasound intensity. From the aspect of energy saving,

ultrasound of pulse mode is usually better than the continuous mode. The “intensity” of pulse mode can be described by **Pulse Ratio** (**PR**), and is illustrated by Equation 3.

$$PR = \frac{t_{on}}{t_{on} + t_{off}} \tag{3}$$

where, t_{on} refers to irradiation time, t_{off} is the gap between two irradiation time, and $t_{on} + t_{off}$ is the total processing time. When t_{off} equals zero, it represents a continuous mode. As shown from the results of the experiments, a pulse ratio of 0.7 is the optimum choice. In the experiments of ultrasound initiated emulsion polymerization, the main effect of ultrasound is to generate sufficient free radicals, and the effect of emulsifying is less important because the intensity of the ultrasound applied in this study is quite high so that the mixture is emulsified in a very short time. Therefore, a continuous mode is a waste of energy and not enough free radicals can be generated at a low pulse ratio.

Increased ultrasound power over a specific range will help to increase the rate of polymerization due to increased free radical generation speed and enhanced diffusion of monomers from droplets to micelles. However, high power of ultrasound which exceeds the specific range will have adverse effects on the polymerization. Number of active cavitation bubbles generated by high power ultrasound will decrease because of the effects of acoustic decoupling and bubble coalescence (Korkut et al., 2013).

For the diameter of the probe of horn ultrasound, a 19mm probe is more suitable for common application because it consumes less energy at the same conversion compared to a 13mm

probe. A 13mm probe performs better than 19mm one especially when aiming to achieve high conversion rate (Korkut et al., 2013).

Bhanvase et al. (2011) carried research on ultrasound assisted semi-batch emulsion polymerization of PMMA to identify the role that ultrasound and initiator play in such experiments. In ultrasound initiated polymerization reactions, because of the absence of chemical initiators, free radicals are generated by cavities created by ultrasound. The life of cavities is extremely short, only a few microseconds. During the period, cavities grow and collapse, and in the process of collapse, the local temperature and pressure will increase dramatically to over 10,000 K and over 1000 atm. In such condition, the decomposition of solvent, monomer, surfactant molecules generates free radicals (Bhanvase et al., 2011). However, such a process of initiation requires high intensity of ultrasound which consumes lots of energy, but at the same time, the efficiency is quite low because most of free radicals recombine to form stable molecules. The addition of chemical initiators (potassium persulfate, PPS) into the ultrasound irradiated emulsion polymerization system can successfully solve the problem. In the semi-batch polymerization reaction, MMA monomers are introduced into the reactor in portions, and both chemical initiators and high intensity ultrasound irradiation are applied for initiation. Results of the experiments have indicated that PMMA nano particles with diameter of 50nm are obtained, and the polymerization rate can be increased from $0.56gL^{-1}min^{-1}$ to $1.33gL^{-1}min^{-1}$ by addition of initiator. Under this condition, the decomposition of initiator and diffusion of radicals are enhanced by ultrasound irradiation so that the reaction speed can be increased (Bhanvase et al., 2011). As for the semi-batch method of reaction, results have shown similar conclusions as for batch reactions in terms of surfactant concentration, monomer

concentration, and reaction temperature, which has been described above. The smaller diameter of PMMA particle size (~50nm) might be the advantage of semi-batch reactions as He et al. (2003) successfully synthesized very fine particles through a differential addition method.

Combined use of thermal initiation (PPS) and ultrasound initiation was also applied to emulsion polymerization of PMMA and PMMA/$CaCO_3$ nano composites by Prasad et al. (2013). For MMA only polymerization, 7.5g MMA, 0.55g SDS, and 69g water are mixed, and for MMA-$CaCO_3$ reaction system, another 0.3g $CaCO_3$ is added into the reactor. Inorganic compounds present in the polymer products have advantages in abrasion resistance, thermal resistance and anticorrosion. The mechanisms of ultrasound initiated polymerization of PMMA and PMMA/$CaCO_3$ are shown in Figure 11 and Figure 12 respectively.

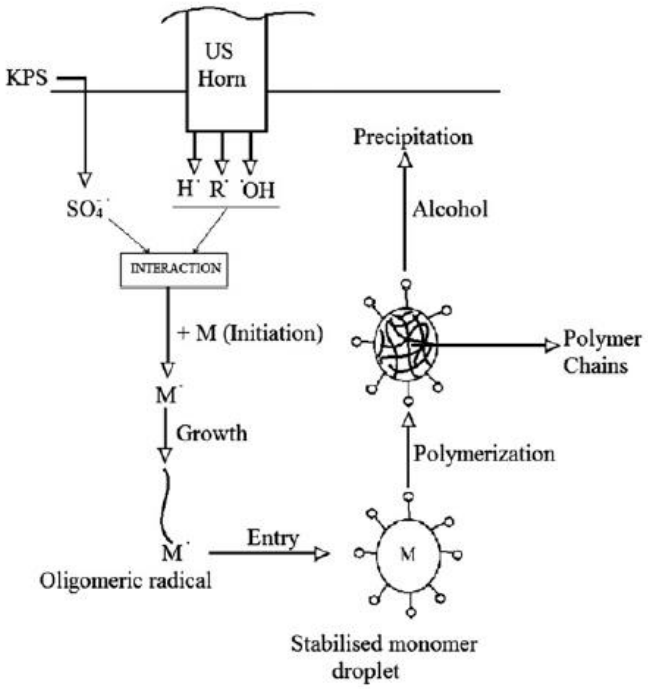

Figure 11. Mechanism of ultrasound initiated polymerization of MMA (Prasad et al., 2013)

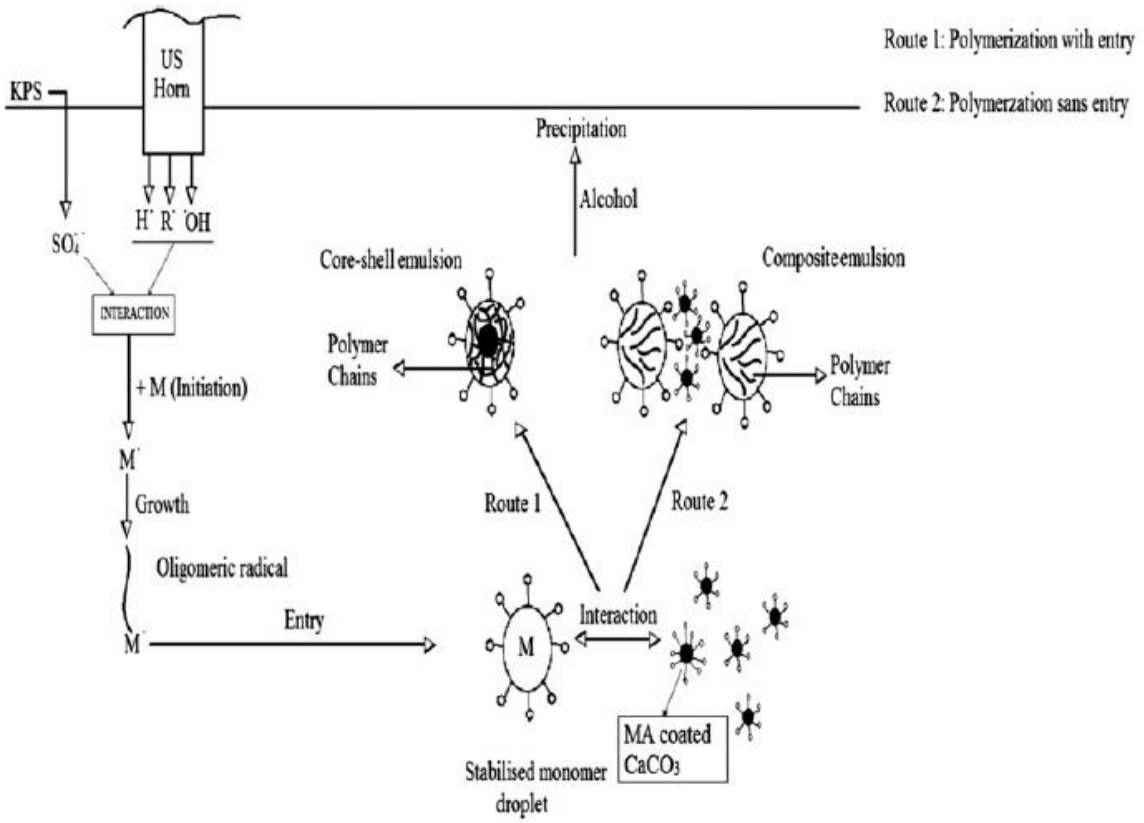

Figure 12. Mechanism of ultrasound initiated polymerization of PMMA/$CaCO_3$ (Prasad et al., 2013)

Three sets of initiation methods are applied to the experiments: (1) thermal initiation (PPS); (2) ultrasound initiation; (3) combination of thermal initiation and ultrasound initiation. The main effect of combined initiation is the increased conversion compared to (1) and (2). Results indicate that the conversion of (1) for PMMA is 72%, for PMMA/ $CaCO_3$ is 76%. Conversion of (2) for PMMA is 69%, for PMMA/ $CaCO_3$ is 66%. Conversion of (3) for PMMA has been increased to 87%, and for PMMA/ $CaCO_3$ it is increased to 86%. All the particles are within the size of 60nm to 130nm (Prasad et al., 2013).

In another paper of Parra et al. (2008), a redox initiator was applied for emulsion polymerization of PMMA along with high frequency ultrasound irradiation. Redox initiation and thermal initiation are two effective conventional initiations. Compared with thermal initiation, redox initiation system has advantages in low temperature initiation (0℃~50℃) and reasonable generation velocity of free radicals. High intensity ultrasound irradiation is another effective method for low temperature initiation, and it can also be combined with conventional initiation methods. Similar to the work of Bhanvase et al. (2011), in which thermal initiation and ultrasound initiation were combined, the combination of redox initiation and ultrasound initiation was studied in this paper. Ammonium peroxidisulfate, initiator, sodium metabisulfate, reductive agent, and ferrous iron sulfate, acting as catalyst, were used to form a redox initiation system. Ultrasound with frequency of 20 kHz was applied to the reaction as well. The reaction temperature was set at a low level (25 ℃)

Unlike the system of combined use of thermal initiation and ultrasound initiation, in which the polymerization rate increases due to the enhanced decomposition rate of initiator by ultrasound, results showed that no significant effects were found with respect to the polymerization with ultrasound initiation alone when an ionic surfactant was used (Parra et al., 2008). It was also discovered that the effect of joint initiation varies with the type of surfactant. When an ionic surfactant is used, no significant effect can be observed because in this case, molecules of the ionic surfactant are broken down to form free radicals so that a continuous free radical source exists. But for non-ionic surfactants, addition of a redox initiator is very important because non-ionic surfactant molecules can hardly be broken down to free radicals since the chemical bond is strong. The morphology of particles synthesized with or without a

redox initiation system was found to be different. For ionic surfactants, particles synthesized without redox initiation seem to have smaller particle size (40-50nm) and narrower distribution than those synthesized via redox initiation (2-4μm). For non-ionic surfactants, particles synthesized without redox initiation seem to produce larger particles (80nm-2μm) and wider distribution than those synthesized without redox initiation (50nm-1.2μm). There is also another difference between ionic and non-ionic surfactants as well, and particles synthesized with ionic surfactants are affected more by redox initiation than those with non-ionic surfactants (Parra et al., 2008).

As recommended above, mini emulsion polymerization is another way to produce nano polymer particles. Ultrasound initiated mini emulsion polymerization of methacrylate was carried out by Teo et al. (2007). Methyl methacrylate (MMA), *n*-butyl methacrylate (BMA), and 2-ethylhexyl methacrylate (2EHMA) were used as monomers. The recipe for the experiments is 7.5g monomer, 69g water, and 0.55g SDS, and the reaction temperature was kept at 30℃. Argon stream was used to bubble through the mixture, to provide protection from oxygen. Ultrasound provided by a 19mm probe was applied to the reaction to generate a uniform emulsion at first, and then pulse mode (7s on, 3s off, Pulse Rate is 0.7) was used to initiate the polymerization. The corresponding ultrasound intensity was 8W/cm^2.

Particles with a diameter ranging from 70nm to 130nm were obtained. Results from the experiments have shown that ultrasound initiated mini emulsion polymerization of methacrylate follows a similar mechanism to that of conventional mini emulsion polymerization. Particles continuously grow during the process of polymerization, and the only difference is

that the radicals are produced by a cavitation effect rather thermal initiators. The order of polymerization rate for three methacrylate monomers is 2EHMA>BMA>MMA (Teo et al., 2007).

The main purposes for the experiments carried in this research is to find an effective and simple method of synthesizing nano sized PMMA particles with small particle size and narrow distribution and to find a method suitable for mass production or for real factorial application. In this study, the combination of both ultrasound initiation and thermal initiation are used for the high polymerization rate, and different methods of polymerization and emulsifying methods are studied.

3. Experimental

3.1 Materials

Commercially available monomer Methyl Methacrylate (MMA, containing ≤30ppm MEHQ as inhibitor, 99%, Sigma-Aldrich) was used without any further treatment. The analytical-grade initiators are Potassium Persulfate (PPS or KPS, Water-Soluble, ≥99%, Sigma-Aldrich) and 2, 2-azobisisobutyronitrile (AIBN, Oil-Soluble, 98%, Sigma -Aldrich), and were used as received. The emulsifier (or surfactant) was reagent-grade Sodium Dodecyl Sulfate (SDS, 99%, Sigma-Aldrich), De-ionized Water was supplied by the Chemical Engineering Department, University of Waterloo.

3.2 Apparatus

Probe/Horn Ultrasound (Fisher Scientific^{TM} Model 120 Sonic Dismembrator, 120W, 20 kHz) equipped with 1/8 inch probe, and a hot plate equipped with a magnetic stirring, round bottom three-neck flask, a peristaltic pump and ultrasound cleaner were used for the polymerization experiments.

3.3 Polymerization of PMMA

Poly Methyl Methacrylate was synthesized by three methods, Differential Addition Method, Batch Reaction Method, and Pre-Mixing Separation Method with five different emulsifying methods, Magnetic Stirring, Bath Ultrasound, Probe Ultrasound (Horn Ultrasound), Magnetic Stirring + Probe Ultrasound, and Bath Ultrasound + Probe Ultrasound. Different concentrations

of surfactant, different concentration of monomer, and different temperatures were examined for certain experiments. Other experiments like initiator-free tests were also carried out. All the details will be illustrated in each section of the Results and Discussion.

3.4 Characterization

The solid content (***S %***) was determined by weighting gravimetric method. A volume of 10 ml sample was taken out and weighted before and after drying in an oven. ***S %*** is calculated by Equation (4).

$$S\%=W_1 / W_2 \times 100\% \tag{4}$$

where W_1 is the weight of dried PMMA particles of certain volume of latex sample. It is calculated by total solid weight deducting the weight of surfactant, since the total volume of the latex after reaction, the volume of latex taken for sample drying, and the total amount of SDS added to the system are known. W_2 is the weight of a certain volume of latex taken for the sample.

The conversion rate (X_m) is determined by the same of solid content and is capsulated by Equation (5).

$$X_m = \frac{W_1}{M_{(total)} \times \frac{l_1}{L}} \times 100\% \tag{5}$$

where $\boldsymbol{M_{(total)}}$ is the total weight of MMA monomers added to the reaction system (density of MMA is 0.9440 g/cm^3). $\boldsymbol{I_1}$ is the volume of latex taken for sample, and $\boldsymbol{L}$ is the total volume of latex after reaction.

The mean particle size and the polydispersity (PD) were determined using Dynamic Light Scattering device (Brookhaven Instruments Corporation) at the angle of 90°, 20℃. The particle size obtained by this instrument is the hydrodynamic diameter (*z*-average diameter, effective diameter). The value of PD is defined by Equation (6).

$$PD = \frac{\mu}{\Gamma^2} \tag{6}$$

where $\boldsymbol{\mu}$ is proportional to the variance of the intensity weighted diffusion coefficient, and $\boldsymbol{\Gamma}$ varies with the relaxation of the intensity fluctuation of scattered light. A small PD value refers to a narrower distribution of particle size, and PD is equal to zero for an identical distribution situation.

4. Results & Discussion

Experiments were carried out to find reasonable ways for fine & uniform particle synthesis and for mass production of PMMA. Since various types of polymerization methods and emulsifying methods were tested to find the right way to reach the goal, results are categorized by those methods used for synthesis, and some comparison will be made to see the differences. There will be three main polymerization methods, batch reaction, pre-mixing separation, and differential addition. Five emulsifying methods were applied for the batch reaction method and pre-mixing separation method because some parts of the results obtained by the two methods approaches the main goals of this study so that more experiments were carried out to obtain more detailed information. A pre-mixing separation method seems to have advantages in producing fine & uniform particles, while the batch reaction method is more suitable for mass production. Other parameters like monomer/water ration, concentration of surfactant and initiator type were also studied for those methods which provide significant results.

4.1 Batch Reaction Method

A batch reaction is the simplest way of synthesizing nano sized polymer particles. In the process of a batch reaction, initiators, surfactant, monomer, and solvent are mixed and emulsified by a prescribed method. Reactions take place in the three neck glass flask. The normal recipe is listed below.

Initiator(PPS or AIBN)	Solvent(Water)	Monomer(MMA)	Surfactant(SDS)
0.16g	120ml	14ml	1.4g

For this batch method, different emulsifying methods will be applied to the reaction system, so that the differences can be seen from the results. The usual reaction time is set to be 1h & 15min, which contains 15 min for rising temperature and 1h hour for reaction, and a cooling method of ice water will be applied after reaction. The temperature for the reaction will be 70 ℃. Any changes to the parameters listed above will be noted in the Tables of results.

4.1.1 Magnetic Stirring

Magnetic stirring is the most commonly used method of emulsifying. The higher agitation speed of magnetic stirring refers to higher shear force and energy. Both 100rpm and 300 rpm stirring rates were examined in the experiments, and double the amount of MMA are also examined in the series of the experiments. The results obtained are shown in Table 1.

Table 1. Results of Batch Reaction Method with Magnetic Stirring

Sample No.	Effective Diameter (nm)	PD	Agitation Speed (rpm)	Amount of MMA (ml)
32	39.5	0.055	300	14
33	50.8	0.04	300	28
34	22.3	0.137	100	14
35	25.5	0.162	100	28

Reaction Condition: 120 ml Water, 1.4g SDS, 0.16g PPS, 14/28 ml MMA; Temperature=70 ℃; Reaction Time=75 min.

The results of the experiments have shown that higher agitation speed leads to larger particle

size with a narrower distribution, and lower agitation speed leads to smaller particle size with a wider distribution. At the very beginning of the reaction, MMA will float on the top of the SDS solution, and can only be mixed after agitation starts. Higher agitation speed can mix more MMA with the SDS solution and make it more even; however, there will always be a part of the MMA left on the top of SDS solution, which becomes a floating transparent object. It can be seen from the results that the addition of more MMA has a big influence on the particle size when the agitation speed is 300 rpm, but has less effect on particle size when the agitation speed is lower than 100 rpm. This is because more MMA can be mixed into the solvent at a higher agitation speed, which makes particles grow larger, and at a lower agitation speed, more MMA monomers become large floating objects. This can also explain the difference between the particle sizes at the two different agitation speeds.

4.1.2 Bath Ultrasound

Bath ultrasound is generated by a bath ultrasound cleaner, in which the power of the bath ultrasound cannot be modified. The tank of the cleaner is filled with water and the reactor is placed in the middle of the tank. Ultrasound is generated from the wall of the tank and immerses into the reactor. The reactor is heated by hot water in the tank.

Table 2. Results of Batch Reaction Method with Bath Ultrasound

Sample No.	Effective Diameter (nm)	PD	Reaction Time	Amount of MMA (ml)	Initiator Type
16	72.5	0.100	75min	14	AIBN
17	95.0	0.033	7h	14	AIBN
19	108.4	0.073	75min	28	AIBN
20	77.2	0.044	75min	14	AIBN
21	87.0	0.135	2h	14	AIBN
22	52.8	0.140	75min	14	PPS
23	49.7	0.133	75min	14	PPS

Reaction Condition: 120 ml Water, 1.4g SDS, 0.16g PPS/AIBN, 14/28 ml MMA; Temperature=70 ℃; Reaction Time=75 min/2 h/ 7 h.

Results in Table 2 show that water soluble (PPS) initiator is better than an oil soluble initiator (AIBN) in producing fine nano particles, which is the same as for a conventional emulsion polymerization. Because of this, PPS is use for almost all other experiments (Sample Number less than 25) instead of AIBN. By using this method, the problem of floating objects can be dissolved, but the particle size is larger than those obtained by the magnetic stirring method even when using a water soluble initiator. The intensity of the bath ultrasound is not high enough to generate cavitation in the latex, and micelles and droplets of monomers cannot be further broken down by the “force” of ultrasound. Essentially, bath ultrasound does not act very differently from magnetic stirring. Addition of double the amount of monomer will result in an increase in the particle size, while extending the reaction time can narrow the distribution, which is shown quite obviously for Sample 17 and Sample 19.

4.1.3 Probe Ultrasound

Ultrasound is generated at the tip of the probe, which is connected to a convertor, and then linked to a generator. The probe is placed in the three neck flask and the center of the mixed liquid of the reactor. Usually, a probe ultrasound generator is more powerful than a bath ultrasound generator. The frequency of the generator is 20K Hz, which is fixed, and the power of ultrasound can be controlled by modifying the amplitude of the ultrasound, which has a range from 20% to 100%. As we know, the intensity of sound is proportional to the square of the amplitude, frequency square, and speed of sound. (Eqn.7)

$$I \propto c \bullet A^2 \bullet f^2 \tag{7}$$

In Equation (7), ***I*** is the intensity of ultrasound. **c** is speed of sound in specific medium and for here, the medium is water. **A** represents the amplitude of ultrasound wave. ***f*** is the frequency of ultrasound.

The intensity of 40% amplitude is 4 times more than the intensity at a 20% level. The actual power of every corresponding percentage of amplitude exactly follows the rule of intensity of sound at low intensity (less than 60%), but appears to be lower than the predicted value of intensity calculated by the intensity law of ultrasound (Figure 13).

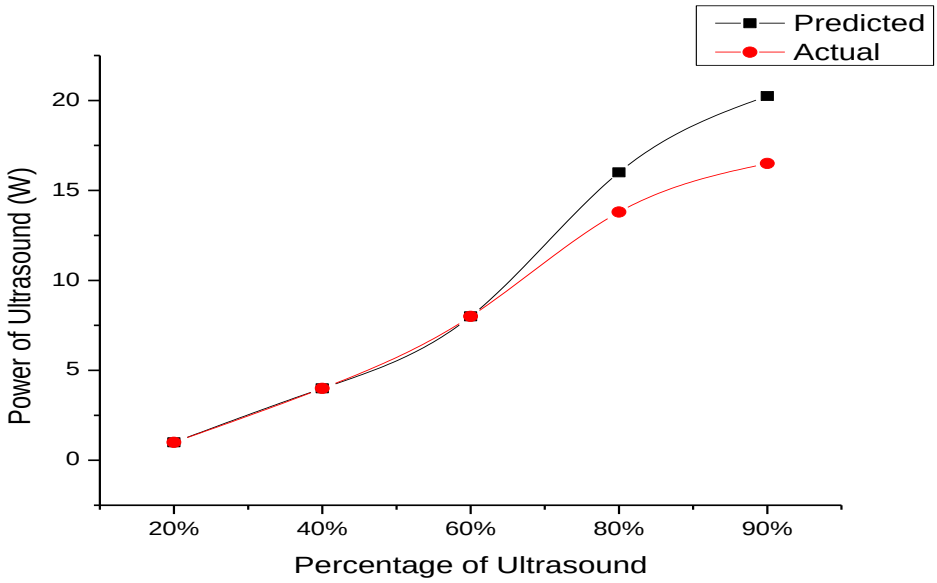

Figure 13. Power of Ultrasound with the Percentage of Amplitude of the Ultrasound Wave

All the experiments done by probe ultrasound are even and only have one phase after the reaction, which is an advantage compared to the magnetic stirring method. The results of the batch reaction with probe ultrasound as the emulsifying method are shown in Table 3. There are two main effects of probe ultrasound, the conventional stirring effect like bath ultrasound, and the cavitation effect which is the most important aspect of emulsifying. Tiny bubbles are generated by ultrasound at the tip of the probe, and exist only a few microseconds. The elimination of bubbles will cause the temperature and pressure to rise to a very high level (10,000 K, 1000atm) around that spot over a small range. Molecules of solvent, monomers, initiators, and surfactant will be broken down into free radicals in such an environment, which is the main mechanism for ultrasound initiated polymerization. However, in this study, the power of ultrasound is not high enough to generate enough free radicals to initiate the polymerization continuously with a relatively high reaction rate.

Table 3. Results of Batch Reaction Method with Probe Ultrasound

Sample No.	Effective Diameter(nm)	PD	Percentage of ultrasound amplitude	Ultrasound power (W)	Temperature (℃)	Reaction Time (min)	Amount of MMA (ml)
38	29.2	0.117	20%	~1	70	75	14
39	20.3	0.126	40%	~4	70	75	14
40	22.6	0.151	60%	~8	70	75	14
41	31.5	0.137	20%	~1	70	75	14
42	43.1	0.141	80%	~13.8	70	75	14
43	47.6	0.173	90%	~16.5	70	75	14
44	37.6	0.046	40%	~8	70	75	28
74	46.6	0.127	80%	~13.8	60	75	14
75	21.7	0.118	60%	~8	60	75	14
81	41.7	0.186	80%	~13.8	70	45	14
83	40.6	0.108	80%	~13.8	70	30	14

Reaction Condition: 120 ml Water, 1.4g SDS, 0.16g PPS, 14/28 ml MMA; Temperature=60℃/70 ℃; Reaction Time=30 min/45 min /75 min.

No significant sign of polymerization was observed as the reaction was carried without initiator or the temperature was far lower than the decomposition temperature of the chemical initiators. In this study, reactions can only be carried out with both additional chemical initiators and high temperature (at least 60℃). Nevertheless, the effect of cavitation for generating

smaller droplets, avoiding collapse of nano PMMA particles and Ostwald ripening is still quite useful in the experiments. Usage of probe ultrasound of low power still helps a lot in producing small PMMA nano particles with narrow distribution effectively and efficiently. At the same time, since additional chemical initiator was used, the polymerization rate is much higher than those polymerization reactions initiated only by ultrasound at ambient temperature.

The distribution of different intensity of ultrasound is quite close to each other. The change of particle size with power of intensity is shown below in Figure 14. The bottom of the curve in Figure 14 is a prediction of the trend.

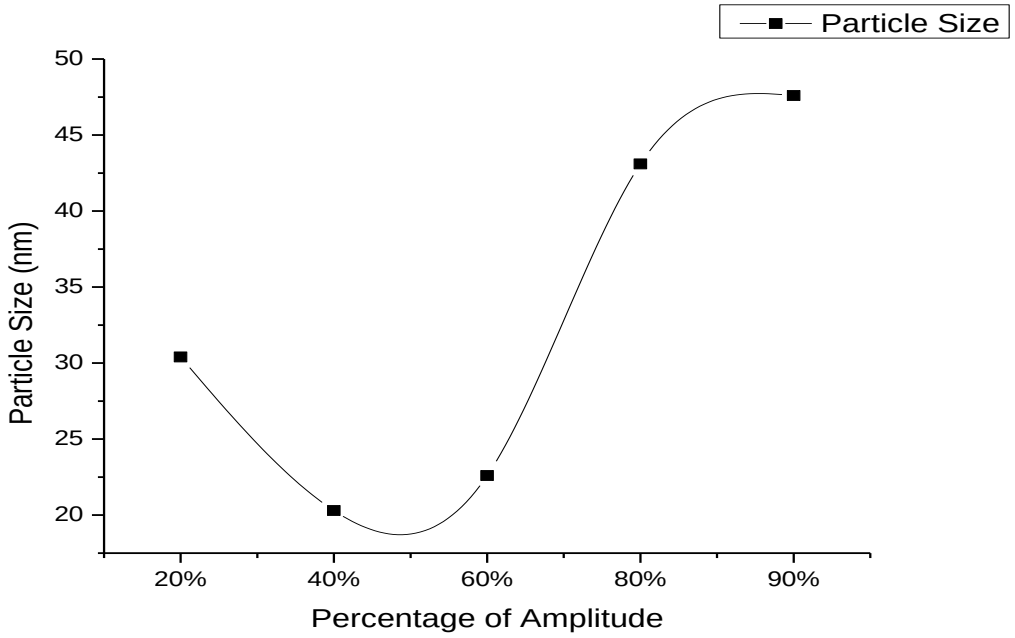

Figure 14. Change of Particle Size with Intensity of Ultrasound

Reaction Condition: 120 ml Water, 1.4g SDS, 0.16g PPS, 14 ml MMA; Temperature=70 ℃; Reaction Time=75 min.

Particle size which decreases with an increase of the ultrasound power firstly shows that the ultrasound dose helps to decrease the particle size while the distribution remains similar. However, with an increase in the intensity of ultrasound, the effects of ultrasound on accelerating the reaction rate and decomposition rate of initiator become more significant, which leads to the implosion of MMA particles. As is well known, implosion will dramatically increase reaction rate and particle size, and it is one of the main reasons for the increase of particle size with intensity of ultrasound when the percentage of amplitude reaches 60% or more. Another reason for obtaining large particles is the gel effect of polymerization, while the foam generated by higher intensity of the probe ultrasound may also contribute to large particle size.

It is also quite obvious that the addition of more MMA causes an increase in particle size. When 28ml MMA is added to the reaction system and 80% amplitude is applied, the whole system will bump because of the large amount of heat released by implosion of the MMA monomers. The conversion rate of the experiments is very high (close to 100%), and the solid content is around 10% for 14ml MMA, 5.3% for 7ml (halved) MMA, and 18.2% for 28ml (doubled) MMA. The polymerization rate is rather high, and the reaction can be finished in 30 minutes (see sample 83). While addition of MMA is doubled, the solid content is almost doubled as well, but the conversion rate is not affected a lot. As reported by other researchers, more MMA monomers will result in higher polymerization rate.

Comparison can also be made between magnetic stirring and probe ultrasound. Table 4 has listed some of the results of samples from both probe ultrasound method and magnetic stirring method.

Table 4. Comparison between Magnetic Stirring and Probe Ultrasound

Sample No.	Effective Diameter (nm)	PD	Emulsifying Method	Amount of MMA (ml)	Notes
32	39.5	0.055	Magnetic Stirring	14	300rpm
34	22.3	0.137	Magnetic Stirring	14	100rpm
39	20.3	0.126	Probe Ultrasound	14	40% AMPL
33	50.8	0.040	Magnetic stirring	28	300rpm
35	25.5	0.162	Magnetic stirring	28	100rpm
44	37.6	0.046	Probe Ultrasound	28	40% AMPL

Reaction Condition: 120 ml Water, 1.4g SDS, 0.16g PPS, 14/28 ml MMA; Temperature=70 ℃; Reaction Time=75 min.

As it can be seen from the results of Sample 32, Sample 34 and Sample 39, the emulsifying method of probe ultrasound can significantly decrease the particle size of nano poly-(methyl methacrylate) particles. Although Sample 34 has similar particle size to Sample 39, there will still be a few floating objects on the surface of Sample 34, which means the actual conversation rate (the percentage of MMA monomers that have been converted to PMMA nano particles) is lower than Sample 39. For Sample 33, Sample 35 and Sample 44, in which the situation when the addition of MMA monomers has been doubled, probe ultrasound can still work efficiently to decrease the particle size. For Sample 35, a large amount of floating objects are obtained after reaction, which refers to that the mixing is not as good as when probe ultrasound is used, and the particle size is small only because only a part of MMA is converted to nano sized particles.

Another big problem for magnetic stirring in the traditional stirring method for synthesizing nano sized polymer particles is that when it is applied to real factorial production, the stirring rate can only reach as high as 50 rpm, which will limit the use of the stirring method a lot.

4.1.4 Probe Ultrasound + Magnetic stirring

Magnetic stirring and probe ultrasound are used as combined so that a more powerful emulsifying method can be formed in order to discover one way to make the particle size even smaller. Probe ultrasound has the power range from 20% amplitude to 80% amplitude, and magnetic stirring is used as 200 rpm and 100 rpm to assist the mixing process. Consequences are shown in Table 5. The change of particle size with the emulsifying power is shown in Figure 15.

Table 5. Results of Batch Reaction Method with Probe Ultrasound + Magnetic Stirring

Sample No.	Effective Diameter (nm)	PD	Percentage of Ultrasound Amplitude	Ultrasound Power (W)	Round Per Minute(rpm)	Reaction Time (min)	Weight of SDS (g)
53	41.1	0.069	20%	~1	200	75	1.4
54	42.2	0.098	40%	~4	200	75	1.4
55	42.2	0.066	60%	~8	200	75	1.4
56	39.2	0.105	80%	~13.8	200	75	1.4
57	52.1	0.145	80%	~13.8	200	75	0.7
58	25.6	0.155	20%	~1	100	75	1.4
59	43.3	0.066	40%	~4	100	75	1.4
60	43.0	0.091	60%	~8	100	75	1.4
61	43.5	0.095	80%	~13.8	100	75	1.4
82	45.7	0.097	80%	~13.8	100	45	1.4
84	46.1	0.120	80%	~13.8	100	30	1.4

Reaction Condition: 120 ml Water, 0.7g/1.4g SDS, 0.16g PPS, 14 ml MMA; Temperature=70 ℃.

Reaction Time=30/45/75 min.

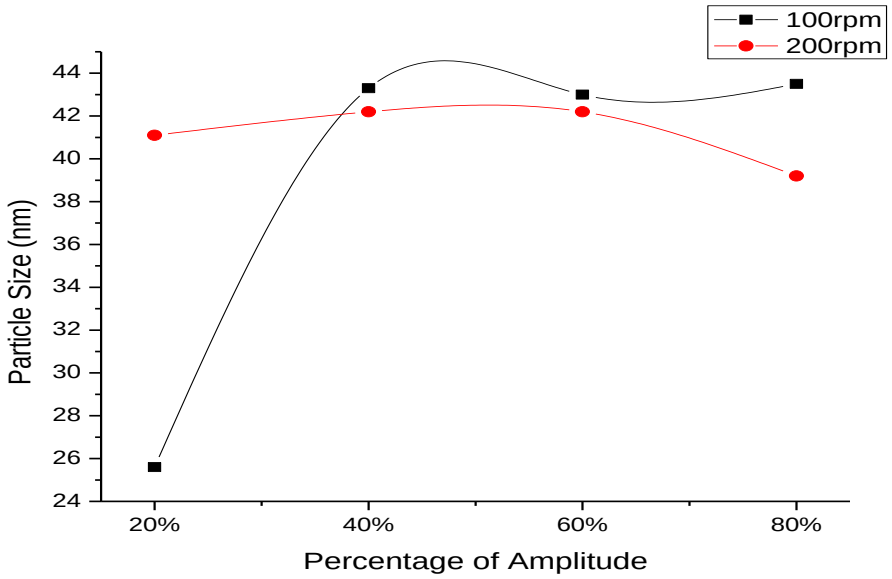

Figure 15. Change of Particle Size with Percentage of Amplitude and Agitation Speed

Reaction Condition: 120 ml Water, 1.4g SDS, 0.16g PPS, 14 ml MMA; Temperature=70 ℃; Reaction Time=75 min.

The diameters of all the particles produced are close to each other except Sample 57 and Sample 58. The size does not change a lot with the increase in power of the probe ultrasound or magnetic stirring. All these results are close to the result of Sample 42, which uses probe ultrasound as the emulsifying method at 80% amplitude. For Sample 42, as discussed previously, a too powerful ultrasound wave causes implosion, so the assumption can be made that this emulsifying method of probe ultrasound plus magnetic stirring has very similar effects for the reaction. These experiments reveal that it may be possible to achieve all the benefits of ultrasound emulsifying with the combination of lower power ultrasound and lower agitation speed so that more energy can be saved. As a proof to this assumption, the result of Sample 58,

which used 20% amplitude plus 100rpm magnetic stirring, is close to the result of sample 40, which used 60% amplitude probe ultrasound.

Another explanation for the increased particle size observed in this section can be attributed to the vast foam generated by combination of stirring and ultrasound. As reported by other researchers, foams will obstruct the diffusion of free radicals between micelles and the solvent phase, which results in a lower polymerization rate, and will also enhance the gel effect of the reaction, while surrounded by foams, as propagating polymer chains are much more difficult to terminate.

Similar to the probe ultrasound emulsifying method, the conversion rate reaches a very high value (nearly 100%) in a very short period of time (30 min, seen from sample 84). Nevertheless, a slight decrease in particle size can be observed from sample 84, 82 and 61. The reason for such a phenomenon is probably that when the conversion reaches the maximum, more surfactant molecules are absorbed by PMMA particles for stabilization, so that foams are eliminated. With the cavitation effect, oversize particles are broken down to smaller ones, so the particle size slightly decreases.

4.1.5 Probe Ultrasound + Bath Ultrasound

Experiments on this method of emulsifying have the same purpose as those with probe ultrasound plus magnetic stirring, which has been discussed above. Results are listed in Table 6 and Figure 16.

Table 6. Results of Batch Reaction Method with Probe Ultrasound + Bath Ultrasound

Sample No.	Effective Diameter (nm)	PD	Percentage of Probe Ultrasound Amplitude	Probe Ultrasound Power (W)	Notes
66	46.4	0.082	20%	~1	
67	46.9	0.154	40%	~4	
68	49.0	0.194	60%	~8	
69	57.5	0.226	80%	~13.8	

Reaction Condition: 120 ml Water, 1.4g SDS, 0.16g PPS, 14 ml MMA; Temperature=70 ℃; Reaction Time=75 min.

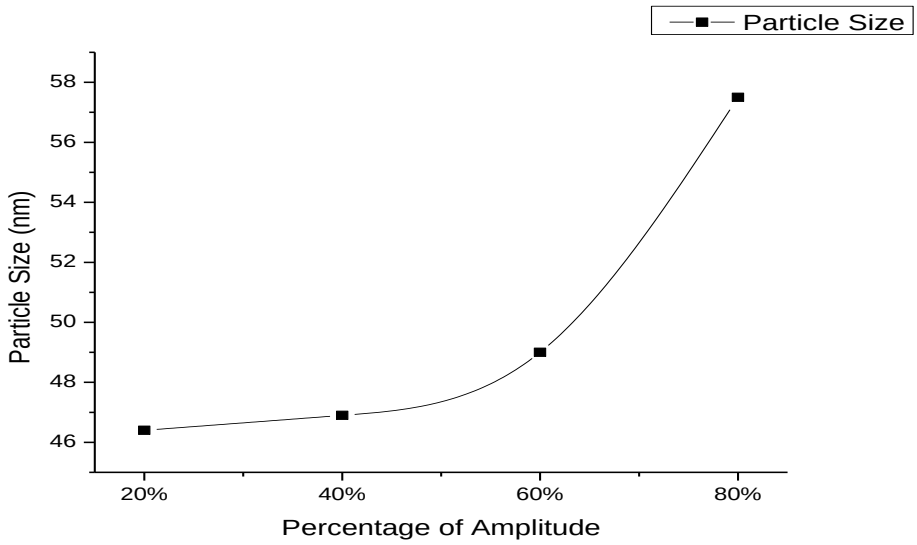

Figure 16. Change of Particle Size with Percentage of Amplitude of Combined Emulsifying Method of Probe Ultrasound + Bath Ultrasound

Reaction Condition: 120 ml Water, 1.4g SDS, 0.16g PPS, 14 ml MMA; Temperature=70 ℃; Reaction Time=75 min.

It is quite obvious that the combination of two types of ultrasound resources has the same effects on the results as the combination of probe ultrasound and magnetic stirring, and is even

more powerful. As the results of probe ultrasound plus magnetic stirring emulsifying method are close to the results of the 80% probe ultrasound emulsifying method, the results of probe ultrasound plus bath ultrasound emulsifying method are close to the results of the 90% probe ultrasound method. Too powerful emulsifying method results in implosion and because of that, the reaction rate and particle size increase sharply. The increase of particle size is not desirable; however, the increase of reaction rate is beneficial for massive production. With further study, it may be possible to obtain a larger amount of nano polymer particles of a certain particle size within a very short period by using ultrasound or other combinations involving ultrasound.

For all the data presented above, the conclusion is that ultrasound can help in producing finer particles with a narrow size distribution and simple reaction method, such as the batch method. However, if the emulsifying method becomes too powerful, side effects also exist due to implosion. For a certain intensity range of emulsifying, especially for combination of probe ultrasound and bath ultrasound and combination of probe ultrasound and magnetic stirring, particle size seems to be fixed, which can be clearly seen in Table 6.

Table 7. Fixed particle size for certain intensity range of combined emulsifying method

Sample No.	Effective Diameter (nm)	Type of combination
53	41.1	20% AMPL Probe Ultrasound + 200rpm Magnetic Stirring
54	42.2	40% AMPL Probe Ultrasound + 200rpm Magnetic Stirring
55	42.2	60% AMPL Probe Ultrasound + 200rpm Magnetic Stirring
59	43.3	40% AMPL Probe Ultrasound + 100rpm Magnetic Stirring
60	43.0	60% AMPL Probe Ultrasound + 100rpm Magnetic Stirring
61	43.5	80% AMPL Probe Ultrasound + 100rpm Magnetic Stirring
66	46.4	20% AMPL Probe Ultrasound + Bath Ultrasound
67	46.9	40% AMPL Probe Ultrasound + Bath Ultrasound

Reaction Condition: 120 ml Water, 1.4g SDS, 0.16g PPS, 14ml MMA; Temperature=70 ℃; Reaction Time=75 min.

While synthesizing PMMA nano particles with the combined emulsifying method, keeping it at the lowest energy cost emulsifying level can save a large amount of energy. This also explains the narrower PD of Sample 33 and Sample 44. While double the amount of MMA has been added into the reaction system, and the particle size is limited by the combined emulsifying method; more MMA monomer can help more particles grow as large as it can be in that situation, which narrows the distribution. Synthesis of particles with a certain particle size can be achieved by a certain recipe and emulsifying method. The conversion rate of ultrasound assistant batch reaction is quite high (almost 100%), which could be an obvious advantage for this reaction method.

4.2 Pre-Mixing Separation Method

In the laboratory, PMMA nano particles have been synthesized by a differential addition method. In that way, the MMA monomer was added into the reaction system in a differential manner by using a peristaltic pump. Monomers are slowly dissolved into the SDS solution so that very fine particles can be obtained. However, it is not efficient and is complicated for operation. Making some changes to the dissolution process might help to synthesize fine particles in a better way. The recipe is listed below is the same as that for the batch reaction except for the addition of initiator.

Initiator(PPS or AIBN)	Solvent(Water)	Monomer(MMA)	Surfactant(SDS)
0.16g	120ml	14ml	1.4g

Solvent, monomer and surfactant are mixed firstly by a certain emulsifying method. For this process, a large amount of experiments have shown that different emulsifying methods do not affect the final results of mixing and separating. No matter in which way they are mixed, the emulsion will be transferred into a separation funnel and become two layers after a few hours. The upper layer is white, in which water is dissolved in MMA, and the bottom layer is transparent, in which MMA is dissolved in water. Under this circumstance, the bottom layer can be considered as a saturated MMA solution and is separated out to perform the reaction with addition of 0.16g PPS as initiator after the separation process. All these emulsifying methods applied to the batch reaction will also be used in this pre-mixing separation synthesis method. All the results will be discussed below.

The primary purpose of such method is to create a “starved” environment for polymerization. In this situation, the under layer solution contains only micelles and monomers dissolved in water,

and no monomer droplets exist, which is different from conventional emulsion polymerization. By cutting off the supply of MMA monomers, particles with small size and narrow distribution can be obtained.

4.2.1 Magnetic Stirring

Magnetic stirring at 200 rpm is applied to the separated lower layer mixture. AIBN is used as initiator, and additional SDS of 1.4g is added to the mixture to eliminate precipitation after reaction. Precipitation of PMMA occurs when there is no additional SDS; because the mixture synthesized using the emulsifying method of magnetic stirring cannot stay stable after applying the cooling method.

Table 8. Results of Pre-mixing Separation Method with Magnetic Stirring

Sample No.	Effective Diameter (nm)	PD	Initiator Type
4	24.5	0.065	AIBN
6	27.6	0.038	AIBN
7	27.3	0.045	AIBN
8	27.9	0.034	AIBN
9	27.8	0.058	AIBN

Reaction Condition: Concentration of SDS ([SDS]) =0.01148 g/ml; Additional SDS=1.4g; 0.16g AIBN; Agitation Speed=200rpm; Temperature=70 ℃; Reaction Time$=75$ min.

The results in Table 8 do not show large differences from each other, and that might be an advantage for the “starved” environment created for the polymerization.

4.2.2 Bath Ultrasound

As is done for the batch reaction, ultrasound is generated by an ultrasonic cleaner filled with water with a three neck flask immersed in the center of the sink of the ultrasonic cleaner. The reactor is heated by water bath. Results are shown in Table 9.

Table 9. Results of Pre-mixing Separation Method with Bath Ultrasound

Sample No.	Effective Diameter (nm)	PD	Initiator Type
10	26.7	0.070	AIBN
11	25.5	0.124	AIBN
13	24.7	0.099	AIBN
14	24.8	0.081	AIBN
24	26.8	0.106	PPS
26	26.2	0.066	PPS
27A	27.0	0.059	PPS
27B	26.7	0.067	PPS

Reaction Condition: Concentration of SDS ([SDS]) =0.01148 g/ml; 0.16g PPS/AIBN; Temperature=70 ℃; Reaction Time=75 min.

The SDS concentration of the bottom layer is calculated to be 0.01148g/ml. Sample 26, 27A and 27B provide results for three different ways of mixing, which however provide very similar particle size and distribution. The diameter of particles is quite small and the distribution is narrow. Compared to the batch method, they provide the advantages of the pre-mixing separation method. Experiments with water soluble initiators tend to have a narrower distribution, but the particle size still seems to be stable, and precipitation is observed even without additional SDS, which is an advantage to the magnetic stirring method.

4.2.3 Probe Ultrasound

Usually, probe ultrasound is considered to be more powerful than bath ultrasound. During the reaction, a probe will be placed in the center of the separated down layer solution with water saturated with MMA. The results of these experiments are listed in Table 10 and Figure 17. The bottom of the curve in Figure 17 is a prediction of the trend.

Table 10. Results of Pre-mixing Separation Method with Probe Ultrasound

Sample No.	Effective Diameter (nm)	PD	Percentage of Ultrasound Amplitude	Probe Ultrasound Power (W)	Reaction Time (min)	Notes
48	24.5	0.082	20%	~1	75	
50	21.0	0.095	40%	~4	75	
51	19.3	0.122	60%	~8	75	Precipitation
52	40.9	0.032	80%	~13.8	75	Precipitation
85	16.9	0.135	80%	~13.8	45	Cooling by air

Reaction Condition: Concentration of SDS ([SDS]) =0.01148 g/ml; 0.16g PPS; Temperature=70 ℃. Reaction Time=45/75 min.

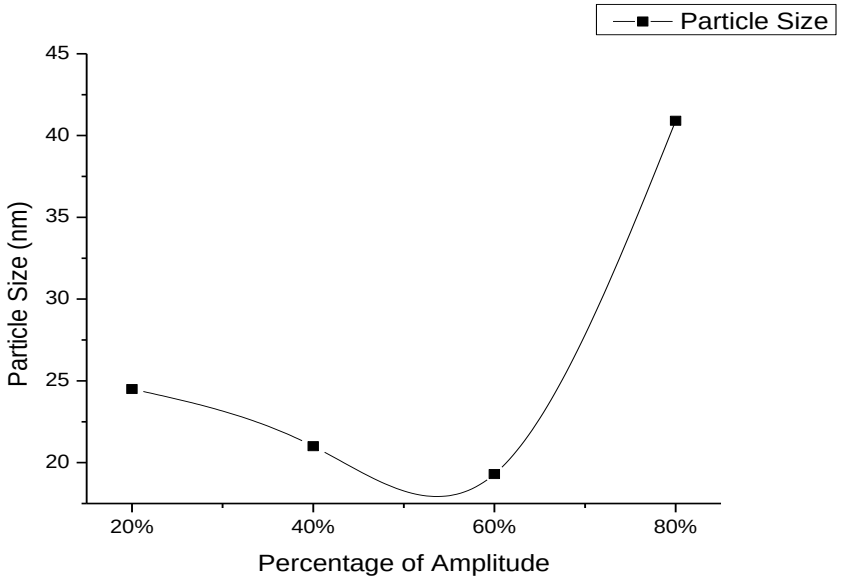

Figure 17. Change of Particle Size with Percentage of Amplitude with Probe Ultrasound of Pre-mixing Separation Method

Reaction Condition: Concentration of SDS ([SDS]) =0.01148 g/ml; 0.16g PPS; Temperature=70 ℃; Reaction Time=75 min.

While the power of probe ultrasound is low, it does help reduce the particle size a little, which can be clearly seen from Sample 48 and Sample 50. However, with the increasing power of probe ultrasound, the same problem of implosion appears, which leads to large particles, and some of them collapse to become precipitate. Under these circumstances, the particle size and PD obtained from the liquid phase cannot reflect the actual results of the reaction. Such phenomenon may be a result of the cooling method applied after reaction because large amounts of precipitates can be observed if the latex is cooled down with ice water, while the precipitate will vanish after reheating the latex to a temperature of 70 ℃. As seen from sample 85, a shorter period of reaction time can produce particles, and mild cooling method can avoid

large amounts of precipitates.

4.2.4 Probe Ultrasound + Magnetic Stirring

This combination is also applied in the batch reaction, but in the pre-mixing separation method section, the agitation speed for magnetic stirring was only carried out at 100rpm because even 100rpm is too powerful. In future, experiments should be done at lower agitation (less than 100rpm) for larger scale production of nano polymer particles synthesis. Results are shown in Table 11.

Table 11. Results of Pre-mixing Separation Method with Probe Ultrasound + Magnetic Stirring

Sample No.	Effective Diameter (nm)	PD	Percentage of Ultrasound Amplitude	Probe Ultrasound Power (W)	Agitation Speed (rpm)	Reaction Time (min)	Notes
62	23.4	0.111	20%	~1	100	75	Huge Particles Exist
63	22	0.097	40%	~4	100	75	Huge Particles Exist
64	19.5	0.134	60%	~8	100	75	Precipitation
65	20.0	0.049	80%	~13.8	100	75	Precipitation
86	16.2	0.156	80%	~13.8	100	45	Cooling by air

Reaction Condition: Concentration of SDS ([SDS]) =0.01148 g/ml; 0.16g PPS; Temperature=70 ℃. Reaction Time=45/75 min.

As can be seen from the Table 11 above, all the samples are affected by implosion, which results in large particles and even precipitation with an increase in power. Similar to the probe

ultrasound emulsifying method, the reaction can be finished within a shorter reaction time with finer particles, and the cooling method applied to the latex does affect the formation of precipitate at high intensity of the emulsifying method. Latex samples obtained by the pre-mixing separation method are not as stable as those obtained by the batch reaction.

4.2.5 Probe Ultrasound + Bath Ultrasound

Experiments were carried out at 20%, 40%, 60% and 80% amplitude of probe ultrasound. The results are shown below in Table 12.

Table 12. Results of Pre-mixing Separation Method with Probe Ultrasound + Bath Ultrasound

Sample No.	Effective Diameter (nm)	PD	Percentage of Probe Ultrasound Amplitude	Probe Ultrasound Power (W)	Notes
70	21.5	0.125	20%	~1	
71	24.5	0.146	40%	~4	Huge Particles Exist
72	19.1	0.107	60%	~8	Huge Particles Exist, Precipitation
73	18.9	0.156	80%	~13.8	Huge Particles Exist, Precipitation

Reaction Condition: Concentration of SDS ([SDS]) =0.01148 g/ml; 0.16g PPS; Temperature=70 ℃; Reaction Time=75 min.

The results have verified the prediction of over power. For 20% amplitude of probe ultrasound plus bath ultrasound, it still helps a little to reduce the particle size of the pre-mixing separation method, and the problem of implosion is not that serious. However, with an increase of probe ultrasound power, the problem still cannot be avoided.

Since the bottom layer is saturated with the MMA monomer solution; the over power emulsifying force not only leads to larger particle size, but also creates precipitate in the reaction system. In the section of the pre-mixing separation method, keeping the emulsifying power at an appropriate level to obtain fine and narrow distributed nano particles is the wisest choice. The solid content for such a method is lower than that obtained by the batch reaction, which is around 3%, however, it has ab advantage in particle size and distribution.

4.3 Differential Addition Method

The primary purpose of this study is to improve the differential addition method for synthesizing PMMA nano particles by applying ultrasound to the reaction system, so that the efficiency of the process can be greatly enhanced. The recipe is the same as for the other two methods.

Initiator(PPS or AIBN)	Solvent(Water)	Monomer(MMA)	Surfactant(SDS)
0.16g	120ml	14ml	1.4g

In this method, initiator, surfactant, and water were mixed together at the very beginning, and were raised to a temperature of 70℃. The monomer was added to the reactor drop wise by using a peristaltic pump. The length of time for dropping is 1 hour, and there is another 15 or 30 minutes for the reaction after the dropping process is finished. After that, a cooling process

using ice water is applied to the reaction system.

However, for the ultrasound assistant methods of emulsifying, the differential addition method is not as successful as for the other two methods, so that further study was not carried for this method. Data of the samples collected is listed below in Table 13.

Table 13. Results of Differential Addition Method

Sample No.	Effective Diameter (nm)	PD	Percentage of Probe Ultrasound Amplitude	Probe Ultrasound Power (W)	Agitation Speed (rpm)	Reaction Time
76	211.0	0.232	80%	~13.8	N/A	15min
77	178.0	0.177	80%	~13.8	200	15min
78	126.8	0.206	80%	~13.8	N/A	15min
79	135.1	0.190	80%	~13.8	200	15min
80	144.8	0.186	80%	~13.8	200	30min

Reaction Condition: 120ml Water, 1.4g SDS, 0.16g PPS, 14ml MMA; Dropping Time=1 h; Temperature=70 ℃. Reaction Time=15/30 min.

Results and phenomena of the experiments show that unlike for the batch reactions, for which the conversion rate is as high as 100%, most of the monomers added to the reaction system were not converted to PMMA and the conversion rate is quite low. The particle size of such a method is much higher than that of the other two methods no matter which type of emulsifying method is applied. Since the conversion is low, the diameter obtained is more likely to be the diameter of micelles and droplets in the latex. For the same reaction of 1 hour 15 minutes, the batch reaction can efficiently produce PMMA particles with a small particle size and narrow size distribution, and the operation is much simpler, so that the differential addition method does not have any advantages over the other two polymerization methods.

5. Conclusion & Recommendation

Nanosized poly-(methyl methacrylate) particles are obtained by micro-emulsion polymerization with ultrasound assistance. The batch reaction is shown to be the simplest and fastest way of synthesizing such particles, and the pre-mixing separation method can produce even smaller particles with a narrow size distribution although the solid content (~3%) is lower than that obtained from batch reaction (~10%). The differential addition method is not as effective as the other methods, and further research needs to be carried out.

For the batch reaction method, fine particles with narrow size distribution and high conversion (~100%) can be obtained by probe ultrasound emulsifying only. The optimal intensity of probe ultrasound is at 40% amplitude. Overpowered emulsifying methods tend to make particle sizes larger because of explosive polymerization and a gel effect enhanced by foams generated during emulsifying. Addition of more monomers will increase the particle size and polymerization rate, while less monomer will have an inverse effect. Extension of the polymerization time can make the particles more uniform, while a high conversion rate can be reached quickly. As results shown, such method is quite suitable for mass production of PMMA nano particles with high polymerization rate and conversion and reasonable particle size and size distribution.

In the pre-mixing separation method, the monomer supply is cut off by eliminating large monomer droplets. Particles obtained are smaller and more uniform than those obtained by the batch reaction. Similar to the batch reaction method, emulsifying with overpower will lead

to large particles, and the strict cooling method is responsible for vast precipitation. Further study should be carried out for more details about the mechanisms. The differential addition method is not as successful as the other two methods, so more experiments should be done by modifying the parameters for the reaction and studying the mechanism for differential emulsion polymerization with ultrasound assistance. Results have shown that this method appears more suitable for synthesizing fine and uniform particles rather than mass production.

In this thesis, the creativity is that a stationary “starved” micro-emulsion is created by using pre-mixing separation method for fine and uniform particles synthesis, and a batch reaction system with low power ultrasound irradiation and chemical initiators is created for mass production of PMMA particles, which differs from polymerization initiated by high intensity ultrasound. The contributions of this thesis are that uniform PMMA particles with a size of less than 20 nm are successfully synthesized through ultrasound assisted micro-emulsion polymerization, and the method used for mass production approaches the real application of PMMA nano particles synthesis with high polymerization rate, high conversion, and relative simpler operation.

Methods of ultrasound assistant emulsion polymerization can also be applied to other types of synthesis, like different monomers, copolymers, porous polymers, core-shell structures and so on. More research can be carried out for real industrial applications of ultrasound assistance or initiated polymerization.

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