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The Effect of Nano-SiO_2 Colloid on Soap-free Emulsion Polymerization of Methyl Methacrylate and Hydroxyethyl Methacrylate

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Soap-free emulsion polymerization of methyl methacrylate (MMA) and hydroxyethyl methacrylate (HEMA) was carried out in the presence of colloidal nano-SiO_2 particles. The effect of nano-SiO_2 level on the monomer conversion, polymerization rate (Rp), and emulsion stability was investigated. The viscosity, particle size distribution of the emulsions, surface tension, and ionic conductivity of these systems were determined. Upon the introduction of the nano-SiO_2 particles into this system, the Rp and monomer conversion increased and the average particle size of the P(MMA-HEMA) emulsion decreased in comparison to emulsions formed in the absence of nano-SiO_2. However, the particle size distribution became broader to some degree. Scanning electron microscope observations demonstrated that the shape of these latex particles were uniformly spherical. The surface tension and ionic conductivity of the system increased significantly after polymerization, but the presence of nano-SiO_2 resulted in an increase in surface tension and a decrease in ionic conductivity in comparison to the particle–free system.

Keywords: Soap-free emulsion polymerization, nano-SiO_2 colloid, methyl methacrylate, hydrophilic monomer, polymerization rate, particle size

1 Introduction

Polymer/inorganic nanocomposites have attracted much interest in recent years because they have a number of potential applications. These composites combine the excellent properties of both organic and inorganic components, such as the flexibility and toughness of the polymer matrix, and the particular optical, electrical, thermal, chemical activity and catalytic properties of the inorganic component. They are likely to become one of the fastest developing materials in the new century. In the past decades, there has been a great deal of work done by many research groups on the preparation, characterization, and application of the polymer/inorganic nanocomposites (1–3). Polymer/inorganic nanocomposites can be prepared through many methods, such as sol-gel polymerization (1, 4–8), free-radical copolymerization (1, 5, 9, 10), emulsion polymerization (2, 11–20) and self-assembly methods (4, 21–23). Among these methods, emulsion polymerization in the presence of inorganic nanoparticles has become the most frequently used technique to synthesize polymer/inorganic nanocomposites as functional coatings because they are environment-friendly, simple, and easy to control the reaction conditions.

Owing to its low toxicity, high stability, high thermal resistance, specific optical and electrical properties, nano-SiO_2 is an attractive material for the preparation polymer/inorganic nanocomposites. In recent years, considerable efforts have been devoted to the synthesis of polymer/inorganic nanocomposites in the presence of silica sol. For instance, Zhang et al. (24) reported the synthesis of SiO_2/polystyrene nanocomposite particles by miniemulsion polymerization. Core-shell or other interesting morphology composite particles were obtained depending on the size of the silica particles and the surfactant concentration employed. Cheng et al. (25) obtained a series of SiO_2/PMMA composite particles with different morphologies via conventional emulsion polymerization aided by acid–base interaction between the silanol groups of unmodified silica particles and the amino groups of 4-vinylpyridine. They controlled the morphologies of composite particles, such as multi core–shell, raspberry-like and conventional core–shell structures, by modulating the emulsifier content, the monomer/silica ratio, and the monomer feed conditions. Mizutani et al. (20) described the process of synthesizing

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spherical nanocomposites consisting of silica core and polyacrylate shell by an emulsion polymerization. Wada et al. (26) discussed the properties of organic–inorganic composite materials prepared from acrylic emulsions and colloidal silica. Qi et al. (27) synthesized poly(butyl acrylate)/ silica and poly(butyl acrylate)/silica/poly(methyl methacrylate) composite particles by emulsion polymerization of butyl acrylate (BA) in the presence of silica particles pre-absorbed with 2,2-azobis(2-amidinopropane) dihydrochloride (AIBA) initiator and subsequent MMA emulsion polymerization in the presence of PBA/silica composite particles. However, the majority of these works focused primarily on the preparation of nanocomposites and the effect of the nanoparticles on emulsion polymerization in the presence of emulsifiers. Only a few papers have reported on silica-polymer nanocomposites formed by soap-free emulsion polymerization, and the effect of the nanoparticles on the kinetics of the soap-free emulsion polymerization systems (28–30). Very recently, Bon etal reported that nanosized SiO_2 could provide the colloidal stability by replacing the role of surfactants. The resulting emulsion was armed with a layer of nanoparticles and was used to make multilayered nanocomposite (31).

In this paper, soap-free emulsion polymerization of methyl methacrylate (MMA) containing the hydrophilic monomer hydroxyethyl methacrylate (HEMA) as the stability agent in the presence of nano-SiO_2 is carried out. The effects of nano-SiO_2 colloidal particles level on the emulsion stability, monomer conversion, polymerization rate, particle size and distribution, surface tension and ionic conductivity of the soap-free emulsion polymerization are investigated. Based on this academic research, a novel acrylate emulsion with more excellent properties and stability is anticipated.

2 Experimental

2.1 Materials

Methyl methacrylate (MMA) and ammonium peroxydisulfate [$(NH_4)_2S_2O_8$, APS] were purchased from the Xilong Chemical Plant in Shantou, Guangdong Province (China). Hydroxyethyl methacrylate (HEMA) was obtained from Tianjin Chemical Reagent Research Institute (China). Nano-SiO_2 colloidal solution (solid content 33%, pH 9 and particle size 130 nm) was provided by Beijing Zhongke Nano-technology Co., Ltd (China). In these materials, MMA was distilled under reduced pressure and APS was recrystallized before use. The other materials were used as received. Deionized water was used in all the experiments.

2.2 Emulsion Preparation

Emulsion polymerization was carried out in a 250 ml glass reactor fitted with a reflux condenser, stainless-steel stirrer, nitrogen gas inlet, and thermometer. The solid content of the emulsion was 10% by weight. The sequence of reagent addition used to charge the reactor was water, nano-SiO_2 colloid, and MMA and HEMA pre-mixture. In order to initiate the polymerization, the reaction vessel was purged with nitrogen gas for 30 min, the system was heated to the appropriate temperature, and then the APS initiator was added into the system. At various intervals, a sample was taken out of the reactor, the polymerization reaction was stopped with a drop of aqueous hydroquinone solution, and the conversion of monomer was determined. Finally, the viscosity, particle size, and size distribution of the resultant emulsions, ionic conductivity, and surface tension of the system before and after polymerization were tested. At different runs, the loading levels of nano-SiO_2 were varied.

2.3 Characterization

The monomer conversion and coagulum were determined gravimetrically. The emulsion particle size and size distribution of diluted samples were determined using a Zetasizer Nano-ZS90 laser instrument from Malvern Co., UK. The viscosity of the emulsions was measured with a Brookfield DV-II+ Pro rotating viscometer (USA). The ionic conductivity and surface tension were measured by DDS-11A conductivity tester (Shanghai Rex Xinjing Instrument Co., Ltd. China) and BZY-1 automatic interfacial tension tester (Shanghai Hengping Instrument and Meter Factory, China). The morphology of the emulsions was determined with the scanning electron microscope (JEOL Ltd, Japan).

3 Results and Discussion

3.1 Polymerization Conditions

Due to the absence of an emulsion-stabilizing emulsifier, it is difficult to obtain stable emulsion with a high solid content. By incorporating the hydroxyl monomer HEMA in the MMA soap-free emulsion polymerization, the copolymerization may form a crosslinking network and thus enhance the stability of the resultant emulsion to some extent. That is, because the hydrophilic OH groups of the HEMA monomer are most likely to be located at the surface of the polymer particles, it may be effective for stabilizing the emulsion polymerization process.

In this work, the soap-free emulsion polymerization was carried out at various MMA-HEMA ratios under different reaction conditions. It can be seen from the results in Table 1 that monomer conversion is low and plenty of undesired coagulate is formed when the HEMA level is relatively high (MMA/HEMA weight ratio of 3:1 or 5:1). This is because in the system with a relatively higher HEMA level, the strong hydrophilicity leads to homopolymerization and coagulation of HEMA that affects the stability of the emulsion. Increasing the MMA to HEMA ratio to 9:1 and 19:1

Table 1. The effect of hydrophilic monomer HEMA on the soap-free emulsion polymerization of MMA in the absence of nano SiO_2

Monomer ratio MMA:HEMA	*Reaction temperature °C*	*Monomer conversion %*	*Coagulum %*	*Emulsion stability*
3:1	75	34.7	100.00	Coagulate
5:1	75	26.4	16.03	Coagulate
9:1	75	39.1	1.97	Stable
19:1	70	61.8	0.15	Stable
19:1	75	85.4	0.17	Stable

improves the stability of the emulsion, increases the conversion of monomer, and greatly reduces the formation of coagulum.

Furthermore, the reaction temperature has a very important influence on the emulsion polymerization. When the reaction temperature is 70°C and the MMA: HEMA weight ratio is 19: 1, the monomer conversion is only 61.8% after a reaction time of 5 h, while at a reaction temperature of 75°C, the monomer conversion is 85.4% and the emulsion system remains stable. Higher temperature accelerates the polymerization rate, which leads to higher monomer conversion at the fixed time. Accordingly, we subsequently carried out the soap-free emulsion polymerization a 19:1 weight ratio of MMA/HEMA in the presence of nano-SiO_2 at reaction temperature 75°C.

3.2 Stability of the Emulsion

The effects of nano-SiO_2 level on the solid content of the emulsion, monomer conversion, coagulum formation and the viscosity of the emulsion are presented in Table 2. From Table 2, we can see that increasing the nano-SiO_2 loading level up to 10 wt% increases the solid content of the emulsion and the degree of monomer conversion in comparison to the reaction system in absence of nano-SiO_2. This is because the nano-SiO_2 particles can play a role as emulsion stabilizer in the soap-free emulsion polymerization. The organic monomer most likely polymerizes at the surface of the inorganic particles; at the same time, the presence of nano-SiO_2 has little effect on coagulum formation and the viscosity of the soap-free emulsion. In these polymerization systems, the coagulum is always lower than 1%, which means that these systems are stable.

Table 2. The effect of nano-SiO_2 level on soap-free emulsion polymerization of MMA-HEMA mixtures*

*SiO_2 level** %*	*Solid content %*	*Monomer conversion %*	*Coagulum %*	*Viscosity mPa·S*
0	8.67	86.7	0.62	4.02
2.5	9.49	92.5	0.73	4.74
5.0	10.4	98.3	0.32	3.72
10.0	10.6	95.9	0.36	3.42

*MMA to HEMA ratio is 19:1 and the reaction temperature is 75°C.
**Based on the total monomer weight.

3.3 Polymerization Rate of Soap-free Emulsion Polymerization

Plots of monomer conversion vs. time for the soap-free emulsion polymerization of 19:1 mixtures of MMA-HEMA are illustrated in Figure 1. It is clearly seen that nano-SiO_2 can enhance the degree of monomer conversion and accelerate the reaction to some extent in the soap-free emulsion polymerization reaction. At the beginning of the polymerization, the reaction rate in the presence of nano-SiO_2 is faster than the system without nano-SiO_2, and the final monomer conversion are also higher. This can be explained by adsorption of monomer and enhanced polymerization at the surface of the nano-SiO_2 particles. The higher loading of the nano-SiO_2 up to 10%, the faster the initial polymerization rate. However, beyond a nano-SiO_2 level 5% the monomer conversion cannot be increased continuously.

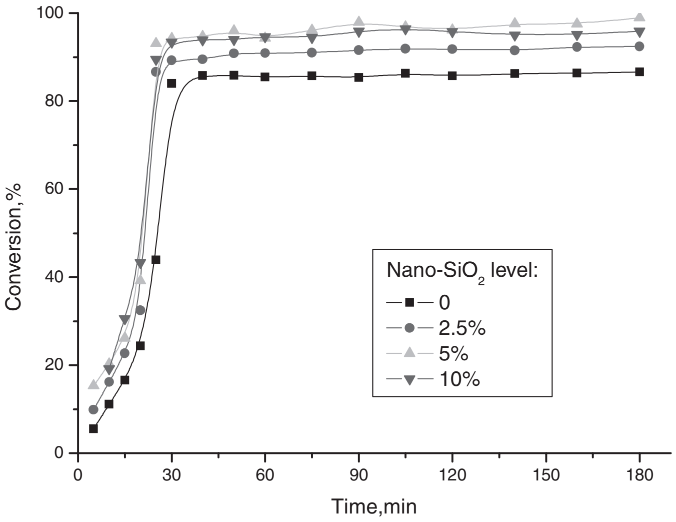

Fig. 1. The effect of silica level on monomer conversion of soap-free emulsion polymerization.

Table 3. The effect of silica level on the size and distribution of the emulsion

Nano-SiO_2 level/%	*Average size/nm*	*PDI*
0	374	0.013
2.5	275	0.024
5.0	261	0.067
10.0	270	0.035

3.4 Particle Size and Size Distribution

Table 3 and Figure 2 provide the size and size distributions of P(MMA-HEMA) particles formed in soap-free emulsions with or without nano-SiO_2 particles. It is clearly seen from Table 3 and Figure 2 that, nano-SiO_2 particles have a very important influence on the size and size distribution of the composites particles. The pure P(MMA-HEMA) soap-free emulsion has the largest mean particle size, but the narrowest particle distribution index (PDI) in these systems. Upon the addition of nano-SiO_2 particles in the soap-free emulsion polymerization, the obtained composites particles have smaller mean size than that without nano-SiO_2 particles, but the PDI is higher. With the increase of nano-SiO_2 level, the size and size distribution of the latex particles do not change much. This is because the nano-SiO_2 particles play a role as emulsion stabilizer in the soap-free emulsion. The monomer polymerizes at the surface of the nanoparticles and at the same time, monomer polymerizes in the micelles of the water phase that are produced by oligomer. Thus, these two kinds of polymerization sites produce smaller particle size and a larger size distribution. With increasing of nano-SiO_2 level, the quantity of the latex particles increases and the composites particle size may become smaller. However, the aggregation between the latex particles increases the particle size of the emulsion. In the mean time, the inorganic particles aggregate partly in the system containing nano-SiO_2 particles, so the particle size of the composites is almost the same, and the size distribution is wider than the one without nano-SiO_2 particles.

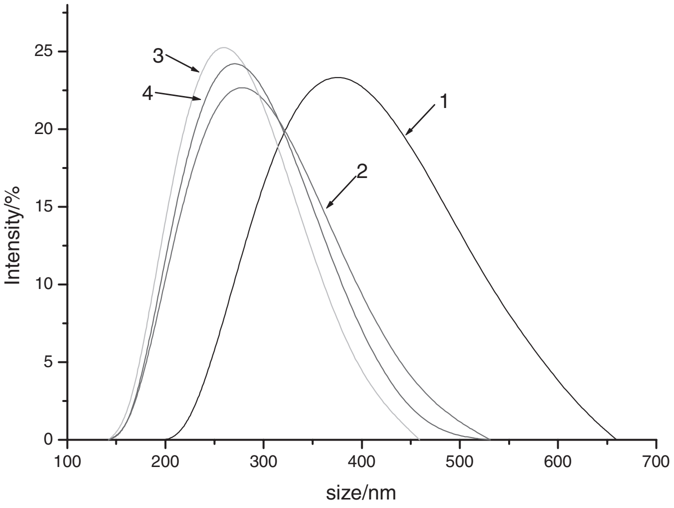

Fig. 2. Particle size distribution of soap-free emulsion at different nano-SiO_2levels: 1, 0%; 2, 2.5%; 3, 5.0%; 4, 10.0%).

3.5 Morphology of Latex Particles

SEM images of P(MMA-HEMA) particles formed at different nano-SiO_2 levels are illustrated in Figure 3. It is clearly seen that the shape of all the latex particles are uniformly spherical, but the particle size of these soap-free emulsions are different. The particle sizes of the emulsions with nano-SiO_2 are much smaller than the emulsion without nano-SiO_2. Furthermore, there is not much difference in the particle size of the emulsions formed at different levels of nano-SiO_2. The SEM results are in good agreement with those of the laser particle analysis.

3.6 Surface Tension and Ionic Conductivity

The surface tension and ionic conductivity of these systems before and after polymerization are provided in Table 4. From Table 4, we can see that nano-SiO_2 particles have an important influence on the surface tension and ionic conductivity of these systems. With the increase of nano-SiO_2 level, the surface tension and ionic conductivity of the pre-emulsion increase continuously. This is due to the high surface tension of nano-SiO_2 and electrical charge distributed at the surface of the nanoparticles. The surface tensions of emulsions obtained with or without nano-SiO_2 are all increased after polymerization. The surface tension differs greatly compared with that of the pre-emulsion before polymerization. This can be explained by hydrophilic HEMA monomers tending to locate at the surface of the latex particles when no nano-SiO_2 is present. Upon adding the nano-SiO_2 particles to the polymerization system, the aggregated nano-SiO_2 particles are divided into individual particles, which increase the surface tension greatly. Nevertheless, not all of the nanoparticles are separated, which can be seen from the results for the product formed at the 10% nanoparticles level. In that situation, the surface tension of the emulsion is almost the same as that of 5% nano-SiO_2 level.

Table 4. Effect of SiO_2 level on surface tension and ionic conductivity of the emulsion before and after polymerization

Level of Nano-SiO_2, %	*Surface tension, mN/m*		*Ionic conductivity, $\mu S/cm$*	
	Before	*After*	*Before*	*After*
0	27.0	34.0	5.9	1596
2.5	28.9	49.1	66.5	1533
5.0	29.6	56.5	129.8	1368
10.0	36.8	55.6	212.0	1478

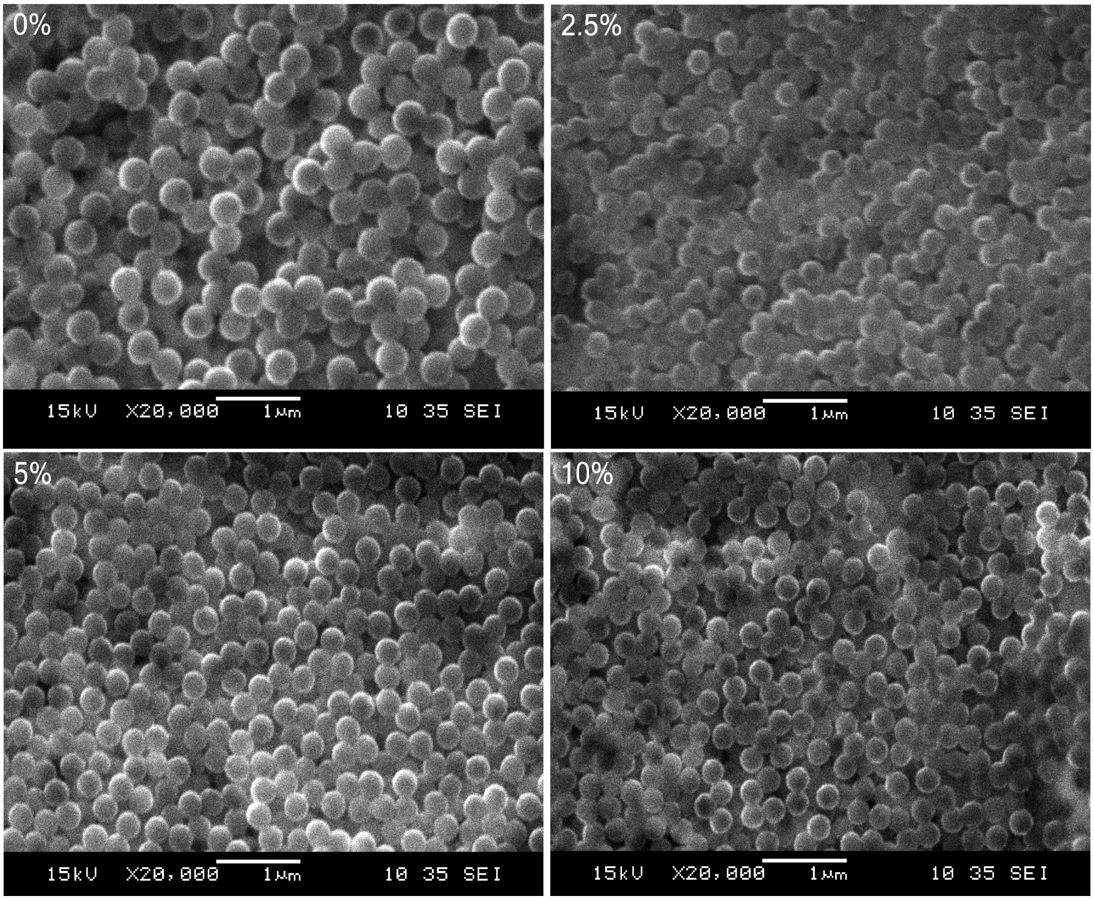

Fig. 3. SEM micrographs of soap-free emulsion particles formed at different levels of nano-SiO_2; the HEMA to MMA ratio in each case was 19:1 and the reaction temperature was 75°C.

Due to the large amount of charge distributed at the surface of the nano-SiO_2 particles, the conductivity of the pre-emulsion increased somewhat with the increase of nano-SiO_2 level. After polymerization, the ionic conductivity increases remarkably. That is due to the increase of the charge density at the polymer particle surface after polymerization produced by decomposition of initiator. The adsorptive interactions of the nano-SiO_2 particles with the polymer decrease this trend, and the conductivity of the emulsion decreases.

4 Conclusions

The effect of nano-SiO_2 colloids on the soap-free emulsion polymerization of MMA-HEMA mixtures has been investigated. The results demonstrate that the nano-SiO_2 level accelerates the polymerization rate and increases monomer conversion at loading levels of 2.5 to 10 wt%. The soap-free P(MMA-HEMA) emulsions with nano-SiO_2 have smaller average particle sizes but broader particle size distributions than that of the pure P(MMA-HEMA) emulsion. SEM micrographs of P(MMA-HEMA) soap-free emulsion particles confirm this, and the shapes of all the latex particles are uniformly spherical. The addition of nano-SiO_2 increases the surface tension of the reaction system before and after polymerization. In addition, nano-SiO_2 increases the ionic conductivity of the emulsion before polymerization but decreases the conductivity after polymerization.

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