

Preparation of Crosslinked Composite Nanoparticles

Wen-Fang Liu, Zhao-Xia Guo, Jian Yu

Department of Chemical Engineering, School of Materials Science and Engineering, Institute of Polymer Science and Engineering, Tsinghua University, Beijing 100084, China

Received 20 April 2004; accepted 18 August 2004

DOI 10.1002/app.21910

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Crosslinked composite nanoparticles were prepared by adding a trifunctional monomer (trimethylol propane trimethacrylate) or a difunctional monomer (divinyl benzene) as a crosslinker into the emulsion polymerization system of styrene in the presence of inorganic nanosilica. A coupling agent, 3-methacryloxypropyltrimethoxysilane (MPS), was added along with the monomer, crosslinker, and silica to improve the interfacial interaction between silica and polymer and thus to obtain high binding efficiency. The role of MPS was examined. The effects of crosslinkers on the kinetics of emulsion polymerization, monomer conversion, and yield were investigated. The mor-

phology of the composite particles was observed by TEM. The particle size and size distribution of composite latex particles were measured by the dynamic light scattering method. The binding efficiency and swelling ratio were determined by relixing the sample in xylene using a Soxhlet extraction apparatus. FTIR spectra and TGA verified the participation of crosslinker and silica. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1538–1544, 2005

Key words: nanocomposites; crosslinking; polystyrene; emulsion polymerization; dynamic light scattering

INTRODUCTION

The preparation of organic–inorganic composite particles is an important field of research. Much of the investigative activity in the past decade has been aimed at obtaining inorganic powders, coated with an organic polymer layer. Such systems are expected to exhibit properties other than the sum of the properties of the individual components, such as better dispersion of particles in the polymeric matrix, improved mechanical properties, and so forth.¹

In many cases, encapsulation is achieved by physical sedimentation or adsorption and the encapsulated polymer remains on the surface of the inorganic particles without chemical bonding. In some applications, such as engineering plastics, the failure deriving from the weak encapsulated layer can degrade the tear strength of the composite material. This degradation can be alleviated by crosslinking the polymer to force chemical links across the weak interface.² Also, crosslinking can prevent the physically adsorbed polymer shell from being melted away during high-temperature processing or dissolving in solvent during usage.

A few studies have been reported concerning encapsulation of inorganic particles by crosslinked polymers. Huang³ encapsulated iron oxide with crosslinked

polyacrylamide through inverse emulsion polymerization; these particles were subsequently used as seed to prepare aqueous hydrophobic magnetic latex particles, and the dissolution of the hydrophilic polymer shell was avoided by crosslinking. Park and Ruckenstein⁴ encapsulated submicron sizes of alumina and fumed silica particles by crosslinked polyacrylamide in concentrated emulsion polymerization, and a crosslinker was added to form a network of thin layers that enclosed the droplet containing the solid particles. Lin et al.⁵ prepared crosslinked poly(acrylic acid)/mica in aqueous solution, which could be used as a water absorbent as a consequence of crosslinking. Similarly, Wu et al.⁶ carried out graft copolymerization of acrylic acid with a crosslinker in the presence of montmorillonite ultrafine powder, yielding a superabsorbent composite. Supsakulchai et al.⁷ prepared composite particles consisting of titanium dioxide encapsulated by crosslinked polystyrene by a suspension polymerization, in which a crosslinking agent, divinylbenzene (DVB), was added to improve the hydrophobicity of the oil phase and the brittleness of composite particles. This group of studies provide micrometer- or submicron-size composite particles in which the inorganic core is tightly encapsulated by a crosslinked polymer shell.

Tight encapsulation is often preferable in view of applications of the composite particles to prevent the desorption of the polymer shell. Apart from the method of crosslinking, tight encapsulation can also be obtained by grafting of polymer onto the surface of inorganic particles during encapsulation.⁸ In this ap-

Correspondence to: J. Yu (yujian03@mails.tsinghua.edu.cn).

proach, a silane coupling agent bearing a double bond (e.g., γ -methacryloxypropyltrimethoxysilane) is often used to pretreat inorganic particles to introduce polymerizable bonds onto the surface of inorganic particles, which then reacts as a comonomer during the polymerization of vinyl monomers.^{8–11} The commonly used polymerization techniques are emulsion, suspension, and dispersion polymerizations. Besides, grafting of polymers onto inorganic particles through living polymerization can lead to encapsulation with an ideal core/shell structure.^{12–14}

In a preliminary work, we attempted to encapsulate nanometer silica by crosslinked polystyrene using a trifunctional crosslinking agent, trimethylol propane trimethacrylate (TMPTMA), in an emulsion polymerization system. The binding efficiency is not very high (typically 60%). To increase the binding efficiency and obtain tightly encapsulated composite nanoparticles, a small amount of coupling agent, 3-methacryloxypropyltrimethoxysilane (MPS) was used in this work by adopting the idea of grafting mentioned earlier. An *in situ* process, in which MPS is added along with the monomer, crosslinker, and silica, is envisaged to simplify the procedure. The role of MPS was examined and the kinetics of crosslinking emulsion polymerization was measured. The products were characterized by binding efficiency, swelling ratio, FT-IR, transmission electron microscopy (TEM), dynamic light scattering (DLS), and TGA technologies.

EXPERIMENTAL

Materials

Nanometer silica (particle size: 10 ± 5 nm) was a gift from Zhoushan Mingri Nanomaterial Ltd. (China). MPS, TMPTMA, DVB, sodium dodecyl sulfonate (SDS), poly(ethylene glycol), decyl phenyl ether (OP-10), and AlCl_3 were used as commercially supplied. Styrene was distilled under reduced pressure and ammonium persulfate (APS) was recrystallized before use. Deionized water was used as a polymerization medium.

Emulsion polymerization

Emulsion polymerization was carried out in a 250-mL four-neck flask, equipped with reflux condenser, thermometer, mechanical stirrer, and N_2 inlet, to which was charged deionized water (440 wt % to St), 70% of APS (0.5 wt % to St), SDS (5.5 wt % to St), and OP-10 (0.7 wt % to St). The temperature of the mixture was raised to 60°C. About 30% of a mixture of silica (3.7 wt % to St), styrene (15 mL), MPS (5 wt % to silica), and TMPTMA or DVB (0–7 wt % to St) was added after ultrasonic treatment for 10 min. After stirring for 20 min at 60°C, the temperature was increased to and maintained at 80°C for 0.5 h, after which the remain-

der of the mixture and initiator was added dropwise over 20 min. It was held at 80°C for 1 h, then increased to and held at 90°C for 0.5 h. After withdrawing the water bath, the emulsion was demulsified with 20% aqueous AlCl_3 , and the product was collected, washed with hot water, and dried for further analysis.

Monomer conversion and yield

Monomer conversion was determined by a gravimetric method. The yield was the weight ratio of the polymer and inorganic component to the monomer and inorganic powder.

Monomer conversion (%)

$$= \frac{\text{Total solids content (\%)} - \text{Initial involatile components content (\%)}}{\text{Initial monomer content (\%)}} \times 100 \quad (1)$$

Yield (%)

$$= \frac{\text{Weight of the dried product (g)}}{\text{Weight of initial monomers and silica (g)}} \times 100 \quad (2)$$

Transmission electron microscopy

Morphologies of the original silica and composite particles were observed using a CM 120 electron microscope (Philips, Eindhoven, The Netherlands). For the transmission electron microscopy (TEM) experiment, a powder sample dispersed in ethanol, or a highly diluted dispersion of the sample made from emulsion diluted with water, was cast onto a carbon-coated copper grid and allowed to dry.

Particle size and distribution

Particle size (\bar{D}_p) and polydispersity index (PDI) of latex were measured with a Zetasizer HS3000 laser light-scattering instrument (Malvern Instruments, Malvern, UK), commonly called the dynamic light scattering (DLS) method. The obtained particle size is an intensity-weighted mean diameter, which is also called “z-average diameter.” The PDI is defined as relative variance, which is an expression of the width of the particle size distribution, and calculated from a cumulants analysis of the DLS measured intensity autocorrelation function. PDI is dimensionless and is close to zero (0.000–0.020) for monodisperse or nearly monodisperse samples, small (0.020–0.080) for narrow distributions, and larger for broader distributions.

Binding efficiency and swelling ratio

The binding efficiency was defined as the percentage of unremovable polymer by the solvent (xylene). To

TABLE I
Characterization of Polymerization in the Presence and Absence of MPS^a

| MPS ^b (wt %) | Monomer conversion (%) | Yield (%) | Binding efficiency (%) |
|----------------------------|---------------------------|--------------|---------------------------|
| 0 | 95.9 | 82.3 | 62.5 |
| 5 | 95.6 | 86.9 | 95.6 |

^a Composition: St/TMPTMA/SiO₂/SDS/OP/APS/H₂O = 100/5/3.7/5.5/0.7/0.5/440 (weight ratio).

^b Based on silica.

remove any nontightly encapsulated polymer, the dried sample was extracted for 12 h with xylene using a Soxhlet apparatus. Binding efficiency was calculated according to eq. (3). The swelling ratio as a measure of crosslinking density of a crosslinked composite is the weight ratio of swollen (A_1) to dried sample after extraction (A_0).¹⁵

Binding efficiency (%)

$$= \frac{\text{Unextractable PS by xylene (g)}}{\text{PS formed (g)}} \times 100 \quad (3)$$

$$\text{Swelling ratio (\%)} = \frac{A_1 \text{ (g)}}{A_0 \text{ (g)}} \times 100 \quad (4)$$

Infrared spectra and thermogravimetric analysis

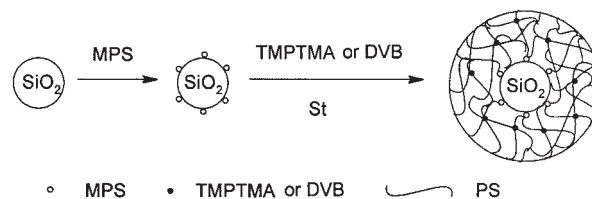
Composite particles after Soxhlet extraction were first swollen in chloroform. Then a small amount of gel was milled with dried KBr together and pressed into a pellet, after which the infrared spectra of the sample were recorded on a Nicolet 560 FTIR spectrometer (Nicolet Instrument Technologies, Madison, WI). Thermogravimetric analysis (TGA) was performed on a TA 2050 instrument (TA Instruments, New Castle, DE) at a heating rate of 20°C/min in flowing N₂.

RESULTS AND DISCUSSION

The role of MPS

Emulsion crosslinking polymerization in the presence of silica with and without MPS was carried out. The monomer conversion, yield, and binding efficiency were measured and the results are listed in Table I. As expected, the addition of MPS (5 wt % relative to silica) substantially improves the binding efficiency from 62.5 to 95.6%. In addition, MPS has no obvious influence on monomer conversion and yield.

It is known that MPS can easily react with silanol groups of silica through formation of a covalent bond, which introduces double bonds onto the silica surface. Such modified silica can then react as a comonomer in the polymerization of vinyl monomers, forming covalent



Scheme 1 Illustration of the encapsulation process in the presence of a coupling agent.

ent bonds (and thus a strong interface) between silica and polymer. Because of the hydrophilicity of the siloxane groups, which are easily hydrolyzed into silanol groups, it is considered that MPS preferably moves to the silica surface and reacts with silica before polymerization starts (see Scheme 1). To examine this expectation, a process—similar to the typical polymerization procedure—was carried out in the presence of an inhibitor, benzoquinone. Silica was then isolated and extracted with xylene in a Soxhlet apparatus for 12 h. The FTIR spectrum of the dried sample shows a weak broad peak at 1709 cm⁻¹, corresponding to the characteristic peak of carbonyl group. The shifting of this peak (relative to that of MPS) indicates grafting of MPS onto the silica surface. Therefore, MPS can play the role of coupling agent by forming covalent bonds at the interface between silica and polystyrene. Because the amount of MPS is small (5 wt % to silica), it mainly acts as coupling agent, although the possibility of acting as crosslinker cannot be excluded because of the presence of three siloxane groups in its structure, which undergo condensation and thus form a network.

Kinetics of polymerization

The kinetic behaviors of emulsion polymerization with and without crosslinkers, TMPTMA, or DVB, were investigated and are shown in Figures 1 and 2,

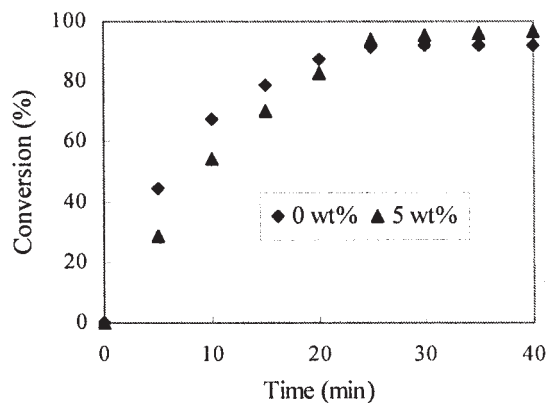


Figure 1 Kinetic curves for the emulsion polymerization of styrene with and without TMPTMA.

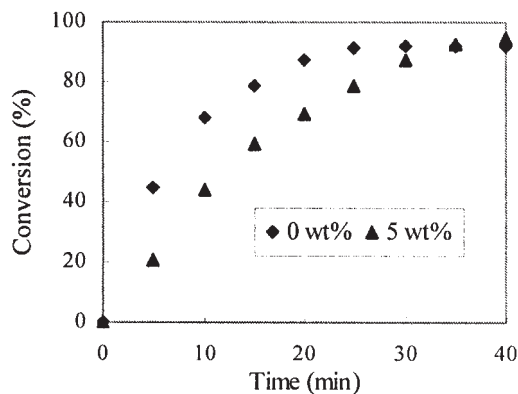


Figure 2 Kinetic curves for the emulsion polymerization of styrene with and without DVB.

respectively. It can be seen that the polymerization rate in the presence of crosslinkers is lower than that without crosslinkers, especially in the DVB system. This may be a result of the decreased monomer concentration at the reaction loci in the crosslinking reaction. The equilibrium monomer concentration in the particle or the particle shell would be governed by the crosslinking density of polymer matrix.¹⁶ As a reflection of particle shrinkage caused by the progress of crosslinking, monomer molecules show a trend of migrating from the interior to the particle surface, leading to a decrease of monomer concentration at the reaction loci. The fact that this trend is more obvious in the DVB system than in that of TMPTMA is not difficult to explain, given that the molecule of DVB is stiffer than TMPTMA because of the aromatic structure.

In the presence of TMPTMA or DVB, the monomer conversion reaches 97–99% within 120 min, which is slightly higher than that without crosslinkers (92%). This is reasonable given that the steric effect promoted

TABLE II
Average Particle Size (D_p) and Polydispersity Index (PDI) for Composite Particles with Different Amounts of Crosslinkers

| TMPTMA (wt %) | DVB (wt %) | D_p^a (nm) | PDI ^a |
|---------------|------------|--------------|------------------|
| 0 | 0 | 64 | 0.033 |
| 3 | 0 | 60 | 0.079 |
| 5 | 0 | 52 | 0.124 |
| 7 | 0 | 43 | 0.128 |
| 0 | 3 | 47 | 0.156 |
| 0 | 5 | 47 | 0.200 |
| 0 | 7 | 46 | 0.227 |

^a Measured by DLS method.

by network formation hinders the termination reaction of growing polymer radicals, especially at the later stage of the polymerization.¹⁷ A similar effect was reported when DVB was used in the suspension polymerization of styrene.⁷ In addition, the addition of crosslinkers has no effect on the yield, which is 85–87%.

Morphology, particle size, and distribution

As a direct evidence of encapsulation, TEM microphotographs of original silica and silica encapsulated by PS with 5 wt % TMPTMA or DVB are shown in Figure 3(a)–(c). Compared to original silica [Fig. 3(a)], the shape of composite particles changes from irregular to spherical, the size of composite particles increases from 10 to 40 nm, and the tendency of the agglomeration of nanometer silica particles is greatly reduced. Because the size of original silica is too small and the mole mass of silicon atom is not much larger than that of the carbon atom, the encapsulated silica particles cannot be recognized. However, we could still draw such a conclusion that nanosilica has been successfully

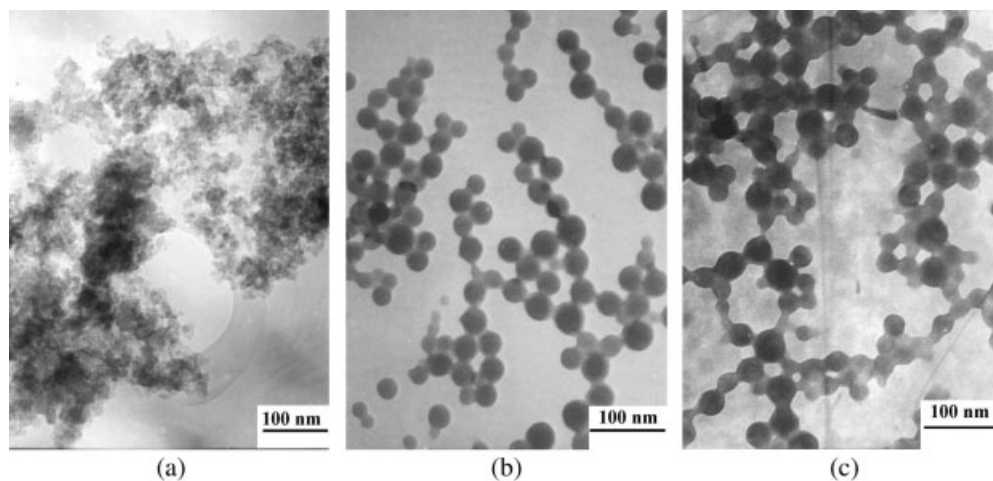


Figure 3 TEM micrographs of (a) original silica and silica encapsulated by PS with (b) 5 wt % TMPTMA and (c) 5 wt % DVB.

TABLE III
Binding Efficiency (BE) and Swelling Ratio (SR) for
Composite Particles with Different
Amounts of Crosslinkers

| TMPTMA (wt %) | DVB (wt %) | BE ^a (%) | SR ^b (%) |
|---------------|------------|---------------------|---------------------|
| 0 | 0 | 95.6 | 2110 |
| 3 | 0 | 93.4 | 748 |
| 5 | 0 | 95.9 | 710 |
| 7 | 0 | 98.2 | 632 |
| 0 | 3 | 95.8 | 666 |
| 0 | 5 | 97.4 | 646 |
| 0 | 7 | 99.0 | 628 |

^a Calculated according to eq. (2).

^b Calculated according to eq. (3).

encapsulated by crosslinked polystyrene from the fact that no free silica particles are observed in Figure 3(b) and (c).

The size and size distribution of composite latex particles with different amounts of crosslinkers were determined by DLS method and listed in Table II.

It can be seen that the size of particles decreases from 64 to 43 nm when the amount of TMPTMA increases from 0 to 7 wt %, indicating that the structure of composite particles is more compact when using more crosslinkers. However, when the amount of DVB varies from 3 to 7 wt %, the size of particles does not change (47 nm) because the mole fraction of functional groups in 3 wt % DVB is already larger than that in 7 wt % TMPTMA and particle size is already at the extreme value around this point.

The size distribution of composite particles for each sample is narrow (maximum 0.2), which is larger with

a crosslinker (TMPTMA or DVB). The larger distribution of crosslinked particles may be attributed to the formation of new particles during polymerization resulting from two aspects: one is the slower polymerization rate arising from the presence of crosslinker as discussed earlier; the other is the release of emulsifier and monomer molecules from large crosslinked composite particles at the later stage of polymerization as a result of particle shrinkage caused by the crosslinking process.¹⁶

Binding efficiency and swelling ratio

To determine the percentage of strongly encapsulated polymer and crosslinking density, the binding efficiency (BE) and swelling ratio (SR) were measured and results are listed in Table III, which shows that the binding efficiency is high for all the samples tested, which may be attributed to the presence of 5 wt % MPS. However, the swelling ratios decreased dramatically when a crosslinker (TMPTMA or DVB) was used. Without the use of any crosslinker, the swelling ratio is 2110%, and the silica particles, which are insoluble in any solvent, act as crosslinking points. When TMPTMA or DVB is used, the swelling ratio decreases to about 630–750%. The decrease in swelling ratio indicates crosslinking of the polymer shell.

FTIR spectra and TGA

Composite particles were characterized by FTIR and TGA, to verify the participation of crosslinker and

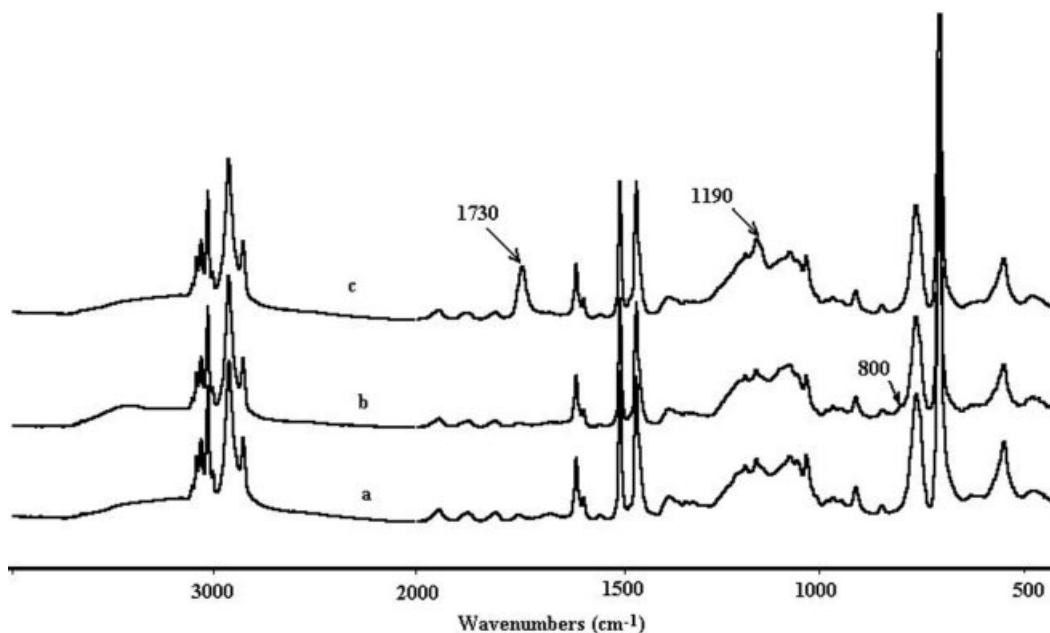


Figure 4 FTIR spectra for composite particles (a) without crosslinkers, (b) with 5 wt % DVB, and (c) with 5 wt % TMPTMA.

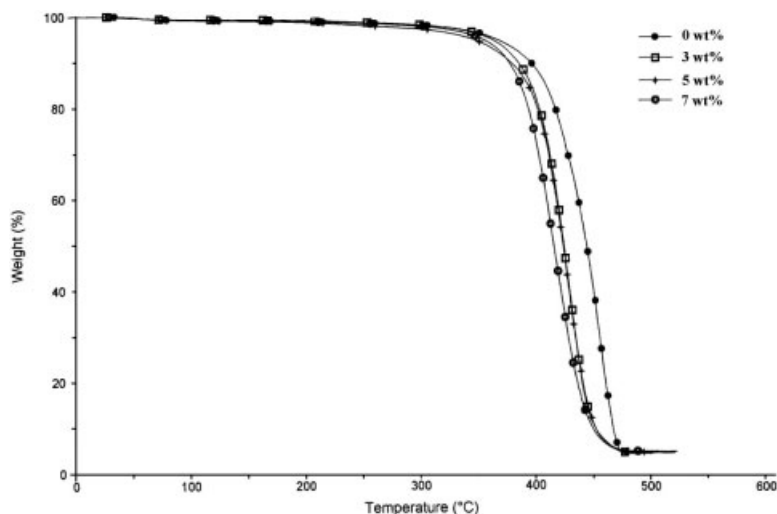


Figure 5 TG curves for composite particles with different amounts of TMPTMA.

silica. Figure 4(a)–(c) shows FTIR spectra of silica encapsulated by PS without crosslinkers and with 5 wt % TMPTMA or DVB. First, the characteristic peaks of PS and silica can be found in all the spectra, indicating tight encapsulation of silica by PS, because any physically adsorbed polymer has been removed by Soxhlet extraction with xylene before the IR measurement. As verification of the introduction of DVB, a weak peak at 800 cm^{-1} [Fig. 4(b)], attributed to the distortion vibrations of aromatic C—H bond, is recognizable. In Figure 4(c), a strong absorption peak appears at 1730 cm^{-1} and a very small absorption peak at 1190 cm^{-1} compared to Figure 4(a), corresponding to the extension vibrations of carbonyl (C=O) and C—O bond in the ester group, respectively, which provides the proof for the presence of TMPTMA.

TG curves with different amounts of TMPTMA and DVB are shown in Figures 5 and 6, respectively. Residual weights of both kinds of systems at temperatures up to 500°C are 4.0 and 4.5%, which are slightly higher than the theoretical value of silica content (3.5%).

CONCLUSIONS

Crosslinked composite nanoparticles were prepared using a polyfunctional monomer (TMPTMA or DVB) and a small amount of coupling agent (MPS) in the emulsion polymerization system of styrene in the presence of inorganic nanosilica. It was confirmed that MPS can effectively improve the binding efficiency from 62.5 to 95.6% when added along with the mono-

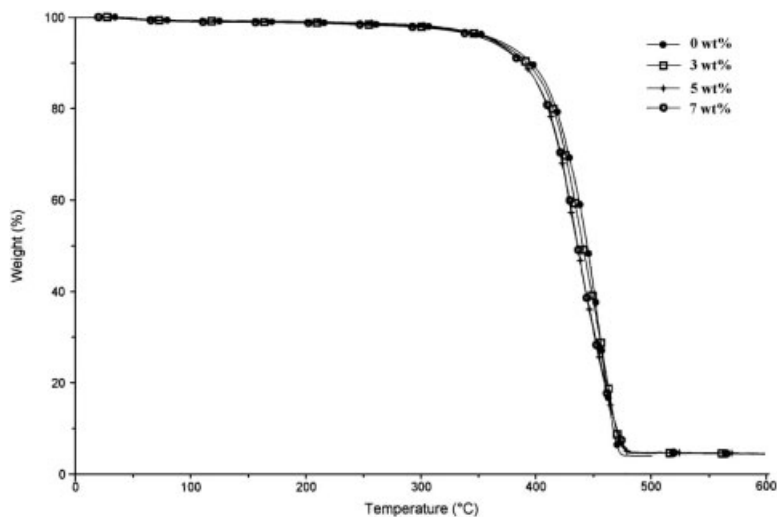


Figure 6 TG curves for composite particles with different amounts of DVB.

mer, crosslinker, and silica. In the presence of TMPTMA or DVB, the polymerization rate is lower than that without crosslinkers; however, the monomer conversion reaches, respectively, 97 and 94% within 120 min, which is slightly higher than that without crosslinkers (92%). In addition, crosslinkers have no effect on the yield (i.e., 85–87%). As observed by TEM, composite particles are either spherical or ellipsoidal in shape, and no free silica particles are observed. Particle sizes obtained by the DLS method decrease with increasing amounts of crosslinkers, indicating that the structure of composite particles becomes more compact. When using TMPTMA or DVB, size distribution becomes a bit broader, deriving from a lower polymerization rate and the release of emulsifier and monomer molecules from large crosslinked composite particles at the later stage of polymerization. Attributed to the presence of 5 wt % MPS, binding efficiency is always high and has no noticeable change when using more crosslinkers. However, the swelling ratio for all samples using crosslinkers is much lower (630–750%) than that without crosslinkers (2110%), indicating crosslinking of the polymer shell. FTIR and TGA can further confirm the participation of crosslinker and silica.

References

1. Van Herk, A. M. *Polymeric Dispersions: Principles and Applications*, Asua, J. M., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1997.
2. Kendall, K.; Sherliker, F. R. *Br Polym J* 1980, 12, 85.
3. Huang, T. C. C. Ph.D. Thesis, Lehigh University, Bethlehem, PA, 1986.
4. Park, J. S.; Ruckenstein, E. *Polymer* 1990, 31, 175.
5. Lin, J. M.; Wu, J. H.; Yang, Z. F.; Pu, M. L. *Macromol Rapid Commun* 2001, 22, 422.
6. Wu, J. H.; Lin, J. M.; Li, G. Q.; Wei, C. R. *Polym Int* 2001, 50, 1050.
7. Supsakulchai, A.; Ma, G. H.; Nagai, M.; Omi, S. *J Microencapsul* 2003, 20, 1.
8. Bourgeat-Lami, E.; Espiard, P.; Guyot, A.; Gauthier, C.; David, L.; Vigier, G. *Angew Makromol Chem* 1996, 242, 105.
9. Bourgeat-Lami, E.; Lang, J. *J Colloid Interface Sci* 1998, 197, 293.
10. Yu, J.; Yu, J.; Gao, Y. F.; Guo, Z. X. *Chin J Polym Sci* 2002, 20, 71.
11. Yu, J.; Yu, J.; Guo, Z. X.; Gao, Y. F. *Macromol Rapid Commun* 2001, 22, 1261.
12. von Werne, T.; Patten, T. E. *J Am Chem Soc* 2001, 123, 7497.
13. Mori, H.; Seng, D. C.; Zhang, M. F.; Müller, A. H. E. *Langmuir* 2002, 18, 3682.
14. Pyun, J.; Jia, S. J.; Kowalewski, T.; Patterson, G. D.; Matyjaszewski, K. *Macromolecules* 2003, 36, 5094.
15. Uhl, F. M.; Levchik, G. F.; Levchik, S. V.; Dick, C.; Liggat, J. J.; Snape, C. E.; Wilkie, C. A. *Polym Degrad Stab* 2001, 71, 317.
16. Matsumoto, A.; Kodama, K.; Aota, H.; Capek, I. *Eur Polym Mater* 1999, 35, 1509.
17. Tobita, H.; Kumagai, M.; Aoyagi, N. *Polymer* 2000, 41, 481.