Study on Ultrasonic Induced Encapsulating Emulsion Polymerization in the Presence of Nanoparticles

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ABSTRACT: In this paper, the ultrasonic induced encapsulating emulsion polymerization technique was used to prepare polymer/inorganic nanoparticle composites. The main affecting factors in ultrasonic induced encapsulating emulsion polymerization were studied systematically. The experimental results suggested that the pH value, the type of monomers, the type, content, and surface properties of nanoparticles, the type and concentration of surfactant have great influence on the ultrasonic induced encapsulating emulsion polymerization and the obtained latex stability. If selecting cationic emulsifier (such as cetyl trimethylammonium bromide), low water soluble monomer (such as *n*-butyl acrylate and styrene), and hydrophobic nano silica, the inorganic nanoparticles could be encapsulated by polymers through ultrasonic irradiation successfully under alkalescent condition, forming a novel polymer/inorganic nanoparticles composite. The mechanism of ultrasonic induced encapsulating emulsion polymerization and the composite latex stabilization are proposed. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1130–1139, 2001

Key words: ultrasonic induced encapsulating emulsion polymerization; inorganic nanoparticles; stability; nanocomposite

INTRODUCTION

Nanomaterials have many attractive features and therefore are regarded as the most prospective materials in the coming 21st century. Particularly, polymer/inorganic nanoparticle composites have drawn more and more attentions recently, because this kind of material can combine the merits of polymer and inorganic nanoparticles, and in this way the expensive nanoparticles can be utilized most efficiently and economically. However, the big challenge encountered in making polymer/inorganic nanoparticle composites is that the nanoparticles cannot be dispersed in polymer matrix at the nano level by conventional techniques, because the surface energy of the tiny particles is very high, and these particles tend to agglomerate during mixing. In our previous paper,[1] we reported that a novel technique, ultrasonic irradiation, could be employed to deal with this problem and to make polymer/inorganic nanoparticle composites.

Ultrasound is a wave of frequency $2 \times 10^4 \sim 10^9$ Hz. When ultrasonic wave passes through a liquid medium, a large number of microbubbles form, grow, and collapse in a very short time about a few microseconds, which is called ultrasonic cavitation. Sonochemical theory calculation and the elegantly designed experiments[2] suggested that ultrasonic cavitation can generate lo-

cal temperature as high as 5000 K, and local pressure as high as 500 atm, and heating and cooling rate greater than 10^9 K/s, a very rigorous environment that can induce some chemical reactions that cannot take place under normal conditions. Therefore, ultrasound has been extensively applied in dispersion, crushing, activation of materials, as well as in initiating polymerization.[3] That is, ultrasonic irradiation is a unique technique that has multifunctions of dispersion, pulverizing, and activation. By taking these advantages, ultrasonic induced encapsulating emulsion polymerization of monomer in presence of nanoparticles could be developed. This is a new way to prepare polymer/inorganic nanoparticle composites. As demonstrated in our previous paper,[1] the inorganic nanoparticles in the aqueous solution can redisperse more effectively through ultrasonic irradiation than by conventional stirring; subjected to ultrasonic irradiation, n-butyl acrylate (BA) and methyl methacrylate (MMA) monomers can be polymerized without any chemical initiator, and ultrasonic induced encapsulating emulsion polymerization of BA monomer in the presence of nano silica could produce poly(butyl acrylate) (PBA)/nano silica composite, in which nano silica were encapsulated by PBA and nano silica reach nano level dispersion in PBA matrix. All these encouraging results confirm that ultrasonic irradiation is an effective and novel technique to prepare polymer/inorganic nanoparticle composites.

As a part of a systematic study, this paper continues to study the main affecting factors on ultrasonic induced encapsulating emulsion polymerization—namely, pH values of emulsion, type of monomer, type, content and surface properties of nanoparticles, type and concentration of surfactant—aiming at optimizing the conditions for preparing polymer/inorganic nanoparticles composites through ultrasonic irradiation, and providing a mechanism for such unconventional encapsulating polymerization.

EXPERIMENTAL

Materials

Nanoparticles: SiO_2, 10–15 nm, Al_2O_3, 17 nm, TiO_2, 27 nm, Zhousan Nanomaterial Limited Company, Zhejiang, China.

n-Butyl acrylate (BA): CP, Tianjin Chemical Reagents Factory, was washed three times with 10% aqueous solution of sodium hydroxide, and distilled water to remove the inhibitor hydroquinone, dried with anhydrous sodium sulfate, then vacuum distilled.

Cetyl trimethylammonium bromide (CTAB): AR, Beijing Chemical Reagent Company, China.

Sodium laury sulfonte (SLS): CP, Shanghai Xiangde Chemical Factory, China.

Polyvinyl alcohol (PVA): 0588 $M_W = 22,000$, CP, Chongqing Weinilun Factory, China.

Polyvinylpyridine (PVP): K30 $M_W = 40,000$, CP Aldrich.

Apparatus

The reaction apparatus was described in the previous paper.[1] Ultrasonic irradiation was carried out with the probe of the ultrasonic horn immersed directly in the mixture emulsion system. During the polymerization, thermostated water was circulated to maintain a constant temperature, and constant N_2 purging rate.

### Ultrasonic Induced Encapsulating Emulsion Polymerization

A certain amount of purified monomer, surfactant aqueous solution, and nanoparticles were introduced into the reaction vessel, deoxygenated by bubbling with oxygen-free nitrogen for 2 min in the reaction vessel, and water was circulated to maintain a certain temperature. Then the ultrasound generator was switched on and the emulsion was subjected to ultrasonic irradiation. After a certain reaction time, ultrasonic irradiation was stopped. Half of the prepared polymer emulsion was stored for dispersion stability observation, and the rest was poured into ice-cold methanol to coagulate and deemulsify, then the precipitated material was filtered, washed, dried under vacuum condition, and weighed to ascertain the conversion gravimetrically in the usual way.

Characterization

IR analysis of the samples were performed on a Nicolet 560 Fourier transform infrared (FTIR) spectrometer.

The C, O, and N content of the nanoparticles was determined by element analysis with an Italy Carlo Erba 1106 Element Analysis Instrument to obtain the content of the emulsifier adsorbed on the surface of nanoparticles.

The dispersion stability of nanoparticles in the aqueous solution was characterized by spectrophotometry with a 721 Spectrophotometer.
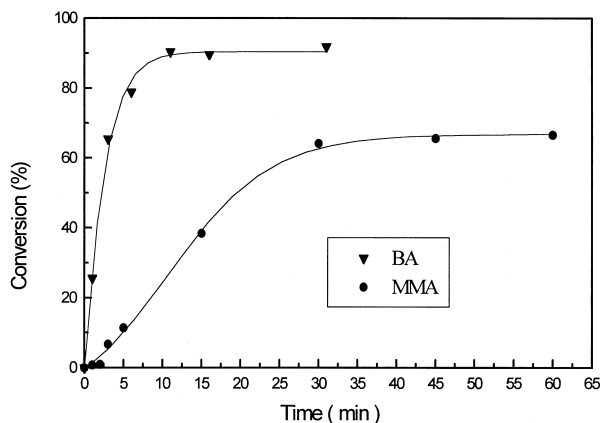
Figure 1 The time-conversion curves of ultrasonic induced emulsion polymerization of monomer MMA and BA.

The charge property of nanoparticles was determined by electrophoretic analysis with a DYY-III-4 Electrophoresis Apparatus.

RESULTS AND DISCUSSION

As we reported in our previous paper,[1] by taking advantages of the multieffects of ultrasonic irradiation, namely, dispersion, pulverization, activation of particles as well as initiation of polymerization of monomer, a novel polymer/inorganic nanoparticles composites could be prepared. This study will focus on the main affecting factors on ultrasonic induced encapsulating emulsion polymerization.

Ultrasonic Induced Emulsion Polymerization of BA and MMA

The premise condition for ultrasonic induced encapsulating emulsion polymerization of monomers is that ultrasound can initiate polymerization of monomers without any chemical initiator. First, the ultrasonic induced emulsion polymerization of monomer BA and MMA was studied. The time conversion curves for such two kinds of monomers are shown in Figure 1. From Figure 1, it can be seen that the conversion of BA amounts to 91% in 11 min, and the conversion of MMA amounts to 65% in 30 min. As mentioned above, ultrasonic cavitation can generate very high local temperature and pressure, a very rigorous environment for chemical reaction.[2] Under these rigorous conditions radicals can be generated due to

decomposition of water, monomer, surfactant, or rupture of polymer chains to initiate further chemical reaction, e.g., polymerization of monomer. It should be noted that the polymerization rate of monomer BA is much faster than that of monomer MMA, probably due to the different cavitation properties of BA and MMA, which have different vapor pressure (the pressure P_v of BA is 6.638 mmHg at 30°C, the pressure P_v of MMA is 51.764 mmHg at 30°C). According to eqs. (1) and (2),[4] T_{max} and P_{max} generated in the BA system is much higher than those monomers with higher vapor pressure, such as MMA, so the number of radicals produced by ultrasonic cavitation is significantly increased. This leads to the dramatic difference between the MMA and BA systems in ultrasonic induced emulsion polymerization.

$$T_{max} = T_b P_m (\gamma - 1)/P_v \qquad (1)$$

$$P_{max} = P_v [P_m (\gamma - 1)/P_v]^{\gamma/\gamma - 1} \qquad (2)$$

where T_{max} is the highest temperature generated during collapsing of cavitation bubbles, P_{max} is the highest pressure generated during collapsing of cavitation bubbles, P_m is the atmosphere pressure, γ is the ration of specific heat capacities of solvent vapor, and P_v is the vapor pressure of solvent at reaction medium temperature T_b.

Ultrasonic Induced Encapsulating Emulsion Polymerization

BA System

Effect of pH Value of Emulsion. Table I shows the effect of pH value of emulsion on the conversion of monomer and the stability of the composite latex obtained through ultrasonic induced encapsulating emulsion polymerization of BA in presence of SiO_2 nanoparticles. It is clear that pH value of

Table I   The Effect of pH of the Emulsion on the Conversion of BA and the Latex Stability

pH	Conductivity	Stability	Conversion
2.19	3.883	×	90.37%
4.30	0.218	×	90.37%
7.20	0.827	○	52.84%
8.60	1.436	○	36.44%
9.30	2.172	×	52.36%

○ good, — moderate, × poor

Table II Results of Element Analysis of Nano Silica Absorbing CTAB[a]

|	N%	C%	H%
No NaOH	—	1.81	1.21
0.05% NaOH	0.94	17.06	3.74

[a] Nano silica that absorbed CTAB were washed 15 times by centrifugal separation

emulsion plays a key role in the stability of nano-composite latex. Only when the emulsion is weak basic, i.e., pH 7 ~ 9, the stability of the nanocomposite latex is good. From the conversion data, we can see that the acid medium favors the conversion of monomer, and the polymerization rate in the acid medium is higher than that in the basic medium. This indicates a difference of polymerization in acid and basic medium. As we know, the adsorption of surfactant on the inorganic particles can be improved by adjusting pH value.[5] Generally, the positive charged particles adsorb the anionic surfactant more easily in the acid medium, whereas the negative charged particles adsorb the cationic surfactant more easily in the basic. Nano silica used in this paper was negative charged as suggested through electrophoresis experiment, therefore it will favor the adsorption of cationic surfactant CTAB on the nano silica in basic medium as confirmed by element analysis. The data listed in Table II demonstrate that under the weak basic condition, CTAB absorbed on the nano silica amounts to 20 wt % of the whole nanoparticles. Also, in the presence of NaOH, the adsorption of CTAB on the surface of nano SiO_2 (surface modified with 2,2-methylchlorosilicane) under ultrasonic irradiation were studied by FTIR. As shown in Figure 2(b), the strong peaks of —CH_2 and —CH_3 of CTAB appear, suggesting that CTAB was strongly absorbed on the surface of nanoparticles. However, in neutral or acid medium, the CTAB absorbed on the nano silica was not detected by element analysis after the same procedure as in the basic medium, indicating that in the acidic medium, it is difficult for the cationic surfactant CTAB to be absorbed on the surface of the negative charged nanoparticles; therefore, the polymerization mainly occurs in the conventional micelle formed by the self-aggregation of surfactant molecules, and the polymerization rate is high, but the obtained polymer contributes little to the stabilization of nanoparticles. On the other hand, in the basic medium, it is much more easily

for the cationic surfactant and hydrophobic monomer to be absorbed on the surface of nanoparticles, forming the admicelle (composed of two layers of surfactant molecules). In such a case, the polymerization will mainly occur in the admicelle, i.e., encapsulating emulsion polymerization initiated by ultrasound, and the polymerization rate is slower than that of polymerization which occurred in the micelle. But the obtained polymer encapsulates the nanoparticles, contributing greatly to the stabilization of nanoparticles, because the polymer layer formed on the surface of nanoparticles prevents the self-aggregation of the nanoparticles and has steric stabilizing effect. However, in the case of the strong basic medium, pH > 10, the conductivity and ionic strength of the system are very high, and the electrical double layer will be compressed, the latex particles become unstable.

Effect of Type and Concentration of Surfactant. Surfactant plays important roles in ultrasonic induced encapsulating emulsion polymerization. These effects are listed as follows:

- Surfactant will decrease the interface tension of the medium, so cavitation bubbles are easily formed in the presence of surfactant, which is helpful to enhance the rate of radicals formation and the number of radicals.
- The surfactant molecules aggregated in the interfacial region of cavitation bubbles can be
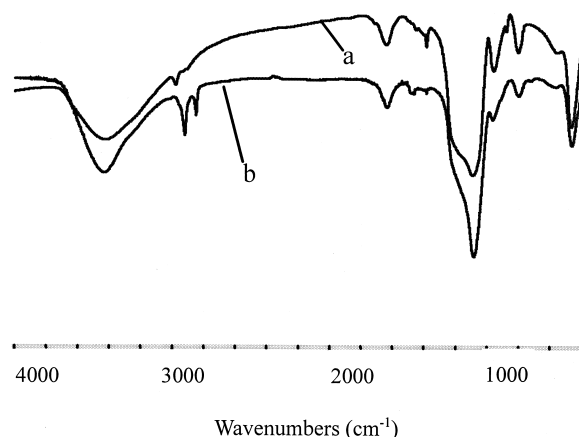
Figure 2 FTIR spectra of (a) pure hydrophobic nano silica and (b) hydrophobic nano silica that absorbed CTAB in 0.05% NaOH solution under ultrasonic irradiation The nano silica were washed 15 times with water by centrifugal separation.
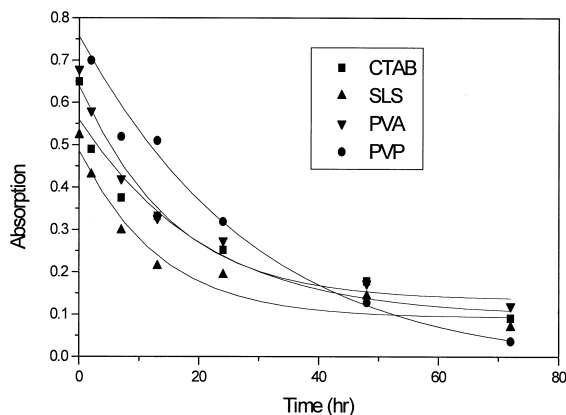
Figure 3 Absorbance–time curves of nano silica at the wavelength of 600 nm in 1% CTAB, 1% SLS, 1% PVA, and 1% PVP aqueous solution.

decomposed to produce radicals under ultrasonic irradiation.

- Surfactant can be absorbed on the surface of the nanoparticles, and produce double layer admicelle to capture radicals. The admicelle is the main locus of ultrasonic induced encapsulating emulsion polymerization.
- When surfactant was absorbed on the surface of nanoparticles, the surface of nanoparticles will become more hydrophobic, which favors to the absorption of hydrophobic monomer on the nanoparticles.
- Surfactant has the electrostatic stability effect on the nanocomposite latex particles.

Electrophoresis experiments show that nano silica is negative, so we select the cationic surfactant CTAB in this study. Absorbance–time curves of nano silica in CTAB, SLS, PVP, and PVA solution are shown in Figure 3 respectively. Clearly, the dispersion stability of nano silica in CTAB solution is the best among those systems.

Effect of CTAB concentration on the conversion during ultrasonic induced encapsulating emulsion polymerization of BA is shown in Figure 4. Clearly, with the increase of surfactant concentration, the conversion of monomer in 20 min increases. The results suggest that the increase in surfactant concentration favors an increase in the polymerization rate. However, when the concentration reaches 0.7%, the conversion of monomer in 20 min will keep constant. Besides, the latex dispersion stability is good when the surfactant concentration is 0.5, 1, and 1.5%. If the surfactant concentration is less than 0.5%, coagulum is eas-
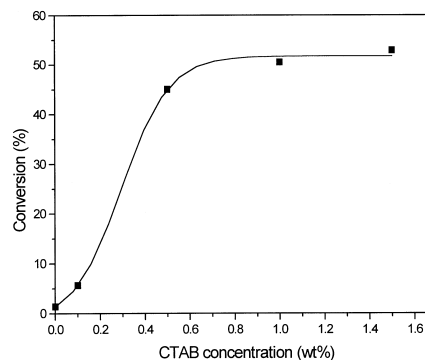
Figure 4 Effect of CTAB concentration on the conversion in 20 min during ultrasonic induced encapsulating emulsion polymerization of BA.

ily produced during the reaction. On the other hand, if the surfactant concentration is too high, foam is easily produced during the reaction, which hinders the ultrasonic cavitation.

Effect of the Type of Nanoparticles. We conducted the ultrasonic induced encapsulating emulsion polymerization of BA in the presence of nano SiO_2, nano Al_2O_3, and nano TiO_2. The results are shown in Table III. Clearly, the stability of nano silica is the best among the three different nanocomposite latexes because it has the lowest density and the smallest particle size. Among the three kinds of nanoparticles, the cationic surfactant CTAB and hydrophobic monomer are more easily absorbed on the surface of nano silica, contributing to ultrasonic induced encapsulating emulsion polymerization, and therefore to the stability of nano silica. From the conversion data, the polymerization rate in the presence of TiO_2 or Al_2O_3 is higher than that in the presence of SiO_2, indicating that in the presence of nano SiO_2, the encapsulating emulsion polymerization is dominant, while in the presence of TiO_2 or Al_2O_3, polymerization mainly takes place in the micelle formed by self-aggregation of surfactant molecules.

Table III   Effect of the Type of Nanoparticle on the Conversion and the Latex Stability

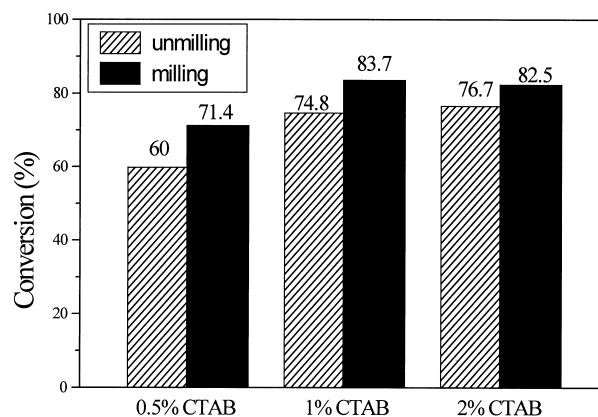| Nanoparticle (diameter)	Stability	Conversion
TiO_2 (27 nm)	×	76.79%
Al_2O_3 (17 nm)	×	71.38%
SiO_2 (10 nm)	○	27.88%

Table IV Effect of Surface Properties on the Conversion and the Latex Stability in the Ultrasonic Induced Encapsulation Emulsion Polymerization of BA

Surface Properties	Stability	Conversion
Hydrophilic porous SiO_2	—	41.54%
Amphilic porous SiO_2	—	42.14%
Hydrophobic porous SiO_2	○	27.88%
Spherical SiO_2	—	65.55%

Figure 5 Comparison of conversion of BA after 20 min ultrasonic irradiation in presence of nano silica through milling and unmilling with emulsifier.

Effect of Surface Properties of Nanoparticles. The ultrasonic induced encapsulating emulsion polymerization of BA in the presence of hydrophilic porous SiO_2, hydrophobic porous SiO_2, amphilic SiO_2, and spherical SiO_2 were conducted respectively. The results are shown in Table IV. In presence of hydrophilic porous SiO_2, amphilic SiO_2, and spherical SiO_2, the nanoparticles will deposit in several days from the prepared composite latex. However, in presence of hydrophobic porous SiO_2, the stability of the prepared nanocomposite latex is much better, the deposition of nanoparticles will not occur in several months. The hydrophile–lipophile balance (HLB) value of CTAB calculated according to the Davies methods[6] is about 7.4, indicating it tend to be hydrophobic; compared with other types of nano silica, the absorption of CTAB on the hydrophobic nano silica is stronger. In addition, CTAB is more easily absorbed by porous nano silica than by spherical silica. So, for hydrophobic and porous nano silica, the encapsulating emulsion polymerization is dominative, the polymerization rate is relatively slower, and the latex stability is better.

Moreover, we conducted ultrasonic induced encapsulating emulsion polymerization after pretreating the nano silica by milling it with surfactant CTAB and drying at different CTAB content. Compared with those unmilling systems (directly adding), the obtained latex stability is better, and the conversion in the same time is enhanced, as shown in Figure 5. This is probably due to the increase in the surface activation by milling.

Effect of the Content of Nanoparticles on Polymerization. Without Surfactant. The effect of content of nanoparticles on the conversion in the ultrasonic induced polymerization of monomer BA is shown in Figure 6. Clearly, ultrasonic induced polymerization of monomer BA can take place in presence of only nanoparticles, monomer and wa-

ter, without surfactant and chemical initiator. It suggests that the monomer or water can be decomposed under ultrasonic cavitation although the conversion is not high, only about 2.4%. With increase of the content of nano silica, the conversion of monomer first increases, and then decreases. When the content of nanoparticles is about 0.5%, the conversion amounts to 17%. This fact indicates that in the absence of surfactant, instead of micelle, inorganic nanoparticles can become the nuclei and capture the radicals to further initiate the encapsulating polymerization. In the absence of nanoparticles, i.e., there are only monomer and water, the size of monomer droplets is big, about $5 \sim 20~\mu m$, and the number of monomer droplets is small, so the efficiency of their ability to capture the radicals is too low to be
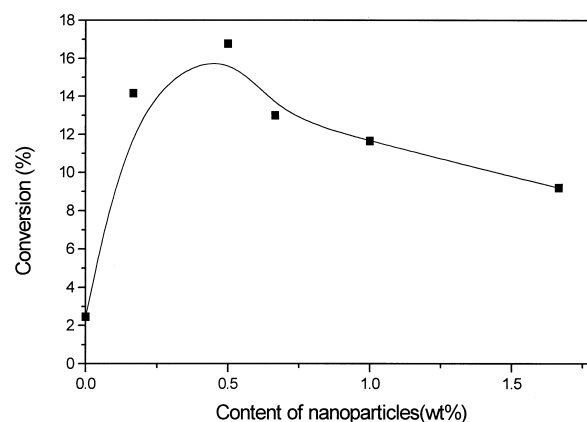
Figure 6 Effect of content of nanoparticles on the conversion in the ultrasonic induced polymerization of monomer BA.
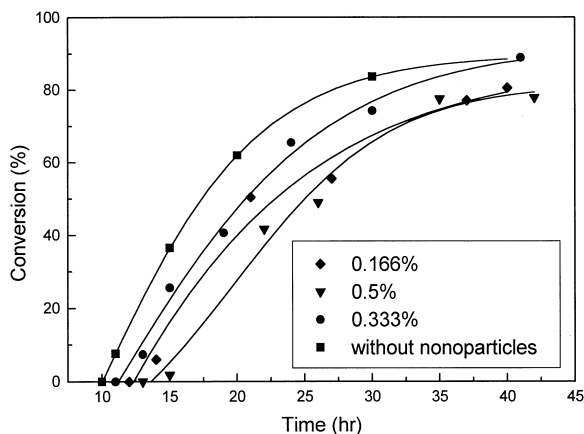
Figure 7 Effect of content of nanoparticles on the polymerization rate in the ultrasonic induced emulsion polymerization of monomer BA.

taken into account. The chain propagation was attributed to homogeneous nucleation, i.e., the nuclei is produced by precipitation of the oligomer radicals from the aqueous phase, but the water solubility of BA is very low, about 0.01 mol/L (45°C), which results in the small number of homogeneous nuclei, and the number of radicals produced by ultrasonic cavitation is not very high, so the polymerization rate is low. If added appropriately, the nanoparticles can be dispersed at nanometer scale under ultrasonic irradiation, and a certain amount of monomer can be absorbed on the surface of nanoparticles due to their big specific surface area and high surface activity, and the radicals produced by ultrasonic irradiation can be captured to initiate the chain propagation, so the polymerization rate was enhanced. Clearly, in a range, the more nanoparticles, the more nuclei produced, leading to an increase in polymerization rate. However, if further increasing content of nanopaticles, the dispersion of nanoparticles under ultrasonic irradiation is not very efficient, so the surface area of the nanoparticles does not increase linearly, and the chance of collision between the particles increases, leading to the termination of the absorbed radicals, which makes the efficiency of radicals initiation decrease, and then the polymerization rate decreases.

With Surfactant. Effect of content of nanoparticles on the conversion in the ultrasonic induced emulsion polymerization of BA in presence of surfactant CTAB is shown in Figure 7. Compared with the polymerization without surfactant (see Fig. 6), the polymerization rate significantly increases. There are two reasons for this. First, in absence of surfactant, the number of radicals is small and cannot be completely captured to initiate the chain propagation. Second, without the electrostatic stability of the surfactant, the produced particles will aggregate seriously and then deposit. The effect of content of nanoparticles on the polymerization is complicated. From Figure 7, the order of polymerization rate can be listed as follows based on the content of nanoparticles: R_p (0) > R_p (0.333%) > R_p (0.166%) > R_p (0.5%). The reasons: when nanoparticles were introduced into the reaction medium, a large amount of surfactant and monomer were absorbed on the surface of the nanoparticles, the encapsulating emulsion polymerization on the surface of nanoparticles takes place predominantly. So, compared with the case in the absence of nanoparticles (i.e., polymerization takes place in the micelle), the termination rate is faster and the overall polymerization rate is slower. With the increase of the content of nanoparticles, reaction loci increases, and polymerization rate of the encapsulating emulsion polymerization on the surface of nanoparticles was enhanced. However, if further increasing in the content of nanopaticles, similar to the case in the absence of surfactant, the dispersion of nanoparticles under ultrasonic irradiation are not very efficient, and the surface area of nanoparticles does not increase linearly. At the same time, the chance of collision between the particles increases, which can lead to the termination of the absorbed radicals, and make the efficiency of radicals initiation decrease, thus the polymerization rate decrease.

MMA System

pH Value. Ultrasonic induced encapsulating emulsion polymerization of MMA at different pH value were conducted; the results are shown in Table V. From Table V, the conversion of MMA in

Table V   Effect of pH Value on the Conversion and the Latex Stability in the Ultrasonic Induced Capsulation Emulsion Polymerization of MMA

pH	Stability	Conversion
4.30	×	16.21%
7.20	×	22.50%
8.60	×	16.01%
9.30	×	29.39%

Table VI   Effect of Surface Properties of Nanoparticles on the Conversion and the Latex Stability in the Ultrasonic Induced Capsulation Emulsion Polymerization of MMA

Surface Properties	Stability	Conversion
Hydrophilic porous SiO_2	×	27.69%
Hydrophobic porous SiO_2	×	16.25%

Table VII   Effect of Ratio of St and BA on the Latex Stability and Conversion in the Ultrasonic Induced Encapsulating Emulsion Polymerization

Ratio	Stability	Conversion
Pure St	○	6.71%
St : BA = 1 : 1	○	26.51%
St : BA = 1 : 3	○	29.91%
Pure BA	○	74.34%

20 min is low and the polymerization rate is slower than that of BA. This was attributed to the different cavitation properties as we mentioned above. Surprisingly, very different from the BA system, whether in weak acid medium or in weak basic medium, the composite latex is not stable. This is because, when CTAB molecules were absorbed on the surface of nanoparticles, the surface of nanoparticles become hydrophobic; relatively hydrophilic monomer MMA is difficult to aggregate on the hydrophobic surface of nanoparticles. So, the encapsulating emulsion polymerization is difficult. The chain propagation reaction mainly occurs in the latex particles, resulting from the micelle (heterogeneous nucleation) and the oligomer radicals (homogenous nucleation).

Effect of Surface Properties of Nanoparticles. The ultrasonic induced encapsulating emulsion polymerization of MMA in the presence of hydrophilic porous SiO_2 or hydrophobic porous SiO_2 were conducted respectively. The results are shown in Table VI. The prepared composite latex is still not stable. The encapsulating emulsion polymerization is difficult whether in the presence of hydrophilic SiO_2 or hydrophobic SiO_2. The surface of hydrophilic SiO_2 or hydrophobic SiO_2 will become hydrophobic once absorbing the cationic surfactant CTAB; thus MMA is difficult to aggregate on the hydrophobic surface of nanoparticles.

St System

The ultrasonic induced emulsion polymerizations of styrene were conducted; the results are shown in Table VII. The prepared composite latex is stable, suggesting that encapsulating emulsion polymerization of St can occur. Besides, the polymerization rate of St is slow. This is because the activity of St radicals is low compared with acrylate monomer, and the chain propagation rate is slow. Unexpectedly, colored compounds are produced in ultrasonic induced polymerization.

Ultrasonic Induced Copolymerization

St + BA

The copolymerization of St and BA was conducted. The results are shown in Table VII. It is clear that the stability of the nanocomposite latex is good, and with the increase of St content, the conversion of monomers decreases. The experimental results provide some basis to prepare copolymer/nanoparticles composite latex with some special properties.

MMA + BA

The copolymerization of MMA and BA were conducted, as shown in Table VIII. With the increase of MMA content, the conversion of monomer decreases, and the stability of composite latex decreases, this is in agreement with our former conclusion.

Possible Mechanism of Ultrasonic Induced Encapsulating Emulsion Polymerization

Based on the experimental results mentioned above, we proposed the mechanism of ultrasonic induced encapsulating emulsion polymerization as follows:

Table VIII   Effect of Ratio of MMA and BA on the Latex Stability and Conversion in the Ultrasonic Induced Encapsulating Emulsion Polymerization

Ratio	Stability	Conversion
Pure MMA	×	—
MMA : BA = 1 : 1	×	16.41%
MMA : BA = 1 : 3	×	11.36%
Pure BA	○	40.64%
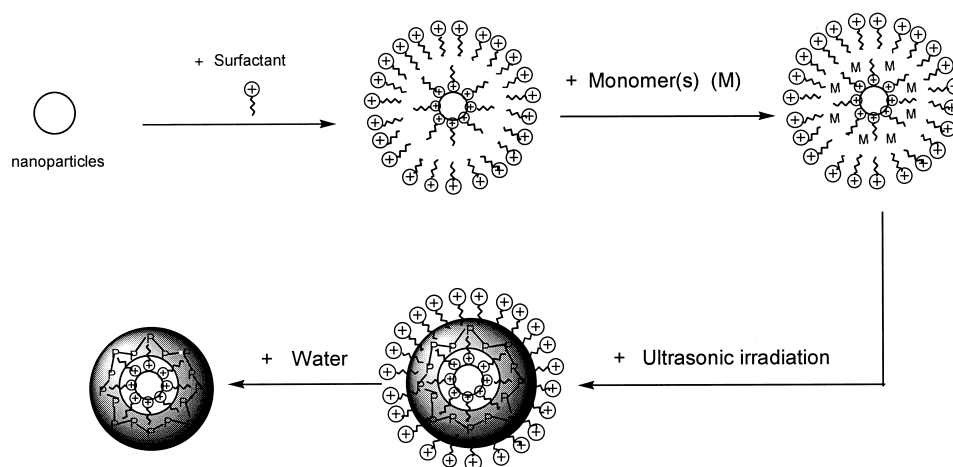
Figure 8   Schematic illustration of the ultrasonic induced encapsulating emulsion polymerization in the admicelles formed on the nanoparticles.

- The formation of radicals: ultrasonic cavitation can generate very rigorous environment, local temperature up to 5000 K, local pressure up to 500 atm, etc.[2] Under such rigorous conditions radicals can be generated due to decomposition of solvent, monomer, or rupture of polymer chains to initiate further chemical reaction, e.g., polymerization of monomer.

- Polymerization reaction (chain propagation and termination): there are three ways in the ultrasonic induced encapsulating emulsion polymerization:

  1. The polymerization reaction occurs in the bilayer admicelle formed on the surface of nanoparticles.[7] The process can be depicted as Figure 8. Since the size of nanoparticle is very small and the specific surface area is so large, under appropriate operating conditions, a large amount of cationic surfactant can strongly be adsorbed on the surface of nanoparticles with negative charge. The adsorbed surfactant molecular is considered as a local bilayer structure with a lower layer of head groups adsorbed on the substrate surface and an upper layer of head groups in contact with solution, which is called admicelles.[6] When surfactant molecules are adsorbed on the surface of nanoparticles, the surface of nanoparticles becomes hydrophobic, which favors the adsorption of a hydrophobic monomer such as BA. At the same time, the presence of admicelles promotes the adsolubilization of the monomer in the admicelles, and prevents the formation of general micelles, which are formed by self–aggregation of surfactant molecule. Those formed admicelles can capture the radicals produced by ultrasonic cavitation to initiate the encapsulating emulsion polymerization of monomer on the surface of nanoparticles in the admicelles. Once the reaction has started, additional monomer from the bulk solution diffuses into the admicelles. By adjusting the operating conditions, the polymerization in the admicelle is dominant, and the competitive polymerization in the bulk solution can be limited.

  2. Polymerization initiated by the active sites of nanoparticles. The intense shock wave and stream resulting from ultrasonic cavitation can produce active sites on the surface of nanoparticles to initiate the polymerization of monomer. On the other hand, surfactant, water monomer and the formed polymer on the surface of nanoparticles can be decomposed to produce radicals and in situ initiate the polymerization of monomer.

  3. Polymerization occurs in the micelles formed by self-aggregation of surfactant molecular. This is similar to the conventional emulsion polymerization except that the radicals are produced via ultrasonic irradiation rather than from decomposition of conventional chemical initiator. To get the nanoparticles encapsulated by poly-

mer, this kind of polymerization should be avoided.

Mechanism of Stabilization of Nanoparticles

The experimental results in this study suggest that it is difficult for nanoparticles to be stabilized in water, surfactant aqueous solution, water soluble polymer aqueous solution, and polymer emulsion. However, once the encapsulating polymer layer on the surface of nanoparticles was formed through ultrasonic induced encapsulating emulsion polymerization, the polymer/inorganic nanoparticle composite latex is long-term stable. The main reasons may be as follows:

- The positive charged CTAB surfactant molecules are absorbed on the nanoparticle surfaces, forming two molecule layers, which has an electrostatic stabilizing effect. Without surfactant, the nanoparticle cannot be stable.
- The polymer on the nanoparticle surface forms a polymer encapsulating layer of certain thickness, which has a steric stabilizing effect. Without the polymer encapsulating layer, the nanoparticles are unstable also.

CONCLUSION

Ultrasonic induced encapsulating emulsion polymerization of BA, MMA, and St in the presence of nanoparticles such as SiO_2, Al_2O_3, and TiO_2 offers a new way to prepare polymer/inorganic nanoparticle composites. The pH value, the type of mono- mer, the type, content, and surface properties of nanoparticles, the type and concentration of surfactant have significant effects on the ultrasonic induced encapsulating emulsion polymerization. By adjusting these affecting factors, the encapsulating polymerization can occur predominantly on the nanoparticle surface. The obtained latex particles are long-term stable. In this way novel polymer/inorganic nanocomposite materials can be prepared. The possible mechanism of ultrasonic induced encapsulating emulsion polymerization and stabilization of the composite latex are also proposed.

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