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ORIGINAL CONTRIBUTION

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Preparation and morphology of SiO_2/PMMA nanohybrids by microemulsion polymerization

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Abstract Polymethylmethacrylate/SiO2 nanocomposite particles were prepared through microemulsion polymerization by using the silica particles coated with 3-(trimethoxysilyl) propyl methacrylate (MSMA) in both acidic and alkaline conditions. Core-shell and other interesting morphology nanocomposite particles were obtained depending on the pH of the microemulsion, the amount of silanol, and the coupling agent concentration employed. Then, by combining a modified microemulsion polymerization process, i.e., an additional monomer-adding process, the solid contents of the polymer/inorganic nanocomposite microemulsion could greatly increase. Thus, by adjusting these parameters and polymerization process, it was possible to control the morphology and size of the nanocomposites.

Keywords Morphology · Microemulsion polymerization · Silica · Nanocomposite

Introduction

In recent years, considerable efforts have been expended on the elaboration of organic/inorganic nanocomposite materials. Such materials can be obtained as colloidal suspensions with a variety of morphologies. The interest in colloidal nanocomposites has gained much importance owing to their remarkable properties that can be obtained by an appropriate combination in structures of the organic and inorganic components inside the nanoparticles. Core-shell nanocomposites with different interesting morphologies have also formed the subject of numerous investigations, which have been largely spurred by the applicability of such materials in the areas of coatings, catalysis, and diagnostics [1–8].

To date, the most important route to organic/inorganic core-shell nanocomposite polymer shell and inorganic core is via heterophase polymerization, more specifically through the control of structure and morphology, and by seeded emulsion polymerization in different ways [10–18]. A typical method is to synthesize core-shell nanoparticles based on the charge attraction between particles, in which one kind of particle consisting of initiated monomers and stabilized by the emulsifier hold charges opposite to the surface charges of the inorganic core particles.

Polymerized latex can also be mixed with and coated directly onto inorganic beads through acid-base interaction. Lami and Guyot [18] used a cationic initiator [e.g., 2,2'-Azo-bis-iso-butyronitrile (AIBA)] and anionic silica particles to synthesize silica/polymethylmethacrylate (PMMA) nanocomposite. They also obtained the same results by mixing cationic PMMA with anionic silica particles.

Surface modification of minerals and polymers is another useful method. In this process, polymerization is performed directly in the presence of inorganic particles without the interactions of charges. Examples of emulsion, miniemulsion, suspension, and dispersion polymerizations for preparing nanoparticles can be found in the literature. For example, silica nanoparticles are encapsulated with polystyrene (PS) and PMMA by dispersion polymerization in polar media and by emulsion polymerization using a cationic azo initiator, respectively [14–22]. Bai Yang and his coworkers obtained monodispersed silica-polystyrene core-shell microspheres through emulsion polymerization of styrene (St) on the surface of 3-(trimethoxysilyl)propyl methacrylate (MPS) grafted silica nanoparticles [21]. The research focus of the modification is mainly on the methods of the physicochemical processes. The silica-polymer particles are usually prepared in neutral or alkalescent systems. However, the effect of pH on the morphology of silica-polymer core-shell nanocomposites has seldom been discussed in detail [22, 23].

We have developed a convenient method to prepare silica/PMMA nanocomposites in either acidic (pH 2) or alkalescent (pH 9) microemulsion by using coupling agents to graft silica nanoparticles. Here, we report the study of the morphology of silica-polymer nanocomposites obtained in different acidity and the investigation of the influence of silica content and initiator type on the structure of nanocomposites. In this study, we also worked on increasing polymer content in the reaction system by using a modified microemulsion polymerization process [24, 25]. We found that the stability of the emulsion in an acidic condition is quite different from that in alkaline condition in the case of high solid content.

Experimental

Materials

Methyl methacrylate (MMA, analytical reagent grade), sulfuric acid (analytical reagent grade), tetrahydrofuran (THF, analytical reagent grade), sodium dodecyl sulfate (SDS), γ-methacryloxypropyltrimethoxy silane (MSMA), and potassium persulfate (KPS) were purchased from Shanghai Chemical Reagent Company. Octadecyltrimethyl ammonium bromide (OTAC) (99% pure, analytical reagent grade) was purchased from Shanghai Jingwei Co., Ltd. MMA and THF were distilled under reduced pressure before polymerization. KPS was purified by recrystallization from water. The silica nanoparticles were prefabricated from water glass, and the method was developed in our previous work [26–28].Water glass (highly purified, containing 9.15 wt% Na_2O and 28.55 wt% SiO_2) was purchased from Jiading Water Glass Factory, Shanghai, China, and used as received. Deionized water was used for all experiments.

Preparation of silica/PMMA latex

The preparation of silica acid precursor was performed according to Refs. [26–28]. A given amount of MSMA was drop-wisely added into the silica acid precursor under vigorous mechanical stirring at room temperature. The reaction was stopped after 12 h, and the product was grafted silica nanoparticles.

The microemulsion polymerization of silica-polymer hybrid was conducted in a 250-ml four-necked flask with a stirrer and a condenser. Ming's method was used with some modifications [29]. First, 80 ml of H_2O, 2.0 g of surfactant, and 5.0 g of monomer were mixed in the reactor, and the pH of the mixture was adjusted to the desired value by adding $NH_3{\cdot}H_2O$ and CH_3COOH. Then, the required amount of silica nanoparticles was added, and the pH of the mixture was readjusted. Under pure nitrogen atmosphere, the reactor was heated to 75°C, while 10 ml aqueous solution of initiator KPS (0.30 wt% of monomer) was introduced into the system. After reacting for 1 h, the remaining monomer was slowly added to the flask. The reaction was allowed to continue at 75°C for 1–2 h.

Characterization

The electrophoretic mobility of the silica acid precursor was determined using a laser electrophoresis zeta (Z) potential analyzer (Zetasizer III from Malvern Instruments). The analysis was carried out at 20°C. Diluted solution of the silica sol was added into a 10.3-N NaCl solution, and the pH of the suspension was adjusted by using decimolar HCl and NaOH standard solutions.

Fourier-transform infrared spectroscopy (FTIR) was carried out on a Bruker Vector-22 FTIR spectrometer. Before FTIR measurement, both SiO_2 particles and SiO_2 particles grafted with MSMA were subjected to Soxhlet extraction with ethanol for 72 h and then dried at 60°C in vacuum for 6 h to remove ethanol.

Particle size was determined by dynamic light scattering on an L&G Microtrac Particle Analyzer (9200 series) from Leeds & Northrup Co. Microlatex samples were diluted with deionized water to about 0.1 wt% of polymer concentration. From the measurement, *Z*-average diameters were obtained. The monomer conversion was determined by gravimetry.

Transmission electron microscope (TEM) experiments were performed with a JEOL 2,000 FX microscope (accelerating voltage of 200 kV). To prepare TEM samples, the carbon-coated grid was wetted with a small drop of 2% phosphotungstic acid for 30 min; afterwards, samples were deposited on the grid and left to dry at room temperature before analysis.

Thermal gravimetric analysis (TGA) measurement was done with a Pyris1 TGA instrument (PerkinElmer Instruments Corp., USA) under nitrogen atmosphere from room temperature to 800°C at a heating rate of 20°C/min. The percentage of grafting (PG) was determined by the following equation as described in Ref. [22]:

$$\text{percentage of grafting}(\%) = \frac{\text{polymer graftede}(\text{g})}{\text{silica used}(\text{g})} \times 100\%$$

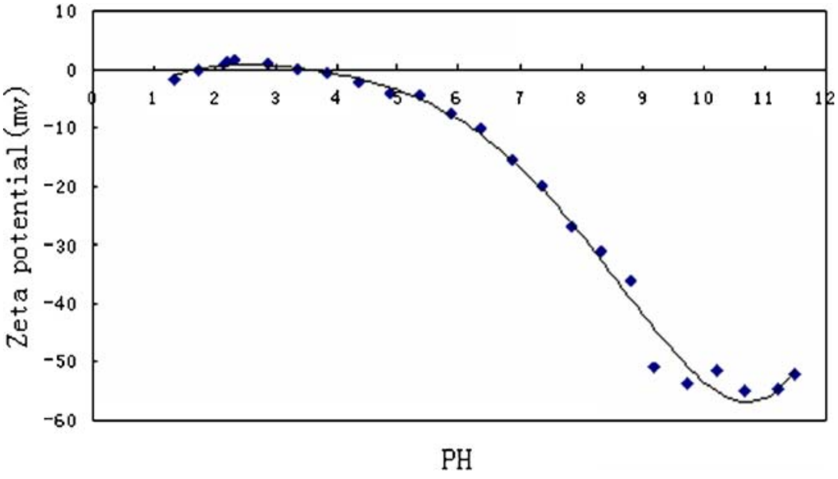

Fig. 1 The zeta potential of the silica nanoparticles at different pH values

The conversion of MMA ($C\%$) was determined by means of the gravity method and calculated using the following equation:

$$C\% = \frac{\mathrm{M2} - \mathrm{M1Y}}{M1X} \times 100\%,$$

where M_1 is the mass of polymerized emulsion sample, M_2 is the mass of solid after drying, X is the mass percentage of MMA based on total input materials, and Y is the mass percentage of emulsifier, initiator, and silica based on total input materials.

Results and discussion

Z potential measurements

Electrophoresis is a convenient method to characterize the surface properties of polymers and metal oxide colloids. For the silica acid derived from water glass, the evolution of Z potential as a function of pH is shown in Fig. 1. It shows that the Z potential is in the vicinity of zero when pH is lower than 4, and specifically, at about pH 2–3, it reaches the isoelectrical point where the negative and positive charges created by the silanol groups are equal on the surface of the silica particles. At that point, the silanol groups with the structure of Si-OH are stable. As the pH value increases from 4, the Z potential becomes more and

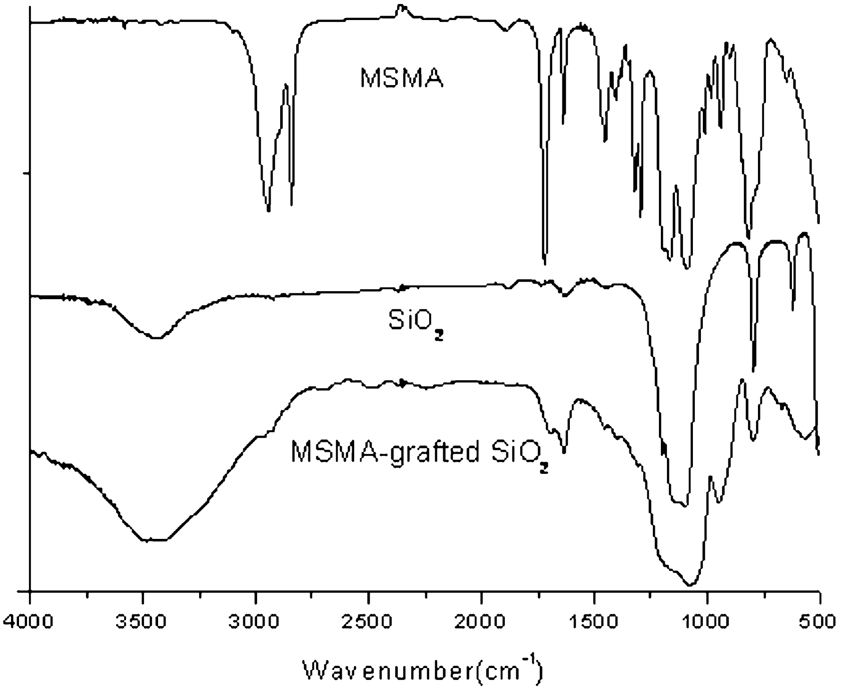

Fig. 2 FTIR spectra of the coupling agents MSMA, pure silica, and MSMA grafted silica

more negative, indicating the increase in negative charges on the particle surface. Because of the equilibrium of the SiOH/SiO$^-$ acid/base dissociation, more negative charges will result in higher surface energy and higher numbers of SiO$^-$ species. In addition, the condensation of silanol groups (Si-OH) will be catalyzed by Louis base as shown in the following equations [30]:

$$\mathrm{Si-OH+OH-\rightarrow SiO^{-}+H2O} \tag{1}$$

$$\mathrm{SiO^{-}\ +\ Si-OH\rightarrow Si-O-Si+OH^{-}} \tag{2}$$

Therefore, in a basic system, the ionized silanol groups can initiate silanols' cross-linking reaction, form the oxygen bridging between the unstable nanoparticles, and probably induce agglomeration.

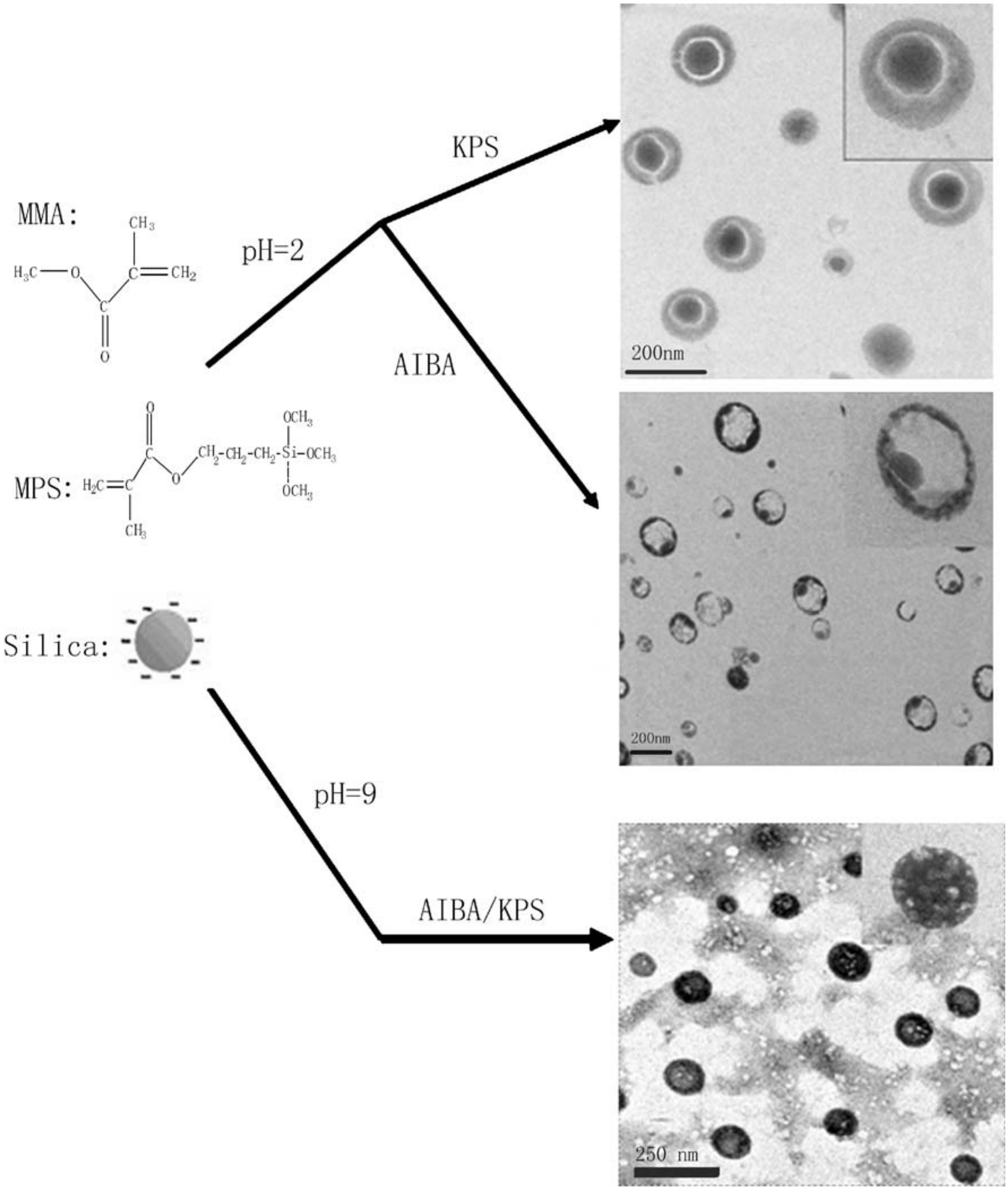

Fig. 3 Silica/PMMA nanocomposite latex particles obtained under different pH values using AIBA/KPS as initiator

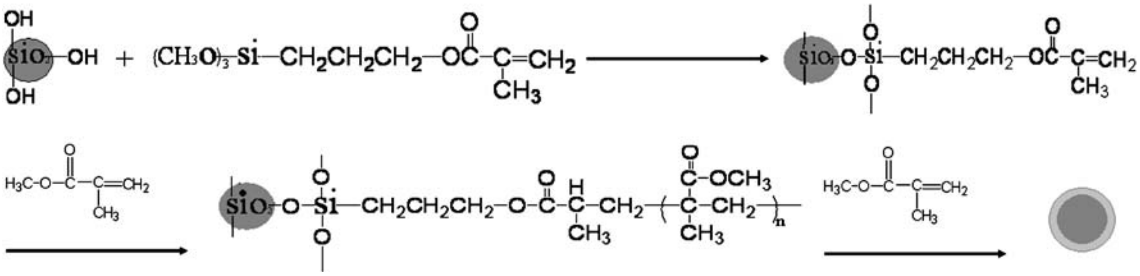

Fig. 4 Schematic illustration of the synthesis route of silica/PMMA nanocomposite latex

FTIR measurements

Silica particles with and without coupling agent MSMA were characterized by Fourier-transform infrared spectroscopy. Figure 2 is an FTIR spectra of pure coupling agent MSMA, silicon oxide, and MSMA grafted silicon oxide. The peaks at 2,960, 2,840, and 1,720 cm^{-1} are assigned to the stretching of C-H bonds and C=O bonds, respectively, while the absorption band at 1,411 cm^{-1} is ascribed to the unhydrolyzed $SiOCH_3$, and the band at 1,640 cm^{-1} is ascribed to the residual water. The spectral difference between pure silica particles and silica particles grafted with MSMA is clearly recognizable. Typical MSMA bands such as the band at 1,720 cm^{-1} of C=O bond and the band at 2,900 cm^{-1} of C-H bond are reflected at the spectrum of MSMA grafted silica particles. These phenomena unambiguously demonstrate that the coupling agent MSMA was indeed attached to the surface of the silica particles via chemical bonds.

TEM measurement

In the presence of silica nanoparticles grafted with coupling agent, MSMA was copolymerized with MMA in acidic and alkaline microemulsions with negative and positive initiators separately. The morphology of the nanohybrids was characterized by TEM. Figure 3 presents the structures of the particles observed from reaction systems of different pH values. The core-shell microspheres were obtained in an acidic condition, and each microsphere had a single silica core wrapped in a polymer shell, whereas the alveolate nanoparticles were formed spontaneously in alkaline microemulsion with irregular shapes of compound grains.

The morphologic diversity of the nanohybrid is probably due to the different surface potentials on the particles at different reaction systems. As discussed before, the Z potential is a function of system acidity. In an acidic system, the Z potential is near zero. The condensation of Si-OH between particles can hardly be carried out during copolymerization. Once MMA reacts with the coupling agent grafted on the inorganic particle, the polymer chain is anchored on the particle and covers the individual core to form a uniform core-shell microsphere. However, when positive-initiator AIBA is used, the silica cores seem to be strongly attached to the polymer surface and leave the center of the microsphere. It is likely due to some remaining fragments of the initiator on the particle surface with positive charges when the monomer had polymerized.

For the silica nanoparticles in alkaline systems, with the quick falling-off of Z potential as shown in Fig. 1, the silanol groups (Si-OH) were hydrolyzed to $Si\text{-}O^-$ and condensed with each other according to the two-step mechanism discussed in "Z potential measurements". Because of the fast reaction rate of the microemulsion polymerization [29], the cross-linking of silica particles would occur in the process of copolymerization of MMA with coupling agent on the surface of inorganic moiety. Therefore, microspheres thus formed have a honeycomb-like structure (Fig. 4).

Table 1 The effect of silica and coupling agent content on the size and appearance of polymerized nanocomposite

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
pH	2	2	2	9	9	9
Silica content (g)	0.75	0.75	1.5	0.75	0.75	1.5
MSMA content (g)	0.15	0.3	0.15	0.15	0.3	0.15
Emulsion appearance	Transparent	Transparent	Transparent	Transparent	Precipitate	Precipitate
Nanocomposite size (nm)	57	274	70	109.5	>1,000	>1,000
PG (%)	122	–	–	144	–	–

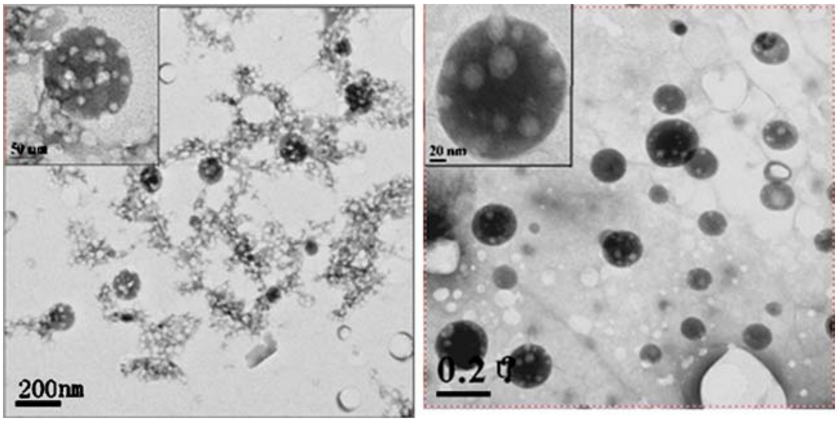

Fig. 5 TEM pictures of the silica/PMMA nanocomposites in system nos. 2 (*left*) and 3 (*right*)

The effect of silica and coupling agent contents on the morphology of silica/PMMA nanocomposite

To study the effect of silica and the coupling agent contents on the morphology and stability of nanohybrids, the amount of silica and the coupling agent were varied separately in both acidic and alkaline conditions. As displayed in system no. 3 in Table 1, at a given amount of coupling agent, doubling the amount of silica content only slightly increased the size of nanohybrid because these inorganic nanoparticles were stable in an acidic system. In the case of a double amount of MSMA with constant silica acid content, the apparent size of polymerized nanohybrid increased remarkably. The coupling agent has three $SiOCH_3$ groups in each molecule that not only couples with the polymer and SiO_2 but also condenses with each other. In addition, there were some polymer particles not tethered to silica in each system due to the relatively high polymer/silica ratio. Increasing the amount of coupling agent enhanced the chance of forming MSMA-copolymer particles, which can be further cross-linked to become particles with the morphology shown in Fig. 5 (left). It is the cross-linked microspheres that contributed to the increase in the apparent particle size of the emulsion (no. 2 of Table 1). By comparing Fig. 5 to Fig. 3, it can be seen that the core-shell structure of the nanohybrid seemed worsened when either silica or coupling agent content was increased. Obviously, there is an optimum reactant ratio for forming well-defined core-shell structures. The excessive amount of coupling agent or silica acid promotes cross-link reactions or condensation reactions, resulting in poor core-shell structures.

When preparing in basic medium, the silica nanoparticles can both couple with PMMA via MSMA and condense with each other (Eqs. 1 and 2). Therefore, increasing either silica or MSMA content would induce agglomeration and reduce the stability of the emulsion, which was observed in system nos. 5 and 6.

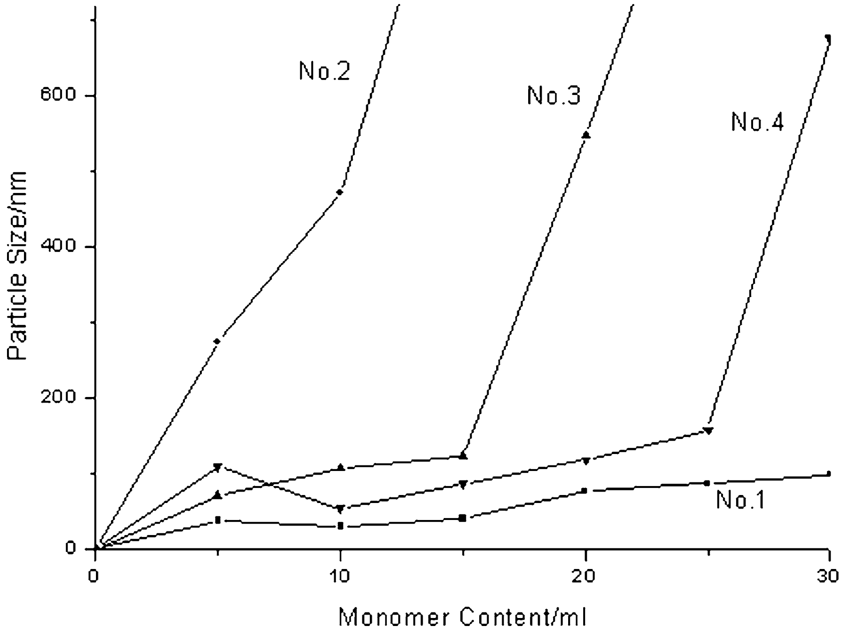

Fig. 6 The relationship between particle size and monomer amount of system nos. 1–4

The effect of solid content and microspheres' morphology on emulsion stability

System nos. 1 and 4 in Table 1 are stable and well-dispersed nanohybrid microemulsions but have low solid contents. It is desirable to enhance the solid contents for applications such as paint. However, it is usually difficult to synthesize nanohybrid emulsions of either high polymer content or high inorganic content due to the phase separation and aggregation of microspheres. Therefore, we designed a modified microemulsion polymerization procedure to obtain higher solid content, which has been reported elsewhere [29]. In the present study, the modified method was applied to increase the solid content by adding additional MMA to the stable nanohybrid emulsions (system nos. 1–4). The size of particles vs the amount of added additional monomer was plotted in Fig. 6. For system nos. 1 and 4, which were synthesized in acidic and basic conditions, respectively, their statistical particle sizes decreased at the beginning of the addition of the extra monomers. In those systems, there should be some free micelles available in which the newly added monomers polymerized and formed many new small particles, which led to the decrease of the statistical particle size. In fact, before the monomer dropping, not all the polymerized monomer was attached to the silica. The polymer grafting efficiencies are similar for nos. 1 and 4, as shown in Table 1. Therefore, there had already existed some free polymer particles in the emulsion system. As more monomers were introduced into the system, the amount of free micelle diminished and was finally exhausted. Then, the added monomer would polymerize on nanohybrid microspheres and the abovementioned new particles, which resulted in the increase in the size of the microsphere. However, in system no. 1, the increase in particle size is small in comparison with that in system no. 4. This indicates that the core-shell microspheres in system no. 1 are more stable than the cellular structure in system no. 4. However, because the stable emulsion system could be formed at the end of monomer dropping, the monomer conversions for nos. 1 and 4 were 94.1 and 90.6%, respectively, both more than 90%.

For system nos. 2 and 3, the double amount of silanol or the couple agent enhanced the possibility of agglomeration between the particles in the system. Therefore, the adding and heating of the additional monomers resulted in swelling of particles and in agglomeration between the swollen particles, which in turn led to the rapid increase in particle size and, finally, to the precipitation in emulsion system. The monomer conversions of these two systems were both under 80% after the monomer dropping because of the precipitation of monomer swollen particles.

Conclusion

Silanol nanoparticles obtained via sol-gel methods in an acidic condition from water glass were used as the inorganic parts of the hybrids. Nanocomposite microemulsion, based on the charge attraction between silanol particles and cation initiators, were synthesized in both acidic and alkaline conditions through the use of coupling agents. In general, at low pH values such as pH 2, the surface of silanol precursor has few charges, and as a result, every hybrid particle has only one silica core, while at high pH values such as pH 9, the large negative surface charge causes autocondensation between silanols and thus leads to the formation of cellular structures in the hybrids.

The structure of the hybrid is also affected by the amount of silanol and the coupling agent in the system. Increasing either silanol or the coupling agent causes the change of hybrid structures from regular core-shell to cellular structure. The former is more stable than the latter. By the modified method of microemulsion polymerization, i.e., an additional monomer-adding process, we successfully prepared the stable nanoscale polymer/inorganic hybrids microemulsion with high solid contents.

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