Fabrication of Silica/Polystyrene Nanocomposite Microspheres by γ-Ray Irradiation

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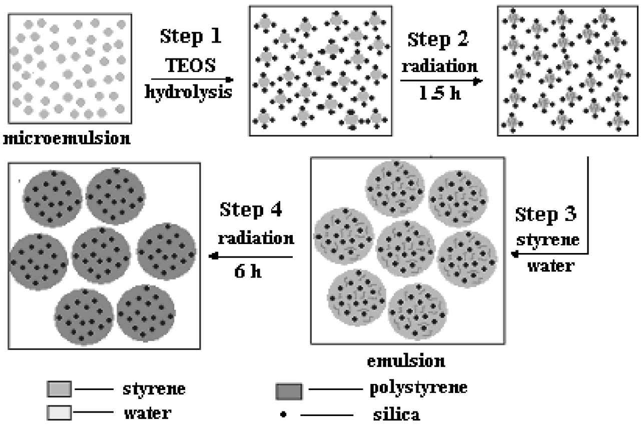
Nanocomposite monodisperse polystyrene microspheres (ca. 90 nm) containing homogeneously dispersed silica nanoparticles (ca. 6 nm) have been successfully produced by combining happily the techniques of microemulsion, emulsion and γ-ray irradiation. The product was characterized with TEM, FTIR, and TGA. A possible formation mechanism of the nanocomposite was proposed.

In the few past years, the synthesis of inorganic/polymer nanocomposites is an area of increasing research activity due to the beneficial synergism of properties that these materials possess. These nanocomposites have been found successful applications in versatile areas such as organic batteries,[1] microelectronics,[2] nonlinear optics,[3] catalysts,[4] and sensors.[5] Many methods have been developed to synthesize inorganic/polymer nanocomposites.[6–8] The major difficulties with scale-up of these methods are as follows: firstly, the polymerization of organic monomer and the formation of inorganic nanoparticles can not be performed in one system, this involves in the separating and redispersing polymer or inorganic nanoparticles, thus, the aggregation of inorganic nanoparticles or polymer can not be avoided; secondly, a relatively high temperature is needed.

Silica/polymer nanocomposite can be applied not only in catalysis and optics but also in chromatography,[9] controlled release,[10] materials additives (fillers),[11] and in many other filed. Although a few strategies do exist for synthesizing this nanocomposite,[8,12,13] it is difficult to make silica nanoparticles to be dispersed well in polymer matrices. Herein we report a novel method to prepare monodisperse polystyrene microspheres (ca. 90 nm) containing homogeneously dispersed silica nanoparticles (ca. 6 nm) at room temperature and under ambient pressure. Scheme 1 shows the overall procedure used to synthesize the nanocomposite. In this new method, the technique of microemulsion, emulsion and γ-ray irradiation was combined skillfully to prepare silica/polystyrene nanocomposite microspheres, and the separation and redispersion of inorganic nanoparticles were avoided.

In a typical synthesis, firstly, a microemulsion was prepared as follows: 10-mL styrene and 1-mL methyl methacrylate was added into an aqueous solution prepared from 10-mL H_2O, 5-mL $NH_3{\cdot}H_2O$ (28%) and 1-mL acrylic acid, and then surfactant poly(ethylene oxide)-10 (10 g) and sodium 12-acryloxy-9-octadecenate (2 g) was titrated into the mixture under stirring. Secondly, after the microemulsion became optically clear, 18-mL tetraethoxysilane (TEOS) was injected and then the reaction mixture was stirred for 48 h at ambient temperature. Thirdly, the reaction mixture was irradiated in the field of 2.59×10^{15} Bq ^{60}Co γ-ray source for 1.5 h with an absorbed dose of 6 kGy. A portion of 20-mL styrene was subsequently added into above mixture and the mixture was poured into 150-mL H_2O under stirring, then a milky-white emulsion finally formed was irradiated for 6 h with an absorbed dose of 18 kGy. After the reaction of emulsion polymerization was complete, the emulsion was destabilized by adding ethanol. Lastly, the precipitate was separated by centrifugation and the resulting particles were further washed with distilled water and ethanol, then dried in vacuum at room temperature for 6 h.



Scheme 1. Illustration of the formation of the silica/polystyrene nanocomposite microspheres.

The size and morphology of the product were investigated by transmission electron microscopy (TEM). TEM images were taken on a Hitachi Model H-800 transmission electron microscope with an accelerating voltage of 200 kV. Fourier transform infrared spectroscopy was carried out on a Bruker Vector-22 FTIR spectrometer. Thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50H instrument.

When TEOS was injected into the microemulsion, silica nanoparticles were formed in aqueous phase of the microemulsion via the reaction of hydrolysis of TEOS and consequent condensation of $Si(OH)_4$ catalyzed by $NH_3{\cdot}H_2O$ (Step 1). After γ-ray irradiation for 1.5 h (Step 2), the conversion of the monomer of styrene is approximately 10%; the microemulsion was then transformed to emulsion by adding styrene and water (Step 3). Finally, the nanocomposite microspheres were obtained by subsequently emulsion polymerization of styrene initiated by γ-ray irradiation (Step 4).

Figure 1 shows the TEM image of the product. The composite microspheres size is reasonably uniform, and the higher magnification image Figure 1b provides excellent evidence for that individual polystyrene microsphere contains homogeneously dispersed multiple silica nanoparticles. The mean diameter of

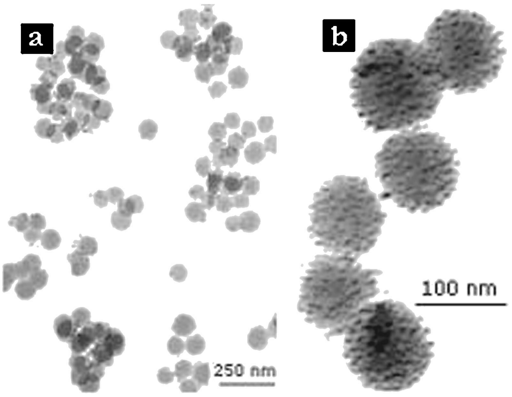


Figure 1. TEM picture of silica/polystyrene nanocomposites. a) low magnification image showing the uniform size of nanocomposite. b) higher magnification image showing polystyrene microspheres (ca. 90 nm) containing homogeneously dispersed silica particles (ca. 6 nm).

these polystyrene microspheres is about 90 nm and that of these silica particles is only 6 nm. Further thermogravimetric analysis for the product indicates silica content of the nanocomposite of 17% by mass, which also generally agrees with that predicted 15%.

FTIR spectrum was also used to examine the nanocomposite and shown in Figure 2. The band at 1095 cm^{-1} dues to the asymmetric stretching vibration mode of the Si–O–Si bridge of the siloxane link[14] and a band at 800 cm^{-1} corresponds to the symmetric stretching of Si–O–Si group. A band at 959 cm^{-1} associated with the presence of Si–OH groups was detected.[15] The eight bands at 699, 757, 1452, 1493, 1601, 2852, 2924, and 3026 cm^{-1} can be assigned to polystyrene. Also, the two bands at 1731 and 1714 cm^{-1} are observed and corresponds separately to the stretching of C=O group of poly(methyl methacrylate) and poly(acrylic acid). This can be contributed to the copolymerization of methyl methacrylate with styrene and acrylic acid. The bands at 1631 and 3424 cm^{-1} can be due to the water introduced by KBr matrix from atmosphere.

Acrylic acid and methyl methacrylate play an important role in the synthesis of the nanocomposite microspheres. In contrast, for the same reactant components but without acrylic acid and/or methyl methacrylate, the encapsulation of silica particles with polystyrene failed and only unattached silica nanoparticles and polystyrene microspheres were obtained. On the one hand, acrylic acid served as a catalyst for the formation of silica and also was absorbed onto silica substrates as a particle-stabilizing agent, thus the diameter of silica particles formed was only 6 nm. However, the diameter of silica particles was 150 nm in the absence of acrylic acid. On the other hand, methyl methacrylate possibly acted as a bridge of silica and polystyrene, across which silica and polystyrene was connected via its copolymerization with acrylic acid and styrene (Step 2 and 3 in Scheme 1) and silica/polystyrene nanocomposite microspheres can be finally obtained, this is also confirmed by FTIR spectrum and TEM image of the product.

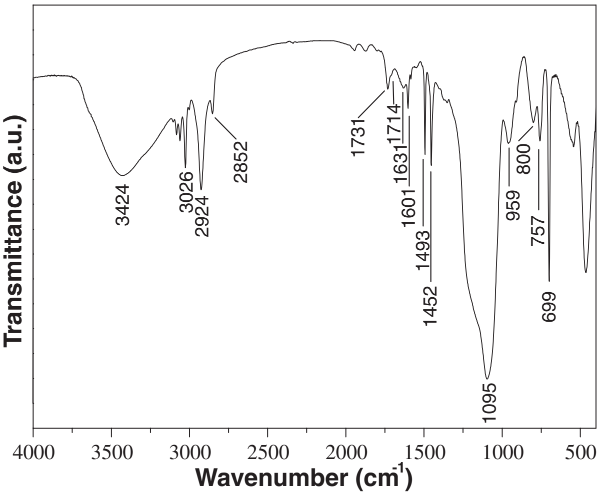


Figure 2. FTIR spectrum of the sample shown in Figure 1.

In summary, a facile route to colloidal polymer nanocomposite via emulsion polymerization of styrene initiated by γ-ray irradiation in the presence of silica nanoparticles is reported. The resulting nanocomposite polystyrene microspheres (ca. 90 nm) contain homogeneously dispersed silica nanoparticles ca. 6 nm). The most important advantage of this new approach is that the aggregation of inorganic nanoparticles has been overcome and all experiment can be carried out at room temperature and under ambient pressure. This method constitutes a promising way to synthesize other inorganic/polymer nanocomposite microspheres.

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