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Preparation of Silica/Poly(*tert*-butylmethacrylate) Core/Shell Nanocomposite Latex Particles

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*Nanocomposite latex particles, with a silica nanoparticle as core and crosslinked poly(*tert*-butylmethacrylate) as shell, were prepared in this work. Silica nanoparticles were first synthesized by a sol-gel process, and then modified by 3-(trimethoxysilyl)propyl methacrylate (MPS) to graft C=C groups on their surfaces. The MPS-modified silica nanoparticles were characterized by elemental analysis, FTIR, and ²⁹Si NMR and ¹³C-NMR spectroscopy; the results showed that the C=C groups were successfully grafted on the surface of the silica nanoparticles and the grafted substance was mostly the oligomer formed by the hydrolysis and condensation reaction of MPS. Silica/poly(*tert*-butylmethacrylate) core/shell nanocomposite latex particles were prepared via seed emulsion polymerization using the MPS-modified silica nanoparticle as seed, *tert*-butylmethacrylate as monomer and ethyleneglycol dimethacrylate as cross-linker. Their core/shell nanocomposite structure and chemical composition were characterized by means of TEM and FTIR, respectively, and the results indicated that silica/poly(*tert*-butylmethacrylate) core/shell nanocomposite latex particles were obtained.*

Keywords inorganic/organic nanocomposite particles, core/shell structure, silica, crosslinked poly(*tert*-butylmethacrylate), 3-(trimethoxysilyl)propyl methacrylate, seed emulsion polymerization

Introduction

In the last decade, many scientists have contributed to the elaboration of nanocomposite materials formed by embedding inorganic particles into polymeric matrices (1–5). Due to their excellent properties synergistically derived from polymer and inorganic materials, very interesting applications of the composite particles can be found in many fields (6, 7). Silica/polymer nanocomposite particles are one type of these composite materials, which have been used extensively in medicine, coatings, agents employed in plastic modification, etc (8). The electroactive silica/polymer nanocomposite particles

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represent a potentially useful material not only for uptaking metal from solution but also for catalytic applications (9).

Although numerous procedures exist, emulsion polymerization is by far the technique mostly frequently used for obtaining composite particles with an inorganic particle core and a polymer shell, due to its advantages such as high reaction rate, good heat dispersion, and relatively sophisticated engineering technology in industrialization (10). Wang et al. (11) obtained long-term stable poly(butylacrylate) latex containing nanosilica through ultrasonic induced encapsulating emulsion polymerization. Zhang et al. (12) used silica nanoparticles grafted by 3-(trimethoxysilyl) propyl methacrylate (MPS) as seeds in the emulsion polymerization and succeeded in preparing monodisperse silica/polystyrene core/shell particles. Bourgeat-Lami and Lang (13) have prepared silica/polystyrene nanocomposite particles by a novel method based on dispersion polymerization of styrene in a water/ethanol (5/95 w/w) medium.

Here, we prepared silica/poly(tert-butylmethacrylate) core/shell nanocomposite particles by seed emulsion polymerization, utilizing the modified silica nanoparticles as seeds, tert-butylmethacrylate as monomer and ethylene glycol dimethacrylate as crosslinker. These core/shell nanocomposite particles have a crosslinked poly(tert-butylmethacrylate) shell which can be hydrolyzed to form pH-sensitive poly(methacrylic acid) shell layers.

Experimental

Materials

3-(trimethoxysilyl) propyl methacrylate(MPS) from Acros Organics, tert-butylmethacrylate(tBMA) and ethyleneglycol dimethacrylate (EGDMA) both from Tokyo Kasei Kogyo and sodium dodecyl sulfate (SDS) from Beijing Chemical Co. were used as received. Other agents were of analytical grade and utilized without further purification. Deionized water was used for all polymerization and treatment processes.

Preparation

Preparation and Modification of Colloidal Silica Nanoparticles. Colloidal silica nanoparticles with average diameters ranging from 80 to 180 nm were prepared in ethanol according to the Stöber method (14). The coupling agent, MPS, was used for modification of the colloidal silica particles: MPS in excess (40 μmol of the coupling agent per square meter surface area of silica nanoparticles, corresponding to five times the silanol surface concentration estimated to be equal to 8 $\mu\text{mol}/\text{m}^2$ (13) was added to the ethanol dispersions of the silica nanoparticles. The dispersions were agitated for 48 h. Residual MPS and ammonia were removed from the dispersions by centrifugation until the absorbance of MPS in the supernatant at 203.5 nm detected by UV spectroscopy approached zero. The ethanol dispersions of MPS-modified silica nanoparticles were transformed into their water dispersions by centrifugation for the seed emulsion polymerization as described below.

Preparation of Core/Shell Structured Microparticles. Silica-poly(tert-butylmethacrylate) core/shell nanocomposite particles were prepared by seed emulsion polymerization. In a typical procedure, the water dispersion of MPS-modified silica nanoparticles was used as seed emulsion, and a certain amount of SDS as emulsifier and NaHCO_3 as buffer agent

were placed in the emulsion. The seed emulsion was deoxygenated by bubbling nitrogen for 30 min, and then heated to 70°C in an oil bath. After APS as initiator was added, the mixture of tBMA and EGDMA was introduced drop by drop into the seed emulsion for 4 h at 70°C.

Characterization

Elemental analysis of carbon and hydrogen (Elementer, Vario EL β) was performed on dry silica nanoparticles and MPS-modified silica nanoparticles. The images of silica nanoparticles and core/shell structured microparticles were obtained by TEM (HITACHI, H-800). The diameters in dry state (D_{dry}) and the hydrodynamic diameters (D_{H}) of silica nanoparticles were measured by TEM and quasi-elastic light scattering (QELS) (Malvern, Zetasizer Nano-ZS), respectively. The solid-state ^{13}C and ^{29}Si NMR spectra of silica nanoparticles were recorded by NMR (Bruker, AV400) to confirm that the grafting of MPS was obtained. The cross-polarization (CP)/magic angle spinning (MAS)/high power dipolar decoupling (DD) techniques were used in all NMR experiments. The MAS rate was 5 kHz. For ^{13}C and ^{29}Si spectroscopy, the contact time were 1 ms and 3 ms, and the repetition time was 4 s and 2 s, respectively. FTIR spectra of core/shell structured nanocomposite particles were measured in the wavenumber range from 4000 to 400 cm^{-1} using a FTIR spectrophotometer (Nicolet, NEXUS-670).

Result and Discussion

Synthesis and Modification of the Colloidal Silica Nanoparticles

Using Stöber's method documented in the literature (14), we easily synthesized the colloidal silica nanoparticles having different sizes depending on the water concentration (see Table 1).

Three reactions are generally used to describe the hydrolysis and condensation of TEOS.

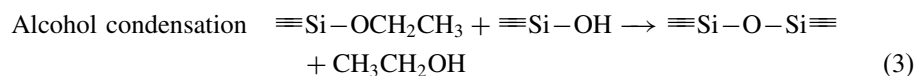
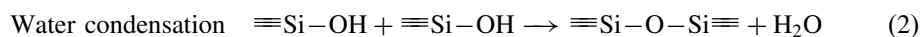
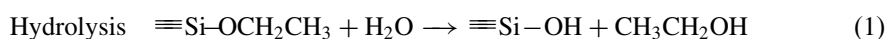


Table 1
Chemical composition and particle size of silica nanoparticles

Silica nanoparticles	[H ₂ O] (M)	Chemical composition (wt%)			Particle size (nm)	
		C	H	OC ₂ H ₅	D_{dry}	D_{H}
SP4	4	0.206	1.592	0.386	65	88.5
SP5	5	0.176	1.584	0.330	105	129.2
SP6	6	0.184	1.575	0.345	130	175.5

Generally it is considered that the condensation reactions (2) and (3) occur after the hydrosis reaction (1), the primary particles begin to form, which then aggregate to form larger final colloidal particles. The percentage of OC_2H_5 groups was obtained from the carbon contents on the assumption that the carbon is due to unhydrolyzed ethoxy groups trapped in the particles as terminal functions. The difference between D_{dry} and D_{H} of the silica nanoparticles, determined respectively by TEM and QELS, results probably from an apparent shrinking of the particles in the TEM experiments. Similar behavior has already been observed in the literature (13, 15). Silica particles obtained by the Stöber's method are known to be porous and this porosity could explain the shrinkage of the small particles under the high vacuum in the TEM experiments (16). Figure 1 shows the silica particles micrographs and their size distribution. For a given concentration of TEOS and ammonia, the particle size increased with the increase of the amount of water used. Simultaneously, the particles become more spherical and regular in shape.

Grafting of the MPS molecule on the silica nanoparticles surface was first evidenced by the increase of carbon content determined by elemental analysis, as shown in Table 2. The weight percentage of the grafted MPS can be calculated assuming that the carbon increase totally came from the grafted MPS (see last column of Table 2). The amount of the grafted MPS increased with the decrease of the size of the silica nanoparticles, which is due to the fact that the total surface area of the nanoparticles increases with the decrease of their sizes causing the enhancement of the concentration of the silanol groups on their surfaces.

Solid-state NMR spectroscopy was used to give evidence of the grafting of MPS. The ^{29}Si CP/MAS NMR spectra of silica particles before grafting and after grafting are given in Figure 2 (a) and (d). In Figure 2 (a), the chemical shift at -91.3 ppm, -100.6 ppm and -110.1 ppm can be assigned to silicon atoms $\text{Q}^2[\text{Si}(2\text{OSi}, 2\text{OH})]$, $\text{Q}^3[\text{Si}(3\text{OSi}, 1\text{OH})]$ and $\text{Q}^4[\text{Si}(4\text{OSi})]$. In Figure 2 (b), the signal of Q^2 , Q^3 and Q^4 silicon atoms still exist, and an additional signal can be found at -65.5 ppm. According to the literature (13), the structure exchange from $\text{Si}-\text{OH}$ bond to $\text{Si}-\text{C}$ bond which corresponds to the transformation of Q silicon into corresponding T silicon, causes a downfield shift of about 45 ppm, therefore, the signal at -66.5 ppm can be attributed to $\text{T}^3[\text{Si}(3\text{OSi}, 1\text{C})]$ silicon, which are the silicon atoms in the MPS molecules. It appears in the spectrum of Figure 2 (b) that the

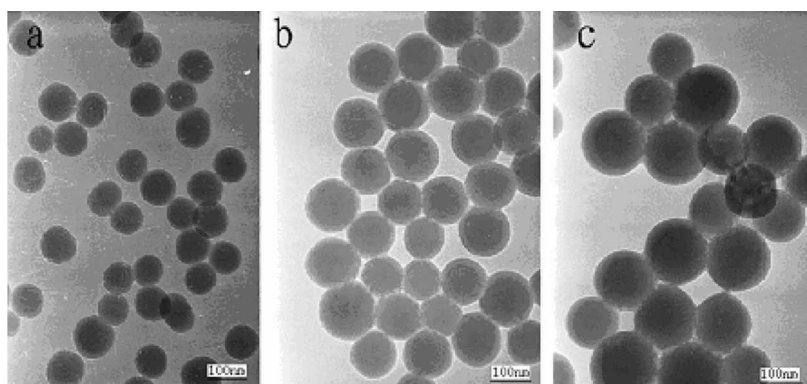


Figure 1. TEM images of silica-nanoparticles prepared using various concentrations of water, (a) 4M; (b) 5M; (c) 6M.

Table 2
Carbon contents of MPS-modified silica nanoparticles

Modified silica nanoparticles	C content before modification (wt%)	C content after modification (wt%)	Grafted MPS content (wt%)
SPM4	0.206	1.77	3.50
SPM5	0.176	1.16	2.20
SPM6	0.184	0.79	1.36

formation of T³ units is predominant while the T¹ species (about -46 ppm), corresponding to the monomeric form, are hardly observed. This indicates that the grafted substance on the modified SiO₂ particles is mostly the oligomer formed by the hydrolysis and condensation reaction of MPS.

Solid-state ¹³C-NMR spectroscopy can also give qualitative proof of the presence of MPS chemically linked to silica, Figure 3 shows the ¹³C CP/MAS NMR spectrum of MPS-modified silica nanoparticles; the assignments are shown in the figure. Except for the signals at 60 ppm and 16 ppm, which are assigned to the (-OCH₂-) (1) and (-OCH₂CH₃-) (2) in the unhydrolyzed ethoxy groups from TEOS, the other signals can be attributed to the carbon atoms of the grafted MPS molecules. The peaks at 136.6 ppm (b) and 123.4 ppm (a) are attributed to the two vinylic carbons and the C=O groups are characterized by the peak at 168.3 ppm. The three peaks at 7.7 ppm (f), 21.7 ppm (e) and 66 ppm (d) have been assigned to the propyl carbons, respectively. The peak characteristic of the methyl group on the double bond (g) is overlapped with the line at 16 ppm.

The result of grafted MPS on the silica nanoparticles is also supported by FTIR spectroscopy (Figure 4) which shows an absorption band (1689 cm⁻¹) attributed to the C=O groups in grafted MPS component.

Preparation of Core/Shell Nanocomposite Particles

A monomer *tert*-butylmethacrylate (tBMA) was polymerized with a crosslinker ethylene glycol dimethacrylate (EGDMA) by seed emulsion polymerization in the presence of the MPS-modified silica as seeds, resulting in the formation of silica/poly

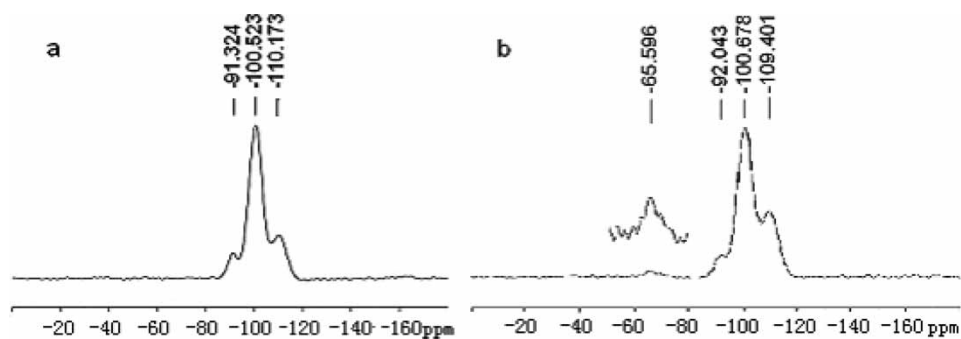


Figure 2. ²⁹Si CPMAS NMR spectra of (a) silica nanoparticles and, (b) MPS-modified silica nanoparticles.

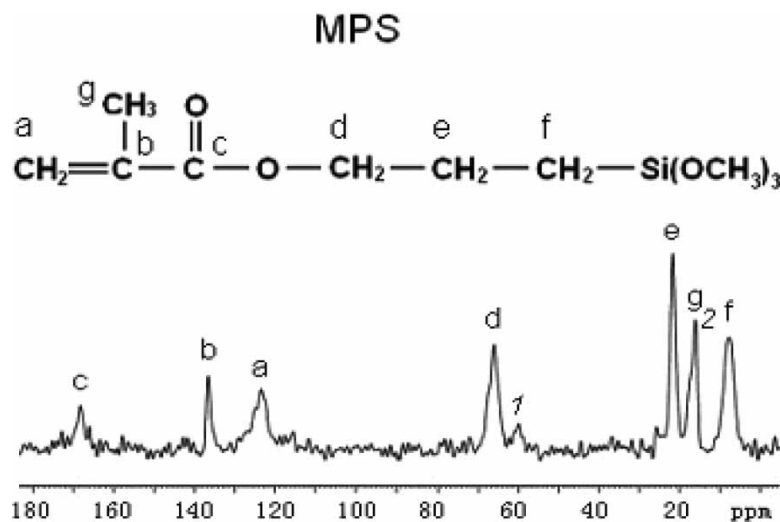


Figure 3. ^{13}C CPMAS NMR spectrum of MPS-modified silica nanoparticles.

(tert-butylmethacrylate) core/shell structured nanocomposite particles. Figure 5 shows the TEM images of the core/shell nanocomposite particles stained by 1.5% phosphotungstic acid (PTA) solution, confirming the core/shell structure of the particles. The small and purely white particles in Figure 5 (a) are poly(tert-butylmethacrylate), which were produced by self-nucleation of the polymer in the process of emulsion polymerization. As the concentrations of the silica nanoparticles used as seeds in the initial stage of the polymerization reaction were increased from 1.0% to 2.0%, the number of the pure polymer particles gradually decreased. The core/shell composite structure of the particles can be evidenced by comparing the spectra of MPS-modified silica nanoparticles,

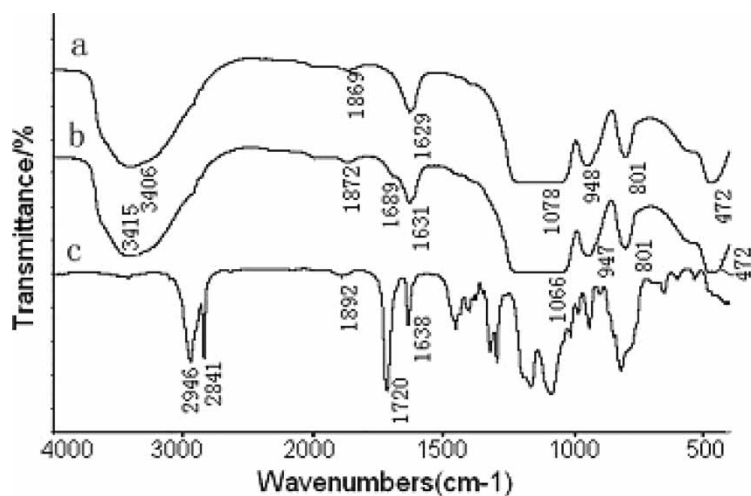


Figure 4. FTIR spectra of (a) silica nanoparticles; (b) MPS-modified silica nanoparticles and (c) pure MPS.

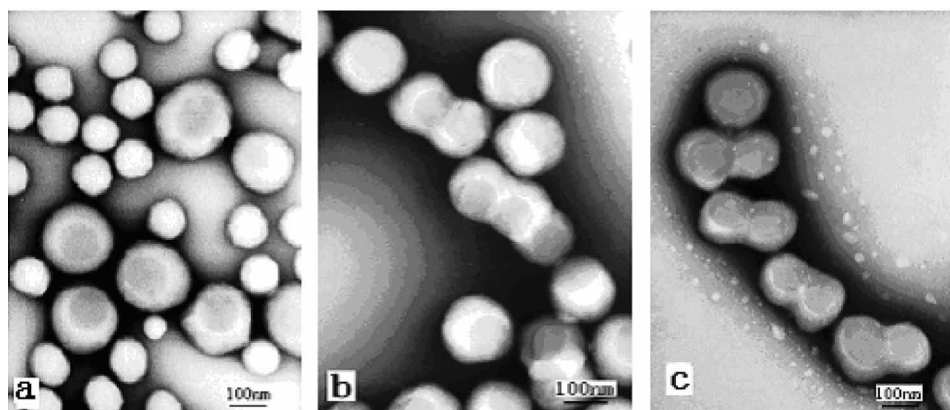


Figure 5. TEM images of the silica/PtBMA core/shell nanocomposite particles prepared using various concentrations of MPS-modified silica nanoparticles as seeds: (a) 1.0%, (b) 1.5% and (c) 2.0%.

tBMA and the nanocomposite particles, as illustrated in Figure 6. The strong peak at 1725 cm^{-1} appearing in the spectrum of the core/shell structured particles was attributed to the carbonyl groups of poly(*tert*-butylmethacrylate) shell layer, and the wide band at 1101 cm^{-1} attributed to the silica core.

Conclusions

MPS can be used for the modification of silica particles to graft C=C groups on their surface; the grafting was confirmed by the results of elemental analysis, NMR spectra and FTIR spectra. The core/shell nanocomposite particles based on silica nanoparticles as core and crosslinked. poly(*tert*-butylmethacrylate) as shell were prepared by seed

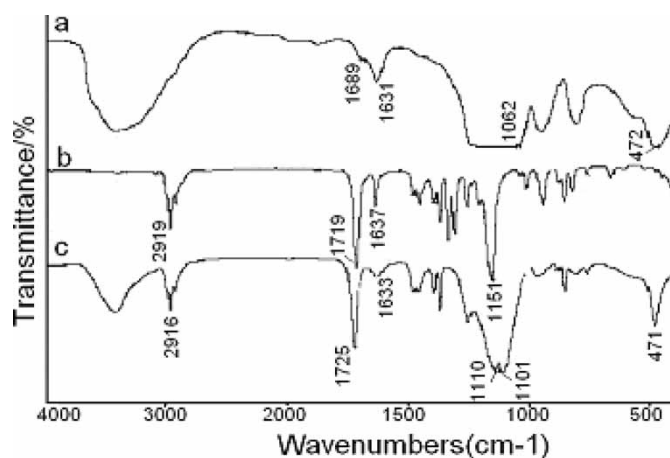


Figure 6. FTIR spectra of (a) MPS-modified silica; (b) tBMA and (c) the core/shell nanocomposite particles.

emulsion polymerization, utilizing modified silica particles as seeds, tert-butylmethacrylate as monomer and ethylene glycol dimethacrylate as crosslinker. Their core/shell composite structure and chemical composition were evidenced by TEM and FTIR results.

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