

GRAFTING OF POLYSTYRENE ONTO A NANOMETER SILICA SURFACE BY MICROEMULSION POLYMERIZATION

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Abstract The grafting of polystyrene onto a nanometer silica surface by microemulsion polymerization is described. Silica was functionalized with 3-methacryloxypropyltrimethoxysilane coupling agent before polymerization. A mixture of ionic and non-ionic surfactants as well as water-soluble and oil-soluble initiators were used. The effect of the amount of silica and ionic surfactant on the graft polymerization was studied. The graft polymerization procedure for styrene was also applied to methyl methacrylate. Composite particles with a core-shell structure were obtained and the yield and grafting efficiency of monomer were high.

Keywords Grafting, Nanometer silica, Microemulsion polymerization

INTRODUCTION

Organic-inorganic nanocomposite materials are of growing interest because they combine the advantages of organic polymers and inorganic nanometer particles. They have diverse applications in different fields such as mechanics, optics, electricity, magnetism, aerospace, thermodynamics, and bionics.

Among the various nanometer inorganic particles (Fe_2O_3 , TiO_2 , CaCO_3 , SiO_2 , ZnO , etc.), silica has been extensively used as a filler in the manufacture of paint, rubber, plastics, binder, functional fiber and so on. However, it is difficult to get silica nanoparticles monodispersed in the polymer matrix, because silica particles agglomerate due to their specific surface area effect and volume effect. Pioneering work has shown that the dispersibility of silica is remarkably improved by grafting polymers onto its surface. The grafted polymer chains also facilitate the filler more compatible with the polymer matrix, thus improving the appearance and the performance of the composite materials^[1].

Polystyrene has been successfully grafted onto nanometer silica bearing initiating groups (azo^[2], perchlorate^[3], peroxy carbonate^[4], peroxy ester^[5] and trichloroacetyl^[6] groups) which were introduced onto the silica surface before graft polymerization in solution or in bulk polymerization. It has also been grafted onto nanometer silica modified with silane coupling agent bearing a double bond by dispersion polymerization in a mixture of ethanol and water^[7, 8]. In the first case, the graft polymerization started from the surface of silica nanometer particles. In the latter case, the modified silica served as the comonomer in the polymerization, and the morphologies obtained include composite particles containing a great number of silica beads, as well as very regular core-shell particles, depending on the type of stabilizer used in the polymerization.

Recent approaches^[9, 10] involve the grafting of polystyrene onto surface-modified nanometer silica using controlled/living radical polymerization. In this method, atom transfer radical polymerization was used to conduct the graft polymerization from the silica nanoparticle macroinitiator. A well-defined core-shell structure was observed from the transmission electron microscopy (TEM) micrographs and its particle size can be

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manipulated by the progress of the reaction^[9].

Emulsion polymerization has been used to prepare polystyrene-silica composite latex^[11]. In this case, silica was pre-coated with a dense layer of hydroxypropyl cellulose, which acted as a binder between the silica surface and the polystyrene molecules. Emulsion polymerization has also been used to graft poly(ethyl acrylate) onto nanometer silica containing functional methacryloyl groups^[12, 13]. TEM study^[13] showed that it did not produce an ideal core-shell morphology, since a heterogeneous structure comprising a relatively large core composed of a few silica particles covered with latex heads was observed.

In this paper, we describe the grafting of polystyrene onto nanometer silica, which has been pre-treated with 3-methacryloxypropyltrimethoxysilane by microemulsion polymerization using a mixture of ionic and non-ionic surfactants. The factors which influence the grafting and the morphology of the composite particles are discussed.

EXPERIMENTAL

Materials and Characterizations

Nanometer silica with a particle size of 10 ± 5 nm was a gift from Zhoushan Mingri Nanomaterial Ltd. (China). The silica was used as received. Styrene (St), 3-methacryloxypropyltrimethoxysilane (MPTMS), phenyl ether, polyethylene glycol, and polyethylene glycol mono-*p*-nonyl phenyl ether (OP) were obtained from Yongchang company and used as received. Styrene (St), methyl methacrylate (MMA) was distilled under reduced pressure before used. 2,2'-Azobis(isobutyronitrile) (AIBN) and ammonium persulfate (APS) were recrystallized before used. Sodium dodecyl sulfonate, sodium dodecyl sulfate and $AlCl_3$ were used without further purification.

Infrared spectra of bare silica (in KBr pellet) and grafted silica (as film, after Soxhlet extraction) were recorded on a Nicolet 560 FT-IR spectrometer. Particle size and size distribution of grafted silica were determined by TEM using a JEOL 200CX electron microscope (the sample was made directly from the microemulsion). Dissolution was performed in xylene at room temperature.

Functionalizaion of SiO_2

MPTMS (5wt% to SiO_2) was introduced dropwise into a flask containing dry silica with rapid stirring for 20 min.

Microemulsion Polymerization

A 250 mL four-necked flask equipped with a reflux condenser, a thermometer, a mechanical stirrer and a N_2 inlet, was charged with 50 mL deionized water, sodium dodecyl sulfonate and OP surfactant. The temperature of the microemulsion was raised to $40^\circ C$, and a mixture of styrene and functionalized silica was added. The temperature of the above reaction mixture was then raised to $60^\circ C$. At this point, 7 mL of 0.6% of APS was added (in all of the experiments, the mol ratio of APS to St is 0.2 mol%). The temperature of the reaction mixture was then raised to $85^\circ C$ and maintained at this temperature for 1.5 h. The temperature was further elevated to $90^\circ C$ and 3 mL of 0.6% APS was added. After half an hour, the reaction mixture was poured into a beaker and 10 mL of 20% aqueous $AlCl_3$ solution was added. The product was collected by suction filtration and washed with hot water, then dried.

Yield, Grafting Ratio and Grafting Efficiency

To remove the ungrafted polymer, the reaction product was extracted with xylene for 12 h using a Soxhlet apparatus. The yield, the grafting ratio and the grafting efficiency were calculated as follows:

$$\text{Yield (\%)} = \frac{\text{Product (g) (before extraction)}}{\text{Total monomer (g) and } SiO_2 \text{ (g)}} \times 100 \quad (1)$$

$$\text{Grafting ratio} = \frac{\text{Polymer grafted (g)}}{SiO_2 \text{ used (g)}} \quad (2)$$

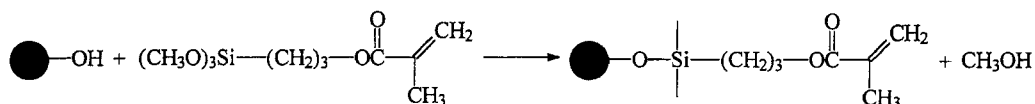
$$\text{Calculated grafting ratio} = \frac{\text{Monomer added (g)}}{SiO_2 \text{ used (g)}} \quad (3)$$

$$\text{Grafting efficiency (\%)} = \frac{\text{Polymer grafted (g)}}{\text{Polymer formed (g)}} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Functionalization of Silica

In order to evaluate the usefulness of silane coupling agent treatment, both bare silica and treated silica were used in the microemulsion polymerization for comparison. As expected, bare silica did not give any polystyrene grafted silica, while treated silica reacted very well under the same reaction conditions. This result is in agreement with that of other researchers' observation. Espiard *et al.*^[11] did not obtain any poly(ethyl acrylate) grafted silica using microemulsion polymerization. It is believed that the silanol groups of silica react with MPTMS through covalent bonding of O—Si to introduce a double bond onto the silica surface, as shown in Scheme 1^[12], which could be considered as comonomer reacting with styrene.



Scheme 1 Functionalization of silica by silane coupling agent

Effect of the Amount of Silica on the Grafting

Due to its marked volume and surface effect, nanometer silica was expected to have a notable effect in the microemulsion polymerization. In this experiment, the amount of silica was studied as a variable while all of the other factors were the same as described in the Experimental section.

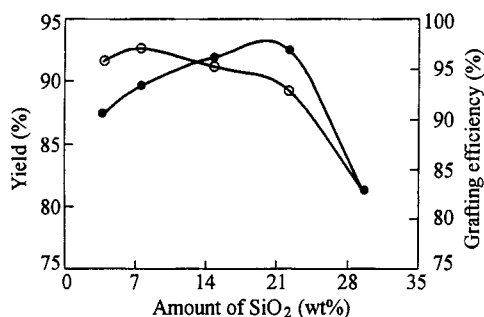


Fig. 1 The effect of amount of silica on the yield and grafting efficiency

● Yield; ○ Grafting efficiency

In this case, the weight ratio of H₂O/St/SDS/OP is 500/140/7/1.

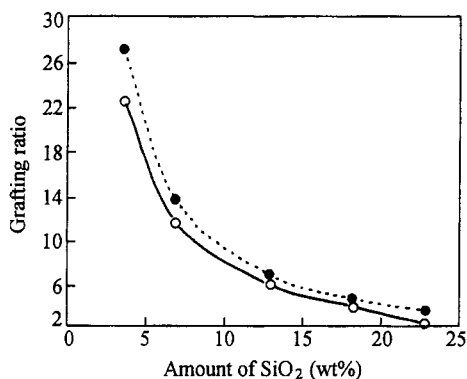


Fig. 2 The effect of amount of silica on the grafting ratio

○ Actual value; ● Calculated value

In this case, the weight ratio of H₂O/St/SDS/OP is 500/140/7/1.

Figure 1 shows the effect of the amount of silica on the grafting of polystyrene onto the silica surface. When the amount of SiO₂ was lower than 18 wt% relative to styrene, the yields were all around 90%, and the grafting efficiencies were all above 90%. A notable decrease both in the yield and the grafting efficiency was observed when the ratio of SiO₂ to styrene was as high as 23 wt%. In this case, we observed that some silica precipitated out from the microemulsion system during graft polymerization; that was one of the reasons for the lower yield. The decrease in grafting efficiency implies that more homopolystyrene was formed. It is noted that the optimum value of SiO₂ content is 13%–18% with the highest grafting efficiency (95%).

The grafting ratio of polystyrene onto silica as a function of the amount of silica is shown on Fig. 2. The

grafting ratio declines as the ratio of SiO_2 to styrene increases, because relatively less styrene was available to SiO_2 particles. When the amount of SiO_2 was about 13%–18% (where the grafting efficiency was the highest), the actual grafting ratio was very close to the calculated value, which means polystyrene formed in the polymerization was almost completely grafted onto the surface of silica. There is an obvious difference between the actual grafting ratio and the calculated one, when SiO_2 was lower to 3% and higher to 23%. Nevertheless, all of the grafting ratios were much higher than that reported in related publications (less than 1.5 (*i.e.* 150%)), in which silica bearing initiating groups such as trichloroacetyl groups^[5] was used.

Effect of the Surfactant

In the early studies, composite surfactants such as ether surfactant and phenyl ether, and sodium alkyl sulfate and polyethylene glycol were used. However, in the presence of silica the conversion of monomer was so low, that only some low molecule weight polystyrene was observed, and the product was difficult to collect. Further study has not been performed; the reason for this phenomenon is still unknown.

In this work, a mixture of ionic surfactant sodium dodecyl sulfonate and non-ionic surfactant OP was used, of which sodium dodecyl sulfonate was the major surfactant. In such a composite surfactant system, these two surfactants could make up a stable microemulsion system. When the amount of sodium dodecyl sulfonate is varied, while all other reaction conditions remain the same, the graft polymerization will be affected. From Fig. 3 and Fig. 4, we can see that the yield, grafting efficiency and grafting ratio reach their maxima when the amount of sodium dodecyl sulfonate ranges between 1.8%–2.4% (mol ratio to styrene).

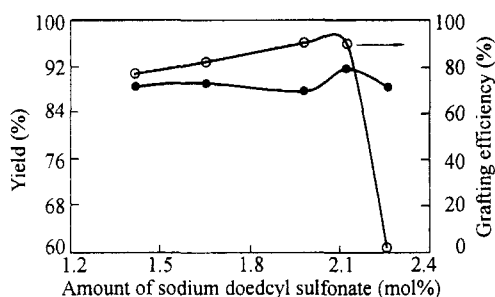


Fig. 3 The effect of sodium alkyl sulfonate on the yield and grafting efficiency

● Yield; ○ Grafting efficiency

Weight ratio of $\text{H}_2\text{O}/\text{St}/\text{SiO}_2/\text{OP}$ is 500/140/5/1

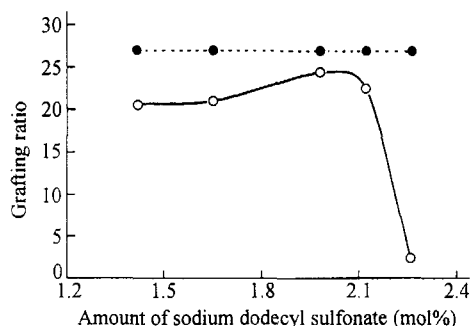


Fig. 4 The effect of sodium alkyl sulfonate on grafting ratio curves

○ Actual grafting ratio; ● Calculated grafting ratio

Weight ratio of $\text{H}_2\text{O}/\text{St}/\text{SiO}_2/\text{OP}$ is 500/140/5/1

When the amount of sodium alkyl sulfonate exceeded the optimal value needed in the polymerization, the yield, however, was still high (*i.e.* the conversion of monomer was still high), and the grafting ratio and grafting efficiency declined sharply. The excess amount of sodium alkyl sulfonate turned into excess pure styrene latex, resulting in the formation of homopolystyrene.

Effect of Initiator and Monomer

In order to make a comparison between the oil-soluble initiator (AIBN) and the water-soluble APS, the two initiators were added into two identical mixtures of monomer and silica, respectively, and keeping all other reaction conditions the same. The results of graft polymerizations with the two types of initiator are shown in Table 1. We can see clearly that the yield, the grafting ratio and the grafting efficiency were close in both cases, although a little bit lower when AIBN was used because in both cases the reactions took place in the latexes and the size of latexes was of equal magnitude.

Table 1. The results for different initiator used in the graft polymerization^a

Initiator	AIBN	APS
Yield (%)	81.34	91.70
Actual grafting ratio	19.00	22.59
Grafting efficiency	87.24	90.56

^a The reactions proceeded under the same conditions, the amount of SiO₂, sodium dodecyl sulfonate and AIBN used were 3.57 wt%, 2.1 mol% and 0.46 mol% (with respect to St).

In order to know whether the conditions found for styrene are also feasible for other vinyl monomers, MMA was used instead of styrene. From Table 2 we can see that the graft polymerization of MMA also proceeded well. Table 2 also shows that the grafting efficiency of styrene is not so high as some values indicated in Fig. 3, because the polymerization condition used in Table 2 is not the optimal condition for styrene. The difference in the results between styrene and MMA is reasonable since the polarity of MMA and St is different, MMA is more soluble in water than styrene, leading to different grafting effects.

Table 2. The results for different monomers used in the graft polymerization^a

Monomer	MMA	St
Yield (%)	82.69	88.50
Grafting efficiency	98.11	76.71
Calculated grafting ratio	28.29	27.03
Actual grafting ratio	22.76	20.66

^a The reactions proceeded under the same conditions with the same amount of sodium dodecyl sulfonate (2.0 mol% to styrene, 1.9 mol% to MMA) and the same amount of SiO₂ (3.7 wt% to styrene, 3.5 wt% to MMA)
The initiator was APS in both cases.

Evidence of Grafting

The FT-IR spectrum of polystyrene grafted SiO₂ has absorption peaks at 1600, 1493, 756 and 698 cm⁻¹ which are the characteristic peaks of polystyrene, indicating that polystyrene has been grafted onto silica, as any ungrafted polystyrene has been removed by Soxhlet extraction with xylene prior to the IR measurement.

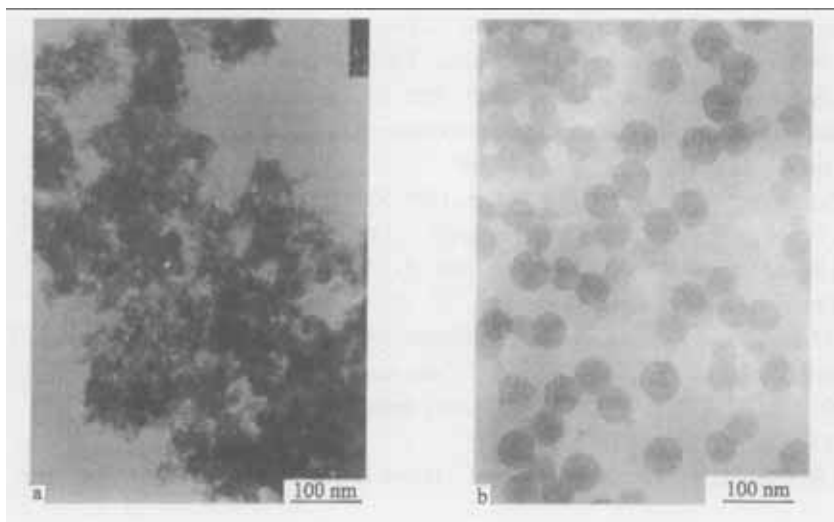


Fig. 5 TEM micrographs of original SiO₂ (a) and polystyrene grafted SiO₂ obtained directly from microemulsion system (b)

In this case, the weight ratio of H₂O/St/SiO₂/SDS/OP is 500/140/5/7/1

The dispersibility of SiO₂ in organic solvents was greatly improved by grafting. The grafted SiO₂ can form a transparent and stable gel in xylene, while ungrafted SiO₂ precipitates completely. This is further evidence in

support of grafting.

Furthermore, as conclusive evidence of grafting, the TEM micrograph is shown in Fig. 5. The shape of original silica (Fig. 5a) was irregular and the surface was rough with a particle size of 10 ± 5 nm. After graft polymerization, the particles became spherical in shape and bigger in size (about 45 nm, Fig. 5b). Thus nanometer composite particles have silica as the core and polystyrene as the dense shell.

It should be noted that the grafting efficiency is much higher in this work than that of related work. Espiard and Guyot used emulsion polymerization to encapsulate nanoparticles of silica with poly(ethyl acrylate). In their work, although silica was also pretreated with MPTMS, it was added to water at the beginning of the procedure (while in our work, it was added together with the monomer to the microemulsion). Their grafting efficiency was much lower, only 9%–48%, when the ratio of silica to monomer was 1.5%–11%^[12]. Bourgeat-Lami *et al.* used dispersion polymerization to encapsulate inorganic silica with polystyrene and only 12% of the total synthesized polystyrene was grafted onto the surface of silica^[7].

CONCLUSIONS

Polystyrene has been successfully grafted onto a nanometer silica surface by microemulsion polymerization using a mixture of ionic and non-ionic surfactants. Functionalization of silica with 3-methacryloxypropyltrimethoxysilane coupling agent prior to graft polymerization was necessary to get silica involved in polymerization as a comonomer. The amounts of silica and ionic surfactant have to be selected carefully in order to get an efficient grafting. Both water-soluble and oil-soluble initiators give good grafting. The graft polymerization process found for styrene is also useful for methyl methacrylate. The grafting efficiency is high (above 80%) when the amount of silica is between 11 wt%–18 wt% (relative to styrene) and the composite particles have a larger size (about 45 nm) compared with the original silica (10 ± 5 nm). This indicates the formation of core-shell structure with silica as the core and polystyrene as the dense shell.

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